THE EFFECT OF BENZOTRIAZOLE ON THE CORROSION
AND ELECTRODEPOSITION OF COPPER

by

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A study has been made of the influence of benzotriazole as a corrosion inhibitor for copper and brass in atmospheric and immersed environments. The effect of benzotriazole as an addition agent in the copper sulphate-sulphuric acid plating bath has been investigated systematically, with a particular emphasis on the correlation between the structure and properties of the coatings.

Benzotriazole has been found to be a good inhibitor and was discovered to act as a weak buffer for copper and brass immersed in acidic, neutral and alkaline solutions. The film formed by pre-dipping copper into a hot aqueous solution of benzotriazole increased the corrosion resistance in many solutions and was particularly beneficial in oxidizing and complexing solutions, as well as in decreasing the rate of oxidation in atmospheric conditions up to about 350°C. Benzotriazole was found to have similar inhibitive properties to Naphthotriazole and was much better than triazole in several environments.

It was established, by using the Stereoscan, that the presence of benzotriazole in the plating solution modified the nucleation and growth of the deposits. With low concentrations adsorption occurred during plating, while with higher additions it was codeposited in a layered structure. In deposits from the plain bath, the grain size decreased while the hardness and tensile stress increased, as the bath temperature was lowered and the current density raised. Deposits from the bath containing benzotriazole had a much smaller grain size and were much harder, the actual hardness varying with the plating parameters in a similar manner to that of the deposits from the plain bath. The internal stress, measured with the Spiral Contractometer, could be tensile or compressive and depended upon the concentration of benzotriazole in the solution and the plating conditions, the range of values being from 164 MN/m² tensile to 121 MN/m² compressive.

The results produced in this work have been analysed in the light of the known theories and correlations produced.
ACKNOWLEDGEMENTS

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INTRODUCTION

The original aim of this thesis was to study the production of copper coatings deposited from the copper sulphate-sulphuric acid plating solution containing benzotriazole. This followed the introductory work of Prall who claimed that the inclusion of codeposited cuprous benzotriazolate increased the corrosion resistance of copper deposits.

The initial investigation in the present work (Chapter 4) was carried out on the inhibitive properties of benzotriazole for copper under atmospheric, high temperature and immersed conditions. The emphasis of the research was later changed from the corrosion resistance of these coatings to the use of benzotriazole as an addition agent in the electrodeposition of copper, after Kendall reported, in his thesis in 1968, that the inherent resistance of these copper coatings was not as good as Prall had suggested. This difference in corrosion behaviour, suggested by Kendall and confirmed in this work, was probably due to the fact that in his work the adsorbed film of benzotriazole was removed from the coatings before corrosion testing, whereas in Prall's work it was not.

The first part of the work on the electrodeposition of copper (Chapter 5) was a study of the modifications produced by benzotriazole on the nucleation, surface appearance and cross-sectional structure of the coatings. The current efficiency and throwing power of the plating bath were measured with and without an addition of benzotriazole and are described in the first part of Chapter 6. An investigation was made into the effect on the grain size, hardness and internal stress produced by varying the purification and composition of both these baths, the bath temperature, current density and solution agitation, in the second part of Chapter 6. These results are discussed in the light of the current theories and examined for correlations between the plating parameters and the resulting properties.

It was expected that the knowledge produced would enable an assessment to be made of the practical use of benzotriazole both as a corrosion inhibitor and as an addition agent in the acid copper plating bath. This
research should also assist in the determination of the optimum
conditions of composition and plating variables for the production
of bright, hard deposits with a low internal stress, which are desirable
for engineering purposes.
1. LITERATURE SURVEY

1.1 Inhibitors

1.1.1 Introduction

The term inhibitor (from the Latin inhibere, to check) may be defined as "a material which, when added in small amount to an environment potentially corrosive to a metal or alloy in contact with it, effectively reduces the corrosion rate by diminishing the tendency of the metal or alloy to react with the environment". Inhibitors may also be applied to metal surfaces in the form of a coating e.g. phosphate and chromate surface treatments.

One of the first known uses of inhibitors was in the Middle Ages when they were used in acidic pickling solutions. Master armourers used acidic solutions to remove scale from metal articles and found that the addition of organic compounds such as flour, bran, yeast, etc. to the acid retarded the metal dissolution and prevented the appearance of pickling brittleness. For a long time, inhibitors were used exclusively for ferrous metals and alloys in liquid media, but more recently they have been applied to many non-ferrous metals, e.g. magnesium, copper, zinc etc. and also used as an addition to paint lacquers, oils and greases. Atmospheric inhibition has been obtained by the use of compounds which volatilize in air and form protective surface films on adjacent metallic surfaces; these substances are particularly useful in the packaging and storage of metals and equipment.

1.1.2 Theory

An inhibitor may be used to reduce the rate of corrosion of a metal by affecting any one of four requirements which must simultaneously be fulfilled when metal dissolution occurs:

1. an anodic region at which corrosion takes place, usually \( M \rightarrow M^{n+} + ne \);
2. a cathodic region where electrons are consumed, usually \( 2H^+ + 2e \rightarrow H_2 \) or \( O_2 + 2H_2O + 4e \rightarrow 4(\text{OH})^- \);
3. an electrolytic contact (aqueous solution) between the anode and cathode;
4. a metallic contact so electrons can flow from the anode to the cathode.

The rate of production of electrons at the anode must be equal to the rate of consumption of electrons at the cathode. Therefore, if the cathodic process is slowed then the anodic or corrosion process is slowed to the same extent.
Many inhibitors operate by forming a film or an adsorbed layer on the metal surface, so changing the anodic or cathodic reactions, or by increasing the electrical resistance at the surface. These film forming and adsorption inhibitors are very important and are now discussed in more detail.

1.1.3. Film Forming Inhibitors

This type of inhibitor can be used to affect the anodic and/or cathodic process and is normally used only in neutral solutions, because it is often not very effective in acidic conditions. Continuous corrosion occurs only if the products at both the anode and the cathode are freely soluble. However, if an addition is made to the solution to produce an insoluble product on the surface, this polarizes, or slows, the rate of the process and reduces the rate of corrosion. The substance, therefore, acts as a film forming inhibitor. If an insoluble cathodic product is formed, the substance is called a cathodic inhibitor, e.g. soluble zinc compounds act in this way giving zinc ions which react with the hydroxyl ions produced at the cathode to form a film of zinc hydroxide on the cathodic region; this process can be summarised by the following equations:

$$O_2 + 2H_2O + 4e \rightarrow 4(OH)^- \quad \text{Zn}^{2+} + 2(OH)^- \rightarrow \text{Zn(OH)}_2$$

If the anodic reaction is stifled, the addition is called an anodic inhibitor, e.g. carbonate ions in water form a protective film on the anodic areas of iron according to the equations:

$$Fe \rightarrow Fe^{2+} + 2e \quad Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3\downarrow$$

followed by $2FeCO_3 + 3H_2O \rightarrow Fe_2O_3 + 2CO_3^{2-} + 6H^+ + 2e$.

An alternative method of producing an anodic oxide film on ferrous surfaces is obtained by anodic protection, which uses an external source of power to induce film formation, thus passivating the surface. Certain inhibitors affect both the anodic and cathodic processes and therefore are called mixed inhibitors, e.g. zinc tetroxy-chromate which gives zinc ions to protect the cathodic areas and chromate ions which protect the anodic areas.
If only part of the anodic area is protected, as occurs when insufficient anodic inhibitor is used, intense attack may occur at the small, unprotected area, because of the high anodic current density, and this often results in rapid pitting of the surface. Therefore, these anodic inhibitors are sometimes called "dangerous" inhibitors. However, when insufficient cathodic inhibitor is used, the rate of the cathodic process is reduced (but not stopped), so the rate of corrosion of the anodic area is also reduced, in this case over the whole large anodic area, so pitting cannot result. Thus, in practice it is necessary to use either a cathodic inhibitor or a sufficient concentration of anodic, or mixed, inhibitor to give complete coverage of the anodic surface.

1.1.4 Adsorption Inhibitors

A different group of inhibitors, which is normally used in acidic conditions, acts by adsorption on to either the metal or the oxide surface. These reacting species may be ions, atoms, radicals or molecules and are bound to the surface; they may subsequently be replaced by a passivating oxide film. The bonding may be loose, and called physical adsorption, or it may be stronger and become chemisorbed.

The differences between physically and chemically adsorbed material are very important and govern the inhibitive properties of those substances. Some of these characteristics have been tabulated by Hackerman:

<table>
<thead>
<tr>
<th>Type of electronic interaction</th>
<th>Physical Adsorption</th>
<th>Chemical Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of electronic interaction</td>
<td>Van der Waals or electrostatic</td>
<td>Actual charge transfer or charge sharing</td>
</tr>
<tr>
<td>Energetics</td>
<td>Low heat of adsorption in water &lt; 10Kcals</td>
<td>High heat &gt; 10Kcal</td>
</tr>
<tr>
<td>Kinetics</td>
<td>Rapid, relatively independent of temperature. Activation energy often traceable to diffusion processes</td>
<td>Slow reaction with activation energy &gt; 6Kcal</td>
</tr>
<tr>
<td>Specificity</td>
<td>Adsorbed species relatively indifferent to nature of adsorbent</td>
<td>Specific interaction with strong dependence on nature of adsorbent</td>
</tr>
<tr>
<td>Reversibility</td>
<td>Adsorbed material readily removed by solvent washing</td>
<td>Adsorption is irreversible and permanent</td>
</tr>
</tbody>
</table>

The weak Van der Waals or electrostatic bonding in physical adsorption accounts for the low energy involved in the process, the high speed of adsorption as well as the easy reversibility and non-specific nature of the reaction.
Corrosion may occur at exposed areas, where the inhibitor is desorbed, because these sites are no longer protected; to prevent this attack a supply of inhibitor must be readily available in the corrosive medium to recover the exposed areas and maintain protection. In contrast, the strong bonding in chemical adsorption explains the higher energies and the irreversibility of the process, as well as the specificity which is due to the fact that chemical bonding depends upon both the inhibitor as well as the surface on to which it adsorbs. Slight variations in the nature of the adsorbing material are not likely to affect the physical adsorption, due to the general surface bonding, but, in chemisorption, these changes may have a significant effect on the electronic movement at the surface.

The adsorption process on the surface of a metal in an aqueous solution depends upon both the polarity of the metal and the nature of the electrolyte. This polarity is present because, when a metal is immersed in water, some dissolution occurs ($M\rightarrow M^{n+} + ne$) and continues until an equilibrium, between the metal and the ions, is reached. This results in the metal gaining a net negative charge (due to the electrons) and the aqueous solution adjacent to it a positive charge (due to the positive metal cations). These positive charges tend to form a plane parallel to the negative charges in the metal surface, and the region between the surface and these cations is called the Helmholtz electrolytic double layer. Between this double layer and the bulk solution there is another region, called the Gouy-Chapman layer, which is more diffuse, up to $10^{-6}$ m thick, and has a net positive charge. The charges in the double layer appear to influence the initial stages of the adsorption and have been discussed in detail by West\textsuperscript{5}, Antropov\textsuperscript{6} and Brasher\textsuperscript{7}.

One important use of adsorption inhibitors, indicating the importance of the surface charges, is in the acids used to remove the scales which either result from the heat treatment (millscale) or form in water pipes. Hydrochloric or sulphuric acid is normally used to dissolve the scales, so the cleaned metal is exposed to corrosion; it is on these areas that the inhibitor is preferentially adsorbed and protects the surface from attack by the acid.
Thus, the use of these inhibitors reduces the corrosion of the exposed metal surface (often by 90%), and minimizes both the loss of acid and also the volume of spray produced by the process. Inhibitors which can be used for restraining the pickling of the scale include amines, thioureas and aldehydes, all of which exist in a charged state in acidic solutions.

If the metal surface has a high negative charge, it preferentially attracts positively charged amines which, under these circumstances, act as very effective inhibitors, whereas the negatively charged thioureas or aldehydes are more suitable for a surface with a lower charge. In both these cases the charge on the metal surface is important in the adsorption and inhibition processes.

1.1.5 Benzotriazole

One of the most important inhibitors for copper is benzotriazole which can also be used as an addition agent in electroplating and it is these properties which are the main subjects of this thesis. The inhibitive aspects are considered now and the use in electrodeposition is covered in a later part of the review. (Section 1.2.7)

The structure and bonding within the benzotriazole molecule, $C_6H_5N_3$, have been widely studied and it is considered to have the arrangement shown in Fig. 1.1.5(i). The apparent dissociation constant has been determined by measuring its absorption spectra with a spectrophotometer in different solutions, and Stenström and Goldsmith found that the dissociation constant was $10^{-8.2}$, i.e. $pK = 8.2$, while Macbeth and Price observed a marked displacement in the absorption spectra, on changing the solvent from alcohol to water, a difference which they attributed to the ionization of benzotriazole that occurred in the water. Benzotriazole, with a free imino-hydrogen atom, has been shown to be strongly associated by Heafield and Hunter. In a recent book, on the dissociation constants of organic compounds in aqueous solutions, Perrin quoted a value of $pK = 8.64$ for benzotriazole and, in a paper on the thermodynamics of proton ionization in dilute aqueous solutions, Hansen et al gave a value of $pK = 8.38 \pm 0.03$.

The structure of benzotriazole in different solutions has been investigated by Fagel and Ewing. They suggested that the type of ion depended upon the acidity of the solution and proposed the three different forms shown in Fig 1.1.5.
However, Tadashi thought that benzotriazole existed in the form of an anion (Fig 1.1.5(iii)) in most solutions. A knowledge of the structure of benzotriazole in water is important in understanding its mode of action as a corrosion inhibitor.

Benzotriazole, \( \text{C}_6\text{H}_5\text{N}_3 \), is a specific corrosion inhibitor for copper and copper alloys. It is commercially available and, at a cost of £1.57 for 100g, provides a cheap and satisfactory inhibitor for most aqueous environments in which a concentration of 0.1 to 1.0 g/l is used. Its physical and chemical properties have been studied by Cotton, who found that in the pure form it melts at about 98-100°C with subsequent sublimation. The solubility in water increases from 1% w/v at 10°C to 20% w/v at 100°C and it is soluble in alkalies, 20% w/v at 20°C in 10% caustic soda, and also in acids, 50% w/v at 20°C in \( 2\text{N} \) hydrochloric acid. Benzotriazole is very stable in water and alkalies, but less so in acid solutions.
Benzotriazole has been used to inhibit the corrosion of copper and copper alloys in both atmospheric and immersed conditions for at least ten years. Surfaces exposed to the vapour, or covered with a lacquer containing this inhibitor, have successfully resisted atmospheric corrosion for several years. When added to aqueous solutions, pastes etc. it gives a marked decrease in the rate of corrosion.

These uses have been described in recent reviews in *Corrosion Engineering* (by Tadashi in Japanese) and in *Anti-corrosion* (by Walker). The fact that at least 44 patents have been granted indicates the extensive use of this inhibitor.

On metal surfaces, benzotriazole is thought to be chemically absorbed and is characterized by the properties described earlier by Hackerman. Morito and Suetaka studied the structure of the surface film formed by benzotriazole and copper and concluded that a cuprous benzotriazole compound was produced by the substitution of a hydrogen atom in the nitrogen-hydrogen group with a cuprous ion. The plane of the molecule was found to be parallel to the copper surface. Cotton concluded that the film formed is inert, stable and long lasting, so it is often possible to obtain corrosion protection over a considerable period without replenishment of the inhibitor.

A film is produced on copper surfaces in air and in close proximity to benzotriazole and prevents discolouration of the metal, which makes it particularly useful in the packaging and storage of copper articles; this vapour treatment is very suitable for components which cannot be wetted, e.g. electrical equipment. The inhibitor may be contained as a solid in packages, or the articles may be wrapped in paper which has been either impregnated with the solid or immersed in a solution of benzotriazole; after this treatment, the surfaces can withstand staining in many atmospheres, including sulphur dioxide, salt mist and hydrogen sulphide. This use of benzotriazole in the storage and transport of copper has been described by Cotton and Scholes.

Copper tarnishes or stains in the atmosphere when it is used for exterior surfaces, such as architectural metal-work, e.g. building facades, pillars, window frames and plaques.
After several years of research BMMRA have produced a transparent coating offering good resistance to outdoor exposure, including sunlight. This lacquer is called "Incralac" and is based on a specific acrylic resin with an addition of benzotriazole. Incralac became commercially available in Britain in 1964, is now widely used and has been found to give protection for more than five years. The recommended application, which must be on to a clean dry surface, is by spraying to give a minimum dry film thickness of at least $25 \times 10^{-6} \text{m}$. Because this acrylic coating is rather soft, another lacquer, based on polyurethane containing 1.5wt% inhibitor, was developed in 1967 and this gives a much harder coating. The use in other lacquers has been described recently by Christie and Carter and also Spindel.

Benzotriazole may be applied to metal surfaces by immersing the article in a hot, aqueous solution and then air drying. This technique has been used in the stabilizing of bronze objects to avoid "Bronze disease", which is an unstable form of patina resulting from the conversion of cuprous chloride on the alloy surface and often in pits and cracks. It is important to remove or stabilize this corrosion product, particularly on articles for decorative purposes. Brinch Madsen used either a benzotriazole wash or Incralac to stabilize the surface and prevent further corrosion of bronze antiques from Denmark, Egypt, England, India, Iraq and Persia with very satisfactory results. This widely employed immersion treatment inhibits the surface of copper and copper alloys which can then be used for domestic objects, because of the increased resistance to corrosion in many different environments.

However, the most extensive application of benzotriazole is as an addition to aqueous environments. It is the subject of a number of patents in antifreeze solutions, liquids used in enclosed heating and cooling systems, hydraulic fluids and detergents. The addition of 1% of the inhibitor to polishing waxes, alkaline cleaning solutions, oils and greases has prevented the rapid tarnishing of copper and copper alloy surfaces. The effectiveness of benzotriazole as a corrosion inhibitor in aqueous chloride solutions has been widely studied. Evans thought that the inhibition was due to the formation of basic copper chloride which interacts with benzotriazole to form a "blocking substance". Bonora et al., who found that benzotriazole had a marked influence on the polarization of both the anodic and cathodic processes of copper immersed in a 0.1 sodium chloride solution, also considered that benzotriazole stabilized the surface film. Tunturi showed that the inhibitor completely eliminated any weight losses of copper immersed in a 3% sodium chloride solution at 60°C.
Cotton and Scholes found that benzotriazole was a more effective inhibitor in aqueous solutions than several other similar compounds including indazole, bensimidazole, indole and methyl benzotriazole.

Many acids have been used to remove tarnish and to clean copper surfaces: the addition of 1% to 10% benzotriazole, plus 5% to 25% thiourea, to these acids has been found to inhibit corrosion of these cleaned surfaces, so the use of these mixtures in surface cleaning solutions has been patented. Benzotriazole alone has been found to satisfactorily prevent the corrosion of freshly pickled copper surfaces, although Bharucha did report the formation of visible compounds on the surface of the metal. Ross and Berry have investigated the effect of benzotriazole on the corrosion of copper in 10% sulphuric acid in a circulating flow system. A maximum inhibitor efficiency of 95% was observed, with a concentration of 0.01 M under stagnant conditions and low flow rates, irrespective of whether the acid was aerated or not. The effect of increasing the flow rate depended upon the presence or absence of dissolved oxygen. With no oxygen, the efficiency was unaffected and remained about 95%. However, the inhibitor efficiency was much lower in the presence of oxygen, with a value of 35% at a concentration of 0.01 M, and this was further reduced by the introduction of turbulent flow. Therefore, the presence of oxygen decreased the efficiency of benzotriazole as a corrosion inhibitor.

The presence of trace amounts of dissolved copper occurring naturally in waters, or from corrosion of copper surfaces, is often found to be harmful. One indication of copper ions is the bluish-green staining that may occur in sanitary fittings. As little as 0.1 parts per million of dissolved copper in water can produce a breakdown of passivity and pitting of aluminium, because the copper is deposited on to the aluminium surface and gives bimetallic corrosion. Pitting may also occur by a similar mechanism on zinc, galvanized steel, iron and steel. It is, therefore, potentially dangerous to connect copper with these metals in a water system or, to run water from copper surfaces on to these metals, for example, copper roofing with aluminium guttering is a bad combination. Dissolved copper may also have a detrimental effect in colouring or contaminating the products from the textile, food or soap industries. It can act as a catalyst in the oxidation and breakdown of antifreezes and accelerate the chemical degradation of rubber, important in the rubber hoses in car cooling systems.
In most of the above examples benzotriazole can be used to stabilize the copper in the solutions and prevent the possible detrimental effects. Wall and Davies used 100 ppm of benzotriazole to reduce the rise in the conductivity produced by dissolved copper ions in closed circuit, water cooled stators used in the power industry. In this system, if the conductivity rose above a critical value, there was the possibility of excessive energy losses, or even flashovers in the coolers, because high voltages of 6 to 8 kV were used. They found that the use of benzotriazole prevented the necessity of expensive equipment for the continuous removal of dissolved copper from the waters.

The structure and thickness of films formed by benzotriazole on copper mirrors have been studied by Poling, who used infrared reflectance spectra techniques. He correlated this information with the oxidation and reduction corrosion reactions in aqueous solutions obtained from polarization curves. These studies indicated that the thickness of the surface films was equivalent to several molecular layers of the benzotriazole complex. The initial stage in the growth of the surface film on the copper was the formation of a chemisorbed monolayer. Film thickening then occurred by the movement of copper ions in the metal to the electrolyte surface, where they reacted with the physically adsorbed benzotriazole molecules to form the insoluble copper benzotriazole complex on the surface. Because of the plentiful supply of inhibitor in the solution, the growth of the film was controlled by the availability of copper ions from the metal at the copper solution interface. Poling was able to form thick copper-benzotriazole films (400-5,000 Å), by immersing copper in benzotriazole solutions which were corrosive and increased the supply of copper ions, or contained a copper salt. These surface layers were much thicker than those used by other workers (< 50 Å) and gave excellent corrosion protection to immersed copper and also reduced the rate of oxidation of copper in air. An addition of 0.01 wt% benzotriazole to thin transformer oils was found to produce a similar thick protective film on copper in contact with it. This film prevented the corrosion of the copper and consequently the production of copper ions which promote the deterioration of the oil; therefore, the inhibitor protected both the copper and the oil.
Polarization techniques have been used to investigate the effect of benzotriazole on the anodic and cathodic reactions of copper in various solutions. By comparing the cathodic curves produced in this way, Poling showed that the films formed in oxygen-free solutions were much more protective than those obtained when oxygen was present. He also found that the anodic processes were inhibited by the high electrolyte resistance of the thick surface film. He deduced that, as well as acting as a physical barrier at the anode, the film inhibited the cathodic hydrogen evolution reaction much more effectively than the oxygen reduction reaction. These conclusions of Poling are supported by the results of Ross and Berry, who measured the rate of corrosion of copper in flowing solutions of sulphuric acid. They found that, in the deoxygenated acid, benzotriazole was very effective and reduced the corrosion by 95% but, in the presence of dissolved oxygen, the efficiency dropped to 35% or less. Thus, in the deoxygenated acid, in which the predominating cathodic process was the evolution of hydrogen, good protection was obtained because the benzotriazole inhibited this process. However, in the oxygenated acid the main cathodic reaction was the reduction of oxygen, which was not inhibited, so the benzotriazole was not nearly as effective.

In contrast, other workers have used polarization curves to study the inhibition produced by benzotriazole and they arrived at different conclusions. Dugdale and Cotton decided that benzotriazole specifically inhibited the oxygen reduction process and did not affect the hydrogen evolution process. However, in a later paper, Cotton and Giles stated that the effect on the oxygen process was very slight, and the main role of the benzotriazole was in the passivation of the copper surface. This is in good agreement with the results of Mansfeld et al., who suggested that a chemisorbed film was formed, giving passivity on the copper surface, and also that the oxygen reduction process was inhibited.
The other main difference in the results reported was that Poling produced surface films which were much thicker than those of the other workers. Mansfeld et al. duplicated, as closely as possible, Poling's experiments, but were not able to obtain films thicker than 60 Å and reported that they could not explain this discrepancy in the thickness. This disagreement must be due to some important difference in the experimental technique used to form these surface films of copper-benzotriazole.

It was generally agreed that benzotriazole formed a surface film on the copper and this produced some inhibition or even passivation. The experiments of Ross and Berry, performed in sulphuric acid, clearly indicated any changes in the hydrogen evolution reaction which is the chief cathodic process. The other workers used sodium chloride solutions, in which the predominant process was the oxygen reduction reaction, and changes in the hydrogen reaction would not be very marked. However, in the experiments of Poling, the thick films may have behaved in a peculiar manner and not in the same way as the much thinner ones. Therefore, in different circumstances, either of the cathodic processes may be inhibited and be reinforced by the formation of a protective surface film.

Benzotriazole can also be used to prevent dezincification of brass and as an inhibitor for cadmium and silver and as a restrainer in photographic emulsions and developers. With its sodium salt, it has been found to inhibit the corrosion of cast iron and steel in neutral solutions. It has been used as an addition agent in electroplating solutions of zinc, nickel, and copper. This application in the electrodeposition of copper from the acid sulphate bath will be discussed later (in Section 1.2.7)
1.2 Electrodeposition

1.2.1 General Theory

The theory of electrodeposition is now covered in considerable detail, because it is relevant to the major part of this thesis. The solubility of a metal can be altered by varying the potential of a metal in an electrolyte, and the change is indicated in the Pourbaix Diagram. This is a diagram in which the potential of a metal is plotted against the pH of water, and it is constructed from thermodynamic and solubility data. The stability of the metal is indicated by regions of corrosion or dissolution of the metal, immunity (or negligible corrosion, the concentration of the metal ions being less than $10^{-6}$ g.ion/l) and passivity (in which the metal is covered with a protective film, often oxide).

For copper in a solution of copper ions the equilibrium potential, $E$, between the metal and its ions,

$$\text{Cu}^{2+} + 2e \rightarrow \text{Cu}$$

is given by the Nernst Equation:

$$E = E^o + \frac{RT}{nF} \log_{10} \frac{a_{\text{Cu}^{2+}}}{a^0_{\text{Cu}^{2+}}}$$

For copper at 298°K this becomes:

$$E = +0.34 + 0.0295 \log_{10} a_{\text{Cu}^{2+}}$$

Where $E = \text{actual electrode potential}$

$E^o = \text{standard electrode potential}$

$R = \text{gas constant, } 8.314 \text{ joules/deg.mole.}$

$T = \text{temperature in degrees absolute, } 298^0\text{A}$

$n = \text{number of electrons}$

$F = \text{Faraday} = 96,500 \text{ coulombs}$

$a_{M^{n+}} = \text{activity of metal ions}$

If the potential of copper is raised from the standard equilibrium value, $E^o = +0.34V$, by an external source, then the activity and the concentration of the copper ions must increase to achieve a new equilibrium. This is obtained by the dissolution of copper, which occurs until equilibrium is again reached, and this dissolution is called the anodic process. If the potential is lowered, deposition of metal ions occurs until equilibrium is attained and this is the cathodic process. These are the thermodynamic aspects of electrodeposition and indicate the relative stability of a metal and its ions at different potentials, but the rates of these processes are not given.
The rate of deposition is a function of the current density at the cathode. When a metal is in equilibrium with its own ions, a very small current flows in each direction and this is called the exchange current, although no net current passes. As the potential of the metal is changed from the standard equilibrium value, $E^0$, a net current flows and the variation in the potential, $\Delta E$, the overvoltage, is given by $\Delta E = E^0 - E$. This change from the standard equilibrium value of an electrode is also called the polarization, and it is equated with the current density, for potentials greater than 0.05V, by the Tafel Equation:

$$\eta = a + b \log i$$

Where $\eta$ = polarization, $a, b$ = constants, $i$ = current density

The total polarization of a cell may be subdivided into three main types:

1. Activation polarization, which is concerned with the charge transfer step in the inner part of the electrolytic double layer;
2. Concentration polarization, which is related to the changes in the concentration of the electrolyte in the anodic and cathodic regions;
3. Resistance polarization, which covers the resistance in the electrolyte together with any films on the surface of the electrodes.

Knowledge of these individual forms of polarization is important, but it is the total value that is the main consideration in electroplating. It forms part of the voltage drop across the cell, which determines the current, and hence the anodic and cathodic current densities. Therefore, any factors which increase the polarization, such as the formation of surface films, decrease the rates of dissolution and deposition.

The current efficiency may also affect the rate of deposition of a metal at the cathode. This is that fraction of the total current which is used to deposit metal at the electrode, while the remaining current may liberate hydrogen or react with impurities at the surface. For the normal copper sulphate-sulphuric acid plating bath, the current efficiency depends upon the polarization and is usually almost 100%.
1.2.2 Crystal Growth from the Vapour Phase

The earliest work on the growth mechanisms of metal deposits on metal substrates was carried out from the vapour phase. The conclusions from these studies, which will now be discussed, were then modified and developed for the nucleation and growth processes in electrodeposition.

The essential ideas of the growth of perfect crystals were put forward by Gibbs in 1878 and extensively developed by many others\textsuperscript{83-86}. It was considered that an atom in the vapour landed on a metal surface and then diffused to a suitable lattice site, such as those at the edges of monomolecular steps and particularly at kinks in these steps. Growth continued until all these stepped surfaces had disappeared and a perfect lattice plane had been produced. Further crystal growth then depended upon the formation of two dimensional nuclei, consisting of new molecular layers on the surface. The probability of the formation of these new nuclei is very dependent upon the supersaturation of the vapour; below a critical value (about 25-50\%) it is quite negligible, but increases very rapidly above this value\textsuperscript{87,88}. However, real crystals grow at supersaturations of 1\% or lower, at which no nucleation should occur, according to this theory\textsuperscript{89}.

Frenkel\textsuperscript{90} suggested that the surfaces of perfect crystals above the absolute zero of temperature have a certain roughness, produced by thermal fluctuations, and he proved that these surfaces would contain a large number of kinks; this was later confirmed\textsuperscript{89}. For continual growth, a high degree of saturation is still necessary to give a supply of new nuclei. However, this formation of new nuclei is unnecessary, if the imperfections on the crystal surface include screw dislocations which produce self perpetuating growth steps\textsuperscript{87,91}. These dislocations have been widely observed in deposits\textsuperscript{91-93} and are the basis of the modern theory\textsuperscript{89,94-97}.
1.2.3. **Crystal Growth by Electrodeposition**

The main differences between electrodeposition and vapour deposition have been listed by Bockris and Damjanovic\(^7\) as:

1. the existence of an electric field;
2. the presence of adsorbed layers of anions, water molecules and metal adions;
3. the particles which reach the surface are charged and not neutral;
4. the velocity of arrival of ions at a cathode is much slower than from a vapour.

However, although these differences exist, there are some similarities in the mechanisms of growth, such as growth on screw dislocations, which will be discussed later.

The principal growth forms on single crystal faces have been reviewed by Bockris and Damjanovic\(^7\) and may be in the form of layers\(^3,98\), blocks\(^98-100\), pyramids\(^93,100,101\), ridges\(^98-100\), spirals\(^93,102\), dendrites\(^103,104\), whiskers\(^105,106\), and many polycrystalline. Most of these features are very dependent upon the plating variables, polarization, substrate morphology, temperature and particularly impurities which may be adsorbed on the surface\(^93,98,107,106\).

Polycrystalline growth may be considered to consist of three stages\(^109\):

1. the initial growth, which is determined by the structure of the substrate (in thin deposits only);
2. a transitional stage, in which twinning may occur giving polycrystalline structure;
3. the final stage, in which the structure of the deposit is characteristic of the conditions of deposition and independent of the substrate (in thick deposits). The thickness at which the transition occurs depends upon the plating conditions, and, if the current density is increased, it takes place earlier in thinner coatings\(^110\).

One fundamental aspect of the process of electrodeposition is the method of transfer of the hydrated ions in the solution to the lattice sites. Bockris and Reddy\(^111\) suggested that an indirect path, involving surface diffusion, is more probable than the direct discharge of the ion at the lattice site. After the ion is adsorbed on the surface, it must move to the growth site, probably by surface diffusion to a step site and then via the step to the kink site,
where it is incorporated in the lattice. This surface diffusion is considered to be the rate controlling step in the electrodeposition of copper at potential near to the reversible value.

In the deposition of copper from the cupric ion, it is thought improbable that the transfer of two charges can occur in one step. Mattson and Bockris have found that the process is from the cupric ion to the cuprous ion and then to copper. It is the first of these changes, cupric to cuprous, which is the rate controlling step, and this has been confirmed by using a rotating disc cathode to assist the diffusion processes.
1.2.4

Nucleation and the Early Stages of Growth of Copper Electrodeposits

The nucleation and growth of deposits appear to have a significant effect on their physical and chemical properties, so that a considerable amount of work has been carried out in this field of study. Pick et al.\(^{99}\) have extensively investigated the structure of copper deposited from purified copper sulphate-sulphuric acid solutions on to copper single crystals of different orientations. In the very early stages of deposition, isolated growth centres or layers developed, which were bounded by facets with low crystallographic indices. The growth of surface features varied considerably, both in the appearance and the nature of the dominant crystal faces, and depended upon the crystallographic orientation of the cathode surface, while the surface topography was found to coarsen as the plating time increased. The nucleation\(^{117}\) of copper deposits was assisted by the presence of impurities and involved the spreading of flat disc-like nuclei, as would be expected from the classical mechanisms already discussed.

Deposits on copper single crystals have a structure which depends upon the plating conditions\(^{118-120}\) and have the same three characteristic stages of growth\(^{121}\) (epitaxial, twin and polycrystalline) as have been previously reported for silver\(^{110}\). The thickness just prior to polycrystalline growth has been hyperbolically related to the current density\(^{121}\), high current density giving the thinner deposits. At low current densities the rate of discharge of metal ions was sufficiently slow for the atoms to arrive at the correct lattice sites, so that few nuclei formed and these grew laterally to give flat surfaces. Therefore, this epitaxial growth continued to large thicknesses of the coating. At higher current densities more nuclei formed epitaxially and grew, but did not join together perfectly and faults were produced\(^{122,123}\).

The above work supported the prediction of Burger\(^{124}\), that if the rate of addition of atoms to a surface is sufficiently high, there is an increased probability that atoms arriving at twin positions remain, are joined by others and grow. Deformation of the deposit may occur as the concentration of the twins, stacking faults and dislocations increases. Rearrangement in the structure and the formation of nuclei with different orientations give polycrystalline growth and perhaps internal stress.
1.2.5 The Structure of Copper Deposits

The structure of deposits is very important because it has a profound effect on the properties of the coatings, for example, the hardness and stress may be very high for deposits with small grain size. There have been many attempts to classify the different types of structure produced during plating, but it is often difficult to distinguish between similar structures, as they depend upon the plating conditions and different combinations and transitional forms may occur.

Weil and Read \(^{125}\) divided the microstructures of metals, including copper, deposited from pure plating solutions (without addition agents) into those without and those with a preferred direction of growth. A more comprehensive classification, was suggested by Fischer \(^{126}\), on the basis of the growth habit, as seen under the optical microscope:

1. field orientated isolation type growth of single crystals, which may be very large with dendritic branching;
2. basis orientated reproduction growth, in which the crystallites in the coating are parallel to those in the substrate and normally occurs if few nuclei form on a chemically polished cathode and large crystallites are allowed to grow;
3. field orientated texture type, which shows marked preferential growth in the direction of the lines of the electric field, normally with a fibrous texture;
4. twinning intermediate type, i.e. the transition between the basis and the field orientated growth discussed in Section 1.2.4;
5. unorientated dispersion growth, which shows a random arrangement with no preferred orientation.

The first two groups are not normally observed in commercial plating, because these forms of growth are easily inhibited by the presence of impurities. Field orientated isolation growth gives individual crystals, which do not form the continuous coatings required in practice, so that growth of the single crystals is deliberately inhibited by the use of certain addition agents and better deposits are formed.
The second group, basis orientated deposits, are produced from pure solutions on chemically or electrochemically cleaned surfaces, where the orientation effect of the base metal affects the deposit. The mechanically polished surface normally used in commercial plating is covered with a Beilby layer of unorientated crystals and metal oxide, so that basal orientation of the deposit is prevented. In copper plating from the pure acid bath, the basis orientated reproduction growth is encouraged by the use of a low current density and high bath temperature with a chemically clean substrate. The use of low concentrations of an addition agent such as 0.16 g/l acridine$^{127}$, 0.017 g/l chloride ion$^{128}$ or 1.0 g/l p-phenolsulphuric acid$^{129}$ may give a similar growth structure with grain refinement.

Field orientated texture growth can be obtained from the copper sulphate bath at low temperatures, or by the use of an addition agent, e.g. 1.3 g/l asparagine$^{130}$, 0.09 g/l β-naphthoquinoline$^{131}$, 0.1 g/l gelatine$^{132}$ or 0.1 g/l thiourea$^{133}$. Unorientated dispersion growth, with a grain size that is too small to observe with an optical microscope, has been plated from the copper sulphate bath, with a higher concentration of the same addition agents which gave the field orientated texture previously described, e.g. 13.0 g/l asparagine$^{134}$, 0.2 g/l gelatine$^{132}$, 1.8 g/l β-naphthoquinoline$^{131}$ or 12.9 g/l quinoline$^{127}$. The use of 0.012 g/l benzotriazole$^{69}$ has also been found to give this type of structure.

Fischer did not mention the banded deposit which has been described by Lamb and Valentine$^{134}$ and is often obtained in deposits from the copper sulphate bath with an addition agent, e.g. 0.024 to 0.08 g/l benzotriazole$^{69}$, 6.5 g/l asparagine$^{135}$, 9.2 g/l brucine$^{135}$ or 0.04 g/l thiourea with 0.8 g/l molasses$^{136}$.

From these classifications, it is obvious that impurities or addition agents have a very considerable effect on the structure of electrodeposits. The use of these chemicals is very important, because the modifications produced in the structure alter the physical and chemical properties of the coatings. In commercial plating, the careful use and control of addition agents gives deposits with desirable properties, e.g. increased brightness or hardness, and the use of these compounds will now be discussed.
1.2.6 The Use of Addition Agents in Electroplating

The presence of small amounts of certain substances in plating baths may, as has already been mentioned, have a marked effect on the nucleation and growth mechanisms, as well as on the properties of the deposits. These substances may occur naturally in the plating bath and are called impurities, or may be deliberately used as addition agents to give some desired improvement in the deposit, such as a smooth or hard surface.

It is rare in normal practice for a metal to be electroplated in a perfectly pure form. Brenner¹³⁷ found that all electrodeposited metals contained minute impurities of hydrogen, oxygen and other elements derived from the bath, but these did not appreciably affect the properties. However, under certain circumstances, the impurity content was much higher (several percent) and the properties of these deposits were considerably changed.

The presence of hydrogen, codeposited from the acid bath in nickel and chromium electrodeposits, has been proved by the method of vacuum heating followed by analysis. This gas in the deposit produces a strained lattice which results in internal stresses in the coatings, as well as increasing the hardness¹³⁸. The presence of high concentrations of other impurities may have a similar effect on the hardness, for example, as much as 10.7% bromide has been reported in copper deposits from a bromide bath¹³⁹.

Addition agents can be used to modify the brightness, levelness, hardness, adhesion, strength, electrical resistance, internal stress, porosity and grain size of deposits¹³⁷-¹⁴³. Normally, there is some codeposition of the addition agents which results in the change in the mechanical properties. Thus, Zentner et al¹⁴¹ concluded, from their results on the effect of addition agents, that "substances present in the plating solution affect the properties of the electrodeposit only to the extent that they influence the co-deposition of foreign material". Thus, surface active agents have a much greater effect than compounds which are dispersed homogeneously in the solution and not preferentially adsorbed.

A summary of some of the important effects of addition agents can be represented in the form of a flow chart, Fig 1.2.6, based upon the work of Edwards¹⁴⁴.
Marble, who studied the effect of 76 different addition agents on the mass and structure of copper deposited from the acid bath, concluded that there is no single relationship between the type of the deposit and the chemical nature of the addition agent. This does not necessarily disagree with the observation of Zentner et al, who studied the effect of the chemical nature of the addition agent when incorporated and combined into the deposit, rather than that of the free addition agent in the plating solution. Marble found that the structure of the electrodeposited copper depended upon many factors including the solution composition, current density, temperature and agitation, as well as the presence of addition agents.
Eichkorn and Fischer have discussed the influence of surface active substances on the base and field orientated types of deposit and found that impurity molecules in the plating solution increased the distortions of the lattice and consequently affected the properties of copper electro-deposits, such as the electrical resistance and hardness; this modification of the structure has also been described elsewhere. The adsorption of the impurity molecule on to the cathode surface is very important in the surface diffusion, nucleation and growth of the electrodeposits; this process depends upon both the adsorption energy and the concentration of the impurity in the solution. The type of nucleus formed is modified by the adsorption of the impurity and the distribution is determined by different factors including the activation energy of different sites, the frequency of total nucleation, the preferred nucleation at certain crystallographic sites and the velocity of the growth of such nuclei into preferred crystallographic directions. Generally, as the concentration of impurity increases, the grain size of the deposit decreases, which causes an increase in the disorder, grain boundary density and dislocation density.

It has been suggested that, as the molecular size of the surface active material increases, the degree of adsorption is increased and a greater change is observed in the properties of the deposits. Changes in the structure of an electrodeposit may be caused by several factors. As an increasing area of the surface is covered by adsorbed material, the lateral growth of crystallites may be encouraged and a levelling effect produced as discussed elsewhere. Also, as the density of the coverage increases, the surface tension decreases, so that the rate of nucleation and the probability of a transformation from two dimensional to three dimensional nucleation are both increased. This has been found to happen with copper deposits from the acid bath with increasing concentration of O-phenanthroline. At concentrations of less than $10^{-5}$ mol/l the base orientated type of structure was produced, with less than $5 \times 10^{-4}$ mol/l the field orientated texture was formed and at about $5 \times 10^{-3}$ mol/l the non-orientated dispersion growth occurred. Thus, as the concentration of the inhibitor increases, the nucleation and growth are both affected.
The presence of gelatine is known to affect the nucleation of copper from the acid bath. Adsorption occurs at growth sites and it has been found that only a few molecules of gelatine are required to inhibit pyramidal growth, compared with the much more stable cubic layer growth. The concentration of gelatine decreased as the plating time increased, which suggests that it was codeposited and this has been confirmed by the fact that cross-sections of the deposit have been shown to consist of alternate layers rich in copper and gelatine. This is another example of the banded structure described in Section 1.2.5 and of adsorption affecting both the nucleation and growth mechanisms.

In copper plating from the sulphate bath, addition agents have been used commercially for brightening, surface smoothing, grain refining, increasing the limiting current density and the hardness, reducing treeing and internal stress. However, the conditions for the use of a particular addition have to be evaluated for each application, so that the undesirable characteristics can be avoided, for example, the production of a bright surface is not satisfactory if it is highly stressed and peels.

1.2.7 Benzotriazole as an Addition Agent

Benzotriazole has been found to have a marked effect on the properties of electrodeposited copper. This compound is also a corrosion inhibitor for copper and copper alloys and this property has been discussed in Section 1.1.5. The effect of the addition of this compound to copper plating solutions is the major aspect of this thesis and, therefore, the literature is reviewed comprehensively.

The first work on the use of benzotriazole as an addition agent in the copper sulphate-sulphuric acid plating bath was carried out by Prall and Shreir. This was probably the first deliberate attempt to co-deposit a known corrosion inhibitor in a metallic coating. If the plated surfaces
were exposed to corrosive environments, which would allow the deposit to release the inhibitor, an improved corrosion resistance would be obtained. This was observed when the coatings were immersed in hydrochloric sulphuric acid and the codeposited cuprous benzotriazolate was slowly oxidized by dissolved oxygen to give cupric ions and benzotriazole, which inhibited the rate of corrosion of the copper deposits.

The effect of benzotriazole on the surface topography has been studied by Prall, who found that the copper deposited was coherent and highly reflective when the concentration of the addition agent was about 0.24 g/l. At very low concentrations the deposits were coarsely crystalline, but with more than 0.024 g/l they became more reflective.

When cross-sections of the deposits were examined, a layered or banded structure was observed if the plating solutions contained more than 0.048 g/l, but below this there was no banding. However, banding could be induced into deposits with less than 0.048 g/l, by switching off the current to allow a surface film of benzotriazole to form, and then plating again. The cross-sectioned deposit showed a band for every occasion that the current had been switched off, provided that a sufficient period of time was allowed for adsorption and film growth. It has been found elsewhere that this film produces a weak bond with the metal surface and the deposits subsequently plated were easily detached without damage. This procedure has been utilized in the stripping of copper coatings from substrates for use in the production of foils and other electroformed articles.

Prall and Shreir were able to prove that the copper deposited from these solutions contained undecomposed benzotriazole, which was recovered and determined quantitatively by a process of solvent extraction followed by a displacement reaction with silver ions. In this manner they analysed the deposits and found that the inclusion concentration was a function of both the electrolyte composition and the plating variables. The inclusion content of benzotriazole in mg per lg copper varied with the following:
(1) The concentration of benzotriazole in the plating solution, from 0.010 mg (with 0.00008 g/l) to 2.925 mg (with 0.240 g/l);

(2) the plating bath temperature, showing a decrease from 2.560 mg at 25°C to 1.390 mg at 45°C and then an increase to 5.010 mg at 75°C;

(3) the current density, from 0 mg with 700A/m² to 3.065 mg with 25A/m²;

(4) the concentration of copper sulphate which ranged from 4.5 mg with 20 g/l to 5.0 mg with 30g/l and then to 1.7 mg with 350 g/l;

(5) the concentration of sulphuric acid, showing a rise from 0.860 mg with 0.35 ml/l to 2.720 ml/l and then a drop to 0 mg with 250 ml/l.

Agitation of the cathode increased the brightness of the deposits and gave a pronounced increase in the inclusion content from 2.650 mg with a still cathode to 6.295 mg when the amplitude of the cathode was 2 x 10⁻³ m. Air agitation of 23.0 ml/s resulted in an even higher inclusion of 7.740 mg and very bright deposits. Solution agitation produced an initial decrease (2.700 mg to 1.070 mg), followed by an increase to 4.870 mg. Therefore, it follows that by varying the plating conditions, the amount of the inclusion can be carefully controlled, together with the surface brightness and appearance.

Prall also proposed a physical model to explain the banded structure and different inclusion concentrations found in these deposits.

The following possible mechanisms for the entry of benzotriazole into the copper deposits were also considered:

(1) benzotriazole chelates with the copper surface, which is continually being re-formed during deposition, so becomes included in the growth;

(2) soluble complexes of cupric benzotriazolate which exist in the solution may become included in the deposit;

(3) the benzotriazole reacts with the transient cuprous ions (present during the deposition process) to form an insoluble complex on the plating surface, which then becomes included in the deposit.

The first mechanism appeared to be supported by the fact that film formation occurred when copper was immersed in a benzotriazole solution. The diffusion of benzotriazole to the metal surface is the main factor affecting
the inclusion content in this process. It was, however, discounted because the inclusion content was found to depend upon many other factors which do not affect the diffusion processes in the solution, such as the concentrations of copper sulphate and sulphuric acid in the plating bath. The second mechanism was not supported by the decrease in the amount of inclusion with an increase in the copper sulphate concentration of the bath. Also, the fact that the inclusion content was related linearly with the cuprous ion concentration, and only to the square root of the cupric ion concentration, suggests that the inclusion was cuprous benzotriazolate.

In the deposits from solutions containing different volumes of sulphuric acid, the maximum inclusion content was in the range where cuprous benzotriazolate is precipitated (about pH = 1), whereas, above a pH of about two, a turquoise precipitate of the cupric complex was observed, accompanied by a decrease in the inclusion concentration (2.72 mg at pH = 1.52, 1.27 mg at pH = 2.05, and 0.86 mg at pH = 2.38). Therefore, it was thought more probable that the cuprous, and not the cupric form, became included in the deposit. Factors such as agitation, which increase the diffusion of benzotriazole in the solution, assist the formation of the complex and increase the amount of inclusion.

The formation of the cuprous and cupric complexes in different solutions has also been studied by Gerenrot and Eichies\textsuperscript{72}. They found that in the acid bath the cuprous form was present with up to 0.25 g/l benzotriazolate in the solution, but above this level the cupric compound was produced. This is in agreement with Prall and Shreir\textsuperscript{69}, who used solutions with up to 0.24 g/l and found the cuprous form was stable.

The mechanical properties of these deposits were not studied by Prall\textsuperscript{71}, except for the observation that certain coatings were stressed. He found that by varying the concentration of the copper sulphate in the bath, the stress could be varied from tensile (60 g/l) to zero (125 g/l) and to compressive (180 g/l), but the magnitude of these stresses was not determined. Several
physical and chemical properties of these deposits have been investigated
by Kendall\textsuperscript{68}, who studied the internal stress, hardness, strength and
corrosion resistance.

Kendall\textsuperscript{68} used 125 g/l analar copper sulphate and 49 g/l microanalar
sulphuric acid in his plating solution, which was purified by refluxing with
hydrogen peroxide to oxidize impurities, then treated with activated charcoal
to absorb them. The anode and cathode were separated by a porous pot to
prevent any decomposed anodic products from affecting the deposition processes
at the cathode.

The surface of the pure deposits was coarse and angular, but an addition of
up to 0.024 g/l benzotriazole produced grain refinement and a mat finish\textsuperscript{68}.
With 0.048 g/l the deposits were bright and had a fine nodular growth, the
nodules becoming larger and flatter as the concentration increased to 0.24 g/l
at which value a bright surface was produced. Epitaxial growth from the
substrate was eliminated by an addition of 0.01 g/l, and a similar change
has been observed with other addition agents\textsuperscript{167}. Cross-sections of the
deposits showed that banding started at concentrations above 0.06 g/l, which
is in close agreement with the figure of 0.048 g/l quoted by Prall\textsuperscript{71}.

The internal stress in copper coatings was measured by Kendall\textsuperscript{68} with the
spiral contractometer and continuous readings were taken up to a deposit
thickness of $3.8 \times 10^{-5}$ m. These results are summarized for the maximum
thickness in Table 1.2.7 (a) overleaf.
These results indicate that a compressive stress is favoured by:

1. a high bath temperature;
2. a low current density;
3. a high concentration of benzotriazole in the solution.

However, the tensile stress value of 68.9 MN/m² seems to be very high for copper deposited from the plain bath at 25°C and with a current density of 200 A/m². Using similar conditions Fischer et al. obtained a tensile stress of 9.65 MN/m² and Safranek quoted a range from 5.5 to 30 MN/m²; and other values are given in Tables 1.3.3 (a) and (b); therefore, the stress in solutions containing benzotriazole was investigated in this work.
The hardness of coatings was measured with a GKN microhardness tester and some of the results are given in Table 1.2.7 (b)

<table>
<thead>
<tr>
<th>Conc. of Benzotriazole g/l</th>
<th>Current Density A/m²</th>
<th>Temperature °C</th>
<th>Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>200</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>0.06</td>
<td>&quot;</td>
<td>&quot;</td>
<td>207</td>
</tr>
<tr>
<td>0.22</td>
<td>&quot;</td>
<td>&quot;</td>
<td>201</td>
</tr>
<tr>
<td>0</td>
<td>&quot;</td>
<td>45</td>
<td>60</td>
</tr>
<tr>
<td>0.22</td>
<td>&quot;</td>
<td>&quot;</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 1.2.7 (b)

At a bath temperature of 25°C the hardness rose with concentration to a value of HV 207 with 0.06 g/l and then fell; however, at 45°C, the hardness gradually increased to HV 150 with 0.22 g/l but, at this temperature, no decrease was observed. An increase in temperature produced a reduction in the hardness at all the concentrations used.

The tensile strength of the coating was measured after removal from the substrate. The strength of the pure deposits was 296 MN/m², which increased to 469 MN/m² with an addition of 0.01 g/l benzotriazole. However, the value fell with higher concentrations to a constant value of 255 MN/m² which is below that for the pure deposits; with more than 0.03 g/l the deposits were too brittle to test. A similar peak has been observed with copper deposits using Rochelle Salt (potassium sodium tartrate) as an addition agent. However, the most important conclusion from this work was that Kendall found that the deposits containing cuprous benzotriazolate did not resist corrosion as well as the pure copper deposits. The coating also tarnished rapidly under wet atmospheric conditions. This observation was based upon both corrosion tests and polarization experiments on plated surfaces which had been polished to remove the film of benzotriazole adsorbed from the plating solution, and they were then soaked in water for 30 minutes to remove any surface effect.
He considered that two processes controlled the inhibitive properties of the codeposited cuprous benzotriazolate. The first was the availability of a sufficiently high concentration of the inhibitor in the deposit; the second was the ability of the benzotriazole, released from the deposit, to distribute itself rapidly over the whole area exposed to the corrosive environment. The results in his work indicated that there was an insufficient concentration of the inhibitor in the deposits and also that it did not cover the total area rapidly. These results do not seem to confirm the preliminary tests of Prall, who only washed the plated specimens and used them without the surface polishing. Therefore, his specimens were covered with the insoluble adsorbed layer of benzotriazole from the plating bath which, probably by itself, could give the corrosion protection recorded. In his work Kendall allowed only the codeposited cuprous benzotriazolate below the plated surface to act as an inhibitor. Thus, it appears that benzotriazole can act as an inhibitor when adsorbed on the plated surface, but it is unable to give protection when codeposited within the coating.

It may be concluded that the addition of benzotriazole to the acid copper sulphate bath modified the structure and properties and produced a deposit with:

(1) a bright surface;
(2) a banded structure;
(3) the incorporation of undecomposed benzotriazole in the form of cuprous benzotriazolate;
(4) an increased internal stress, in either a compressive or a tensile direction;
(5) an increased hardness;
(6) an increased tensile strength;

The magnitude of each of these changes depended upon the concentration of benzotriazole used in the solution and the plating conditions.

All the above results were obtained using highly purified solutions with the copper anodes surrounded by porous pots which isolated any decomposition products formed by the benzotriazole at the anode from the electrolyte. In this present work, laboratory grade chemicals were used and the anodes were not isolated, in order that the results obtained would be more relevant to commercial applications. All the above modifications to the plated copper
were systematically investigated, except the determination of the inclusion content, comprehensively covered by Prall, and the tensile strength.

1.3. Properties of Electrodeposits

1.3.1 Introduction

It is well established that the properties of a plated metal, such as the grain size, hardness and internal stress, are mainly determined by the composition of the plating bath and the conditions of deposition. Because the properties are largely dependent upon the structure of the coating, the relationships between the properties and the structure have been widely studied. Several general rules, indicating the effect of plating variables on the grain size, have been formulated by Butts and De Nora and these are now summarized.

The grain size of a deposit decreases with:

(1) an increase in the current density;
(2) a decrease in the bath temperature;
(3) a decrease in the concentration of the metal ion;
(4) an increase in the cathodic potential;
(5) the presence of addition agents;
(6) the presence of other ions, especially those forming a complex ion of the metal being deposited;
(7) an increase in the stirring rate or agitation, although an increase in the grain size has sometimes been observed.

The grain structure of very thin deposits tends to follow that of the basis metal during epitaxial growth but, at a greater thickness, it changes according to the plating conditions. However, none of the above conditions of electrolysis appears to be an independent variable, so that a change in one normally affects at least one of the others and it is difficult to isolate the separate effects.

The grain size has a very pronounced effect on many of the other physical and mechanical properties of an electrodeposited metal. These effects have been widely studied, in order to determine the most suitable plating condition necessary to obtain the desired properties, for a particular metal coating.
Many workers have found a strong correlation between a high hardness and a small grain size, or factors which produce a small grain size. Several papers have been published, including those by MacNaughton and Hothersall, Arkharov and Nemnonov, Hofer and Hintermann, and all suggested that the hardness was connected to the grain size. MacNaughton and Hothersall thought that different packing within the crystal lattice could account for variations in the hardness for a given grain size. Jindal and Armstrong produced the following equation, which is similar to the Hall-Petch formula, relating the hardness and the average grain diameter:

\[ H = H_0 + kd^{\frac{1}{2}} \]

Where
- \( H \) = hardness number e.g. HV
- \( H_0 \) = a constant characteristic of dislocation blocking
- \( d \) = average grain diameter
- \( k \) = a constant related to the penetrability of the boundaries for moving dislocations.

This equation has been found to be satisfactory for electrodeposited iron, as well as for heat treated metals. Mohrheim has produced a different equation for pyrometallurgical iron:

\[ H = a + b \log_{10}d \]

Where
- \( H \) = hardness number e.g. HV
- \( d \) = average grain diameter
- \( a, b \) = experimental constants

Semi-logarithmic relationships have also been reported between the hardness and crystal size of nickel deposits, but no quantitative relationship was given.

The mean grain diameter has been related to the yield strength of a metal. Bragg suggested an equation of the form:

\[ S \propto \frac{1}{d - d_0} \]

Where
- \( S \) = yield strength
- \( d \) = average grain diameter
- \( d_0 \) = limiting grain diameter
Baldwin proposed the experimentally determined relationship:

\[ S = k d^{-1/5} \]

Where \( S \) = yield strength

\( k \) = a characteristic constant

\( d \) = average grain diameter.

Several workers have noted a correlation between a small grain size and a high tensile stress in electrodeposits, and the stress itself has been associated with an increased hardness. Riedel used X-ray analysis to measure the stress in copper deposited from different baths, and found that the hardness and internal stress were closely related.

The effect of different plating variables on the grain size, internal stress and microhardness of copper deposits will now be reviewed, because these are particularly important and relevant to the present work.

1.3.2 Grain Size

There is not much published work on the variation of grain size in electrodeposits produced by different plating conditions. The early studies have been comprehensively reviewed by Butts and DeNora, who listed the effects of different variables on the grain size of deposits, which are summarized in Section 1.3.1. From their own results they showed that the grain size, measured by the intercept method, decreased with the current density and increased with the bath temperature. The change in the mean grain diameter was from about \( 5 \times 10^{-5} \text{m} \) (with \( 600 \text{A/m}^2 \)) to about \( 12 \times 10^{-6} \text{m} \) (with \( 750 \text{A/m}^2 \)) at \( 20^\circ \text{C} \). With a current density of \( 500 \text{A/m}^2 \) the grain size increased with the bath temperature from \( 1.4 \times 10^{-6} \text{m} \) (\( 20^\circ \text{C} \)) to \( 2 \times 10^{-6} \text{m} \) (\( 30^\circ \text{C} \)) and \( 3 \times 10^{-6} \text{m} \) (\( 50^\circ \text{C} \)); a larger increase was observed at higher current densities. In a recent article, Lamb et al confirmed that the grain size decreased with a decrease in temperature or with an increase in current density, but unfortunately they did not give any quantitative data. The use of addition agents in the plating bath has been found to produce a considerable decrease in the grain size of the deposit.
The effects of these three variables, current density, bath temperature and role of addition agents, are particularly important and are now discussed further. An increase in the current density, at a fixed temperature, increases the rate of arrival of ions at the cathodic surface: this causes less surface diffusion and results in more nucleation and a smaller grain size. An increase in the bath temperature, at a fixed current density, raises the ionic mobility and surface diffusion, so results in a larger grain size. The addition agents, which are normally surface active, preferentially adsorb on the cathodic surface, prevent epitaxial growth, encourage the formation of nuclei and a smaller grain size.

1.3.3. Internal Stress

The internal stress in an electrodeposited coating is of particular interest, because it may cause such harmful effects as the cracking, peeling and blistering of the deposit, which lead to the corrosion of the substrate metal; other undesirable properties include geometrical distortion of electroformed components, poor adhesion and fatigue, as well as an increased hardness, brittleness and porosity. The factors which affect the internal stress in deposits have been investigated because of the above undesirable characteristics.

Metals are normally deposited in a stressed condition. This is probably due to the small volume change in the deposit that occurs during, or soon after, plating and results in an internal stress, if it is restrained by the basis metal. The stress may be tensile, and tend to contract the deposit, or compressive, and tend to expand the deposit. The numerical value given to the internal stress is the force per unit area acting in a direction parallel to the plated surface; it may be as high as 2,270 MN/m² (tensile) for chromium or 276 MN/m² (compressive) for tin-nickel.

The literature up to 1968, on the measurement and proposed theories of internal stress, has been covered in detail by the author in a monograph and in a review by Weil. Similarly, the engineering aspects of internal stress are not discussed because they are in another article, which is bound at the end of this thesis.

The simplest and the most widely used mechanical means of measuring the internal stress in electrodeposits is based upon a flexible cathode. The
cathode, which is a thin metal strip insulated on one side, bends when plated on the other side and the stress in the coating is calculated from the deformation. There are several bent strip methods and these may be divided according to whether the cathode is free to move during deposition or not. If it is free to move, as in the Brenner Senderoff Spiral Contractometer \(^{192}\), the stress in the first few layers of the metal deposited is allowed to relieve itself by bending the substrate and the next layers are plated on a bent surface. The value of the stress obtained is appropriate to that on a thin deformable substrate, for example, in electroforming. If the strip is restrained, as in the Hoar-Arrowsmith Apparatus \(^{193}\), each layer is plated on to a relatively flat, unrelieved surface and the stress value obtained is more applicable to deposition on to thick substrates, for example, car bumpers. Normally the methods in which the cathode moves give a lower value for the stress than those with a fixed cathode. Details about the operation of the Hoar-Arrowsmith Apparatus and the Brenner Senderoff Spiral Contractometer, which were both used in this work, are given in the experimental sections 2.4.5.

A brief summary of the theories which have been proposed to explain the origin of stress is now included. One of the earliest theories \(^{194}\) was that the internal stress in the deposit depended upon the difference in the lattice parameters of the substrate and deposit. Although a correlation was shown between these parameters, neither the stress in a metal deposited on a substrate of the same metal nor the stress in very thick coatings could be explained, so this theory is only applied to very thin coatings. Most of the other theories are based upon the formation of a metastable deposit, which changes in volume immediately after deposition and results in a stress being formed. The excess energy theory assumes that the ions in the electrolytic double layer, on the surface of the cathode, are at a high temperature and are deposited to form a thermally expanded lattice which gives a tensile stress on cooling. This can only explain the formation of a tensile stress and never a compressive stress. The hydrogen theory considers that codeposited hydrogen is incorporated into the deposit and causes a temporary expansion in the plated metal. The hydrogen subsequently diffuses away and the deposit contracts to give a tensile stress. Hydrogen undoubtedly
plays an important role in the formation of stress in those metals which are codeposited with hydrogen, such as chromium and nickel, but this theory is not a probable cause for the stress in copper, when plated without hydrogen at a current efficiency of approximately 100%.

Most of the other theories are based upon the inclusion in the deposit of water molecules or foreign particles, either impurities or addition agents. The presence of these substances in deposited metals has been confirmed for many systems, including the incorporation of cuprous benzotriazolate in copper plated from the acid bath containing benzotriazole. These compounds can have several effects and may:

1. be deposited in a deformed state, (resulting from the electrostatic charge in the cathodic double layer), and then change to a more stable form;
2. diffuse in the coating and give a volume change;
3. change their shape, or form compounds with the metal;
4. concentrate at grain boundaries and act as wedges between the grains;
5. affect the number and distribution of dislocations in the deposit, which may create local stress fields.

All these theories may, individually or collectively, create either compressive or tensile stresses in the deposited metal. In a recent review of the origins of stress in electrodeposits, Weil stated that "it appears that there is not one single cause of internal stress". Then, by a process of elimination, he concluded that the dislocation theory could explain all the observed phenomena in a logical way. However, the stress in a deposit may be the result of several effects, which vary in relative importance according to the plating conditions or deposit thickness. Therefore, it may be misleading to suggest that only one theory can explain all the observed features.

The internal stress in a specific metal deposit depends to a large extent upon the thickness of the coating, the current density and temperature used during deposition and the composition of the bath. These factors will now be discussed, with particular reference to electrodeposited copper from the copper sulphate-sulphuric acid bath.
The stress in very thin deposits is greatly influenced by the substrate and often leads to very high stresses. The stress normally decreases with an increase in the deposit thickness and Kushner\textsuperscript{179} has proposed the following equation to account for this relationship:

\[ S = A + Be^{-kt} \]

Where

- \( S \) = average stress in deposit, psi
- \( t \) = deposit thickness, ins
- \( A \) = equilibrium or a minimum value of stress, psi
- \( B \) = stress due to initial influence of substrate, psi
- \( k \) = constant

Thus in nickel deposits, the stress reaches a practically constant value of about \( 1.2 \times 10^{-4} \) m according to Brenner and Senderoff\textsuperscript{192}, whereas Kushner\textsuperscript{179} suggests a lower value of \( 2.5 \times 10^{-5} \) to \( 5.0 \times 10^{-5} \) m.

The high stress in very thin coatings may be due to the lattice mismatch between the deposit and the substrate: this decreases in influence as the thickness increases. In thicker coatings the stress may decrease due to:

1. the reduction in the concentration of impurities, or addition agents, in the bath, due to their incorporation in the deposit;
2. the change in the pH of the solution;
3. the oxidation or reduction of constituents of the bath, particularly organic, at the electrodes;
4. the production of suspended particles at the anode.

The mismatch theory cannot explain the high stress when the same metal is used for both the coating and also the substrate. The most probable of the remaining possibilities is (1), because purification of a plating solution reduces the internal stress\textsuperscript{138,179}. The other effects can be minimized and a decrease in the stress can still be observed with an increase in the deposit thickness. The relationship between the stress and current density varies from metal to metal, but in general, it appears that the stress increases with current density, for example, in deposits of iron\textsuperscript{195}, zinc\textsuperscript{196} and nickel\textsuperscript{197}. An increase in the current density raised the tensile stress in copper deposits from an acid sulphate bath without any additions, according to several workers\textsuperscript{180,184,198-200}, and some of their results are shown in Table 1.3.3 (a).
From these values, it can readily be seen that copper is deposited with a low tensile, or compressive, stress when a small current density is used. As the current density increases, the stress changes in a tensile direction, with a tensile stress increasing and a compressive stress decreasing and then becoming tensile. The results of Lamb et al. 187, who used the same bath at temperatures of 20°C and 45°C, indicate that the stress becomes more compressive at higher bath temperatures and the change in the stress, due to an increase in the current density, is less.

One explanation for the increase in the tensile stress with current density is that, at high current densities, rapid deposition of the metal ions occurs under non-equilibrium conditions. Under these circumstances a distorted lattice is formed, probably with a reduced grain size and a higher internal stress.
This correlation between a high tensile stress and a small grain size has already been discussed in Section 1.3.1.

The internal stress normally decreases with the bath temperature and, as early as 1909, Stoney measured this effect and found a decrease from 67.6 - 72.5 MN/m² at 10-15°C to 30.0 - 33.1 MN/m² at 80-90°C, for nickel deposits. Similar decreases have been found by other workers for nickel, iron and cobalt. For copper from the acid sulphate bath without additions, a decrease in the tensile stress has been observed as the temperature was raised as shown in Table 1.3.3 (b).

<table>
<thead>
<tr>
<th>Bath Temperature °C</th>
<th>1</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyslov and Samartsev</td>
<td>46.9T</td>
<td>18.6T</td>
<td>29.6T</td>
<td>15.2T</td>
<td>10.3T</td>
<td>3.79T</td>
<td>2.21C</td>
</tr>
<tr>
<td>&quot;</td>
<td>29.6T</td>
<td>15.2T</td>
<td>10.3T</td>
<td>3.79T</td>
<td>4.83T</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.450</td>
<td>4.830</td>
<td>**</td>
<td>**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shibasaki</td>
<td>29.3T</td>
<td>29.6T</td>
<td>17.9T</td>
<td>0</td>
<td>7.8C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

T = Tensile stress
C = Compressive Stress
* Current Density 400A/m²
** Same bath composition as* but at current density 200A/m²

From these results, it may be concluded that an increase in the bath temperature causes the stress in a deposit to change in a compressive direction; thus a tensile stress decreases, and may change to a compressive stress, while a compressive stress increases.

The decrease in the tensile stress in a deposit, resulting from an increase in the bath temperature, may be due to deposition under conditions closer to...
equilibrium. At the higher temperatures, the ions have a greater mobility and are able to diffuse more easily to those lattice sites with the lowest energy, so that a deposit with a larger grain size and lower stress is formed.

Only a little work has been carried out to determine the effect on the internal stress of copper deposits, produced by variations in the concentration of copper sulphate or sulphuric acid. Van der Sommen\textsuperscript{207} reported that the stress increased with the concentration of copper sulphate, but he measured only relative, and not absolute, values. Lamb et al.\textsuperscript{147}, who studied the effect of three different concentrations of copper sulphate, found that the change depended upon the plating conditions and there was a significant decrease in the stress at a low bath temperature (20°C), from 22.7 MN/m\textsuperscript{2} with 67 g/l copper sulphate, to 10.3 MN/m\textsuperscript{2} with 187 g/l. However, the changes were not significant when higher bath temperatures or lower current densities were used. The literature on the effect of varying the concentration of sulphuric acid is conflicting. Fedot'ev and Khonikevich\textsuperscript{208} found that the stress decreased from 18.6 MN/m\textsuperscript{2} (0 g/l) to 4.89 MN/m\textsuperscript{2} (25 g/l) and then increased to 23.4 MN/m\textsuperscript{2} (200 g/l sulphuric acid). Lamb and Valentine\textsuperscript{185} found a small and not very significant increase in the stress with an increase in the acid concentration. It may be concluded that the stress in the deposits decreased as the concentration of copper sulphate was increased: the effect of varying the concentration of sulphuric acid in the bath was uncertain.

The presence of addition agents in the copper sulphate-sulphuric acid plating bath often produces a marked increase in the stress. Many compounds have been studied and the stresses produced depend upon the concentrations used, as indicated in Table 1.3.3(c)
From these and other results, it may be concluded that many addition agents produce a tensile stress when a low concentration is used, and a compressive stress with a high concentration.

The values of the stress produced in thin copper deposits with benzotriazole, and measured by Kendall, are much higher (207 MN/m² tensile and 138 MN/m² compressive) than those found with other addition agents, and this was one of the reasons that the use of this compound was studied in this work.

The internal tensile stress in a deposit appears to increase with:

1. a decrease in the deposit thickness;
2. an increase in the current density;
3. a decrease in the bath temperature;
4. a decrease in the concentration of copper sulphate in the plating solution. The presence of addition agents may produce a tensile or a compressive stress, but an increase in the concentration of the addition agent appears to change a tensile into a compressive stress.

### Table 1.3.3 (c)

<table>
<thead>
<tr>
<th>Addition Agent</th>
<th>Concentration g/l</th>
<th>Stress MN/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelatine</td>
<td>0.05 0.26 0.50</td>
<td>48.9T 0 24.8C</td>
</tr>
<tr>
<td>Thiourea</td>
<td>0.025 0.10 0.3</td>
<td>77.2T 46.2C</td>
</tr>
<tr>
<td>β Naphthoquinoline</td>
<td>0.08 0.20</td>
<td>103T 0</td>
</tr>
<tr>
<td>Rochelle Salt</td>
<td>0 0.01 0.05 0.134</td>
<td>18.6T 39.3T 9.65T</td>
</tr>
</tbody>
</table>

T = Tensile Stress
C = Compressive Stress
1.3.4 Hardness

Fischer has shown that the hardness of an electrodeposited metal nearly always exceeds that obtained by other methods. This is illustrated by the following hardnesses for electrodeposited metals and annealed or rolled metals, respectively: chromium HV 400 to 950 and 220 to 350, platinum HV 600 to 680 and 50 to 130, rhodium HV 580 to 680 and 100 to 180.

However, it is difficult to compare the hardness values obtained by different authors, because incompatible methods and units are often used, e.g. scratch and indentation hardnesses. One common method of describing the hardness is in terms of the depth of penetration of a loaded sphere or diamond tetrahedron. The hardness value is obtained by dividing the load by the area of the imprint; the value is usually expressed in kilograms per square millimeter Kg/mm$^2$ or Vickers Hardness Number HV.

Hard coatings are often used in applications requiring wear resistance, such as the use of nickel for the internal plating of aluminium valves, the surfaces of pump spindles, hydraulic rams, screws and the surface of aeroplane propellers. Because of their excellent electrical conductivity, hard copper deposits are used for electrodes in spot and seam welding and other electrical components, such as contacts, commutators and printed circuits. The good thermal conductivity allows these copper deposits to be used for injection moulds and press tools for plastics and dies for stamping thin sheet. Hard deposits, particularly of nickel and chromium, may be used to build up worn, corroded and overmachined components, and the rear axles of buses have often been treated in this way.

The hardness of a deposited metal often increases as the current density is raised and has been recorded for iron, chromium and nickel. Copper deposits from a bath with no addition agents are much softer and lie within a range of hardness from HV 60 to 160. Increases in the hardness with current density have been found for copper deposits and the values are given in Table 1.3.4 (a).
From the values quoted, it can be seen that the hardness of the deposits rises as the current density increases. The measurements of Lamb et al. indicate that purification of the solution considerably reduced the hardness. However, with other purified baths of different composition, they concluded that there was no consistent relationship because, in some experiments, an increase was observed and in others a decrease.

It may be concluded that, with a particular bath, an increase in the current density produces harder deposits. It has already been noted, in Section 1.3.2, that an increase in the current density decreased the grain size of the plated metal, and several workers have found a correlation between a small grain size and a high hardness. The most probable explanation for this effect is that, in a deposit with a small grain size, there are many grain boundaries blocking the slip planes, along which deformation of the crystals would normally occur. The presence of incorporated impurities or addition agents would increase both the magnitude of this blocking effect and the hardness. Tikhonov has calculated that the dislocation density in a copper electrodeposit was about $4.4 \times 10^9 \text{ cm}^{-2}$ and it has been suggested that the effect of these dislocations, together with incorporated foreign particles, was to decrease the mobility during deformation and to increase the hardness and the internal stress.

The hardness of metal deposits usually falls as the plating temperature is increased, as observed with chromium, iron, and nickel. The effect of temperature on the hardness of copper deposits from the sulphate bath is not very well understood, as illustrated by the results given in Table 1.3.4(b).
The work of Butts and DeNora suggests that an increase in the hardness of the deposit was followed by a decrease, as the bath temperature was raised. However, the predominant trend appears to be that an increase in the bath temperature results in a small decrease in the deposit hardness. This is probably due to the fact that, at higher temperatures, the ions are more mobile and form deposits with a larger grain size (see Section 1.3.2); this larger grain size normally results in a lower hardness, for reasons which have already been discussed in the previous section on the effect of current density on hardness.

It is difficult to assess the effect on the hardness of changes in the composition of the plating bath, because different conditions for deposition have been used. No significant change was observed by Lamb et al. in the hardness of copper deposits produced from baths containing different concentrations of copper sulphate. They found that the hardness could either increase, or decrease, with the acidity of the bath, but concluded that the predominant effect was that the hardness of the copper deposits increased with the sulphuric acid concentration.

The presence of addition agents in the copper sulphate plating bath normally increases the hardness of the deposits. In certain cases very hard deposits have been produced and some of these are included in the Table 1.3.4 (c).
<table>
<thead>
<tr>
<th>Addition Agent</th>
<th>Concentration g/l</th>
<th>Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asparagine</td>
<td>15</td>
<td>271</td>
</tr>
<tr>
<td>Gelatine</td>
<td>0.1</td>
<td>305</td>
</tr>
<tr>
<td>Rochelle Salt</td>
<td>0.2</td>
<td>276</td>
</tr>
<tr>
<td>Thiourea</td>
<td>0.2</td>
<td>350</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>15</td>
<td>212</td>
</tr>
<tr>
<td>Naphthalene disulphonic acid and thiourea</td>
<td>0.5</td>
<td>260</td>
</tr>
<tr>
<td>Quinoline and chloride ions</td>
<td>12.9</td>
<td>217</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conc. of gelatine g/l</th>
<th>Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at</td>
</tr>
<tr>
<td></td>
<td>Temperature $^\circ$C</td>
</tr>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>0</td>
<td>99</td>
</tr>
<tr>
<td>0.02</td>
<td>145</td>
</tr>
<tr>
<td>0.10</td>
<td>215</td>
</tr>
<tr>
<td>0.10</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 1.3.4 (c)

Sammour has studied the effect produced on the hardness of copper deposits by changes in the current density, bath temperature and concentration of gelatine and the results are given in Table 1.3.4 (d)
From his results in Table 1.3.4 (d), it can be seen that an increase in the current density and a decrease in the bath temperature produce harder copper deposits, when the bath contained gelatine. An increase in the concentration of the gelatine in the solution also raised the hardness and a similar effect has been observed elsewhere with thiourea and Rochelle salt. Kendall measured the hardness at 25°C and 45°C and found a maximum hardness was reached with a concentration of 0.06 g/l benzotriazole at a bath temperature of 25°C, but observed no peak at 45°C. However, he did not systematically study either the current density or the bath temperature (except at 25°C and 45°C), and both these effects are investigated in this work.

The hardness of electrodeposits appears to increase with:

1. an increase in the concentration of sulphuric acid in the bath;
2. an increase in the current density;
3. a decrease in the bath temperature;
4. an increase in the concentration of addition agents in the solution.

1.3.5 The Effect of Time on Changes in Internal Stress and Microhardness

Both the internal stress and the hardness of electrodeposited metals, as well as the electrical resistance, have been found to change with time, over a period of several days after the plating current had been switched off.

This effect has been observed in the internal stress of nickel, chromium, and copper, and has been called the stress after-effect. If the metal is under tensile stress, this changes with time and becomes more tensile but, in compression, it becomes less compressively stressed, i.e. the stress always changes in a tensile direction.

Nishihara et al., in their studies of the stress after-effect, found that the stress changed when the cathode was removed from the electrolyte. The tensile stress increased in nickel, chromium and copper deposits, whereas the compressive stress in copper (from a sulphate bath containing glue) and in zinc decreased. It is worth noting that electrodeposited lead, from a
fluosilicic bath containing glue, had a very small compressive stress immediately after plating, which then became tensile\textsuperscript{231}. A similar change from compressive to tensile stress has been noticed by Jahn\textsuperscript{232}.

The hardness of several electrodeposited metals has been found to decrease with time after the cessation of plating. The hardness of silver\textsuperscript{235} fell from HV 105-90 to 65-50 and the microhardness and electrical resistance of electrolytic iron\textsuperscript{236} have both fallen with time. Binder and Fischer\textsuperscript{233} found that the hardness of copper, deposited from the sulphate bath containing \(\beta\)-naphthoquinoline, decreased linearly from HV 225 to 145 in 100 days at room temperature. This softening process, which they called self annealing, was accelerated if the specimens were exposed to X-rays.

Several theories have been proposed to explain these changes in internal stresses, hardness and electrical resistance. Vagramyan and Tsareva\textsuperscript{228} have attributed this phenomenon to the fact that surface atoms, which are more mobile than those in the bulk metal, can move and alter the stress after the current has been switched off. Polukerov and Kuznetsov\textsuperscript{234} suggested that the effects were due to spontaneous changes in the crystal structure, such as an ordering process in the copper lattice. Kushner\textsuperscript{179} associated the adsorption of impurity molecules on the grain boundaries with the internal stress: thus, according to his theory, a high concentration would produce a compressive stress and a low addition a tensile stress. He explained the stress after-effect as probably due to dissolution, caused by the formation of concentration cells in the diffusion layer between prominent areas (cathodes) and recessed areas, such as grain boundaries (anodes). Dissolution of both the metal and the foreign matter occurred at the anodic areas, caused the stress to rise and also supplied the metal ions, which were then deposited at the cathodic regions. In this way the compressive stresses were changed to a greater extent (9.2% and 17%) than the tensile stresses (2.3% and 6.7%), as a result of the greater dissolution of the codeposited impurity.

However, the results of Nishihara et al\textsuperscript{231} indicated that the stress changed after the cathode had been removed from the plating solution. This meant that the theory of Kushner\textsuperscript{179}, involving dissolution and deposition of copper in the electrolyte, could not explain their observations and could not be the only reason for the stress after-effect. They suggested that the
codeposition and incorporation of hydrogen in the coating was the major cause of stress in electrodeposits and that the release of this hydrogen, after plating and the removal of the cathode from the solution, resulted in the stress change. They analysed copper which had been plated from the sulphate bath and found that hydrogen was present. This hydrogen could not have been the only reason for the decrease in the stress in copper deposits, because very low concentrations have been determined by Foley (0.001 to 0.003%) and by Safranek (less than 0.001%). With such low quantities, the diffusion of hydrogen is not a probable cause of either the internal stress, or changes in it, for copper deposits. Thus, the role of hydrogen in the formation of stress in copper deposits from the sulphate bath is uncertain; the differences observed may be due to the fact that different plating conditions were used in the actual deposition.

The internal stress has also been found to depend upon the time of ageing of the addition agent in the electrolyte. Vagramyan and Tsareva found that the stress in copper deposits from a freshly prepared solution, containing a mixture of naphthalene disulphonic acid (0.5 g/l) and thiourea (0.005 g/l), was much lower than that plated from a similar bath which had been stored for a year. They suggested that the reason for this change was that the naphthalene disulphonic acid oxidized during storage to give oxidation products which were more effective than the pure additive in raising the stress. However, Allsop found that the stress in copper deposits decreased as the plating solutions aged and Brenner and Senderoff observed that the stress in nickel deposits, from a modified Watts bath, decreased from 427 MN/m² to 103 MN/m², after standing overnight at 54°C.

It can be seen from the above literature survey that the stress, hardness and electrical resistance of deposits plated from electrolytes containing addition agents may alter with time. These effects may be summarized as follows:

1. a tensile stress increased after plating;
2. a compressive stress decreased after plating;
3. both the hardness and electrical resistance of deposits decreased after plating;
4. a stored or 'aged' solution gave deposits with a stress which was
different from that obtained with a freshly prepared solution.

1.3.6 The Effect of Ultrasonic Agitation on the Deposits

Ultrasonic agitation of an electrolyte produces a marked change in several plating parameters, including the throwing power and limiting current density. This form of agitation has also been found to improve the quality of the deposits and alter the physical and mechanical properties, such as the internal stress and the hardness and, therefore, has been widely studied 241-247.

The main effects of the vibration of the electrolyte are to lower the activation polarization and to decrease the thickness of the diffusion layer at the electrode surface, which in turn, reduces the concentration polarization. According to Yeager and Hovorka 243, the use of ultrasonics completely eliminated the diffusion layer at both electrodes in certain plating baths. This reduction in the polarization, which has already been discussed in the section on the general theory of electrodeposition, enables a higher current density to be used to give a good deposit, so that a faster rate of deposition can be employed. Agitation has increased the limiting or maximum current density which can be used to produce a satisfactory copper deposit from the sulphate bath; in one bath 244 the change was observed to be from 500 to 1,600 A/m², and from 1,500 to 12,500 A/m² in another 245. Another advantage is that the use of ultrasonic vibrations encourages the formation, on the cathodic surface, of molecular hydrogen from atomic hydrogen; this reduces the tendency for atomic hydrogen to enter the metal and produce embrittlement of the plated article. The increased rate of deposition and improved surface quality has been observed with deposits of cadmium, copper, chromium, gold, nickel, silver and zinc and some alloys, although no details are given regarding their physical and mechanical properties 246.

In another paper 247, the present author reviews the use of ultrasonics to increase the maximum current density, the throwing power (which is a measure of the ability of the bath to produce a uniform thickness of deposit on irregular surfaces) and the cathodic current efficiency; the hardness and internal stress of the coating are also discussed. The microhardness 247 of many deposited metals, including copper, cadmium, gold, silver and zinc, was increased using agitated electrolytes. For nickel the changes in hardness were from HV 215 to 310 and from HV 260 to 400, and for chromium
from HV 740 to 920. The application of ultrasonics was reported to reduce
the stress, cracking and peeling of nickel deposits and improve the
adhesion. A considerable decrease in the porosity of nickel and cobalt
coatings was also observed.

The main advantages of the use of ultrasonics can be summarized as follows:

1. an increase in the rate of deposition;
2. a rise in the cathodic current efficiency;
3. harder deposits;
4. an improved surface reflectivity and adhesion;
5. a decreased internal stress and porosity;

The chief disadvantage is the high cost of installing the equipment to
generate these vibrations.

1.3.7 The Throwing Power of a Solution

The term throwing power, or throwing efficiency, is a measure of the
ability of a plating solution to produce deposits of more or less uniform
thickness. This property of the solution is important and is normally
specified because the minimum deposit thickness on an article may control
the rate of corrosion of the substrate. If it is possible to plate the
whole surface with this minimum thickness, a considerable saving of metal,
plating current and time can be achieved. For this reason, there is a
growing demand for quantitative knowledge about the throwing power of
different solutions. The throwing power of a solution is thought to
depend mainly upon the following three factors:

1. the cathodic polarization;
2. the conductance of the solution;
3. the change in the current efficiency with change in current density.

These will now be discussed individually.

1. The cathodic polarization is particularly important and a large increase
   in it, with a corresponding increase in the current density, appears
   essential to a good throwing power. The protruding parts of the cathode
   surface receive a greater current density because they are closer to the
   anode; this produces a higher concentration polarization and encourages
deposition at other sheltered areas, which otherwise would have a lower
current density, a reduced concentration of copper ions and a decreased
cathodic polarization. Thus, a high local polarization over some areas
promotes plating at other areas and increases the throwing power.
If the throwing power depended only upon the distance between one anode and two cathodes as well as Ohm's law, a change in the conductivity of the solution would have no effect. However, an increase in the conductivity could alter other factors, such as the polarization. Thus an addition of sulphuric acid to a copper sulphate solution increases the conductivity, suppresses the ionization of the copper salt, reduces the copper ion concentration and increases the cathodic polarization. This increase in the polarization raises the throwing power of the solution.

If the current efficiency of a particular bath varies with the current density, the throwing power is affected. When the current efficiency decreases, as a result of an increase in the current density, this leads to thinner deposits than expected on the prominent areas and a higher throwing power.

Because the throwing power depends upon the distribution of the electrodes, the bath temperature and the current density, their values should be specified when results are tabulated. There are several methods of measuring the throwing power of a solution and these have been compared; it appears that the Haring Blum cell is probably the most commonly used. This cell consists of two cathodes, electrically connected together and positioned at opposite ends of a rectangular cell, with an anode between them. The anode-cathode distances are not equal and the ratio of them is called the primary current ratio and is often chosen as five. During deposition, both cathodes increase in weight by an unequal amount and the ratio of these gains is the metal distribution ratio. Both these ratios are employed in different formulae to calculate the throwing power of the bath. The formula suggested by Field is not only the most widely used but is also accepted as the British Standard and takes the form:

\[ T = \frac{(P - M)}{(P + M)} \times 100\% \]

where
- \( T \) = throwing power
- \( P \) = primary current ratio
- \( M \) = metal distribution ratio

This formula gives a throwing power of 100%, when the primary current ratio is 5 and the metal distribution ratio is 1, i.e. if the increase in weight
of each cathode is equal. When the metal distribution ratio is equal to the primary current ratio, as predicted by Ohm’s law, the throwing power is 0%. In the case of no deposition on the electrode further away from the anode, the throwing power is -100%.

It is difficult to make a comparison of the published values of the throwing power, because the figures quoted have been obtained using different cells and formulae. Mohler has found that the range of throwing power was 5% to 20% for the acid copper sulphate bath. Although Winkler observed a very small rise in the throwing power as the current density increased, the majority of workers found a decrease. Raub and Müller measured a decrease from 55% at 50 A/m² to 25% at 600 A/m², and Mathers and Guist a change from 42% at 50 A/m² to 22% at 300 A/m². Haring and Blum quoted the following figures for the metal distribution ratio; this increased with current density from 4.52 (with 1A) to 4.63 (with 4A), with solution temperature from 4.53 at 21°C to 4.89 at 45°C and with solution agitation from 4.53 with a still bath to 4.83 with air agitation. The presence of addition agents in the plating solution may also raise the throwing power by increasing the cathodic polarization. Thus, the overall effect on the throwing power may depend upon the plating variables, such as current density, as illustrated by the separate use of gelatine and molasses, which gave a small increase in the throwing power at low current densities and gave the opposite effect at high current densities.

It may be concluded that a decrease in the throwing power occurs with:

1. an increase in the current density;
2. an increase in the bath temperature;
3. an increase in the solution agitation;
4. the use of certain addition agents, although others may have the opposite effect.
2. EXPERIMENTAL PROCEDURE

2.1 Introduction

Because of the widespread nature of this work, involving the separate aspects of corrosion and electrodeposition, the type of equipment and the methods used had to be very different. Therefore, in this chapter it was decided to describe separately the techniques and equipment employed for each of these fields, starting with the determination of the properties of the benzotriazole.

The experimental procedure used to measure the solubility of benzotriazole in distilled water is described and followed by the techniques applied to study the effect of different concentrations of benzotriazole on the conductivity and pH of tap, distilled and deionized water. A description is then given of the methods used to determine the resistance to corrosion and oxidation of copper, produced with and without the use of benzotriazole as an inhibitor.

The remaining parts of the chapter are concerned with the electrodeposition of copper from the copper sulphate-sulphuric acid plating bath both with and without benzotriazole. An explanation is given of the control of the plating conditions, such as purification, temperature and agitation. This is followed by a description of the measurement of the properties of the plating solution, such as the current efficiency and throwing power, and then the appearance and properties of the deposits, including grain size, hardness and internal stress.
2.2 Some Properties of Benzotriazole in Water

2.2.1 Solubility of Benzotriazole in Distilled Water

The literature survey (Section 1.1.5) indicated that benzotriazole was very soluble in acids and alkalis above 20°C, but much less soluble in water. Several workers have measured the solubility at different temperatures, but no complete set of data has been obtained and no information has been found for temperatures below 10°C. The solubility of benzotriazole was determined from 0°C to 100°C because it has been used as a corrosion inhibitor at temperatures as low as 0°C (in antifreezes) and up to 100°C in high temperature systems, and in this work as an addition agent in plating solutions over a range from 0°C to about 100°C.

A saturated solution of benzotriazole in distilled water was produced in a boiling tube and brought to the right temperature either by heating in a constant temperature water bath or by cooling in cold water or a freezing mixture. When this temperature was reached, sufficient solid was added so that there was an excess present and the solution was then saturated. The solution was stirred and maintained at the required temperature for an hour to ensure that constant and equilibrium conditions had been reached; about 10 mls of this solution was collected in a hot pipette and poured into a bottle which had previously been dried and weighed. The stopper of the bottle was immediately fitted to prevent evaporation, and the bottle was again weighed to determine the amount of the solution. After this the stopper was removed to allow evaporation; to encourage drying, the bottle was heated to about 30°C, left overnight, cooled in a dessicator and reweighed. It was heated again at 30°C for about an hour and reweighed; if there were no further decrease in the weight it was assumed that the benzotriazole was absolutely dry. The solubility of benzotriazole was calculated from the weight dissolved in a known weight of water at the particular temperature. The process was repeated at different water temperatures and a graph plotted of the solubility v. temperature.
Several experimental difficulties were encountered during the above measurements. Since it was necessary to ensure that the solutions were saturated, they were regularly stirred and then the solid was allowed to settle before a sample of the liquid was taken with a hot pipette. The temperature of the pipette was kept above that of the solution to prevent the precipitation of benzotriazole, which would otherwise occur on the cooler glass surfaces. The drying temperature of the solution was important because, if it were too high, a gel-like solid was formed rather than the needle shaped powder which is the more common form of benzotriazole, and this solid form could possibly have a different weight.

2.2.2 Conductivity of Benzotriazole Solutions

The effect of different concentrations of benzotriazole on the conductivity of deionized, distilled and tap water was measured. This is important because the corrosion inhibition produced by benzotriazole could partially result from a decrease in the conductivity of the solution and an increase in the resistance polarization. Conversely, an increase in the conductivity could increase the corrosion. Another significant effect which has been described by Wall and Davies is that an increase in the conductivity of cooling waters could produce excessive energy losses at the high voltages used in conductors and heat exchange equipment.

The conductivity was measured with a Mullard Conductivity Bridge (Model No.E 7566/3) and a dipping cell for the three waters containing 0 g/l, 0.012 g/l, 0.12 g/l, 1.2 g/l benzotriazole, and also for the saturated solutions. The solutions were agitated slowly with magnet stirrers to assist the dissolution of the benzotriazole and to produce a uniform concentration, and the reading taken at 18°C.

The first set of readings was taken with solutions containing different concentrations of benzotriazole which had been prepared separately prior to the measurement. However, the results with these solutions were irreproducible and it was thought that one possible reason could be the introduction of different impurities from the containers and dissolved gases, such as carbon dioxide, from the atmosphere into the separately prepared solutions. Therefore, all the solutions for one type of water were prepared in the same beaker starting with the lowest concentration and then adding in turn, after each measurement, the appropriate quantity of benzotriazole.
to obtain the required concentration. The experiment was repeated several times because the pH of all three waters was found to vary slightly, and typical values were obtained.

2.2.3 pH of Benzotriazole Solutions

The pH was measured for the same three waters with similar additions of benzotriazole. This was done because it was thought that if the addition of benzotriazole changed the pH of the water, it could affect the stability and protective nature of any surface films on the copper. A change in the pH of the water, to acidic or alkaline values, sometimes causes corrosion of metals, such as zinc, aluminium, lead and others similar amphoteric metals in contact with the copper.

The pH was measured with an E.I.L. pH meter (Model No. 38B), using a glass and calomel electrode. Again the first set of readings were irreproducible and the procedure described in Section 2.2.2 was followed.

2.2.4 Corrosion Inhibition

The rate of corrosion of immersed copper was measured in solutions of different acids, alkalis, salts, dissolved gases and detergents, with and without the addition of benzotriazole. The specimens, with an area of $7 \times 10^{-3}$ m$^2$, were cut from copper sheet, degreased in acetone, pickled in dilute nitric acid, washed in distilled water, air dried, and weighed. The tests were conducted with four specimens in a beaker containing one litre of the solution, which was slowly, magnetically stirred. An identical test was carried out in another glass vessel containing the same solution but with an addition of 0.12 g/l benzotriazole. The rate of stirring was sufficient to simulate slow flow rates which reduce the concentration polarization but do not give excessive aeration. The beakers were covered with clock glass to reduce any evaporation that would otherwise have been quite high at room temperature (about 22°C) over a period of 5 days. After 1, 2 and 5 days the specimens were removed from the solution, washed in distilled water, air dried and weighed. This drying process removed the moisture from the surface, together with any non-adherent surface films, but it did not affect any adherent films, which could be protective. The pH of many of the solutions used was measured, before and after the tests, to discover if the inhibitor had an effect on any change in the pH, during the period of corrosion.
The rate of corrosion was obtained as the average weight loss of the four specimens of copper sheet, with a nominal area of \(7 \times 10^{-3} \text{m}^2\) each, after immersion in a litre of the appropriate stirred solution for a period of 1, 2 and 5 days. For each solution, the efficiency of inhibition produced by the use of 0.12 g/l benzotriazole, was calculated using the formula:

\[
\text{Inhibitor Efficiency} = \frac{(\text{Wt. loss of plain copper} - \text{Wt. loss of copper with inhibitor}) \times 100\%}{\text{Wt. loss of plain copper}}
\]

In the cases where the conditions were very aggressive, i.e., when a high weight loss occurred with the inhibitor, the experiment was repeated using higher concentrations of 0.5 g/l and 1.0 g/l benzotriazole, to determine whether these concentrations were more effective than the lower ones. The above tests were repeated for brass specimens (70% copper, 30% zinc) and the surfaces of these test pieces were also examined for dezincification.

The effect of the pH of a solution on the corrosion inhibition produced by benzotriazole was investigated for copper immersed in sulphuric acid. Sufficient distilled water was carefully added to the concentrated sulphuric acid to produce a range of solutions with pH from -1 to +4. The solutions were slowly magnetically stirred and the specimens were weighed after a period of immersion of 1, 2 and 5 days in the acid, both with and without an addition of 0.119 g/l benzotriazole. The inhibitor efficiency was then calculated for each concentration of the sulphuric acid used.

The inhibition obtained by dipping copper into a hot solution of benzotriazole, previously described in the literature review (Section 1.1.5), was studied for some of the solutions. The specimens were dipped for a period of 5 minutes into a saturated solution of benzotriazole at 60°C and then allowed to dry in air before being weighed and immersed in the test solution. A powdery deposit of benzotriazole was formed on part of the surface of some of the dipped specimens when they were dried. It was necessary to remove this excess benzotriazole before testing because, otherwise, it would have increased the apparent corrosion resistance of the dipped film. The powder was removed by washing in distilled water and the specimens were again dried in air.

The final section of the work on corrosion inhibition was a comparison of benzotriazole with triazole and naphthotriazole (see Fig. 2.2.4). The stain resistance of copper immersed in tap water with and without the above
inhibitors was studied over a period of 21 days. A standard addition of 0.25 M, wt. % of the inhibitor was used and the time period before staining first occurred was recorded. The efficiency of each substance was measured by immersing the copper in ammonium chloride and a few acids with and without an addition of the inhibitor. The degree of inhibition conferred on to copper, by immersion in a hot solution of each of these substrates was also determined in different atmospheres, including salt spray, humidity and sulphur dioxide; after a period of 42 days, the changes in the weight and the surface appearance were recorded.

![Benzotriazole, Triazole, Naphthotriazole](image)

**Fig. 2.2.4 Structure of Benzotriazole, Triazole and Naphthotriazole**

The harmful effect of copper ions in water on aluminium and certain other metallic surfaces has been discussed previously. (Section 1.1.5). This experiment was designed to compare the inhibition produced on copper by the addition of benzotriazole to the water, with that given to copper when dipped in a hot aqueous solution of benzotriazole prior to immersion.

Instead of comparing the very small weight changes which occur over a period of a few days, a comparison was made of the times taken for aluminium foil, immersed in these solutions, to pit. The experiment was carried out with tap, distilled and deionized water.

In order to accelerate the pitting of the aluminium a large surface of copper \((9 \times 10^{-2} \, \text{m}^2)\) was used to give a copious supply of copper ions with a small area of aluminium foil \((6 \times 10^{-4} \, \text{m}^2)\). The copper surface used was the inside of a copper calorimeter that contained a fixed volume \((500 \, \text{mls})\) of water and the aluminium foil. The calorimeters were degreased in acetone, cleaned in nitric acid and thoroughly washed in deionized water; the aluminium foil was also degreased in acetone. For each water, ie. tap, distilled and deionized, three separate tests were conducted with:
(1) plain water and a cleaned calorimeter;

(2) water containing 0.12 g/l benzotriazole and a cleaned calorimeter;

(3) plain water in a treated calorimeter. This calorimeter had been filled with an aqueous 1% solution of benzotriazole at a temperature of 60°C for about 5 minutes, when it was emptied, allowed to air dry and washed in hot water to remove any remaining solid benzotriazole. This procedure is known to produce a protective film on the copper surface (Section 1.1.5).

The aluminium foil was then placed in the calorimeters, which were covered with clock glasses to prevent evaporation of the water, and the aluminium foil examined for pitting at regular intervals of quarter of an hour, and then after longer periods up to a total of about five hundred hours. However, this experimental procedure did not give reproducible results, which was considered to be due to the formation of an incomplete surface film on the copper. To overcome this problem and ensure the production of a satisfactory film, the copper surfaces were immersed in a hotter and more concentrated solution containing about 5% benzotriazole at 80°C for a period of thirty minutes, which gave better results.

2.2.5 Oxidation Resistance of Dipped Copper

It is well known, and has been discussed in Section 1.1.5, that copper which has been dipped in a solution of benzotriazole has an enhanced resistance to oxidation or tarnishing. In this preliminary work the rates of oxidation of a plain and a dipped specimen of copper foil were measured at 300°C.

The rates of oxidation of the copper were determined with a Stanton automatic thermal balance which recorded both the weight change and the temperature of the furnace. So that a direct comparison could be made, two identical experimental runs were performed consecutively with the same temperature setting for a plain specimen and a dipped specimen. The initial work was done with samples of $2 \times 10^{-2} \text{ m} \times 5 \times 10^{-2} \text{ m}$ copper foil, folded into a concertina shape to fit on to the pan of the thermal balance. These specimens were degreased in acetone and air dried but did not give reproducible results. The experiment was repeated with copper of the same area, which had been degreased in acetone and pickled in 50% nitric acid to remove any surface contamination, but again the results did not agree.

Eventually acceptable results were obtained using much larger specimens
(5.6 \times 10^{-2} \text{m} \times 8.0 \times 10^{-2} \text{m}) that were degreased in acetone, cleaned in 50\% nitric acid for 30 seconds, washed in distilled water and air dried. They were then stored in a dry atmosphere for 24 hours to allow the formation of a thin oxide film which would grow at a logarithmic rate and reach a steady thickness in this time. The procedure was repeated with dipped specimens which had been immersed in a hot aqueous solution of benzotriazole (5\% at 80 to 90\degree C) for at least an hour, removed and air dried. It was found necessary to wash the samples in warm water to remove the solid benzotriazole which remained on the surface after the evaporation of the solution. It was considered advisable to check that any difference in the results between the plain and dipped copper was due to the benzotriazole in the solution, and not to dipping into the hot water and the consequent heat treatment. A specimen was cleaned in the normal manner and immersed into hot water (80 to 90\degree C) for an hour and air dried and the rate of oxidation determined.
2.3 Electrodeposition: Control of Plating Conditions

2.3.1 Bath Composition

The plating bath was prepared from general grade chemicals, as supplied by British Drug Houses Ltd., and freshly distilled water prepared in an all glass still. The maximum limits of impurities in the copper sulphate were 0.005% chloride, 0.5% alkalis (sulphated) and 0.08% iron, and in the sulphuric acid, 0.01% non-volatile matter, 0.01% hydrochloric acid, 0.001% nitric acid, 0.0002% arsenic, 0.002% iron, 0.002% lead and 0.1 ml N/1% reducing substances. The composition of the solution chosen was 0.5M copper sulphate (125 ± 1 g/l CuSO$_4$·5H$_2$O) and 0.5M sulphuric acid (49 ± 0.5 g/l H$_2$SO$_4$), because Shreir and Smith have established that this concentration possesses the greatest reproducibility. In order to obtain results which were applicable to commercial plating, general grade and not highly purified chemicals were used. The solutions were made with distilled water, because this was considered to be more constant in composition than tap water.

2.3.2 Purification

The presence of impurities in a plating bath is known to affect the growth and properties of electrodeposited metals, and some of these effects have been discussed in the literature review. Using a purification technique similar to that described below, Brenner and Senderoff observed a decrease in the internal tensile stress of nickel deposits, from 221 MN/m$^2$ to 103 MN/m$^2$, when a bath made of commercial grade salts was purified. In the present work on copper deposits, a decrease in the tensile stress on purification was observed, from 7.25 MN/m$^2$ to 3.45 MN/m$^2$ with a bath containing general grade chemicals, and a smaller change from 14.1 MN/m$^2$ to 10.7 MN/m$^2$ when analytical chemicals were used under different plating conditions. These decreases confirm the importance of impurities on the mechanical properties of the deposits.

A purified solution was used as a reference and also indicated the effect of the presence of impurities in the solution. Ideally the method of purification should be governed by a prior knowledge of all the adverse impurities, but this is not possible in practice. The following procedure for purification has been well established and the deposits plated from this purified solution gave reproducible results.
The solution was boiled for about ten minutes to remove volatile impurities, such as formaldehyde and carbon dioxide\textsuperscript{262,263}. An addition of 10 mls of 100 v/v hydrogen peroxide was then made to each litre of the boiling solution to oxidize any impurities, destroy sulphide ions and eliminate any chloride ions as chlorine gas\textsuperscript{264,265}. This is important because the presence of chloride ions in plating solutions is known to have a marked effect on the mechanical properties of the deposits, particularly for nickel\textsuperscript{240}. The solution was kept boiling for a period of fifteen minutes after the evolution of gas had stopped. This was followed by the addition of 20 g/l of activated charcoal that has been found to adsorb the adsorbable impurities, including gases and any remaining chlorides\textsuperscript{107,108,118,266-269}. The solution was boiled for a further period of fifteen minutes and then filtered with glass wool to remove the charcoal and any other suspended matter, such as dust and insoluble impurities from the anode, which otherwise could produce surface roughness. The solution was subsequently pre-electrolysed, using analar electrodes and a current density of about 200 A/m\textsuperscript{2}, to plate out any metallic impurities, such as antimony, arsenic (which produce rough, brittle surfaces) and zinc\textsuperscript{113,126,239,270-272}. In the present work, the stresses in deposits plated from the purified bath have been in good agreement with one another and those reported elsewhere, over a wide range of values from 124 MN/m\textsuperscript{2} for nickel from the Watts bath to 10.7 MN/m\textsuperscript{2} for copper deposits.

2.3.3. Effect of Solution Agitation

It has been established that the agitation of a plating solution may have a marked effect on the hardness and stress of several electroplated metals\textsuperscript{247}. Preliminary work on copper deposits has shown that ultrasonic vibrations decrease the internal stress, typical values being 7.25 MN/m\textsuperscript{2} for a stirred bath and 3.79 MN/m\textsuperscript{2} for one subject to ultrasonics, under the same plating conditions. Therefore, it was necessary to standardize the agitation of all the plating solutions. Under normal conditions the plating baths were mechanically stirred using a magnet covered in an inert coating. The rate of stirring was sufficiently slow to prevent the formation of a vortex on the surface and excessive aeration. However, it did produce an efficient mixing of the solution and reduced any concentration effects\textsuperscript{273}. In some experiments a comparison was made between the various forms of agitation. When deposition was required from a still solution, the bath was
placed on a sheet of anti-vibration padding to reduce any mixing or other effects resulting from vibrations of the bench. The use of ultrasonic vibration, which has been reviewed in the preceding chapter (Section 1.3.6), was found to eliminate the diffusion layer of a polarized copper electrode, but not to affect its equilibrium potential. The plating solution was ultrasonically agitated by placing it, in a glass beaker, in an ultrasonic tank filled with water. However, during the application of ultrasonic vibrations to the bath, the temperature of the water rose several degrees. To counterbalance this rise in temperature, a water-cooled copper coil was fitted inside the tank and the rate of water flow was regulated, so that there was no noticeable increase in temperature over the maximum plating time which was three hours for the hardness determinations.

2.3.4 Temperature Control

The temperature of the bath is very important, because it affects the plating variables such as polarization. For this reason, it is essential to control the temperature of the electrolyte as accurately as possible during the study of deposition processes. Although it has been suggested by Wilman that the temperature of a metal species at the time of its crystallization is much higher than that of the plating bath, the temperature of the bulk solution is also important. Therefore, irrespective of the significance of this crystallization temperature, it is necessary to maintain the temperature of the plating bath at a constant value, because small changes may have a marked effect on the properties of the resulting deposits, such as the internal stress.

Preliminary work has shown that the internal stress in copper deposits depends upon the temperature of the plating bath. A decrease in the tensile stress was observed from 19.3 MN/m$^2$ at 0°C to 7.25 MN/m$^2$ at 23°C and to 3.1 MN/m$^2$ at 40°C, so it was essential to control carefully the bath temperature. The temperature of the plating bath may rise during electrolysis with solutions of high electrical resistance or with the use of high current densities. It was, therefore, decided that air thermostated enclosures were not suitable, particularly as a wide range of temperatures was required. Constant temperature water baths were found to be satisfactory and only a very small change in temperature ($\pm$1°C) occurred over a period of three hours, when high current densities were used in still solutions.

It was not possible to use a commercial metallic constant temperature water bath for magnetically stirred solutions. For these stirred baths the use
of a five litre beaker as a constant temperature enclosure was found to be satisfactory. The plating solution contained in a beaker, was put in the larger glass vessel and placed on the magnetic stirrer which also served as a hot plate. The temperature of a solution in this arrangement was found to be very constant and a maximum variation of about ± 2°C was observed at 95°C over a time period of three hours. A mixture of water, ice and sodium chloride was used in the outer vessel to produce cold surroundings and constant values as low as -2 ± 1°C were obtained and maintained for up to three hours.

The use of a water cooled coil to keep a constant temperature in the ultrasonic tank has already been discussed (Section 2.3.3). This gave a temperature which could be controlled at about ± 2°C in the temperature range from 10°C to 90°C.

2.3.5 Concentration of the Electrolyte

It is important that the plating bath should contain a sufficient volume of electrolyte to prevent a significant change occurring in the composition, during an experiment. This is particularly relevant in pure solutions, because a change occurs in the metal ion concentration if the rate of deposition at the cathode is not equal to the rate of dissolution at the anode. The incorporation of an addition agent in the deposited metal has been observed and discussed in Section 1.2.6: this may have a considerable effect on the properties of the deposit.

In order to determine whether changes occurred in the plating bath in this present work, a thick copper deposit was plated on to electrodes of an area of 4 x 10⁻³ m² with a current density of 215 A/m² for three hours, using one litre of the copper sulphate-sulphuric acid plating bath containing 0.119 g/l benzotriazole. The deposit was then mounted, cross-sectioned, polished and etched and the microhardness measured at different distances from the substrate. Because no appreciable variation was found in the hardness at different deposit thicknesses, it was concluded that no significant changes occurred in the bath during plating to affect the hardness.

It is known from work by Read and Graham²⁷⁶ that the composition of the cathode layer may be quite different from that of the bulk solution. These differences may be important in this work, particularly when benzotriazole is used; however, ultrasonic vibrations are known to eliminate the diffusion layers at copper electrode surfaces²⁴⁵. Read and Graham²⁷⁶ showed that,
for the copper sulphate system, the following effects occurred:

1. variations in the bulk sulphuric acid concentration affect the cathodic film more than similar bulk copper sulphate changes;

2. a small temperature rise markedly decreases the concentration gradient, because the acid content of the film decreases and the copper ion concentration increases;

3. there can be a variation in the cathodic film composition with a change in the siting of a vertical cathode, despite agitation;

4. an increase in the current density increases the sulphuric acid content and decreases the copper sulphate content of the cathodic film.

It is for reasons such as these, that it is necessary to fix the relative positions of the anode and cathode, to stabilise the plating temperature and to ensure that the current density remains as constant as possible during the experiment.

2.3.6 Electrode Preparation

The cathodes were prepared from thick copper sheet (2.5 x 10^{-3} or 1.7 x 10^{-3}m thick). In the unpurified bath, general laboratory grade copper was used for both electrodes while, in the purified bath, analar grade copper was used for the anodes and the general grade for cathodes. The areas of the anode and cathode were equal unless stated otherwise.

It soon became evident that, unless the surfaces were prepared carefully, the adhesion of the electrodeposited copper was not always good and peeling sometimes occurred with highly stressed deposits. The following procedure was found to give good deposits and reproducible results. The copper surfaces were degreased by immersion in acetone in a beaker that was placed in the ultrasonic tank and subjected to vibrations for about fifteen minutes. This was followed by a quick pickle at room temperature in a mixture of 50% nitric acid and 50% distilled water, to remove any surface films. The specimens were then washed thoroughly in distilled water and air dried.

The specimens were lacquered with 'Lacomit' so that only the required surface area would be plated at the appropriate current density. This lacquer was dried in an air furnace at 100°C for several hours. To ascertain that the Lacomit itself did not introduce any impurities into the plating solution, a comparison was made with another lacquer, 'Collodion'. The stress results, for a parallel pair of experiments using these lacquers
were the same so it was concluded that, as they had very different compositions, no significant impurity was introduced into the electrolyte.

2.3.7 Cathodic Current Distribution

The current distribution on the cathodes should be as uniform as possible to give representative and reproducible results. With a flat cathode, the area to be plated should be as central as possible on the electrode so that the lacquer covers the edges. The anode-cathode separation distance and relative positions were chosen and fixed, because the literature indicated that these values gave the best compromise for planar, equipotential surfaces and optimum current distribution. The anode and cathode in each cell were held in a vertical position with crocodile clips on very thick copper wire which was clamped above the bath, with the electrode surfaces parallel to each other at a fixed distance apart. The spacing of the anode and cathode was 2.5 times the electrode width and this distance has been related to the throwing power. When a contractometer is used to measure the internal stress, the cathode is in the form of a helix and, therefore, a cylindrical, anode is used to give a uniform deposit thickness.

The time of immersion, prior to the commencement of plating and after plating had been completed, were kept as short as possible, to minimize any dissolution of the copper electrodes. The total immersion time of the electrodes in the plating solution is important because, even when no current is flowing, certain reactions may take place at the copper surfaces and alter the nature of the surface and possibly the cathodic and anodic films. Evans suggested that the dissolution of a copper surface in an oxygenated solution may occur thus:

\[ 2 \text{Cu} + 2\text{H}_2\text{SO}_4 + \text{O}_2 = 2 \text{CuSO}_4 + 2\text{H}_2\text{O} \]

In the absence of oxygen, copper can still dissolve until an equilibrium between cuprous and cupric ions is reached. This particular reaction has been established as one of the chief causes of error in the copper coulometer. Local electrochemical corrosion of polycrystalline copper may also occur due to the variations in the electrode potentials of grain boundaries and different crystallographic faces of the copper.

2.3.8 Current Density and Plating Time

A direct current, stabilized power supply instrument was used which was
capable of producing up to thirty volts and a current of three amperes. This instrument was found to provide a constant current over a period of up to three hours which was the longest plating time used for the hardness measurements.

The plating solutions were contained in beakers surrounded by constant temperature water baths. These beakers were arranged in series so that, with electrodes of the same area, the current density in each cell was identical. It was necessary to control the current density carefully because preliminary stress measurements indicated that the internal stress increased considerably with the current density, at a bath temperature of 0°C, as shown in Table 2.3.8.

<table>
<thead>
<tr>
<th>Current Density $A/m^2$</th>
<th>Internal Stress $MN/m^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>1.03</td>
</tr>
<tr>
<td>110</td>
<td>1.72</td>
</tr>
<tr>
<td>215</td>
<td>6.89</td>
</tr>
<tr>
<td>430</td>
<td>19.3</td>
</tr>
<tr>
<td>645</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Table 2.3.8

The plating time was adjusted to give a constant deposit thickness, so that any variation with thickness in the property to be measured was minimized: for these calculations the current efficiency was assumed to be 100% and, under normal conditions, this introduced only a very small error of 1 or 2%. This arrangement was used to investigate the effect of varying either the plating temperature or the agitation of the solution, with a fixed current density.
2.4. Electrodeposition: Measurement of Properties

2.4.1 Determination of Current Efficiency

The current efficiency is the percentage of the total current flowing through a cell that is effectively employed in the cathodic deposition or the anodic dissolution of a metal. If the current efficiency is less than 100%, some of the current is used in secondary reactions, such as the codeposition of hydrogen at the cathode. It is not the economic loss, due to the higher current consumption required to produce a coating of a particular thickness, that is usually considered important, but the influence of the side reactions on the quality of the coatings, e.g. a small volume of hydrogen may produce a high internal stress in the coating.

The standard method of measuring a quantity of electricity is to use a silver coulometer, in which one coulomb of electricity deposits 0.001118 g of silver. For accurate measurements, the current density used in this silver coulometer must normally be about 30A/m², hence it was not practical to use it with current densities of 500A/m² that were used in this work, because extremely large silver electrodes would be required. The use of a commercial coulometer, a Batty instrument, was considered but this had an accuracy of only ± 5%, which was not sufficiently sensitive for these determinations. Therefore, it was decided to set up experiments to measure the relative changes in the current efficiency produced by variations of the current density and the bath temperature.

The effect of varying the current density was first studied by using nine pairs of electrodes of different surface areas, the smallest being 1.64 x 10^{-4} m² and the largest 2.7 x 10^{-3} m². These electrodes were prepared as described in the section on Electrode Preparation (§3.6) and then weighed. They were connected in series in the same plating tank, to ensure a constant temperature, and a current of one ampere was passed for an hour, corresponding to a current density varying from approximately 860A/m² to 55 A/m². After deposition, the electrodes were washed, dried and weighed so that the weight changes for each pair of electrodes could be compared. The results obtained using this technique were unexpected and some cathodes even lost weight. The experiment was, therefore, repeated with each pair of electrodes in a separate beaker; all the beakers were placed in a constant temperature water bath to ensure an identical temperature in each beaker. This arrangement gave satisfactory results, so the process
was repeated at different temperatures from 10°C to 77°C. The variation in the current efficiency was determined by this method using different current densities at a fixed temperature.

To determine the effect of varying the plating on the current efficiency, the current density was fixed by using four cells in series, having all the electrodes of the same area. The solution temperatures were kept constant in water baths at about 10°C, 25°C, 50°C and 85°C and a current of one ampere was again passed for an hour and the current efficiency was calculated. Because approximately the same thickness of copper was deposited on to the specimens, they were then used to give an indication of the variation of hardness with bath temperature.

2.4.2 Metal Distribution Ratio and Throwing Power

In this work the Haring Blum cell was used to determine the metal distribution ratio, from which the throwing power was calculated using the Field formula. The cell consisted of a rectangular box, with internal dimensions $1.5 \times 10^{-1}$ m long, $5 \times 10^{-2}$ m deep, constructed of perspex or polymethyl-methacrylate. Two cathodes of equal area were placed at the opposite ends of the cell and joined together with a thick wire. The anode, which was perforated by five holes to minimize any difference in the concentration polarization on each side, was placed in the cell between the cathodes at a distance of $2.5 \times 10^{-2}$ m from one end and $1.25 \times 10^{-1}$ m from the other. This gave a ratio of distances of 5:1 and is termed the primary current ratio. For each run all the electrodes were cleaned in nitric acid, washed in water, dried in air, and weighed, and then a current of one ampere was passed for 20 minutes. Finally the electrodes were removed from the cell, washed, dried in air and weighed. Three identical cells were used in series with either one, or two, cells in the ultrasonic tank, so that the effect of ultrasonics on the metal distribution and throwing power could be compared with the results from the still solution. However, this arrangement gave irregular values for the metal distribution ratio and throwing power; for two identical experiments with still solutions the metal distribution ratios were 2.97, 2.34, 3.47, 4.24, 3.79 and 4.53.

The experimental technique finally adopted, which gave reproducible results for the metal distribution ratio of 4.05, 3.99 and 4.14, is now described. In each cell, those surfaces of both cathodes that face away
from the anode were lacquered with Lacomit and then dried in an oven. A thick copper wire was soldered on to the top of each cathode and bent so the two free ends in a cell could be connected together with an electrical barrier strip, so minimizing any contact resistance which could affect the current distribution. The other faces of the cathodes were given a quick etch in 50% nitric acid for 30 seconds, washed in distilled water and dried with a hot air fan. For accurate results it was essential to use all the electrodes in a vertical position, with the cathodes flat against the ends of the cell, in positions which could be exactly reproduced from one run to another. This was achieved by the use of very small perspex cubes stuck to the bottom of the cell to locate the ends of the electrodes, and by horizontal perspex bars on top of the cell, to keep the electrodes in a vertical position with the cathodes against the ends of the cell.

To minimize the dissolution of copper in the acid plating solution as described earlier, (Section 2.3.7), the electrodes were positioned in the empty cells and a small potential was applied to prevent corrosion when the appropriate volume of solution was added. The potential was adjusted to give the required current density; after plating for the necessary time, the applied potential was reduced to a very low value to avoid any anodic dissolution and the electrodes were removed from the bath, immediately washed, dried and weighed.

2.4.3 Surface Appearance

The effect on the surface appearance of varying the current density and the bath temperature was investigated for deposits from the unpurified bath. Five current densities 65, 140, 220, 430 and 650 A/m² were used, together with five temperatures, 0, 23, 40, 60 and 80°C; the plating time varied and depended upon the current density, being equivalent to 1 hour with 220 A/m². After plating the specimens in series, they were washed in warm water, dipped in acetone and dried in air. Photographs were taken of all these deposits on a Zeiss microscope at a magnification of x 320.

The effect of different degrees of solution agitation, i.e. still, stirred and ultrasonic, was studied at 23°C with a current density of 430 A/m², using the unpurified bath with and without an addition of benzotriazole. The surfaces of these specimens were photographed at magnifications of x 1 and x 320, as soon as possible after plating, to minimize the extent of cracking and peeling of the coat.
2.4.4 Determination of Grain Size

It has been established by Butts and DeNora\textsuperscript{150} that the grain size of a deposit is mainly influenced by the plating conditions. It is also known that the grain size has a marked effect on the properties of a deposit, such as the internal stress and microhardness. Therefore, the grain size was measured, so that it could be compared with the other properties of the deposit to be investigated.

The grain size of deposits was measured by the linear intercept method on a polished and etched surface. The plated surface was lightly polished with a fine metal polish to remove the protruding areas. The Beilby layer was removed by electropolishing with concentrated phosphoric acid (specific gravity 1.75) at room temperature, using a potential of about three volts and a current density of 200 to 500 A/m\textsuperscript{2}; a polishing time of between two and five minutes was found to be satisfactory. Because the main comparison was made between the grain size and microhardness, the same specimens were used for both measurements. The thickness of the deposits was fixed at 5 x 10\textsuperscript{-5} m since this was the value required for the hardness determination. After polishing, the copper deposits were etched at room temperature with a mixture of 50 mls ammonium hydroxide, 20 mls of hydrogen peroxide (of strength 30 volumes) and 50 mls of water, which left the grain boundaries clearly visible under the microscope. However, the above mentioned etchant stained the surface of deposits from the plating bath containing benzotriazole, so for these coatings alcoholic ferric chloride was used.

The surface line intercept method was used to measure the grain size. The etched surface, showing deposits with a large grain size, was magnified and projected on to a Quantimet television screen, whereas a Vickers Projection microscope with oil immersion (quoted magnification up to x 4,000) was used for finer deposits. A straight edged linear scale (perspex ruler) was superimposed on the magnified image and the number of grain boundary intercepts recorded on the largest possible scale length (3 x 10\textsuperscript{-1} m on the Quantimet and 1.5 x 10\textsuperscript{-1} m on the Vickers).

For both instruments the lower magnification was used, so that the maximum number of intercepts was visible, thus giving the most accurate values. Readings were taken on the central region of the deposit, because this area has the most uniform current distribution. An average value was obtained from transverse, longitudinal and diagonal orientations.
of the scale. This method to determine the mean intercept length followed that described in the ASTM standard\textsuperscript{287}. Several correlation factors have been proposed to obtain the grain diameter from the intercept length and these range from 1.5 to 1.26\textsuperscript{288-291}. However, the mean intercept length is recorded in this work, because it is widely used in the literature\textsuperscript{292}.

2.4. Measurement of Internal Stress

**Modified Hoar Arrowsmith Apparatus\textsuperscript{138}**

During the early stages of this work, the internal stress was measured with a modified form of the Hoar Arrowsmith Apparatus\textsuperscript{138} and the later work with a Brenner Senderoff Spiral Contractometer\textsuperscript{192}. The change of the apparatus was not due to any scientific reason but due to the accidental loss of the Hoar Arrowsmith apparatus that occurred during a move from one laboratory to another. The Hoar Arrowsmith Apparatus has been described in detail elsewhere\textsuperscript{138,193} and is shown in Fig 2.4.5 (a) so a further description is not given here. The modifications that have been made to improve it are now briefly described. The modified form Fig. 2.4.5 (b) incorporates a long, light, thin walled, stainless steel tube attached to the free end of the cathode and this tube supports the mirror, so increasing the sensitivity of the instrument. The electromagnets can be moved along parallel track lines and then clamped into position so that the applied field can be varied depending upon the stresses expected; for high stresses the magnets are moved closer to the strip. The instrument can be calibrated in a vertical position and this prevents the bending of the strip under its own weight, which may occur during calibration in a horizontal position. Weights are placed in the pans attached to the end of the strip by a magnet sheath and rigid struts: the sensitivity can be improved by increasing the distance between the pans. Using this arrangement the gravimetric and magnetic forces are applied to the same position on the strip, which may be close to the top of the deposit to increase the accuracy.

In this apparatus the anode was a strip of metal, with the same dimensions as the cathode, held in a position parallel to the cathode and at a distance of about $4 \times 10^{-2}$ m from the face to be plated. A copper anode was used for copper plating and was of the same grade as the chemicals used for the plating solution, i.e. general or analar quality.

The stress values in copper deposits measured with this instrument were compared with those obtained from the MacNaughton and Hothersall apparatus.
Cathode
A Anode
E Electromagnets
P Pans for calibrating weights
S Magnetic sheath
R Railway lines

Fig. 2.4.5. Hoar Arrowsmith Apparatus and Modified Form
and also the Contractometer. For this comparison a stainless steel strip, measuring approximately 0.12 x 0.01 x 0.0005m, was used as the cathode in the modified apparatus. This strip, and a similar pair for the MacNaughton and Hothersall method, were prepared by the same processes as used for the spiral in the Contractometer (which will be discussed later in this section), namely degreased in acetone and then plated with thin coatings of nickel and copper. Analytical solutions were used and the plating conditions and deposit thickness were standardized for the three stress measurements. The tensile stress values obtained were an average of three separate readings and in close agreement, being 14.5 MN/m² with the MacNaughton and Hothersall method, 13.8 MN/m² with the contractometer and 13.1 MN/m² with the modified apparatus.

The normal cathode in this work was a strip of a platinum 10% iridium alloy, the iridium being added to increase the elasticity and strength of the platinum. To ascertain that the strip was not permanently deformed during the deposition of a stressed coating, the strip was plated with a stressed deposit and then the current was reversed and the coating was anodically dissolved. The fact that the strip returned to the original position, as indicated by the light spot, suggested that there was no permanent deformation. Because the anodic dissolution of the coating could also have removed the nickel and copper plated during the preparation of the strip, it can be assumed that there was either a very low or a zero internal stress in these thin deposits.

Brenner Senderoff Spiral Contractometer

This instrument consists of a cathode strip bent into the form of a helix, the upper end of which is fixed and the lower end is free to rotate, see Fig. 2.4.5 (c). During the plating of a stressed deposit the lower end of the spiral is deflected and this movement is magnified by means of a system of gears and indicated by a dial on top of the instrument. If the deposit on the spiral is in tension the spiral unwinds; if in compressive stress it winds closer.

The spiral is a titanium stabilized 18/8 stainless steel, which requires careful surface preparation before it can be plated with copper from the copper sulphate bath and the procedure followed was similar to that in the article by Brenner and Senderoff, in which they described the instrument. The spiral was degreased by immersion in acetone in an ultrasonic tank and
Fig 2.4.5(c) Brenner Senderoff Spiral Contractometer.
then plated with nickel from the Wood's bath which contained 250 g/l nickel chloride (NiCl₂·6H₂O) and 50 ml/l concentrated hydrochloric acid. The time used was two minutes at 60°C with 200 A/m². This was followed by a flash coating with copper from the cyanide bath using the same plating conditions and time. After preliminary tests, it was not found necessary to lacquer the inner surface of the spiral to prevent deposition, because very little copper was plated on the inside of the spiral.

The helix was clamped to the instrument with lacquered clips and calibrated by applying a weight, on a thread over a pulley, attached to the lower, free end of the helix. The contractometer reading was recorded on the dial, both as the load was increased and decreased, and a graph of load v deflection was plotted. The process was repeated with the spiral twisting in the opposite direction, so that the stress value could be obtained, whichever direction the spiral moved during plating. This graph was found to be a straight line and, from the gradient, the deflection constant K can be calculated. The mean stress in the deposit was calculated from the equation:

\[ S = \frac{2KD}{ptd} \times 485 \]

Where
- \( S \) = mean stress in kN/m²
- \( K \) = constant, gradient of load v deflection curve
- \( D \) = contractometer deflection in degrees
- \( p \) = pitch of the helix in cm
- \( t \) = thickness of the material of the helix in cm
- \( d \) = deposit thickness in cm.

In this work nine spirals were prepared together and stored in a desiccator, to prevent surface corrosion, until required. Three contractometers were used and it was necessary, before every stress determination, to calibrate the spiral when clamped to a particular contractometer. The spirals were connected in series and, after calibration in air, each was immersed in a plating solution contained in a one litre beaker which, in turn, was placed in a three litre glass vessel containing the water which acted as a constant temperature bath. The litre beaker was lined with a clean cylindrical anode, which was used to give a uniformly thick deposit on the spiral. The solutions
were magnetically stirred below the spirals.

Readings were taken of the deflections during plating, after lightly tapping the head of the instrument to overcome friction in the gears. Because different current densities were used, the deflections were recorded after plating times which corresponded to certain deposit thicknesses. The deposit thickness, after plating had finished, was calculated from the weight, area and density of the deposit, because an accurate micrometer reading could not be obtained, as the cathode was curved. The validity of the assumptions made in this, and other methods, has been examined by Abe and West.

2.4.6 Measurement of Microhardness

The preliminary work on the microhardness of copper deposits was carried out with the GKN Microhardness Tester. However, because only two sets of results were obtained with this instrument, its operation is not described but followed that in the manual. The load was 30 g for the copper deposits and 100 g for the deposits containing benzotriazole: this change in the load could have introduced a small inaccuracy into the readings so, after this preliminary work, a fixed load was used in all the subsequent tests. The hardness of the copper was HV 102 and that from a bath containing benzotriazole HV 374, both these values were an average of 7 pairs of readings. Because of the very large increase produced by the benzotriazole, the effect of the separate plating variables, bath temperature, current density, etc, was investigated for both the plain bath and the one containing benzotriazole.

The Akashi Microhardness Tester was used for the later work, because it was then available and more convenient to operate. The surface to be examined is viewed at a magnification of x 20 and the area to be tested is centrally aligned. The carriage supporting the specimen is then slid along rails until it is below the diamond indenter, the carriage is then raised and the load applied for a period of ten seconds. The load is then removed by lowering the carriage, which is moved back under the microscope. The length of the two diagonals of the diamond shaped indentation are measured and the average is calculated. From this value the corresponding Vickers hardness number can be obtained, using the conversion tables provided with the instrument.
Reproducible results can only be obtained if the surface is smooth and a diamond shaped indentation is formed. When the surface is rough a kite shape is produced, with different lengths for the diagonals of the indentation, and in this work, if these pairs of readings were not within \( \pm 3\% \) of each other, the reading was repeated. The surfaces were electro-polished as described in the section on grain size determination. The testing load was chosen as 50 g because this gave a small depth of indentation, and, with the copper specimens used, a diagonal length for the diamond impression of between about 36 x 10\(^{-6}\) m for the softest coatings and 17 x 10\(^{-6}\) m for the hardest (corresponding to Vickers hardness numbers of about HV 70 and 320). The load was determined mainly by the softest coatings and fixed because, although Vickers hardness is generally acknowledged not to depend upon the load, there is some evidence that with very small loads the hardness increases with a decrease in the load\(^{294}\). Therefore, by fixing the load for all the coatings this possible variation was avoided. A thick substrate should be used to avoid any bending produced by internal stress in the deposit during the plating. It should also be at 1.5 times the diagonal length of the indentation (ten times the depth of indentation) according to the instruction manual, so the plating times and current densities were adjusted to give a constant deposit thickness of approximately 5 x 10\(^{-5}\) m. For harder deposits, a thinner deposit thickness would have been suitable, but the thickness was standardized to eliminate the errors arising from any variations in the hardness with deposit thickness.

The cathodes were cut from copper sheet with a thickness of 2.5 x 10\(^{-3}\) m, which was cleaned in the usual way and then lacquered to give an exposed area of 4 x 10\(^{-3}\) m\(^2\). The anodes were of the same area and the electrodes were separated in the plating cell by a distance of 6 x 10\(^{-2}\) m, with the magnetic stirrer placed midway at a fixed distance below the electrodes. One litre of fresh solution was used for each run and, after deposition, the cathodes were immediately removed, rinsed in distilled water, dried and the hardness measured. This was done to minimize the effects of stress relief and/or peeling of the deposit, which would reduce the hardness.

The readings were taken on the central area of the electrodes, where the current density and deposit thickness were most uniform. Each hardness value recorded is an average of at least seven pairs of readings. To check the accuracy and setting of the tester, a specimen of annealed, polished copper sheet was used as a standard before and after each set of readings.
3. PRELIMINARY RESULTS

3.1 Introduction

In the first part of this chapter a description is given of the preliminary work which was done to investigate the effect of benzotriazole on the corrosion of copper immersed in various solutions. Experiments were conducted with copper specimens immersed in the solution being tested and also in a solution containing an addition of benzotriazole. Copper samples which had been treated with a hot solution of benzotriazole prior to the test were compared with the untreated specimens in the same solutions. The oxidation resistance of plain and dipped copper specimens was studied using a thermal balance.

The second part of this chapter covers the electrodeposition of copper from the copper sulphate-sulphuric acid plating bath. An investigation was made into the effect of some plating variables on the current efficiency, metal distribution ratio and throwing power of the solution, as well as the hardness and internal stress of the deposits.

3.2 The Corrosion Inhibition of Copper produced by Benzotriazole.

Introduction.

The literature survey (section 1.1.5) indicated that very small additions of benzotriazole were sufficient to produce a marked reduction in the corrosion of copper, in certain specified solutions. In this preliminary work, the range of solutions used included two acids, hydrochloric and nitric, one base, ammonia, and one salt, sodium chloride, and the effect on the rate of corrosion of an addition of 0.119 g/l benzotriazole to each solution was investigated.

The copper specimens were cleaned, as described previously in the experimental section 2.2.4, and some were pretreated by immersion in a hot solution of benzotriazole at 60°C for about five minutes, to allow a protective film to form on the surface. All the specimens were then dried,
weighed and immersed in a litre of the solution being studied, one set in the plain solution, another set in the solution containing benzotriazole and the third set, that had been pretreated, in the plain solution. After the appropriate time, the specimens were taken out of the solution, washed in hot water to remove any soluble or loose film, dried in air and weighed. The tests were all conducted in still solutions at room temperature (20 ± 3°C).

Results

These are given in Table 3.2.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Weight Change g/5×10⁻³ m² 17 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plain Copper</td>
</tr>
<tr>
<td></td>
<td>Plain Solution</td>
</tr>
<tr>
<td>0.1N Hydrochloric acid</td>
<td>1.5486</td>
</tr>
<tr>
<td>0.1N Nitric acid</td>
<td>0.1407</td>
</tr>
<tr>
<td>3% Ammonia</td>
<td>0.6451</td>
</tr>
<tr>
<td>0.5N Sodium chloride</td>
<td>0.1292*</td>
</tr>
</tbody>
</table>

* Weight loss g/6.0420 m² in 6 days

Discussion

These results indicate that a significant reduction in the rate of corrosion of the copper was produced by the addition of benzotriazole to all the solutions used. However, most of the copper specimens that had been pretreated with the benzotriazole corroded at a faster rate than those which had not been treated. This may be due to the formation of an incomplete protective film on the copper during the pre-treatment, resulting in the production of active-passive cells, which gave an increased rate of corrosion.

Therefore, in the subsequent work the dipped copper surfaces were treated with the hot aqueous benzotriazole solution for a much longer period, about thirty minutes, to encourage the production of a continuous film on the copper. It was also
decided to stir slowly the solution with magnets, in order to reduce any variations in the solution composition or temperature and to give more reproducible values.

Conclusion

From the results it may be concluded that:
(1) the addition of 0.119 g/l benzotriazole to all the solutions produced a marked decrease in corrosion of the copper;
(2) the process of dipping the copper in a hot solution of benzotriazole prior to testing had a marked effect and either increased or decreased the rate of corrosion of the specimens.

3.3. High Temperature Oxidation Resistance of Copper treated with Benzotriazole

Introduction

The use of benzotriazole to prevent copper tarnishing at room temperature is well known and has been discussed in the literature review (section 1.1.5). Cotton\textsuperscript{21} observed that it gave some protection at elevated temperatures but he did not give any quantitative data. The aim of this section of the work was to determine the rate of oxidation of untreated and treated copper specimens at 300\textdegree C. The procedure was that described in section 2.2.5. and all the experiments were duplicated to give an indication of the accuracy. The specimens were immersed in the hot benzotriazole solution for about 30 minutes, as described in section 3.2.

Results

Experiments with Plain Specimens
Area: \(2 \times 10^{-2} \text{m} \times 5 \times 10^{-2} \text{m} \times 2 = 2 \times 10^{-3} \text{m}^2\).
Weight increase at 300\textdegree C: 2.6 mg and 3.4 mg in 800 mins.

Experiment with Plain and Dipper Specimens
Area: \(5.6 \times 10^{-2} \text{m} \times 8.0 \times 10^{-2} \text{m} \times 2 \approx 9 \times 10^{-3} \text{m}^2\)
Weight increase at 300\textdegree C for 500 mins.
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Weight Increase mg.</th>
<th>Specimen 1</th>
<th>Specimen 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain Copper</td>
<td></td>
<td>13.3</td>
<td>12.1</td>
<td>12.7</td>
</tr>
<tr>
<td>Copper dipped into hot water</td>
<td></td>
<td>11.4</td>
<td>11.0</td>
<td>11.2</td>
</tr>
<tr>
<td>Copper dipped into Benzotriazole Solution</td>
<td></td>
<td>5.0</td>
<td>4.6</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Table 3.3

Discussion

The results show that the weight changes at 300°C were very low for specimens with a surface area of $2 \times 10^{-3} \text{m}^2$ and that a small difference in the weight increase gave a large percentage error (about 30%). However, with larger areas ($9 \times 10^{-3} \text{m}^2$) the weight increases were much larger and the errors (about 10%) in the readings of the plain specimens correspondingly smaller. The specimens that had been treated in hot water showed a small difference (14%) from the plain untreated sample, but the gain was much larger than for those treated with benzotriazole.

The benzotriazole treatment produced a marked decrease in the rate of oxidation of the copper samples. Therefore, further work was planned to study the manner in which this reduction in the rate of oxidation was affected by the temperature of oxidation.

Conclusion

The rate of oxidation at 300°C of copper was significantly reduced, if the specimens were dipped into a hot benzotriazole solution and allowed to dry in air prior to oxidation.

3.4 The Effect of Current Density and Ultrasonic Agitation on the Current Efficiency, Metal Distribution Ratio and Throwing Power of the Copper Plating Bath.

Introduction

In this section of the preliminary work the Haring Blum cell was used to investigate the weight changes that occurred at the electrodes, when different current densities were used with still and ultrasonically agitated solutions. Three identical cells were connected in series, with two in the ultrasonic bath and one containing a still solution, or vice versa.
The relative current efficiencies of the anodic and cathodic processes were indicated by the weight loss of the anode and the total weight gain of the two cathodes. The weight changes were measured with three different currents, so that any variation with the current density could be observed.

The metal distribution ratio was calculated from the weight gains of the two cathodes. The throwing power was determined from this ratio, using the Field Formula given in section 1.3.7, for both the still and the ultrasonically agitated solutions at the three different current densities. The experimental details were as described in the experimental section 2.4.2.

Results
These are given in Table 3.4

<table>
<thead>
<tr>
<th>Anodic Current Density</th>
<th>Plating Time</th>
<th>Anode Loss</th>
<th>Cathode 1 Gain M₁</th>
<th>Cathode 2 Gain M₂</th>
<th>Total Cathode Gain M₁ + M₂</th>
<th>Metal Distr. Ratio M₁/M₂</th>
<th>Throwing Power %</th>
<th>Solution Agitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/M</td>
<td>Mins.</td>
<td>g</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>385</td>
<td>10</td>
<td>.4107</td>
<td>.3030</td>
<td>.0927</td>
<td>.3957</td>
<td>3.269</td>
<td>27.61</td>
<td>Still</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.4168</td>
<td>.3408</td>
<td>.0730</td>
<td>.4138</td>
<td>4.668</td>
<td>4.33</td>
<td>Ultrasonic</td>
</tr>
<tr>
<td>195</td>
<td>15</td>
<td>.3062</td>
<td>.2309</td>
<td>.0578</td>
<td>.2887</td>
<td>3.994</td>
<td>14.38</td>
<td>Still</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.3130</td>
<td>.2388</td>
<td>.0516</td>
<td>.2904</td>
<td>4.628</td>
<td>4.88</td>
<td>Ultrasonic</td>
</tr>
<tr>
<td>30</td>
<td>120</td>
<td>.4030</td>
<td>.2874</td>
<td>.0960</td>
<td>.3834</td>
<td>2.994</td>
<td>33.47</td>
<td>Still</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.4118</td>
<td>.3021</td>
<td>.0858</td>
<td>.3879</td>
<td>3.521</td>
<td>22.68</td>
<td>Ultrasonic</td>
</tr>
</tbody>
</table>

Table 3.4

Discussion
From the weight changes recorded in Table 3.4, it is apparent that the accuracy of the metal distribution ratio depends particularly upon the weight change of the cathode further away from the anode. A difference in weight of 1 mg represents an approximate error of only 0.3% for the cathode nearer to the anode, whereas on the other cathode it is 2%. Although
the total weight of copper deposited should not affect the metal distribution ratio, it was decided for future experiments to fix this at one ampere for 20 minutes, or the equivalent.

Conclusion

From the results it may be concluded that:

(1) the weight loss of the anode was greater than the total weight gain of the cathodes at all the current densities used, i.e. the anodic current efficiency was always higher than the cathodic current efficiency;

(2) the anode in the ultrasonic bath lost more weight than in the still bath, i.e. the anodic current efficiency was higher in the ultrasonically agitated solution than in the still solution;

(3) the total weight gain of the cathodes in the ultrasonic bath was greater than in the still bath, i.e. the cathodic current efficiency was higher in the ultrasonically agitated solution than in the still solution;

(4) in the ultrasonic bath the metal distribution ratio was higher and the throwing power was lower than in the still bath;

(5) the metal distribution ratio in the ultrasonic bath increased with current density, whereas a peak was obtained in the still bath at about 170 A/m², the throwing power changing in the opposite manner.

3.5. The Effect of Different Plating Variables on the Hardness of Copper Deposits from the Plain Bath

Introduction

A study was made of the effect on the hardness of varying the concentration of the solution and the plating conditions. In each experiment all the factors, except that being investigated, were kept constant. The concentration of copper sulphate in the plating solution was varied as well as the sulphuric acid, although it was suggested in the literature review section (1.3.4) that this would give only a very small change. The hardness measurements were made on very thick deposits (about 2.5 x 10⁻⁴ m) so that the effect of the substrate could be ignored.
**Results**

In all the experiments a stirred standard bath of 125 g/l copper sulphate and 49 g/l sulphuric acid was used at a temperature of 20°C and with a current density of 215A/m², unless otherwise stated.

### 3.5.1 Effect of Solution Purification

**Bath Temperature 25°C**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard bath made with general grade chemicals</td>
<td>84</td>
</tr>
<tr>
<td>Standard bath made with general grade chemicals and purified</td>
<td>71</td>
</tr>
</tbody>
</table>

### 3.5.2 Effect of Concentration of Copper Sulphate (CuSO₄·5H₂O)

<table>
<thead>
<tr>
<th>Concentration of Copper Sulphate in Bath g/l</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>Powdery</td>
</tr>
<tr>
<td>140</td>
<td>104</td>
</tr>
<tr>
<td>280</td>
<td>58</td>
</tr>
</tbody>
</table>

### 3.5.3 Effect of Concentration of Sulphuric Acid in Bath

<table>
<thead>
<tr>
<th>Concentration of Sulphuric Acid g/l</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Powdery</td>
</tr>
<tr>
<td>25</td>
<td>88</td>
</tr>
<tr>
<td>49</td>
<td>83</td>
</tr>
<tr>
<td>98</td>
<td>78</td>
</tr>
</tbody>
</table>

### 3.5.4 Effect of Bath Temperature

<table>
<thead>
<tr>
<th>Bath Temperature °C</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>102</td>
</tr>
<tr>
<td>23</td>
<td>87</td>
</tr>
<tr>
<td>52</td>
<td>68</td>
</tr>
</tbody>
</table>

### 3.5.5 Effect of Current Density

**Bath Temperature 23°C**

<table>
<thead>
<tr>
<th>Current Density Used A/m²</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>88</td>
</tr>
<tr>
<td>215</td>
<td>95</td>
</tr>
<tr>
<td>430</td>
<td>116</td>
</tr>
</tbody>
</table>
3.5.6 Effect of Solution Agitation
Bath Temperature 18°C

<table>
<thead>
<tr>
<th>Plating Bath</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Still Solution</td>
<td>75</td>
</tr>
<tr>
<td>Stirred Solution</td>
<td>95</td>
</tr>
<tr>
<td>Ultransonic Solution</td>
<td>111</td>
</tr>
</tbody>
</table>

Discussion
The hardness was measured at three different values of the variable being studied, with the plating cells arranged in series, with the exception of the current density in which different currents and plating times were used. Thus, the results can only be compared within each set, because small variations occurred in the current and plating temperature. This is illustrated by the fact that the hardness of the deposit plated from the stirred bath, in the experiment designed to study the effect of solution agitation, was 95 HV as compared with 93 HV when the current density was varied.

Conclusion
From these results it may be concluded that:

1. purification of the plating solution reduced the hardness of the resulting deposit;
2. the hardness was affected by the concentration of copper sulphate in the bath;
3. this hardness was only slightly affected by the concentration of sulphuric acid in the bath;
4. too low a concentration of copper sulphate or sulphuric acid gave a powdery deposit;
5. an increase in the bath temperature decreased the hardness;
6. an increase in the current density increased the hardness;
7. the hardness increased with the type of solution agitation in the following order: still, stirred and ultrasonic.

3.6 The Effect of Different Plating Variables on the Hardness of Copper Deposits from the Bath containing Benzotriazole.

Introduction
In all these experiments the plating bath contained 0.119 g/l (0.001M) benzotriazole, unless otherwise stated. The variables
studied were the same as in the plain bath, namely the concentration of copper sulphate, bath temperature, current density and solution agitation, with the exception of the concentration of sulphuric acid. The effect of agitation was studied with a plain bath and also with additions of 0.012 g/l, and a much higher concentration of 0.24 g/l.

Various additions from 0 to 1.0 g/l benzotriazole were investigated with ultrasonic agitation, and also with a still bath using a purified solution. The hardness of the deposits was measured immediately after plating, and after several days, to ascertain whether any ageing of the deposits had occurred.

Results

In all the experiments a stirred standard bath of 125 g/l copper sulphate and 49 g/l sulphuric acid was used, containing 0.119 g/l benzotriazole at a temperature of 20°C and with a current density of 215 A/m², unless otherwise stated.

3.6.1 Effect of Solution Purification

Bath Temperature 25°C

<table>
<thead>
<tr>
<th>Solution</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard bath made with general grade chemicals</td>
<td>248</td>
</tr>
<tr>
<td>Standard bath made with general grade chemicals and purified</td>
<td>195</td>
</tr>
</tbody>
</table>

3.6.2 Effect of Concentration of Copper Sulphate (CuSO₄·5H₂O)

<table>
<thead>
<tr>
<th>Concentration of Copper Sulphate in Bath g/l</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>187</td>
</tr>
<tr>
<td>140</td>
<td>300</td>
</tr>
<tr>
<td>280</td>
<td>224</td>
</tr>
</tbody>
</table>

3.6.3 Effect of Bath Temperature

<table>
<thead>
<tr>
<th>Bath Temperature °C</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>260</td>
</tr>
<tr>
<td>45</td>
<td>202</td>
</tr>
<tr>
<td>65</td>
<td>161</td>
</tr>
</tbody>
</table>
### 3.6.4 Effect of Current Density
Bath Temperature 23°C

<table>
<thead>
<tr>
<th>Current Density used A/m²</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>228</td>
</tr>
<tr>
<td>520</td>
<td>255</td>
</tr>
<tr>
<td>645</td>
<td>280</td>
</tr>
</tbody>
</table>

### 3.6.5 Effect of Solution Agitation

<table>
<thead>
<tr>
<th>Plating Bath</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Still Solution</td>
</tr>
<tr>
<td>Standard Bath</td>
<td>81</td>
</tr>
<tr>
<td>Standard Bath +0.013 g/l benzotriazole</td>
<td>104</td>
</tr>
<tr>
<td>Standard Bath +0.24 g/l benzotriazole</td>
<td>217</td>
</tr>
</tbody>
</table>
Effect of the Concentration of Benzotriazole and the Ageing of the Deposits.

An ultrasonically agitated, purified bath made from analar grade chemicals was used, at a bath temperature at 25°C and current density 215 A/m².

<table>
<thead>
<tr>
<th>Concentration of benzotriazole in plating bath g/l</th>
<th>Deposit Hardness HV</th>
<th>Ageing % change after 15 days</th>
<th>Surface Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immediately</td>
<td>After 1 day</td>
<td>After 15 days</td>
</tr>
<tr>
<td>0</td>
<td>62.9</td>
<td>62.6</td>
<td>56.5</td>
</tr>
<tr>
<td>0.0005</td>
<td>66</td>
<td>62.6</td>
<td>58</td>
</tr>
<tr>
<td>0.001</td>
<td>67</td>
<td>64.2</td>
<td>61</td>
</tr>
<tr>
<td>0.005</td>
<td>68.8</td>
<td>60</td>
<td>64.2</td>
</tr>
<tr>
<td>0.01</td>
<td>86.7</td>
<td>82.6</td>
<td>80.2</td>
</tr>
<tr>
<td>0.12</td>
<td>105</td>
<td>99.7</td>
<td>99.7</td>
</tr>
<tr>
<td>0.2</td>
<td>110</td>
<td>110</td>
<td>107</td>
</tr>
<tr>
<td>0.3</td>
<td>152</td>
<td>148</td>
<td>143</td>
</tr>
<tr>
<td>0.5</td>
<td>152</td>
<td>148</td>
<td>143</td>
</tr>
<tr>
<td>1.0</td>
<td>156</td>
<td>143</td>
<td>143</td>
</tr>
</tbody>
</table>
A magnetically stirred, purified bath made from analar grade chemicals was used, at a bath temperature of 22°C and current density 215 A/m².

<table>
<thead>
<tr>
<th>Concentration of benzotriazole in plating bath g/l</th>
<th>Deposit Hardness HV</th>
<th>Ageing</th>
<th>Surface Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immediately</td>
<td>After 7 days</td>
<td>% change after 7 days</td>
</tr>
<tr>
<td>0</td>
<td>63.9</td>
<td>61.6</td>
<td>3</td>
</tr>
<tr>
<td>0.001</td>
<td>67.7</td>
<td>66.3</td>
<td>2</td>
</tr>
<tr>
<td>0.005</td>
<td>67.7</td>
<td>61.0</td>
<td>10</td>
</tr>
<tr>
<td>0.01</td>
<td>74.4</td>
<td>71.6</td>
<td>4</td>
</tr>
<tr>
<td>0.05</td>
<td>103</td>
<td>102</td>
<td>1</td>
</tr>
<tr>
<td>0.12</td>
<td>127</td>
<td>116</td>
<td>8</td>
</tr>
<tr>
<td>0.2</td>
<td>155</td>
<td>144</td>
<td>7</td>
</tr>
<tr>
<td>0.3</td>
<td>161</td>
<td>148</td>
<td>8</td>
</tr>
<tr>
<td>0.5</td>
<td>161</td>
<td>152</td>
<td>6</td>
</tr>
<tr>
<td>1.0</td>
<td>161</td>
<td>148</td>
<td>8</td>
</tr>
</tbody>
</table>

These results are not directly comparable - see Discussion.

3.6.7. Effect of Ageing the Solution

Bath Temperature 26°C

<table>
<thead>
<tr>
<th>Solution</th>
<th>Deposit Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh solution with 0.119 g/l benzotriazole</td>
<td>234</td>
</tr>
<tr>
<td>Solution containing 0.119 g/l benzotriazole stored for six months</td>
<td>270</td>
</tr>
</tbody>
</table>

Discussion

All the deposits produced from the bath containing benzotriazole were much harder than those from the corresponding bath without
any addition. It is interesting to note that the bath containing 47 g/l copper sulphate and benzotriazole produced a good metallic deposit whereas, without the addition, a powdery copper was deposited.

The hardness of the deposits increased with the concentration of benzotriazole in the plating solution, whether the bath was still, magnetically stirred or ultra sonically agitated. However, the results showing the effect of concentrations from 0 to 1 g/l benzotriazole cannot be compared with one another because the bath temperatures were not identical. As a result of the very small volumes (150 mls) of solution used, most of the benzotriazole initially present in the bath was codeposited with the copper, before the plating had been completed. Therefore, towards the end of deposition, the copper was plated from solutions with a much lower concentration of benzotriazole than indicated by the initial concentration in the solution.

The ageing of the deposits reduced the hardness by a minimum of 1% and a maximum of 12%. There appears to be little correlation between the percentage decrease and either the benzotriazole concentration or the initial hardness. The surface of deposits, from plating baths containing very low additions of benzotriazole, appeared to be dull and matt. With concentrations of about 0.05 to 0.2 g/l, the deposits were bright, but greater concentrations produced peeling and cracking, suggesting the presence of a high internal stress. However, because of the low quantities used, these observations may not be typical.

Conclusion

From the results it may be concluded that:

(1) the hardness of the deposit increased with the concentration of benzotriazole used;

(2) the presence of benzotriazole increased the limiting or maximum current density that could be used to produce good deposits;

(3) the hardness of the deposits depended upon the concentration of copper sulphate in the bath;
the hardness decreased as the bath temperature increased;
the hardness increased with current density;
the hardness increased with the solution agitation in the order still, stirred and ultrasonic;
the presence of a sufficient concentration of benzotriazole produced bright copper deposits;
a high concentration of benzotriazole resulted in a cracked or peeled deposit;
the hardness of the deposits decreased with time at room temperature (22°C or 25°C), this has been called a self annealing or ageing effect.

3.7 The Effect of Different Plating Variables on the Internal Stress in Copper Deposits from the Plain Bath.

Introduction

In the two previous sections, the influence on the hardness of the electrodeposits produced by varying the plating conditions has been studied. In this, and the next, set of experiments the effect on the internal stress was examined. In the first part of the preliminary work the effect of the purification of the plating solutions on the internal stress in the resulting deposits was investigated. The composition of the solution was fixed at 125 g/l copper sulphate and 49 g/l sulphuric acid, and one bath was made with general grade and another with analar grade chemicals. Part of the analar bath was purified with hydrogen peroxide, activated charcoal and then pre-electrolysed as described in the experimental section (2.3.2). The internal stress in deposits from these solutions, namely general, analar and purified analar grades, were measured with the modified Hoar Arrowsmith apparatus under standardized conditions as described in section 2.4.5. The same purified analar bath was used again and the internal stress was determined and compared with previous values.

The effect of the above purification treatments was studied for baths made with general grade chemicals and also analar grade chemicals; the stress in deposits from all these solutions was determined. The temperature and current density used in the above three experiments were not identical, hence
the three sets of results are not comparable. The relatively low current density and high temperature may account for the rather low stress values produced in the deposits from the bath containing the general grade chemicals.

It was, therefore, decided to investigate the effect on the stress of changes in the plating temperature and the current density. The variation of the stress with the concentration of copper sulphate, solution agitation and deposit thickness was also studied. All these experiments were conducted with general grade chemicals. Because the stress may depend upon the deposit thickness, this was fixed for each set of experiments, although it varied between sets.

Results

In all the experiments a stirred standard bath of 125 g/l copper sulphate and 49 g/l sulphuric acid was used at a temperature of 20°C and with a current density of 215 A/m², unless otherwise stated.

All the stresses recorded in this section are tensile.
### 3.7.1 Effect of Solution Purification

<table>
<thead>
<tr>
<th>Standard Solution</th>
<th>Current Density A/m²</th>
<th>Bath Temperature °C</th>
<th>Deposit Thickness m</th>
<th>Internal Stress MN/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Grade Chemicals</td>
<td>215</td>
<td>20</td>
<td>2.5 x 10⁻⁵</td>
<td>7.24</td>
</tr>
<tr>
<td>General Grade Chemicals purified</td>
<td>215</td>
<td>20</td>
<td>2.5 x 10⁻⁵</td>
<td>3.45</td>
</tr>
<tr>
<td>Analar Grade Chemicals</td>
<td>270</td>
<td>15</td>
<td>3.2 x 10⁻⁵</td>
<td>14.2</td>
</tr>
<tr>
<td>Analar Grade Chemicals purified</td>
<td>270</td>
<td>15</td>
<td>3.2 x 10⁻⁵</td>
<td>10.7</td>
</tr>
<tr>
<td>General Grade Chemicals</td>
<td>380</td>
<td>18</td>
<td>4.5 x 10⁻⁵</td>
<td>18.0</td>
</tr>
<tr>
<td>Analar Grade Chemicals</td>
<td>380</td>
<td>18</td>
<td>4.5 x 10⁻⁵</td>
<td>14.5</td>
</tr>
<tr>
<td>Analar Grade Chemicals purified</td>
<td>380</td>
<td>18</td>
<td>4.5 x 10⁻⁵</td>
<td>10.3</td>
</tr>
<tr>
<td>Analar Grade Chemicals used once</td>
<td>380</td>
<td>18</td>
<td>4.5 x 10⁻⁵</td>
<td>9.65</td>
</tr>
</tbody>
</table>

### 3.7.2 Effect of Concentration of Copper Sulphate (CuSC₄.5H₂O)
Deposit thickness 7.5 x 10⁻⁶ m

<table>
<thead>
<tr>
<th>Concentration of Copper Sulphate in Bath g/l</th>
<th>Internal Stress MN/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>7.58</td>
</tr>
<tr>
<td>330</td>
<td>5.17</td>
</tr>
</tbody>
</table>

### 3.7.3 Effect of Bath Temperature
Deposit thickness 2.5 x 10⁻⁵ m

<table>
<thead>
<tr>
<th>Bath Temperature °C</th>
<th>Internal Stress MN/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.3</td>
</tr>
<tr>
<td>23</td>
<td>7.24</td>
</tr>
<tr>
<td>40</td>
<td>3.10</td>
</tr>
<tr>
<td>60</td>
<td>0.689</td>
</tr>
</tbody>
</table>
3.7.4 Effect of Current Density
Deposit thickness $2.5 \times 10^{-5} \text{m}$

<table>
<thead>
<tr>
<th>Current Density Used A/m$^2$</th>
<th>Internal Stress MN/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>1.03</td>
</tr>
<tr>
<td>110</td>
<td>2.41</td>
</tr>
<tr>
<td>215</td>
<td>6.89</td>
</tr>
<tr>
<td>430</td>
<td>19.3</td>
</tr>
<tr>
<td>645</td>
<td>20.7</td>
</tr>
</tbody>
</table>

3.7.5 Effect of Solution Agitation
Bath temperature 18°C, deposit thickness $1 \times 10^{-6} \text{m}$

<table>
<thead>
<tr>
<th>Current Density A/m$^2$</th>
<th>Internal Stress MN/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>315</td>
<td>4.89</td>
</tr>
<tr>
<td>626</td>
<td>7.79</td>
</tr>
<tr>
<td>780</td>
<td>8.00</td>
</tr>
<tr>
<td>930</td>
<td>9.93</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Stirred bath</th>
<th>Ultrasonically agitated bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Density A/m$^2$</td>
<td>315</td>
<td>626</td>
</tr>
<tr>
<td>Stirred bath</td>
<td>4.89</td>
<td>7.79</td>
</tr>
<tr>
<td>Ultrasonically agitated bath</td>
<td>3.72</td>
<td>4.34</td>
</tr>
</tbody>
</table>

3.7.6 Effect of Deposit Thickness
Bath Temperature 15°C

<table>
<thead>
<tr>
<th>Deposit Thickness m</th>
<th>Internal Stress MN/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.5 \times 10^{-6}$</td>
<td>26.2</td>
</tr>
<tr>
<td>$5 \times 10^{-6}$</td>
<td>25.5</td>
</tr>
<tr>
<td>$7.5 \times 10^{-6}$</td>
<td>24.5</td>
</tr>
<tr>
<td>$10 \times 10^{-6}$</td>
<td>22.7</td>
</tr>
<tr>
<td>$12.5 \times 10^{-6}$</td>
<td>21.1</td>
</tr>
<tr>
<td>$15 \times 10^{-6}$</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Discussion
The work on the effect of purification of the electrolyte showed that, in all the solutions used, the presence of impurities increased the tensile stress. The fact that the stress in the deposit from the analar purified bath did not have the same value (10.3 MN/m$^2$) as that from the same bath
which had been used once \( (9.65 \text{ MN/m}^2) \) is significant, because this means that the same plating solution cannot be used several times, since it does not give reproducible stress values. It was therefore necessary to use a fresh solution for each stress determination, so that large quantities of copper sulphate and sulphuric acid were consumed, and this was one of the reasons that the majority of the main experiments were performed with the cheaper general laboratory grade and not analar grade chemicals. Another reason for this decision was that the results with these chemicals would be more relevant to industrial plating, than if the work were done with highly purified chemicals.

Since the internal stress was so dependent upon the plating conditions, it was necessary in subsequent work to control all these variables, except that being studied, and to quote them when the stress values are recorded.

**Conclusion**

It can be concluded from these results that:

1. copper was normally plated from the plain bath with a tensile stress;
2. purification of the solution reduced the tensile stress;
3. the stress in the deposit depended upon the concentration of copper sulphate in the bath;
4. the stress decreased as the bath temperature increased;
5. the stress increased with the current density;
6. the stress was less in deposits from the ultrasonic bath than from the stirred bath;
7. the stress decreased as the deposit thickness increased.

3.8 The Effect of Different Plating Variables on the Internal Stress in Copper Deposits from the Bath containing Benzotriazole

**Introduction**

It has been shown by Prall \(^{71}\) (see section 1.2.7) that the addition of benzotriazole to the plating bath could promote either compressive or tensile stresses in the deposits, depending upon the plating conditions. Further work was carried out to ascertain the separate effects of the plating
variables on the stress in deposits from the standard bath containing an addition of 0.119 g/l (0.001 M) benzotriazole.

The effect of the purification of an analar plating solution, prior to the addition of benzotriazole, on the resulting stress was investigated. The purification treatment was that described in the experimental section (2.3.2) and was performed before the benzotriazole was added, to avoid any alteration in the concentration or nature of the benzotriazole. Variations in the concentration of the copper sulphate, bath temperature and current density were also made, to study the effect on the resulting internal stress.

The effect on the stress of the ageing of the plating solution containing benzotriazole was also studied. The internal stress was measured in deposits from two samples of an analar solution which had been stored for several weeks. The first sample contained benzotriazole during storage and, therefore, had aged. The second sample did not contain any addition during storage and the benzotriazole was added to this bath immediately before the commencement of plating.

It was also observed that the internal stress, in deposits from the bath containing benzotriazole, changed after the plating current had been switched off, with the plated cathode remaining in the solution. This stress after-effect was studied for deposits showing either a compressive or a tensile stress.

Results

In all the experiments a stirred standard bath of 125 g/l copper sulphate and 49 g/l sulphuric acid was used containing 0.119 g/l benzotriazole at a temperature of 20°C and with a current density of 215 A/m², unless otherwise stated.

3.8.1 Effect of Solution Purification

Internal stress in deposits 7.5 x 10⁻⁶ m thick, plated from a standard bath made using:

(1) analar grade chemicals           24.8 MN/m² (tensile)
(2) analar grade chemicals and purified 13.1 "    "
3.8.2 **Effect of Concentration of Copper Sulphate (CuSO$_4$.2H$_2$O)**

Deposit thickness $7.5 \times 10^{-6}$m  
Bath temperature 22°C  
Current density 195A/m$^2$

<table>
<thead>
<tr>
<th>Concentration of Copper Sulphate in Bath g/l</th>
<th>Internal Stress MN/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>51.7 (tensile)</td>
</tr>
<tr>
<td>80</td>
<td>22.7 (compressive)</td>
</tr>
<tr>
<td>280</td>
<td>34.5 &quot;</td>
</tr>
</tbody>
</table>

3.8.3 **Effect of Bath Temperature**

Deposit thickness $7.5 \times 10^{-6}$m.

<table>
<thead>
<tr>
<th>Bath Temperature °C</th>
<th>Internal Stress MN/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>17.2 (tensile)</td>
</tr>
<tr>
<td>25</td>
<td>22.1 (compressive)</td>
</tr>
<tr>
<td>30</td>
<td>36.5 &quot;</td>
</tr>
</tbody>
</table>

3.8.4 **Effect of Current Density**

Bath temperature 22°C, deposit thickness $7.5 \times 10^{-6}$m.

<table>
<thead>
<tr>
<th>Current Density used A/m$^2$</th>
<th>Internal Stress MN/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>53.8 (compressive)</td>
</tr>
<tr>
<td>325</td>
<td>22.7 (tensile)</td>
</tr>
<tr>
<td>430</td>
<td>35.5 &quot;</td>
</tr>
</tbody>
</table>

3.8.5 **Effect of the Ageing of the Solution**

Deposit thickness $7.5 \times 10^{-6}$m.

Internal stress in deposits plated from an old analar solution containing

(1) fresh benzotriazole 1.72 MN/m$^2$ (compressive)  
(2) aged benzotriazole 11.0 MN/m$^2$ (tensile)
3.8.6 Effect of the Stress After-Effect
Deposit thickness $7.5 \times 10^{-6}$ m

<table>
<thead>
<tr>
<th>Bath Temperature $^\circ$C</th>
<th>Internal Stress MN/m$^2$</th>
<th>End of Plating</th>
<th>After 30 Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>68.3T</td>
<td>77.2T</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>11.0T</td>
<td>14.5T</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>5.17C</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>90.3C</td>
<td>70.0C</td>
<td></td>
</tr>
</tbody>
</table>

T = Tensile Stress
C = Compressive Stress

Discussion

The stress produced in the deposits from the bath containing benzotriazole was much higher than in those from the plain bath. The stress could be either compressive or tensile, thus confirming the work of Prall and Kendall.

Because the timing of the addition of benzotriazole to the plating bath influenced the internal stress in the deposits, the benzotriazole was added to the bath just before the start of plating. In this way the ageing effect was minimized and the resultant stress was modified by the benzotriazole and not by some products of its degradation.

The stress after-effect was larger in the compressively stressed deposits than in those with a tensile stress. This observation is in good agreement with the work of Kushner, who found the same effect in copper and also nickel deposits.

Conclusion

From the results it may be concluded that:

(1) the presence of benzotriazole had a marked effect on both the sign and the magnitude of the internal stress;
(2) purification of the plating bath prior to the addition of the benzotriazole reduced the tensile stress;
(3) the tensile stress became compressive, as the concentration of copper sulphate in the bath increased;
(4) the tensile stress became compressive as the bath temperature was raised;
(5) the compressive stress at low current densities became tensile as the current density was increased;
(6) the ageing of the solution prior to plating increased the stress in a tensile direction;
(7) after the completion of plating a tensile stress increased and a compressive stress decreased.
4. SOME PROPERTIES OF BENZOTRIAZOLES AND ITS EFFECT ON THE CORROSION INHIBITION OF COPPER

4.1 Introduction

The first section of this chapter covers the work done on the solubility of benzotriazole in distilled water, over the temperature range 1 to 97°C. The effect of different concentrations of benzotriazole on the conductivity and pH of tap, distilled and deionized water is then described. The second part is concerned with the corrosion inhibition produced by benzotriazole on copper and brass. This includes the rate of corrosion, as measured by the weight change, of untreated and dipped copper in a wide range of solutions and pH, together with a comparison of the inhibition produced on copper by benzotriazole, triazole and naphthotriazole.

4.2 Solubility of Benzotriazole in Distilled Water

Introduction

The solubility of benzotriazole in distilled water was determined since, in the later work, it was intended to use the benzotriazole as an addition agent in the plating bath over a wide range of temperatures. These measurements were taken in distilled water, because in the subsequent experiments both the corrosion testing solutions and also the plating baths were made with distilled water. The details of the measurements have been described in the experimental section (2.2.1.).

Results

<table>
<thead>
<tr>
<th>Solution Temperature °C</th>
<th>Solubility of Benzotriazole Wt%</th>
<th>Temperature °C</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.01</td>
<td>50</td>
<td>5.30</td>
</tr>
<tr>
<td>7</td>
<td>1.29</td>
<td>67</td>
<td>7.80</td>
</tr>
<tr>
<td>15</td>
<td>1.70</td>
<td>79</td>
<td>11.0</td>
</tr>
<tr>
<td>24</td>
<td>1.98</td>
<td>84</td>
<td>12.4</td>
</tr>
<tr>
<td>25</td>
<td>1.99</td>
<td>89</td>
<td>16.2</td>
</tr>
<tr>
<td>30</td>
<td>3.04</td>
<td>97</td>
<td>19.7</td>
</tr>
<tr>
<td>46.5</td>
<td>4.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2

Discussion

The results are shown in Table 4.2 and are also plotted in a graph, Fig. 4.2, to illustrate the increase in the solubility of benzotriazole in distilled water, which is particularly marked above about 50°C.

Below about 40°C a saturated solution appeared as two phases, a lower white
FIG. 4.2. EFFECT OF WATER TEMPERATURE ON SOLUBILITY OF BENZOTRIAZOLE.
solid and above it a milky aqueous phase. On stirring this solution the solid mixed with the aqueous phase and then settled out. As the solution was heated, a light brown oil began to form below the white solid at 47°C, and at 50°C all the solid had changed to oil. When the oil was stirred it formed globules in the clear aqueous phase and these gradually dropped back to the oily phase. When the solution was cooled, the powder began to form at 45°C and the last traces of the oil changed to the solid at 41°C.

**Conclusion**

The solubility of benzotriazole in distilled water increased with the water temperature as shown in Table 4.2 and the graph, Fig. 4.2.

4.3 Conductivity and pH of Benzotriazole Solutions

**Introduction**

The conductivity and pH of tap, distilled and deionized water were measured by the methods described in the Experimental Sections 2.2.2. and 2.2.3. respectively. The values given below are typical and an average of several measurements taken at 18°C.

**Results**

<table>
<thead>
<tr>
<th>Concentration of Benzotriazole in Solution g/l</th>
<th>Specific Conductivity of Water $10^{-6}$ ohm$^{-1}$ cm$^{-1}$</th>
<th>pH of Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tap</td>
<td>Distilled</td>
</tr>
<tr>
<td>0</td>
<td>346</td>
<td>4.5</td>
</tr>
<tr>
<td>0.0012</td>
<td>350</td>
<td>4.6</td>
</tr>
<tr>
<td>0.012</td>
<td>360</td>
<td>4.9</td>
</tr>
<tr>
<td>0.12</td>
<td>360</td>
<td>5.5</td>
</tr>
<tr>
<td>1.2</td>
<td>370</td>
<td>8.5</td>
</tr>
</tbody>
</table>

**Discussion**

In the three waters used, the addition of benzotriazole increased the specific conductivity and lowered the pH as shown in Fig. 4.3. To understand these results, the structure and the ionization behaviour of benzotriazole in aqueous solutions must be considered.

The low dissociation constant (discussed in Section 1.1.5) means that very little dissociation of benzotriazole occurs when it is dissolved in water. Although this effect is small, it may explain the increase in the specific conductivity of water when benzotriazole is added. The decrease in the pH may result from an increase in the hydrogen ion concentration or a decrease in the hydroxyl ion concentration. However, the increase in the conductivity indicates the presence of more, not fewer, ions, so the pH
FIG. 4.3. EFFECT OF CONCENTRATION OF BENZOTRIAZOLE ON THE pH AND SPECIFIC CONDUCTIVITY OF SOLUTIONS.
change is probably due to the formation of hydrogen ions by the dissolution of benzotriazole.

It therefore appears that the suggestion of Tadashi,\(^1\) that benzotriazole forms the anion \(C_6H_4N_3^-\) and the hydrogen cation, can explain the increase in the conductivity and the decrease in the pH observed when benzotriazole was added to the waters.

**Conclusion.**

The addition of benzotriazole to all three waters gave a marked increase in the specific conductivity and reduced the pH.

### 4.4 Effect of Benzotriazole on Corrosion of Immersed Copper

**Introduction**

In the preliminary work (section 3.2), it was shown that the addition of 0.12 g/l benzotriazole to an aqueous solution decreased the corrosion rate of immersed copper. In this work the effect of benzotriazole on the corrosion rate and the inhibitor efficiency were investigated in a wide range of chemicals, including several acids, salts and bases, as well as solutions containing dissolved gases and detergents. The experimental procedure followed that described in section 2.2. The weight change recorded was an average of four readings.

A loss in weight in this work represented a net dissolution or corrosion of the copper specimens, whereas a weight gain resulted from the formation of an insoluble precipitate on the surface of the copper. Another possibility is that the copper corroded and the ions that were produced reacted with the electrolyte to form a surface film or precipitate: this gave a gain in weight, if the precipitate were heavier than the dissolved copper, or a loss in weight, if it were lighter.

Some idea of the corrosion processes was also given by an examination of the surface of the specimens and the colour of the electrolyte. Thus, a coloured solution and a bright surface indicated corrosion whereas a colourless solution and an unchanged surface suggested inhibition. The formation of coloured precipitates suggested that corrosion followed by precipitation had occurred. These observations were recorded and are discussed in relation to the weight changes.

**Results**

These are given in Table 4.4.

**Discussion**

In the table of results (4.4), a negative weight change represented a net dissolution or corrosion of the copper. A change in weight of 1 mg
<table>
<thead>
<tr>
<th>Solution</th>
<th>Weight change mg/70 cm²</th>
<th>Inhibitor Efficiency % after 5 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>2 days</td>
</tr>
<tr>
<td></td>
<td>No ETA*</td>
<td>With ETA*</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>+0.8</td>
<td>+0.5</td>
</tr>
<tr>
<td>Teepol 3%</td>
<td>+1.1</td>
<td>-1.0</td>
</tr>
<tr>
<td>Tide 5 g/l</td>
<td>-3.4</td>
<td>-0.4</td>
</tr>
<tr>
<td>Ammonia 3%</td>
<td>-112.0</td>
<td>-126.1(1)</td>
</tr>
<tr>
<td>Carbon dioxide (saturated)</td>
<td>-8.5</td>
<td>-0.1</td>
</tr>
<tr>
<td>Hydrogen peroxide 3%</td>
<td>-2.5</td>
<td>-16.7</td>
</tr>
<tr>
<td>Sulphur dioxide (saturated)</td>
<td>-60.4</td>
<td>-2.8</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>-81.2</td>
<td>-7.0</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>-706.7</td>
<td>-818.5</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>-2.1</td>
<td>+0.8</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>+0.5</td>
<td>-2.6</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>+0.2</td>
<td>-1.3</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>-17.2</td>
<td>-0.6</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>-234.1</td>
<td>-50.7</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>-39.5</td>
<td>-2.9</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>-51.7</td>
<td>-8.4</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>-38.4</td>
<td>-6.6</td>
</tr>
</tbody>
</table>

* ETA = 0.12 g/l Benzotriazole
** Corrosion with ETA not significant, very low value
*** Benzotriazole appears to increase the rate of corrosion

(1) Not reproducible
(2) Benzotriazole prevented the staining and/or growth of surface films or precipitates
(3) Benzotriazole prevented the formation of coloured

Table 4.4
over a surface area of $7 \times 10^{-3} \text{m}^2$ was not considered to be significant, because small errors of this order have been found to occur, due to either the accidental removal of parts of the surface film during the drying prior to weighing, or due to retention of moisture on the surface prior to the commencement of the test.

The formation of an insoluble precipitate on the surface of the specimen resulted in a weight gain and this occurred when copper was immersed in plain solutions of Teepol, sodium hydroxide and sodium chloride. However, a small loss in weight occurred with the specimens in solutions of Teepol, sodium hydroxide and sodium sulphate containing benzotriazole. It is probably not correct to suggest that the inhibitor increased the rate of corrosion of copper in these solutions, but rather that it produced no corrosion inhibition. In the second group of solutions, namely hydrogen peroxide, ferric chloride and ammonia, a marked increase in the rate of corrosion was produced by the addition of benzotriazole. The rate of corrosion of copper in ammonia solutions was irreproducible and in some experiments inhibition was observed. In the third group of solutions a marked decrease in the rate of corrosion occurred, moreover, in certain tests an inhibitor efficiency of over 90% was obtained.

The copper specimens immersed in the distilled water which was used to make up all the solutions (pH about 5.1) did not lose weight, stain or produce a sufficient concentration of ions to colour the water, so it is reasonable to assume that very little, if any, corrosion occurred. The presence of benzotriazole in this water increased the weight gain of the specimen, probably by the formation of a surface film. However, under different conditions Wall and Davies found that copper did corrode in distilled water and that benzotriazole acted as a good inhibitor with an efficiency of 92%.

Table 4.4 shows that complete protection of copper was obtained when benzotriazole was added to a solution of sodium chloride and a patent has been taken out on its use to prevent the discolouration of copper in salt solutions. It was this system that Dugdale and Cotton studied with a potentiostat and they showed that benzotriazole was an effective inhibitor. In the Tide solution, benzotriazole prevented surface staining and gave a corrosion inhibitor efficiency of 96% which is in good agreement with the figure of 94% quoted by Unilever for another detergent. The use of benzotriazole in detergents to prevent corrosion, tarnish or discolouration of metals and machinery has been reported elsewhere. For all the acids tested, benzotriazole had a good inhibitor efficiency (40% to
which agrees well with other published data⁴⁴,⁵³.

**Conclusion**

The addition of 0.12 g/l benzotriazole to solutions:

1. reduced the rate of corrosion of copper in Tide, carbon dioxide, sulphur dioxide, sodium chloride, ammonium chloride, acetic, hydrochloric, nitric, phosphoric and sulphuric acid;

2. increased the rate of corrosion of copper in hydrogen peroxide, ferric chloride and ammonia;

3. had little or no effect on the corrosion of copper in sodium hydroxide and sodium sulphate;

4. prevented the formation of stains or coloured surface films on copper in Tide, carbon dioxide, sodium sulphate, sodium chloride, ammonium chloride;

5. prevented the production of coloured ions when copper was immersed in sulphur dioxide, sodium chloride, ammonium chloride and acetic, hydrochloric, nitric, phosphoric and sulphuric acid.

**4.5 Effect of Concentration of Benzotriazole on Corrosion of Immersed Copper**

**Introduction**

In the last section 4.4, it was found that, for many solutions, the use of 0.12 g/l benzotriazole gave a reduction in the rate of corrosion of copper from 40% to 93%. In this section, the effect of higher concentrations, i.e., 0.5 g/l and 1.0 g/l benzotriazole, was investigated on the corrosion of copper immersed in the more aggressive solutions used in section 4.4., namely acetic, hydrochloric, nitric, phosphoric and sulphuric acids and ammonia, ammonium chloride, ferric chloride and sulphur dioxide. As in section 4.4., the weight changes quoted were an average of four readings.

The use of a concentration of benzotriazole higher than 0.12 g/l has been widely suggested in the literature as well as in patents. Thus in "Incralac" the concentration was 1.5 wt %, in anti-freezes the range was from 0.25 wt % up to as high as 80 wt % and in cleaning acids an addition of 1% to 10% was used.

**Results**

These are given in Table 4.5

**Discussion**

These tests showed that the rate of inhibition normally increased with the concentration of benzotriazole and reached a value of at least 90% with 1 g/l, in all the solutions tested except ammonia and ferric chloride.
<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration of Benzo-triazole g/l</th>
<th>Weight Change mg/70 cm²</th>
<th>Inhibitor Efficiency % after 5 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>2 days</td>
<td>5 days</td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-17.2</td>
<td>-30.3</td>
<td>-94.8</td>
</tr>
<tr>
<td>.12</td>
<td>-0.6</td>
<td>-1.1</td>
<td>-6.0</td>
</tr>
<tr>
<td>.5</td>
<td>-1.2</td>
<td>-0.9</td>
<td>-1.3</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.9</td>
<td>-0.7</td>
<td>-0.5</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-81.2</td>
<td>-144.5</td>
<td>-441.3</td>
</tr>
<tr>
<td>.12</td>
<td>-7.0</td>
<td>-25.2</td>
<td>-157.0</td>
</tr>
<tr>
<td>.5</td>
<td>-1.2</td>
<td>-3.0</td>
<td>-6.6</td>
</tr>
<tr>
<td>1.0</td>
<td>+0.4</td>
<td>+0.4</td>
<td>+0.4</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-234.1</td>
<td>-415.9</td>
<td>-507.2</td>
</tr>
<tr>
<td>.12</td>
<td>-50.7</td>
<td>-90.0</td>
<td>-183.9</td>
</tr>
<tr>
<td>.5</td>
<td>-5.9</td>
<td>-15.3</td>
<td>-34.0</td>
</tr>
<tr>
<td>1.0</td>
<td>-2.5</td>
<td>-7.8</td>
<td>-20.3</td>
</tr>
<tr>
<td>Nitric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-39.5</td>
<td>-79.4</td>
<td>-242.6</td>
</tr>
<tr>
<td>.12</td>
<td>-2.9</td>
<td>-8.5</td>
<td>-34.0</td>
</tr>
<tr>
<td>.5</td>
<td>-0.7</td>
<td>-2.1</td>
<td>-12.4</td>
</tr>
<tr>
<td>1.0</td>
<td>-1.5</td>
<td>-3.2</td>
<td>-7.0</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-51.7</td>
<td>-108.0</td>
<td>-294.3</td>
</tr>
<tr>
<td>.12</td>
<td>-8.4</td>
<td>-34.8</td>
<td>-176.0</td>
</tr>
<tr>
<td>.5</td>
<td>-3.7</td>
<td>-4.2</td>
<td>-7.3</td>
</tr>
<tr>
<td>1.0</td>
<td>-3.7</td>
<td>-4.6</td>
<td>-6.6</td>
</tr>
<tr>
<td>Sulphur dioxide (saturated)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-60.4</td>
<td>-103.2</td>
<td>-218.0</td>
</tr>
<tr>
<td>.12</td>
<td>-2.8</td>
<td>-11.6</td>
<td>-47.7</td>
</tr>
<tr>
<td>.5</td>
<td>-0.1</td>
<td>-8.1</td>
<td>-57.2</td>
</tr>
<tr>
<td>1.0</td>
<td>+1.1</td>
<td>-2.4</td>
<td>-23.0</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-38.4</td>
<td>-95.9</td>
<td>-258.0</td>
</tr>
<tr>
<td>.12</td>
<td>-6.6</td>
<td>-29.3</td>
<td>-94.0</td>
</tr>
<tr>
<td>.5</td>
<td>-0.7</td>
<td>-7.3</td>
<td>-81.9</td>
</tr>
<tr>
<td>1.0</td>
<td>+0.4</td>
<td>-0.4</td>
<td>-9.3</td>
</tr>
<tr>
<td>Ammonia 3%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-112.0</td>
<td>-187.1</td>
<td>-339.7</td>
</tr>
<tr>
<td>.12</td>
<td>-126.1</td>
<td>-203.2</td>
<td>-384.4</td>
</tr>
<tr>
<td>.5</td>
<td>-100.7</td>
<td>-167.0</td>
<td>-296.8</td>
</tr>
<tr>
<td>1.0</td>
<td>-88.5</td>
<td>-178.3</td>
<td>-336.1</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-706.7</td>
<td>-687.8</td>
<td>-656.2</td>
</tr>
<tr>
<td>.12</td>
<td>-818.5</td>
<td>-777.3</td>
<td>-874.8</td>
</tr>
<tr>
<td>.5</td>
<td>-243.9</td>
<td>-268.4</td>
<td>-303.6</td>
</tr>
<tr>
<td>1.0</td>
<td>-148.9</td>
<td>-151.1</td>
<td>-159.8</td>
</tr>
</tbody>
</table>

° Concentration $\frac{N}{10}$ unless otherwise stated

Table 4.5
However, in these two solutions, there appeared to be no correlation between a high concentration of inhibition and a low rate of corrosion. For several of the solutions a relatively low inhibitor efficiency was produced with an addition of 0.12 g/l, whereas a large improvement was achieved when the concentration was increased to 0.5 g/l, the best example of this being phosphoric acid for which the values were 40% (0.12 g/l) and 98% (0.5 g/l). It is, therefore, economically viable to use the higher concentrations of inhibitor in these solutions, and this is also indicated in the literature quoted above.

Conclusion
It may be concluded that for immersed copper:
(1) the inhibitor efficiency of benzenetrazole increased with the concentration used up to 90% or more with 1 g/l for solutions of ammonium chloride, sulphur dioxide, acetic, hydrochloric, nitric, phosphoric and sulphuric acids;
(2) benzenetrazole was not a reliable inhibitor for ammonia and ferric chloride solution.

4.6 Effect of Benzenetrazole on Corrosion of Copper in Solutions of Sulphuric Acid with Different pH

Introduction
This experiment was designed to investigate the effect of 0.12 g/l benzenetrazole as a corrosion inhibitor for copper immersed in various concentrations of aerated sulphuric acid with different initial pH. The solutions were produced by diluting concentrated sulphuric acid with distilled water until the desired initial acidity was obtained, as described in the experimental section 2.2.4.

Results

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>1 day No BTA*</th>
<th>1 day With BTA*</th>
<th>2 days No BTA*</th>
<th>2 days With BTA*</th>
<th>5 days No BTA*</th>
<th>5 days With BTA*</th>
<th>Inhibitor Efficiency % after 1</th>
<th>Inhibitor Efficiency % after 2</th>
<th>Inhibitor Efficiency % after 5 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>-32.0</td>
<td>-63.0</td>
<td>-284.0</td>
<td>-218.3</td>
<td>-994.1</td>
<td>-606.9</td>
<td>23</td>
<td>23</td>
<td>36</td>
</tr>
<tr>
<td>0</td>
<td>-21.1</td>
<td>-9.1</td>
<td>-79.5</td>
<td>-18.8</td>
<td>-572.2</td>
<td>-67.6</td>
<td>57</td>
<td>76</td>
<td>88</td>
</tr>
<tr>
<td>1.0</td>
<td>-21.0</td>
<td>+1.5</td>
<td>-42.2</td>
<td>+1.8</td>
<td>-149.1</td>
<td>-2.4</td>
<td>100</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>1.91</td>
<td>-20.0</td>
<td>+1.2</td>
<td>-38.7</td>
<td>+1.9</td>
<td>-62.0</td>
<td>+1.0</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>-2.8</td>
<td>+0.3</td>
<td>-1.5</td>
<td>+0.7</td>
<td>+3.3</td>
<td>+0.6</td>
<td>100</td>
<td>100</td>
<td>**</td>
</tr>
<tr>
<td>3.9</td>
<td>+0.3</td>
<td>+0.9</td>
<td>+1.2</td>
<td>+0.8</td>
<td>+2.8</td>
<td>+0.8</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

*BTA = 0.12 g/l Benzenetrazole  **No weight loss in either test

Table 4.6
FIG. 4.6. EFFECT OF BENZOTRIAZOLE ON THE CORROSION OF COPPER IN SULPHURIC ACID AT DIFFERENT pH's
Discussion
The results are shown in Table 4.6 and are also plotted in graph, Fig. 4.6. The first observation to be made from both sets of experimental tests is the decrease in the rate of corrosion of copper immersed in the different solutions of aerated sulphuric acid, as the pH increased.

In the most acidic sulphuric acid solution (pH = -1), the benzotriazole behaved as a poor inhibitor with a low inhibitor efficiency. However, in the solution with pH = 0, the inhibitor was much better and the efficiency increased with immersion time during the experiment. These improvements with immersion time could be the result of a decrease in the acidity (i.e. increase in the pH), and corrosiveness of the solution during the experiment, (which will be investigated in section 4.8), or due to the formation of a protective surface film by the copper ions produced in the early part of the test. However, with the solution pH = 1.0 a small weight gain was observed after both one and two days but this changed, after 5 days, to a small weight loss. These figures indicate that the solution became more corrosive with immersion time, but this may not be significant, because the weight changes were very small and, therefore, subject to a relatively large experimental error.

Benzotriazole produced a gain in weight for the copper specimens in a sulphuric acid solution of pH = 1.91 after one, two and five days and this represents an inhibitor efficiency of 100%. A similar gain in weight was recorded for the specimens in solutions with a higher pH containing the inhibitor. The copper specimens in the plain solution of pH = 3 showed a weight loss after one and two days followed by an increase after five days, so the causes suggested above, namely an increase in the pH or film formation, may apply. If the plain copper shows an increase in weight during the test the term inhibitor efficiency which is related to weight losses is not applicable.

Conclusion
From the results obtained it may be concluded that:
(1) the rate of corrosion of copper immersed in a plain aerated solution of sulphuric acid decreased as the pH increased;
(2) the relative efficiency of benzotriazole as a corrosion inhibitor for copper in different solutions of sulphuric acid increased as the pH rose.
4.7 A Comparison of the Corrosion of Treated and Untreated, Immersed Copper Surfaces

Introduction
In his literature survey, Cotton\(^1\) stated that copper surfaces which had been directly treated by aqueous solutions of benzotriazole resisted corrosion much better than the untreated surfaces. In this set of experiments the copper specimens used were pretreated by being dipped into a hot aqueous solution of benzotriazole at 60\(^\circ\)C for about five minutes, air dried, and then weighed. The rates of corrosion of these dipped specimens, which were immersed in plain solutions, were compared with those of the untreated specimens in the plain solutions, and also in solutions containing 0.12 g/l benzotriazole (obtained from section 4.4).

Results

<table>
<thead>
<tr>
<th>Solution (^0)</th>
<th>Weight Change in 5 days mg/70 cm(^2) (Inhibitor Efficiency %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plain Copper</td>
</tr>
<tr>
<td></td>
<td>Plain Solution</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>+0.5</td>
</tr>
<tr>
<td>Ammonia 3%</td>
<td>-339.7</td>
</tr>
<tr>
<td>Carbon dioxide (saturated)</td>
<td>-10.2</td>
</tr>
<tr>
<td>Sulphur dioxide (saturated)</td>
<td>-218.0</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>-441.3</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>-556.2</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>-4.5</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>-94.8</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>-507.2</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>-242.6</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>-294.3</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>-258.0</td>
</tr>
</tbody>
</table>

\(^0\) Concentration \(\frac{N}{10}\) unless otherwise stated
*Pretreatment or Benzotriazole appears to increase the rate of corrosion

Discussion
In both the distilled water and the sodium chloride solution, the
dipped copper specimens corroded at a faster rate than the plain copper. This is an unexpected result that could be due to the formation of an incomplete film and the subsequent corrosion resulting from the production of local active-passive cells.

In most of the other tests the dipped copper corroded less than the untreated copper in the plain solution, but more than the untreated copper in the solution containing 0.12 g/l benzotriazole. However, the dipping process gave better protection than the addition of benzotriazole to the solution in sulphur dioxide, phosphoric acid and ammonium chloride solution. Compared with the untreated copper, the dipped specimens showed a significantly reduced rate of corrosion in ammonia and ferric chloride solutions, while the addition of 0.12 g/l benzotriazole actually increased the corrosion.

**Conclusion**

From the results obtained it follows that the dipping of copper specimens prior to testing:

1. increased the rate of corrosion in distilled water and sodium chloride solution;
2. decreased the rate of corrosion in solutions of carbon dioxide, acetic, hydrochloric, nitric and sulphuric acids, but not to the same extent as an addition of 0.12 g/l benzotriazole;
3. reduced the rate of corrosion in solutions of sulphur dioxide, ammonium chloride and phosphoric acid to a greater extent than the addition of 0.12 g/l benzotriazole;
4. reduced the rate of corrosion in ammonia and ferric chloride solutions, whereas the use of 0.12 g/l benzotriazole increased the corrosion.

4.8 **Effect of Benzotriazole on the Change in pH during Corrosion of Copper**

**Introduction**

During the reaction between an acid and a metal, the pH of the acid may change and this can affect the efficiency of an inhibitor. In this section a wide range of solutions was studied in order to ascertain whether the presence of benzotriazole had any effect on the change in the pH during the corrosion of copper. Each solution was made with distilled water and then divided into two portions, one was used without modification and 0.12 g/l benzotriazole was added to the other. The pH was measured with an E.I.L. pH meter (Modèle No. 38B) before the test and after five days of corrosion.

Before each set of measurements, the pH meter was checked with the
appropriate acidic or alkaline buffer solution and the readings for the solutions were taken to the nearest decimal place.

Results

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH of Solution</th>
<th>No Benzotriazole</th>
<th>With Benzotriazole 0.12g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Corrosion</td>
<td>After Corrosion</td>
<td>Change</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>4.8</td>
<td>6.6</td>
<td>+ 1.8</td>
</tr>
<tr>
<td>Tide 5 g/l</td>
<td>10.0</td>
<td>9.4</td>
<td>- 0.6</td>
</tr>
<tr>
<td>Teepol 3%</td>
<td>6.1</td>
<td>7.2</td>
<td>+ 1.1</td>
</tr>
<tr>
<td>Ammonia 3%</td>
<td>10.9</td>
<td>10.4</td>
<td>- 0.5</td>
</tr>
<tr>
<td>Carbon dioxide (saturated)</td>
<td>3.7</td>
<td>6.1</td>
<td>+ 2.4</td>
</tr>
<tr>
<td>Hydrogen peroxide 3%</td>
<td>3.6</td>
<td>8.1</td>
<td>+ 4.5</td>
</tr>
<tr>
<td>Sulphur dioxide (saturated)</td>
<td>1.5</td>
<td>3.2</td>
<td>+ 1.7</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>1.6</td>
<td>3.7</td>
<td>+ 2.1</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>12.3</td>
<td>12.6</td>
<td>+ 0.3</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>5.6</td>
<td>6.3</td>
<td>+ 0.7</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>1.8</td>
<td>3.2</td>
<td>+ 1.4</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>1.4</td>
<td>1.1</td>
<td>- 0.3</td>
</tr>
</tbody>
</table>

°Concentration \( \frac{N}{10} \) unless otherwise stated

Table 4.8

Discussion

From the table 4.8 it can be seen that the addition of the benzotriazole had virtually no effect on the initial pH, except for the solutions of ammonia (-0.2 pH units) and Tide (-0.3 pH units) which became more acidic, cf. section 4.3.

For most of the solutions without benzotriazole, the pH rose during the experiment with a maximum increase of 4.5 for hydrogen peroxide; in only three solutions, ammonia, Tide and sulphuric acid, did the pH fall slightly. In the solutions containing benzotriazole the change was in the same direction as in the plain solutions but it was smaller, or the same, in every case.

The most probable causes for the increase in the pH during the corrosion of the copper are the reactions which occur at the cathode, namely:
In equation (1) the hydrogen ions are consumed to produce hydrogen gas and, therefore, the concentration of hydrogen ions in the solution decreases and the pH increases because:

\[
pH = -\log_{10} a_{\text{H}^+}
\]

where \( a_{\text{H}^+} \) is the activity of the hydrogen ions, which is related to their concentration. In equation (2) hydroxyl ions are produced which increase both the alkalinity and the pH of the solution. Thus, with both these cathodic reactions, the pH of the solution is increased.

**Conclusion**

It may be concluded that:

1. during the corrosion of copper the pH increased in all the solutions tested (except ammonia, Tide and sulphuric acid);
2. the presence of benzotriazole reduced the change in the pH in all the solutions (except ferric chloride, sulphuric acid and Tide, in which it produced no change), i.e. it acted as a buffer.

4.9 Effect of Benzotriazole on Corrosion of Immersed Brass

**Introduction**

The rate of corrosion of brass (70\% copper, 30\% zinc) was determined in various solutions both without and with an addition of 0.12 g/l benzotriazole. The experimental details were similar to those in 4.4.; the specimens, \( 7 \times 10^{-3} \text{m}^2 \) in area, were immersed in magnetically stirred solutions and weighed after 1, 2 and 5 days. The inhibitor efficiency of the benzotriazole was calculated after an immersion period of five days. The solutions used were the same as those in which benzotriazole was found previously (4.4) to be a satisfactory inhibitor for copper.

**Results**

These are given in Table 4.9.

**Discussion**

Brass, unlike copper which is a more noble metal, has been found to corrode when immersed in distilled water. The corrosion was completely inhibited by the addition of 0.12 g/l benzotriazole to the water. A significant decrease of 98\% was recorded in the corrosion rate of brass in a Tide solution when benzotriazole was used and this agrees with other published data. The corrosion inhibition in sodium chloride solution observed in this work has previously been recorded.
<table>
<thead>
<tr>
<th>Solution</th>
<th>Weight change mg/70 cm²</th>
<th>Inhibit Efficiency % after 5 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>2 days</td>
</tr>
<tr>
<td></td>
<td>No BTA* With BTA*</td>
<td>No BTA* With BTA*</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>-0.5  +0.2</td>
<td>-0.4  +1.0</td>
</tr>
<tr>
<td>Tide 5 g/l.</td>
<td>-6.9  0</td>
<td>-7.8  +0.4</td>
</tr>
<tr>
<td>Carbon dioxide (saturated)</td>
<td>-2.4  +0.4</td>
<td>-2.6  +0.1</td>
</tr>
<tr>
<td>Sulphur dioxide (saturated)</td>
<td>-34.7  +6.8</td>
<td>-74.6  +8.8</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>-84.8  -0.4</td>
<td>-140.5  -0.3</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>-1.2  +0.2</td>
<td>-1.5  +0.2</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>-40.5  +0.2</td>
<td>-76.4  +0.3</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>-85.6  -12.7</td>
<td>-444.0  -25.0</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>-64.6  -0.9</td>
<td>-130.4  -4.2</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>-54.6  -11.4</td>
<td>-88.5  -19.5</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>Irreproducible results</td>
<td></td>
</tr>
</tbody>
</table>

*Concentration N/10 unless otherwise stated

* BTA = 0.12 g/l Benzotriazole

** Dezincification observed on surface of specimen after 5 days immersion.

Table 4.9

The addition of 0.12 g/l benzotriazole to all the solutions, except hydrochloric acid, produced a marked decrease in the rate of corrosion of the immersed brass. With three solutions, sulphur dioxide, sodium chloride and ammonium chloride, dezincification, i.e. preferential corrosion of the zinc rich areas, occurred whereas with the inhibitor present this selective attack was not observed. This prevention of dezincification of brass has been reported elsewhere for hydrochloric acid and sodium chloride solution. The experiment with the brass immersed in the hydrochloric acid was repeated but irreproducible results were obtained on each occasion for both the solutions without and with the benzotriazole; the results indicated that the inhibitor actually increased the rate of corrosion. However, the use of a higher concentration of 1% benzotriazole in a 0.5 N solution of hydrochloric acid has been previously reported to give an inhibitor efficiency of 85%.
Conclusion

From the results above it appears that:

(1) benzotriazole is an effective corrosion inhibitor, with an efficiency greater than 80%, for all the solutions tested except sulphur dioxide (37%) and hydrochloric acid, in which the rate of corrosion was increased;

(2) the presence of benzotriazole prevented dezincification of brass in solutions of sulphur dioxide, sodium chloride and ammonium chloride.

4.10 Corrosion Inhibition of Copper in Solutions containing Triazole, Benzotriazole or Naphthotriazole

Introduction

In this section, the inhibitive properties of benzotriazole were compared with those of triazole and naphthotriazole for copper immersed in solutions of ammonium chloride and several acids. These solutions were chosen because they were found previously (Section 4.4) to be corrosive to copper. The specimens were immersed for five days in the solutions and then the weight losses were determined and the efficiency of the corrosion inhibitor calculated.

Results

<table>
<thead>
<tr>
<th>Solution</th>
<th>Weight loss in 5 days mg/70 cm² (Inhibitor Efficiency %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No addition</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>291.0</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>187.4</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>183.0</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>147.7</td>
</tr>
</tbody>
</table>

*Inhibitor prevented formation of coloured ions

Table 4.10

Discussion

The rates of corrosion of the copper in both the plain solution and that containing benzotriazole are lower than the corresponding values after five days immersion in a previous test (4.4). In the earlier work, the specimens were removed from the solution, washed, dried and weighed after one and also two days immersion. This washing of the copper may have removed surface films, and, therefore, increased the rate of corrosion. In the present test, the specimens remained in the solution for five days, so that any
surface films which formed would have caused the maximum amount of polarization of the anodic and/or cathodic reactions, resulting in the lower rate of corrosion.

The concentration of each inhibitor was fixed as 0.001 M, so that the number of molecules present in each solution would be constant. Triazole was found to be satisfactory only for ammonium chloride, whereas both benzotriazole and naphthotriazole were effective in all four solutions. It has been reported elsewhere\textsuperscript{36,37,43} that benzotriazole and naphthotriazole have similar inhibitive effects.

Conclusion
Triazole was a poor inhibitor (except for ammonium chloride solution), whereas both benzotriazole and naphthotriazole were satisfactory in all the solutions tested.

4.11 Stain Resistance of Copper in Tap Water Containing Various Triazoles

Introduction
In the literature survey (section 1.1.5) it was suggested that the addition of a small quantity of benzotriazole to water prevented the formation of a surface tarnish. This section was designed to investigate the stain resistance produced by the use of a fixed concentration of benzotriazole, as compared with triazole and naphthotriazole. The experiment was performed with four copper specimens immersed in each solution.

Results

<table>
<thead>
<tr>
<th>Environment</th>
<th>Immersion Time before Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; + 0.001M Triazole</td>
<td>2 to 4 days</td>
</tr>
<tr>
<td>&quot; &quot; Benzotriazole</td>
<td>10 to 12 days</td>
</tr>
<tr>
<td>&quot; &quot; Naphthotriazole</td>
<td>Did not stain in 21 days</td>
</tr>
</tbody>
</table>

Table 4.11

Discussion
The copper was degreased and given a quick pickle in dilute nitric acid to produce a bright surface which was then subjected to corrosion. In the plain water the surface tarnished in two to four days to the same extent as it did in eleven days in water containing triazole. None of the specimens in water containing benzotriazole or naphthotriazole stained after a period of twenty one days, and the surfaces were only slightly duller than at the beginning of the experiment.
Conclusion
Copper immersed in tap water stained in two to four days, 0.001M triazole in the water increased the time before staining to an average of eleven days, whereas a similar concentration of benzotriazole and naphthotriazole prevented staining for a period of at least twenty one days.

4.12 Atmospheric Stain Resistance of Copper Dipped in various Triazole Solutions

Introduction
In this experiment a comparison was made of the stain resistances, produced by the dipping of copper for a period of five minutes in hot, saturated, aqueous solutions of benzotriazole, triazole and naphthotriazole. The environments used for testing were tap water and atmospheres of salt spray, warm moist air and moist sulphur dioxide. All the tests, except the tap water, were conducted over a period of forty two days and the appearance and weight change were then recorded. For immersion in tap water, the period before staining occurred was noted.

Results

<table>
<thead>
<tr>
<th>Environment</th>
<th>Plain Copper</th>
<th>Copper dipped in Triazole</th>
<th>Copper dipped in Benzotriazole</th>
<th>Copper dipped in Naphthotriazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td>Stained in 2 days</td>
<td>Stained in 10 days</td>
<td>No staining 21 days</td>
<td>No staining 21 days</td>
</tr>
<tr>
<td>Salt Spray 42 days</td>
<td>Badly stained 9.30</td>
<td>Badly stained 12.34</td>
<td>Partially stained 6.72</td>
<td>Partially stained 5.94</td>
</tr>
<tr>
<td>Weight gain*</td>
<td>+11.43</td>
<td>+7.47</td>
<td>+1.52</td>
<td>-1.59</td>
</tr>
<tr>
<td>Humidity 42 days</td>
<td>Badly stained</td>
<td>Badly stained</td>
<td>Partially stained</td>
<td>Not stained</td>
</tr>
<tr>
<td>Weight change*</td>
<td>+14.64</td>
<td>+17.76</td>
<td>Orange coating</td>
<td>Orange coating</td>
</tr>
<tr>
<td>Sulphur Dioxide 42 days</td>
<td>Brown coating 14.64</td>
<td>Brown coating 17.76</td>
<td>Orange coating 13.95</td>
<td>Orange coating 14.25</td>
</tr>
</tbody>
</table>

*Weight change in mg/7 x 10^-3 m^2

Table 4.12

Discussion
For copper immersed in tap water, the results were similar to those obtained by the addition of these inhibitors to water (see Section 4.11). The period before staining was found to increase from two days, with no treatment, to ten days, with the prior dipping in a hot triazole solution. However, this was not nearly as good as the treatment with benzotriazole or naphthotriazole, which prevented staining for at least twenty one days.
In the other environments, dipping in a triazole solution was not very effective in improving either the surface appearance or the weight change. Specimens treated with benzotriazole or naphthotriazole showed an increased resistance to surface staining and a reduced weight gain in every case, except for the naphthotriazole specimen when tested in the humid atmosphere, where it appears that soluble product was produced and a decrease in weight was found.

Conclusion
From these tests with the dipped copper specimens, it may be concluded that the benzotriazole gave slightly better inhibition than naphthotriazole, which was in turn proved to be much better than triazole.

4.13 Effect of Benzotriazole on the Corrosion of Immersed Copper and the Subsequent Pitting of Aluminium

Introduction
In the literature survey (section 1.1.5) some of the detrimental effects of copper ions in water were described. One example that is particularly important in the field of corrosion is the local pitting produced on aluminium surfaces by waters containing dissolved copper ions. If the attack on copper surfaces can be reduced, then the subsequent life of aluminium in contact with water can be increased, because the extent of the pitting depends upon the concentration of the copper ions. The experiment was carried out in the manner described in section 2.2.4.

Results

<table>
<thead>
<tr>
<th>Copper</th>
<th>Water</th>
<th>Time for Aluminium Foil to Pit, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain Copper</td>
<td>Tap Water</td>
<td>1.25, 1, 1.5, 0.75</td>
</tr>
<tr>
<td></td>
<td>Tap Water + Benzotriazole (0.12g/l)</td>
<td>42, 84</td>
</tr>
<tr>
<td>Dipped Copper</td>
<td>Tap Water</td>
<td>340, 440</td>
</tr>
<tr>
<td>Plain Copper</td>
<td>Distilled Water</td>
<td>115, 310</td>
</tr>
<tr>
<td>Plain Copper</td>
<td>Distilled Water + Benzotriazole (0.12g/l)</td>
<td>Did not pit in 480, 500</td>
</tr>
<tr>
<td>Dipped Copper</td>
<td>Distilled Water</td>
<td>&quot;</td>
</tr>
<tr>
<td>Plain Copper</td>
<td>Deionized Water</td>
<td>&quot;</td>
</tr>
<tr>
<td>Plain Copper</td>
<td>Deionized Water + Benzotriazole (0.12g/l)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Dipped Copper</td>
<td>Deionized Water</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Table 4.13
Discussion

Aluminium foil was used in this experiment, so that even slight corrosion of the aluminium would result in perforation. Thus, a comparison of the times to pit the aluminium in a particular water gave an indication of the concentration of the copper ions in that solution, and also the degree of inhibition produced by the benzotriazole on the copper surface.

In tap water, the foil pitted very quickly and the time varied from 0.75 to 1.5 hours in four separate tests. The addition of benzotriazole to this water increased the time to pit to 42 hours, and in another test to 84 hours, an increase of at least 30-fold, whereas dipping the copper prior to the test produced an even better result and gave protection for 340 and 440 hours. In distilled water, the foil pitted in 115 hours and in another test 310 hours, while the addition of benzotriazole or the dipping of the copper prior to the test prevented perforation for at least 480 hours. No perforation occurred in any of the experiments with deionized water during the 480 hour test, which suggests that these waters are not corrosive to copper.

These experiments show that the protection produced by dipping the copper in a benzotriazole solution was more effective than adding benzotriazole to the tap water. In both distilled water and deionized water, the use of benzotriazole has been patented to prevent the galvanic corrosion of different metallic couples, copper-aluminium, copper-zinc and copper-steel.

Conclusion

It may be concluded that:

(1) the tap water was more corrosive than the distilled water, which was more corrosive than the deionized water;
(2) in tap water the addition of benzotriazole gave good protection, but the dipping of the copper in a hot solution of benzotriazole prior to testing gave much better protection;
(3) in distilled water the addition of benzotriazole or the dipping of the copper gave excellent protection;
(4) no pitting occurred in any of the tests using the deionized water.

4.14 High Temperature Oxidation Resistance of Copper Treated with Benzotriazole

Introduction

In the preliminary results (section 3.3), it was shown that at 300°C the oxidation resistance of copper dipped in a benzotriazole solution was much
higher than that of an untreated specimen. In this present section the effect of temperature on the rates of oxidation is determined for both the untreated and dipped samples, with a total surface area of 90 cm\(^2\). The experimental procedure, using a Stanton Thermobalance, was that found to give reproducible results and described in the preliminary work (section 3.3), with the exception that the time period in these experiments was 400 minutes.

**Results**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Weight Gain mg in 400 mins.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plain Copper</td>
</tr>
<tr>
<td>200</td>
<td>1.0</td>
</tr>
<tr>
<td>250</td>
<td>4.5</td>
</tr>
<tr>
<td>275</td>
<td>4.5</td>
</tr>
<tr>
<td>290</td>
<td>6.0</td>
</tr>
<tr>
<td>325</td>
<td>10.6</td>
</tr>
<tr>
<td>350</td>
<td>12.8</td>
</tr>
<tr>
<td>375</td>
<td>23.2</td>
</tr>
<tr>
<td>400</td>
<td>67.3</td>
</tr>
</tbody>
</table>

Table 4.14

**Discussion**

From the above results it can be seen that the dipping of copper into a benzotriazole solution reduced the weight gain, i.e. the rate of oxidation, to a considerable extent. At 200°C both samples showed only a small weight gain (1 mg) which is of the same order as the experimental error, so that it is difficult to decide what effect the benzotriazole treatment produced. Because of this low weight change, no experiment was performed at temperatures below 200°C, where an even smaller rate of oxidation would be expected.

The difference in the weight change between the untreated and dipped specimens does not appear to be directly proportional to the temperature of oxidation. This may be due to the fact that the weight change of the dipped specimens is controlled by two different factors, which have a similar effect on the weight. The presence of the protective surface layer is known to reduce the rate of oxidation or tarnishing at room temperature, and probably has a similar effect at elevated temperatures. At higher temperatures, this surface film may decompose to powdered soot and this
FIG. 4.14. OXIDATION RESISTANCE OF COPPER AT HIGH TEMPERATURES.
would give a small reduction in the weight of the specimen. A sooty film was observed on the dipped copper specimen after it had been oxidized at 400°C for about seven hours, whereas at lower temperatures coloured films were formed on the surface.

One possible source of error is that, if a non-adherent film is produced on the surface of the copper, it may break off and result in a misleading reading. To prevent this, the chart which automatically showed the weight change was carefully examined for small irregular weight losses, which would indicate that flakes of the oxide had dropped off. However, for the above results no such change was observed, so this cause of error can be ignored.

Conclusion
The prior dipping of copper in the benzotriazole solution gave a significant reduction in the rate of oxidation over the temperature range of 200°C up to about 350°C.
5. PHYSICAL EXAMINATION OF THE NUCLEATION, SURFACE AND STRUCTURE OF COPPER ELECTRODEPOSITS

5.1. Introduction

This chapter covers the physical examination of the nucleation and surface topography of electrodeposits from the plain acid copper sulphate bath, both without and with an addition of benzotriazole, which acts as a brightening agent under these conditions. The cross-sectional structures of the coatings plated from these solutions are also studied. An investigation has been made into the effect of variations in the solution temperature, current density and electrolyte agitation on the surface appearance and the structure of the deposits.

5.2. Nucleation of Copper Electrodeposits

Introduction

This section examines the early stages of the growth of deposits from both the plain bath and also the one containing benzotriazole. It has previously been observed, in this work (section 3.6.3.), that the surfaces of coatings from both these solutions were very different and, therefore, it was decided to examine these surfaces in greater detail.

The usual standard plating solution was used (125 g/l copper sulphate and 49 g/l sulphuric acid) and to one bath an addition of 0.119 g/l benzotriazole was made. It is known $^{111,163}$ that the rate of deposition plays an important role in the distribution of the growing crystals and has an effect on the shape of the nuclei and in this work the usual current density, 215 A/m$^2$, was used. With this current density, suitable deposits were formed in a plating time of about twenty seconds. Before plating, the copper cathodes were degreased in acetone and given a quick pickle in 50% nitric acid; after deposition they were washed in water and dried in air, to prevent staining and/or the formation of a surface layer of copper sulphate.

Photographs of the deposits were taken on the Stereoscan at magnifications of about x 60, x 200 and x 1,300, the exact values given on the instrument were recorded. The intermediate magnification was used for both types of deposit, to illustrate the difference in the shape of a single growth centre on an area of the cathode with only a few nuclei. The cross-sectional structure of a nodular growth from the solution containing
benzotriazole was examined on the Stereoscan and the Zeiss microscope.

Results
The results consist of a series of photographs showing the nucleation of copper deposits. These are subdivided into those from the plain bath {Fig. 5.2.(a), (c) and (e)} at magnifications of x 68, x 330 and x 1,375, and those from the solution containing 0.119 g/l benzotriazole {Fig. 5.2.(b), (d) and (f).} at magnifications of x 62, x 130 and x 1,300. Fig. 5.2.(g) shows the etched cross-section of a deposit from the benzotriazole bath.

Discussion
The crystals plated from the plain bath {Fig. 5.2.(a), (c) and (e)} were regular in size, with flat faces and straight edges. This suggests that crystallographically they were single crystals, since they appeared to be the same in shape as those which form when copper sulphate solution evaporates. In the photographs shown, there was no indication of nuclei forming on the faces of the growing crystals, even when viewed at the highest magnification of about x 10,000 (not shown).

The appearance of the deposit from the solution containing benzotriazole was very different. At a low magnification of x 62 {Fig. 5.2.(b)} the growing form was hemispherical with a few larger reniform or 'cauliflower shaped' deposits - at a higher magnification, or x 130 {Fig. 5.2.(d)} , the deposit appeared to consist of several similar sections that in turn could be subdivided into oval shaped segments. These nodules or segments grew out radially until they terminated at intersections, which showed as grain boundaries when a cross-section of this deposit was examined {Fig. 5.2.(f).} At higher magnifications of x 1,300, each of these oval shaped parts appeared to be constructed of parallel flat plate-like or rod sections, which produced a relatively rough surface on each dome.

The fact that the early stages of growth were very different when benzotriazole was used, may explain the contrast which occurred in the surface appearance of much thicker coatings. This in turn may account for the widely deviating physical and chemical properties of deposits from the two different plating baths.

Conclusion
The addition of benzotriazole to the plating solution had a very marked effect on the early stages of growth of the deposit. The crystals plated
FIG. 5.2. NUCLEATION OF COPPER DEPOSITS

Plain bath

Bath with 0.119g/l Benzotriazole
Fig. 5.2 (g) Cross-section of a Copper Deposit Nodule from Bath containing Benzotriazole

(1) Stereoscan photograph x 236
(2) Zeiss photograph x 120
from the plain bath were regular in size and flat faced with straight edges, but those from the bath containing benzotriazole were hemispherical and reniform.

5.3. The Effect of Bath Temperature and Current Density on the Surface Topography of Copper Deposits from the Plain Bath.

Introduction
The effects produced by varying the bath temperature and current density were studied together. In this experiment, a current density of 215 A/m² was passed for three hours through five cells connected in series and maintained at constant temperatures of 0, 23, 40, 60 and 80°C. The plating baths were covered with clock glasses to minimize evaporation, so maintaining a constant composition of solution. The experiment was then repeated, using the appropriate plating times to give the same final thickness of deposit for current densities of 55, 110, 215, 430 and 650 A/m².

One litre of the standard solution (125 g/l copper sulphate and 49 g/l sulphuric acid) was used in each cell, which was magnetically stirred to reduce any temperature gradients and polarization effects. Because the same specimens were to be used for microhardness determination, a copper cathode of 2 x 10⁻³ m thickness was used in each case, to provide a firm base for the deposits. The electrodes were cleaned in the normal manner and lacquered to give an exposed surface area of 4 x 10⁻³ m².

Immediately after plating, the specimens were carefully washed and dried to prevent staining. They were then photographed at a magnification of x 320 using a Zeiss microscope.

Results
The results are presented as a series of twenty-five photographs, Fig. 5.3., which illustrate the effect on the surface topography of the use of different bath temperatures and current densities to form electrodeposits. The two photographs taken on the Stereoscan Fig. 5.3.(a), show a powdery deposit.

Discussion
The photographs in Fig. 5.3. illustrate the effect on the surface topography of either a change in the bath temperature at a fixed current density (rows) or a variation in the current density at a certain bath temperature (columns).

As the bath temperature was increased, the deposit surface became coarser
Fig. 5.3. EFFECT OF TEMPERATURE AND CURRENT DENSITY ON THE SURFACE TOPOGRAPHY OF COPPER DEPOSITS.
Fig. 5.3(a) Appearance of a Powdery Copper Deposit
at all current densities and this type of appearance has been classified as "shiny and crystalline" by Weil and Read. However, at lower temperatures a much finer crystalline surface was produced, which presumably grew from a large number of nuclei of a similar size. The larger crystals formed in the warmer solutions resulted from a smaller number of nuclei on which growth occurred, resulting in larger grains. When deposition occurred under the combined effect of a low bath temperature and a high current density, some hydrogen evolution was observed and slightly powdery coatings were formed. These powdery or "burned" deposits are undesirable and are produced when the current density exceeds a certain maximum or limiting value, which depends upon the plating bath and the temperature; these deposits, shown in Fig. 5.3.(a), will be discussed later.

Conclusion

The formation of a coarsely grained deposit was favoured by the use of a high electrolyte temperature and a low current density. Finely grained coatings were produced by low temperatures and high current densities.

5.4. Effect of Solution Agitation on the Surface Microstructure of Copper Deposits

Introduction

According to the literature survey (section 1.3.6.), agitation of the plating bath has a significant effect on the surface of the resulting deposited metal. In this section, the effect on the surface of the deposits produced by ultrasonic agitation was compared with those produced by magnetic stirring and also those from a still solution.

The copper deposits were plated from the standard bath at 18°C with a current density of 215 A/m² for 15 minutes on to degreased and pickled copper cathodes. The surfaces were examined under a microscope and a typical area selected, from which a one centimeter square was cut for examination on the Stereoscan. A smaller cathode would not have required cutting, but had the disadvantage that much more metal would be deposited at the edges of the electrode than in the centre, and the sample would not be typical of a large plated area. This edge effect sometimes presents a real problem in the plating industry and subsidiary electrodes or 'robbers' are used to obtain a uniform coating. The copper deposits were examined at magnifications of about x 20 and x 100, the actual values
being given by the side of the photographs. The Stereoscan was used to obtain a greater depth of field than can be obtained with a microscope, and gave a three-dimensional view showing the roughness of the plated area.

The experiment was repeated using a still solution of the same composition as above at 18°C, but with a much lower plating current (about 20A/m²) for 2½ hours. The specimens were photographed at magnifications of x 18, x 98, and x 495 and compared with the previous deposits from the still bath, to determine the effect of the current density on the microstructure of the deposits.

Photographs are also shown of the deposits produced under different plating conditions in an earlier experiment on the effect of solution agitation. These specimens were used for microhardness measurements and the copper was plated at 23°C with a current density of 430A/m² for three hours. These photographs clearly illustrate the effect of solution agitation and were taken at a magnification of x 320 on a Zeiss microscope.

Results

These are shown as three pairs of photographs Fig. 5.4. (a) and illustrate the effect of solution agitation on the surface of copper deposits from a still, a stirred and an ultrasonically agitated bath at magnifications of about x 20 and x 100. These coatings were plated at 18°C and a current density of about 215A/m², whereas those in Fig. 5.4. (b) were at a value of about 20A/m². The third set, Fig. 5.4. (c), were produced at a slightly higher temperature, 23°C, and a much higher current density of 430A/m² and were taken on a Zeiss microscope, which unfortunately does not give the same surface detail as the Stereoscan.

Discussion

It can be seen from the photographs of the surfaces shown in Fig. 5.4. (a) and (c) that there was not very much difference in roughness between the deposits produced from the still and the stirred solutions. However, ultrasonic agitation modified the surface appearance which was much more uniform as well as being smoother. Although it cannot be seen from the photographs, the deposit from the ultrasonically agitated bath was brighter than either of the others and this brightness was probably associated with the increased smoothness.
Fig. 5.4.(a) EFFECT OF SOLUTION AGITATION ON SURFACE APPEARANCE OF COPPER DEPOSITS.
FIG. 5.4(b). EFFECT OF A LOW CURRENT DENSITY ON SURFACE APPEARANCE OF COPPER DEPOSITS.
FIG: 5.4 (c) EFFECT OF SOLUTION AGITATION ON SURFACE APPEARANCE OF COPPER DEPOSITS.
The deposits from the static bath, with a low current density, Fig. 5.4. (b) showed a very regular appearance. At the low magnification of x 18, the surface appeared to be very smooth and the evenness is visible in the photograph at magnification x 98. The last photograph (x 495) shows the sharp clean, crystallographic facets of the surface, which appear to be almost parallel to each other. The reason for these regular shapes was probably that at a low rate of deposition the nucleation occurred slowly and the growth was more perfect than for higher deposition rates, because the depositing ions had longer to move over the cathode surface to the growth site, before joining the lattice and continuing the grain growth.

Conclusion

There was not much difference between the surface smoothness of deposits from a static and a magnetically stirred bath. Ultrasonic vibration of the bath under the same conditions gave a much smoother and brighter surface. The effect of a much lower current density was to produce a very uniform deposit consisting of regularly shaped surface crystals.

5.5. Effect of Solution Agitation on the Appearance and Uniformity of Deposits.

Introduction

Mention has been made in the literature survey (section 1.3.6.) of the fact that agitation of the plating solution increased the maximum or limiting current density which could be passed without the formation of a powdery or 'burned' deposit. It also improved the surface smoothness of the coating and usually increased the hardness and reduced the internal stress in the deposits.

The experiment was designed to compare the surface appearance and smoothness of deposits produced from still, magnetically stirred and ultrasonically agitated solutions. The latter property was investigated by examining the etched cross-sections of the coating under a microscope at a high magnification. Both these surface characteristics of the coating were studied for deposits from the plain bath and also from the bath containing benzotriazole. The standard plating solution was used at 23°C, with a current density of 430A/m²; this high current density was chosen because previously it had been observed that it produced deposits which were slightly burned.
Results

These consist of a series of six photographs in Fig. 5.5. which show the cross-sectional microstructure of copper plated from (a) a still bath, (b) a stirred bath and (c) an ultrasonically agitated solution. With each type of agitation, the photographs on the left are of deposits from a plain bath and on the right from an electrolyte containing 0.12 g/l benzotriazole.

Discussion

The edges of the specimen plated from the still plain bath showed some powdery deposit, whereas the copper from the stirred bath was less powdery and that from the ultrasonically agitated solution was perfectly good, with no sign of burning. A comparison between these coatings and those from the bath containing benzotriazole again showed that this addition agent gave a deposit with a brighter surface as well as a high internal stress. These stressed coatings had a tendency to peel away from the substrate, especially that from the still bath, while the one from the ultrasonic solution was the most adherent. It can, therefore, be concluded that the stress was a maximum and/or adhesion was a minimum in the deposits produced from the still bath. However, as the substrates were all cleaned by the same technique prior to plating, it is more probable that the internal stress was reduced by the agitation of the solution: this explanation is supported by the preliminary results (see section 3.7.3.), which indicated that ultrasonic vibrations decreased the stress in copper deposits.

The photographs of the cross-sections of the deposits showed that an increase in the agitation of the solution increased the surface smoothness. This smoothness may be associated with the reduction in the concentration polarization at the cathode produced by the agitation of the solution, and resulting in more mobile ions which were able to move to the most favoured deposition sites. The reverse of this was the formation of whiskers, which gave a very rough coating, and this occurred most readily in static solutions. The presence of benzotriazole in the solution produced a very smooth coating in all three instances. Because the specimens were not all mounted parallel to one another, the thicknesses of the deposits in the various baths appear to be different.
Deposits from still bath

Deposits from stirred bath

Deposits from ultrasonically agitated bath

Deposits from plain bath

Deposits from Benzotriazole bath (0·12 g/1)

FIG. 5.5. EFFECT OF SOLUTION AGITATION AND BENZOTRIAZOLE ON THE STRUCTURE OF DEPOSITS.
Conclusions

An increase in the solution agitation:

1. raised the maximum current density which could be used without forming 'burned' deposits in the plain bath;
2. improved the surface smoothness of the plain deposits;
3. reduced the internal stress and the extent of peeling in deposits from the bath containing benzotriazole;

The effect of the use of benzotriazole on the plating bath:

1. increased the surface brightness of the deposits;
2. improved the surface smoothness of coatings from all three baths;
3. produced highly stressed deposits.

5.6. Effect of Concentration of Benzotriazole in the Bath on the Surface Topography

Introduction

In an earlier section (5.2.) the nucleation of copper deposits from a bath containing 0.12 g/l benzotriazole was investigated. In this part, a study was made of the modifications to the surface topography produced by the addition of different concentrations of benzotriazole to the plating solution.

Small cathodes, 1 x 10^{-2} m x 1 x 10^{-2} m, were used because specimens of this size could be examined in the Stereoscan. Larger cathodes could not be used because, when they were plated and then cut to the required size, the deposit tended to break or flake off. The small cathodes, with a long thin supporting tag, were cut from copper foil, degreased in acetone, given a quick etch in 50% nitric acid and air dried. One side of the foil and both sides of the tag were lacquered with Lacomit and allowed to dry in air. Twelve anodes were prepared in a similar manner; but these had a much larger surface area (1 x 10^{-3} m^2), because specimens of
1 x 10^{-4} m^2 would completely dissolve during the experiment.

The cells were then set up and the electrodes connected in series. Each cell contained one litre of plating solution and the appropriate concentration of benzotriazole, i.e. 0.0001, 0.0005, 0.001, 0.005, 0.01, 0.05, 0.12, 0.2, 0.3, 0.5 or 1.0 g/l. The solutions were magnetically stirred and the plating time was fifteen minutes with a current density of 215 A/m². After deposition, the cathodes were washed in water, dried in air and examined in the Stereoscan.

Results

Photographs of the copper plated from the copper sulphate-sulphuric acid bath containing different concentrations of benzotriazole are shown in Fig. 5.6. (1) and (2), the magnification used was ×1200.

Discussion

The copper deposited from the plain solution without any addition had a coarse, grainy appearance which is typical of coatings from this bath. The lowest concentration of benzotriazole used, 0.0001 g/l, modified the topography and produced truncated crystallites with flat horizontal tops. With more benzotriazole, the fraction of the cathode covered by these flat crystals increased until, with 0.005 g/l, the whole area appeared to be relatively level.

The surface changed at a concentration of about 0.01 g/l from a flat to a nodular appearance. The deposits from solutions containing 0.12, 0.2 and 0.3 g/l benzotriazole were highly reflective and consisted of flattened nodules. With a higher addition, small nodules or particles appeared to grow on the larger nodules; the surface with 0.5 g/l was semi-bright but that with 1 g/l was dark in colour with a matt appearance.

Conclusion

The addition of benzotriazole to the plating bath had a marked effect on the surface of the copper deposits. At low concentrations of 0.0001 to 0.005 g/l, truncated crystals were formed and above about 0.01 g/l a nodular growth occurred. Very reflective surfaces were produced with additions of 0.12, 0.2 and 0.3 g/l benzotriazole.
Concentration of Benzotriazole in solution g/l

\[ a = 0 \quad b = 0.0001 \quad c = 0.0005 \quad d = 0.001 \quad e = 0.005 \quad f = 0.01 \]

FIG. 5. 6. (1) EFFECT OF BENZOTRIAZOLE ON THE SURFACE TOPOGRAPHY.

P. T. O.
FIG. 5.6. (2) EFFECT OF BENZOTRIAZOLE ON THE SURFACE TOPOGRAPHY.

Introduction

The aim of the work described in this section was to compare the cross-sectional structure of copper deposited from plating solutions containing different concentrations of benzotriazole. Copper wire, about $2 \times 10^{-3}$ m in diameter, was used as the cathode and held in a vertical position in the plating tanks. These tanks consisted of litre beakers lined with copper foil which acted as the anode. This arrangement was normally found to give a uniform deposit thickness over the whole surface of the cathode.

The wire was cut into $1.5 \times 10^{-1}$ m lengths and then cleaned in the normal manner (degreased in acetone and pickled in 50% nitric acid). The standard plating solution was used (125 g/l copper sulphate and 49 g/l sulphuric acid) at room temperature (20°C) and with a current density of 260 A/m². The cells, each containing a litre of solution, were connected in series, and a different addition of benzotriazole (indicated on the photograph) was added to each of the baths, which were slowly magnetically stirred to assist dissolution of the benzotriazole and to minimize any variations in the concentration of the bath.

During plating, the current was switched off three times (after about 0.75, 2 and 2.5 hours) for periods of one, five and five minutes respectively, to induce adsorption and banding (which is discussed later). After deposition for three hours, the plated wire was removed from the bath, washed in water, immersed in acetone and air dried. The specimens were then mounted in a cold setting, metallurgical, mounting plastic at room temperature to avoid any changes in the structure of the deposits, which could occur if they were hot mounted. The mount was then cross-sectioned with a hack saw, polished, etched in an alcoholic ferric chloride solution and examined under a microscope. Several etchants were tried including orthophosphoric acid, ammoniacal hydrogen peroxide and acidic ferric chloride solution, but the one chosen appeared to be the best in giving selective attack and showing the layered structure which was present in some of the deposits.

Results

Fig. 5.7. consists of a series of ten photographs of typical cross-sections
Concentration of Benzotriazole in solution g/l
Cross-section magnification approximately x 265

\[ a = 0 \quad b = 0.001 \quad c = 0.005 \quad d = 0.01 \quad e = 0.05 \]
\[ f = 0.12 \quad g = 0.2 \quad h = 0.3 \quad i = 0.5 \quad j = 1.0 \]

FIG. 5.7. EFFECT OF CONCENTRATION OF BENZOTRIAZOLE ON THE STRUCTURE OF DEPOSITS.
of the microstructures of copper deposits plated from solutions containing different concentrations of benzotriazole.

Discussion

The coatings on the copper were all fairly uniform in thickness, with the exception of those from the baths containing 0.5 and 1.0 g/l benzotriazole. The photographs (a) to (h) show part of the surface including the substrate, deposit and mount. However, the deposits from the solutions containing 0.5 and 1.0 g/l benzotriazole, (i) and (j), were very irregular in thickness and the photographs were taken of thick sections of the coating to show the plated structure. The copper plated from baths containing 0.2 g/l benzotriazole or more was not in continuous contact with the substrate, which suggests that the adhesion between the deposit and the base was poor in solutions with a high concentration of addition agent.

As mentioned in the introduction, the plating current was switched off on three separate occasions for periods of one, five and five minutes, which allowed adsorption of benzotriazole on the surface of the coating and encouraged the formation of bands in the deposited metal. The purpose of these bands was to label the position and shape of the surface at different time intervals during plating.

The structure of the plated copper can be divided into five categories being those in which:

I. no indication was given of banding when the current was switched off, {(a) and (b)} ;

II. one fine band was shown when the current was switched off, {(c) and (d)} ;

III. codeposited layers were present in the coating, {(e) and (f)} ;

IV. the deposit was very fine with poor adhesion and cracked when the current had been switched off for more than a minute {(g) and (h)} ;

V. the thickness of the deposit was very variable with poor adhesion and cracks were produced when the current had been switched off, {(i) and (j)} .
In Group I, a thin line indicates the junction between the substrate and the electrodeposit and it appears that the structure was similar on both sides of this line. No indication is given of the thickness at which the current was switched off. The Group II deposits showed one relatively thick line at the surface of the basis metal and a much thinner line, when the current had been switched off for a period of five minutes.

In the other groups of deposits, the benzotriazole had a more pronounced effect on the structure of the plated copper. Group III deposits showed a layered rather than banded structure. In photograph (e) two layers following the substrate are clear and the outer part of the deposit showed only a very slight effect. Prall suggested that benzotriazole was co-deposited with copper as cuprous benzotriazolate in layers which were parallel to one another and the plated surface. The concentration of benzotriazole in the deposits was shown to be dependent upon the concentration in the plating solution and also the position conditions. A similar but more pronounced structure occurred in the deposit (f) from the bath containing 0.12 g/l benzotriazole. In both these deposits, as well as for all the other specimens, the adhesion of the coating to the substrate was good and there was no evidence of cracking or peeling. In all the other coatings from solutions containing 0.2 g/l benzotriazole or more, the adhesion to the substrate was very poor and cracking or peeling occurred when the current had been switched off for several minutes. The Group IV specimens (g and h) had a fine structure with no indication of a layered deposit at the magnification shown or at the higher values which were also used. Group V samples had very poor coatings with an uneven thickness and they were brittle with the deposit flaking off and, therefore, of no practical significance. The deposit (i) showed a very marked layered structure, whereas (j) was very laminated and non-coherent.

The effect of the adsorption of benzotriazole onto a copper surface, either before the start of plating or during a period of time when the current was switched off, was to decrease the adhesion on the surface. If sufficient adsorption occurred, resulting from exposure to a concentrated solution for a short time or a weaker solution for a longer time, a very weak bond was produced and peeling or cracking occur. This
production of poor surface bonding may assist in the easy removal of plated coatings from treated substrates and is the basis of a patent taken out by the Anaconda Brass Company for use in electroforming.

Conclusion

The presence of benzotriazole in the plating solution had a marked effect on the structure of the deposits. If it were present in low concentrations, it could produce banding, whereas higher amounts gave a layered structure. Concentrations above about 0.2 g/l give a deposit with poor adhesion, which could crack or flake away from the substrate or itself, and these coatings have no practical use. The deposits from baths containing 0.05 g/l and 0.12 g/l appeared to contain an optimum amount of benzotriazole and were both adherent and coherent.

5.8. Effect of Surface Topography on the Deposit Brightness

Introduction

It is a well known fact that the brightness of a deposit is related to the surface smoothness. In this section, an attempt was made to produce deposits with different degrees of brightness and then to examine the smoothness of these surfaces.

A matt coating was deposited from the plain bath at 20°C with a current density of about 215 A/m² for a period of three minutes. With the same plating conditions and an addition of 0.12 g/l benzotriazole to the bath, a very bright surface was produced. These coatings were compared with a semi-bright one which had been deposited from a bath containing benzotriazole and used in a previous experiment. Photographs were taken on the Stereoscan of all three deposits at magnifications of x 200 and x 1,000.

Results

The results of this section of the work are a set of photographs, Fig. 5.8., of a matt copper deposit [(a) and (b)], a very bright surface [(c) and (d)] and a semi-bright coating [(e) and (f)].
Matt Copper deposits from plain bath.

Fully bright Copper deposits from bath with Benzotriazole

Semi bright Copper deposits from bath with Benzotriazole

FIG. 5.8. TOPOGRAPHY AND BRIGHTNESS OF COPPER ELECTRODEPOSITS
Discussion

It can be seen from the photographs (a) to (d) that the addition of benzotriazole to the plating bath under the same experimental conditions modified both the type of growth and the surface topography. The deposit from the plain bath consisted of flat faced angular crystals which formed a rough surface and gave only a limited amount of light reflection and, therefore, appeared as a matt coating. From the baths containing benzotriazole, nodular deposits were produced, which gave a smoother surface with a higher degree of light reflection. The difference between the very bright [(c) and (d)] and semi-bright deposits [(e) and (f)] was that in the latter the whole surface was rougher than in the former and consequently reflected less light.

Conclusion

The deposits from a plain acid sulphate bath gave matt copper coatings, whereas those from the solution containing benzotriazole could be either semi-bright or very bright, depending upon the plating conditions.

5.9. X-Ray Examination of the Electrodeposits

Introduction

Electroplated copper coatings were examined by x-ray diffraction techniques, using copper radiation with a nickel filter for both the powder and back-reflection methods. Powder photographs were obtained of deposits from both the plain bath and one containing 0.12 g/l benzotriazole. The back-reflection method, in which only the high angle lines \{331\} and \{420\} are photographed, was used to indicate any preferred orientation in the deposited layers, as well as the presence of any internal stress or very small grain size.

The powdered specimens were prepared by filing a sample of the plated copper (a process which could create some internal stress) and the particles produced were then rinsed in dilute sulphuric acid to dissolve any iron impurities which may have broken off the file. The powder was washed in water, dried in air and sieved, to remove any large particles that would otherwise give spots on the photograph of the diffraction lines. A thin specimen was made by sticking this powder onto a fine glass fibre, which was then placed in a central position in the powder
camera. The camera was loaded with the film in the Straumanis setting and, with this arrangement, an exposure time of about ninety minutes was found sufficient to give diffraction lines of a suitable intensity for examination. A similar process was repeated with filings of a deposit containing benzotriazole both before and after annealing in a vacuum for 200 minutes at 300°C. An x-ray photograph was obtained of a powdery or 'burned' copper deposit which had been produced from the plain bath using a very high current density; in this case, because a very fine powdery deposit was formed, no filing of the copper was necessary.

In the back-reflection technique a flat plated specimen was used. To avoid the diffraction lines of the substrate material appearing on the photograph, it was necessary to plate a certain minimum thickness of copper. This value was determined by depositing copper of increasing thicknesses onto a nickel foil and taking photographs of the x-ray lines, until there were no lines for the nickel on the film. This minimum thickness was found to be equivalent to a plating time of two hundred minutes at a current density of 215A/m². Because the preparation of these specimens did not involve any grinding process, (which could introduce a stress into the particles of copper or produce particles of a very fine size), any line broadening shown by the back-reflection method could be attributed to either the actual stress in the deposit or a very fine grain size in the copper coating. For details of the formation of diffuse lines on x-ray films by either internal stress or a very fine grain size, the reader is referred to the standard textbooks on x-ray diffraction. In order to compare the back-reflection photographs, a silver powder was sprinkled on the surface of the copper specimens and two sets of superimposed lines were obtained on the film. The distance between the specimen and the film was fixed at three centimetres, because this gave suitable spacing of the \{331\} and \{420\} rings for copper on the film.

Results

The results of the x-ray examination of the deposits are shown in Fig. 5.9. The x-ray powder photographs are for:

(a) a plain matt copper deposit;
(b) a burned or powdery copper deposit;
(a) Copper powder  
(b) Powdery or burned copper deposit  
(c) Copper deposit with benzotriazole and annealed  
(d) Copper deposit with benzotriazole

Fig. 5.9  X-Ray Powder Photographs of Copper
Fig. 5.9  Back-Reflection X-Ray Photographs

(e) Analar Copper Foil  
(f) Plain Copper Deposit  
(g) Copper deposited from solution with Benzotriazole
(c) a deposit from a bath containing 0.119 g/l benzotriazole which had been annealed in a vacuum at 300°C for two hundred minutes.

(d) a deposit from a bath containing 0.119 g/l benzotriazole.

The back reflection x-ray photographs are for:

(e) a piece of analar copper foil;

(f) a plain copper deposit;

(g) a deposit from a bath containing 0.119 g/l benzotriazole.

Discussion

The powder photographs of the plain matt deposit, (Fig. 5.9. (a) ), and also the powdery deposit (Fig. 5.9. (b) ), show sharp lines and clearly resolved doublets. The fact that these lines are sharp prove that the filing of the copper deposit did not produce any significant internal stress.

The lines of the powder photograph for the deposit containing benzotriazole were more diffuse (Fig. 5.9. (d)) than the others but they became sharper after the powder had been annealed. This broadening due to the presence of the benzotriazole is also shown, to a slight extent, in the back reflection photograph (Fig. 5.9 (g)) and prevents an accurate determination of the lattice parameter which is normally calculated from the high angle doublets. There was very little preferred orientation in the deposits and it was mainly observed in the coatings produced from solutions containing benzotriazole at low current densities and high bath temperatures. There appeared to be very little, or no, change in the lattice parameter produced by the incorporation of the benzotriazole.

The back reflection lines for the silver power are slightly spotty in Fig. 5.9 (f) because the specimen was not rotated during exposure to the x-rays. These results are further discussed and compared with those from other parts of the work in Section 7.3.

Conclusions

The deposit from the bath containing benzotriazole gave very diffuse x-ray diffraction lines compared with the sharp lines produced by the deposits from the plain bath. The codeposition of benzotriazole had little effect on the lattice parameter and gave only slight preferred orientation when low current densities and high bath temperatures were used.
6. SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE ELECTROPLATING SOLUTION AND OF THE COPPER DEPOSITS

6.1. Introduction

The first part of this chapter covers, in more detail than in the preliminary results, some properties of the electrolyte. A study is made of the effect of varying the plating conditions, such as the current density, electrolyte temperature, bath agitation and presence of benzotriazole, on the current efficiency, the metal distribution ratio and the throwing power of the acidic copper sulphate solution. In the second section the grain size, microhardness and internal stress of deposits from both the plain bath and the one containing benzotriazole are measured. The physical properties of some of these deposits have been measured and correlated with the bath temperature, current density and solution agitation used during the plating.

6.2. Current Efficiency

6.2.1. Introduction

The effect on the current efficiency of changes in the concentration of copper sulphate in the solution, the current density and the solution agitation was investigated. These variables were studied because, if the cathodic current efficiency is low, the corresponding relative thickness of the deposit is also reduced and the current which is not used in depositing the copper may produce hydrogen gas. This hydrogen is co-deposited with the copper and can affect both the hardness and internal stress of the deposit. The current efficiency was required for the calculation of the deposit thickness which, in turn, was used for the determination of the internal stress. It is, therefore, important to measure the cathodic current efficiency because it is related to other properties which are discussed later in this chapter.

One of the difficulties in the measurement of the current efficiency was the determination of the exact quantity of electricity which was passed through the cell, and this has been discussed in section 2.4.1. in the experimental procedure. To overcome this difficulty the results are given as weight changes at the electrodes and are comparable because the cells were connected in series.

6.2.2. Effect of the Concentration of Copper Sulphate in the Electrolyte

Introduction

The effect of varying the concentration of copper sulphate in the electrolyte was studied at a temperature of 22°C with nine different plating cells, each
containing 1 litre of the appropriate electrolyte with 10 to 240 g/l copper sulphate. Each of these solutions contained 49 g/l sulphuric acid and the electrolytes were slowly stirred magnetically. The electrodes were cleaned in the normal manner (section 2.3.6.), weighed and joined in series, placed in the plating cells and a current, equivalent to 215A/m², was passed for about thirty minutes. The electrodes were then removed from the baths, washed in water, dried in air and weighed, particular care being taken to avoid the loss of copper from the burned deposits. This loss was minimized by keeping the powdery cathodes in a horizontal position when washing, drying and weighing.

The process was then repeated for solutions having a similar range of concentrations but with an addition of 0.119 g/l benzotriazole. In this second experiment, a cell containing an electrolyte without benzotriazole was connected in series as a standard, so that the weight changes of the deposits from the bath containing benzotriazole could be adjusted to make a direct comparison possible with the plain bath.

Results

These are given in Table 6.2.2. and plotted in a graph, Fig. 6.2.2.

<table>
<thead>
<tr>
<th>Concentration of Copper Sulphate g/l CuSO₄·5H₂O</th>
<th>Electrode Weight Changes g</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plain Bath</td>
<td>Bath with BTA⁰</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anode Loss</td>
<td>Cathode Gain</td>
<td>Anode Loss</td>
</tr>
<tr>
<td>10</td>
<td>-.3004</td>
<td>.2073</td>
<td>-.2907</td>
</tr>
<tr>
<td>40</td>
<td>-.2922</td>
<td>.2412</td>
<td>-.2768</td>
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<tr>
<td>70</td>
<td>-.2903</td>
<td>.2660</td>
<td>-.2817</td>
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<tr>
<td>100</td>
<td>-.2876</td>
<td>.2772</td>
<td>-.2843</td>
</tr>
<tr>
<td>130</td>
<td>-.2855</td>
<td>.2741</td>
<td>-.2819</td>
</tr>
<tr>
<td>150</td>
<td>-.2834</td>
<td>.2796</td>
<td>-.2849</td>
</tr>
<tr>
<td>180</td>
<td>-.2828</td>
<td>.2775</td>
<td>-.2877</td>
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<tr>
<td>210</td>
<td>-.2884</td>
<td>.2764</td>
<td>-.2883</td>
</tr>
<tr>
<td>240</td>
<td>-.2092</td>
<td>.2778</td>
<td>-.2695</td>
</tr>
</tbody>
</table>

⁰ Bath containing 0.119 g/l benzotriazole

ˣ Powdery deposit produced with gas evolution

Table 6.2.2.
Bath Temperature 20°C  Current Density 215A/m²

FIG. 6.2.2. EFFECT OF CONCENTRATION OF COPPER SULPHATE ON WEIGHT OF COPPER DEPOSITED.
Discussion

During the plating from the baths containing 10 g/l and 40 g/l copper sulphate, evolution of a gas was observed and the deposits were burned, being dark in colour and powdery. The deposition of powdery copper from solutions containing low concentrations of copper sulphate was also observed in the preliminary work on the hardness of the coatings. It was difficult to remove these deposits from the bath and to dry them, without the loss of any copper powder, which would result in an apparent lowering of the cathodic current efficiency. From theoretical considerations and the published literature, it was assumed that the gas was hydrogen. The fact that hydrogen was evolved from these solutions with low concentrations of copper sulphate suggests that there were insufficient copper ions available for deposition in the electrolyte close to the cathode surface, so that the alternative cathodic process of the formation of hydrogen gas occurred.

This formation of hydrogen by the current instead of plating copper is the main reason for the low weights of copper produced on the cathodes, and consequently a low cathodic current efficiency. It appears that the efficiency of the bath with 70 g/l copper sulphate was also less than 100%, although in this case no gas was observed on the cathode surface and the deposits were not powdery. With 100 g/l copper sulphate and above, there was no significant increase in the weight of copper deposited in either bath. Apart from the bath containing 10 g/l copper sulphate, in which much less copper was plated when benzotriazole was present, the addition agent sometimes increased and sometimes decreased the current efficiency, but these changes were normally within the experimental error which was about ± 30 mg or ± 1%.

It may be noted that the weight of copper dissolved from the anodes was, in all cases except one, higher than the weight deposited. This means that the anodic current efficiency is greater than the cathodic current efficiency for all the baths except the one containing 240 g/l copper sulphate, which had a particularly low value, perhaps caused by anodic concentration polarization. This may be due to the dissolution of copper at the anode and cathode before and after applying the current and also to the presence of impurities in the anode, which can dissolve or, if insoluble, fall off the anode surface.
Conclusion

The increase in the concentration of copper sulphate in the bath:

(1) initially caused a significant increase in the cathodic current efficiency and then a steady value was reached at about 100 g/l;

(2) reduced the anodic current efficiency in the plain bath with a marked decrease in the bath containing 240 g/l;

(3) had little effect on the anodic current efficiency in the bath containing benzotriazole, except to lower it at 240 g/l.

In both sets of solutions containing 10 g/l and 40 g/l copper sulphate, hydrogen was evolved during plating and powdery deposits were produced.

The presence of benzotriazole in the solution:

(1) had no effect on the cathodic current efficiency, except to give a large decrease in the bath containing 10 g/l copper sulphate;

(2) reduced the anodic current efficiency at low concentrations of copper sulphate and increased it at the highest concentration, but had little effect at other concentrations.

6.2.3. Effect of Current Density

Introduction

In this section the effect of varying the current density on the weight of copper deposited at the cathode was studied. The same experiment was repeated at four different temperatures, each being controlled by immersing all the plating cells in a constant temperature bath. It was, therefore, not possible to stir these solutions magnetically, so they were used in a still condition. The cells were connected in series so that, using one current with electrodes of different areas, it was possible to vary the current density from one cell to another. A coulometer was connected in series and a total quantity of about 3,600 coulombs of electricity measured on the instrument was passed through the circuit. The procedure for cleaning and weighing the electrodes was the same as that described in section 2.3.6.

Results

These are given in Table 6.2.3 and plotted in a graph, Fig. 6.2.3.
FIG. 6.2.3. EFFECT OF CURRENT DENSITY ON WEIGHT OF COPPER DEPOSITED AT DIFFERENT SOLUTION TEMPERATURES.
Current Density $A/m^2$ & Cathode weight gains g & \\
\begin{tabular}{c|cccc}
 & $11^\circ C$ & $27^\circ C$ & $55^\circ C$ & $77^\circ C$ \\
55 & 1.1276 & 1.1134 & 1.1350 & 0.9662 \\
110 & 1.2320 & 1.1878 & 1.1711 & 1.0450 \\
215 & 1.2370 & 1.1956 & 1.1940 & 1.1022 \\
325 & 1.2332 & 1.1946 & 1.1954 & 1.1250 \\
540 & 1.2344 & 1.1968 & 1.1992 & 1.1542 \\
645 & 1.2360 & 1.1959 & 1.1998 & 1.1634 \\
860 & 1.2368 & 1.1965 & 1.2008 & 1.1732 \\
Table 6.2.3. \\
Nominal quantity of electricity passed coulombs & 3620 & 3620 & 3630 & 3600 \\
\end{tabular}

Discussion

A comparison can only be made between the weight gains of those cathodes connected in series at one temperature. It is, therefore, not possible from these results to determine the effect of changing the bath temperature. Similarly, it is not possible to compare the weight changes in this section with those in the preliminary work (section 3.4.).

At all the four temperatures used, the weight gain of the cathodes rose sharply as the current density was increased from 55 $A/m^2$. For the three lower temperatures, a steady weight was observed at a current density of 215 $A/m^2$ and above. This was particularly advantageous because the value of 215 $A/m^2$ for the current density had been chosen as the standard for this work, and at this value a maximum steady value for the cathodic current efficiency occurred. This increase in the current efficiency with the current density has been observed by Kudryavtsev et al.\(^{297}\).

At a low current density, the current efficiency varied more with local changes in the current density than at a higher current density. This relationship between the current density and current efficiency is a determining factor for the throwing power. The change in current efficiency meant that on a rough surface proportionally more metal was deposited at
the projecting points (with the higher current density) than on the recessed points. Therefore, if the current efficiency were the only controlling factor, the metal distribution ratio would be higher and the throwing power would be lower at low current densities, the change being more pronounced at higher temperatures.

**Conclusion**

At low current densities, the cathodic current efficiency increased with the current density for all the bath temperatures used. However, a constant value was obtained at, and above, a current density of 215 A/m², in all the baths except the one at 77°C, which showed a steady increase.

**6.2.4. Effect of Electrolyte Temperature**

**Introduction**

The effect of varying the temperature of the plating bath on the weight of copper deposited at the cathode was investigated at four different current densities. In this experiment, sixteen plating cells were arranged in series and both the temperature and current density varied, so that the effect of both could be studied.

Four cells, containing solutions, were immersed in each of four constant temperature water tanks. The current density was modified in each of the four cells by using electrodes of different areas. This arrangement gave four cells at each temperature and four cells at each current density. The electrode preparation followed the description in section 2.3.6. The experiment was repeated four times and the values given below are typical weight gains.

**Results**

These are given in Table 6.2.4. and plotted in a graph, Fig. 6.2.4.

<table>
<thead>
<tr>
<th>Solution Temperature (°C)</th>
<th>Cathodic Weight Gain g at Current Densities A/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>0.6873</td>
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<tr>
<td>21</td>
<td>0.6824</td>
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<tr>
<td>35</td>
<td>0.6850</td>
</tr>
<tr>
<td>60</td>
<td>0.6687</td>
</tr>
</tbody>
</table>

*x Burned or powdery deposits

Table 6.2.4.
FIG. 6.2.4. EFFECT OF SOLUTION TEMPERATURE ON WEIGHT OF COPPER DEPOSITED AT DIFFERENT CURRENT DENSITIES.
Discussion

The deposits formed at the lowest temperature (3°C) with current densities of 215 and 430 A/m² were burned and powdery. These coatings were lighter in weight than the others, probably due to the production of hydrogen gas which was not, however, observed during plating. The coating produced at 110 A/m² was lighter than that at 55 A/m², so some powdery copper and hydrogen may have been produced, but neither was visible. The current efficiency for both those cathodes was, therefore, lower than for the electrodes plated at higher temperatures.

At all four current densities, the weights of copper deposited at 21°C and 35°C were about the same, and were higher than those plated at a bath temperature of 60°C. Therefore, the cathodic current efficiency fell as the temperature rose above 35°C, an effect which may have been due to the fact that the rate of corrosion or dissolution of a metal increases with the temperature of the electrolyte. This corrosion would be lower at high current densities, at which there would be appreciable concentration polarization preventing dissolution, but this polarization would not occur at lower densities.

A comparison between the effects of an increase in the current density at different temperatures shows that the cathodic current efficiency increased with the current density, except in the cases where burned deposits were formed. This observation, from only four values of the current density, agrees with the conclusion in an earlier section 6.2.3.

Conclusion

The cathodic current efficiency was found to:

(1) be low at low temperatures with medium and high current densities (215 A/m² and above) at which burned deposits were formed;

(2) decrease as the temperature rose above about 35°C;

(3) increase with current density, except at 3°C.

6.2.5. Effect of Solution Agitation

Introduction

It has been noted in the literature survey (section 1.3.6.) and in the preliminary work (section 3.4.) that the agitation of a plating solution
increased the cathodic current efficiency. In this part of the work, the effect of ultrasonic vibrations on both the anodic and cathodic current efficiencies is compared with those of the still bath. The comparison was made at a series of different plating current densities from 30 to 385 A/m², the solutions being at room temperature (20°C).

Three Haring-Blum cells, (described in section 2.4.) were used in series with one or two cells placed in the ultrasonic tank and the remainder contained a still plating solution. The area of the electrodes exposed to the solution was 2.5 x 10⁻³ m² and the volume of electrolyte was about 370 mls. The electrodes were prepared as described in section 2.3.6. and the current passed for the appropriate time to give approximately the same weight change in every case, except one which was accidentally allowed to plate for a longer time.

Results

These are given in Table 6.2.5.

Discussion

The results are given in rows of three and subdivided into anodic weight losses and cathodic weight gains for the cells used in series. No comparison can be made between the weight changes at different current densities, because the quantity of electricity could not be precisely controlled.

The amount of copper dissolved from the anode was generally greater than the amount deposited on the cathode, at current densities of 130 A/m² and above. The anodic current efficiency, therefore, was higher in these cases than the corresponding cathodic value. However, at the lower current densities of 30 and 65 A/m², the weight of copper deposited from the still bath was sometimes higher than the weight dissolved at the anode. For almost all the current densities the weight loss of the anodes in solutions subjected to ultrasonic vibrations was greater than that in the still solutions, showing that ultrasonic vibrations increase the anodic current efficiency, which is in agreement with the results in the preliminary work (section 3.4.).

At current densities below 130 A/m², the use of ultrasonic agitation decreased the weight of copper deposited, compared with the still solutions. However, at 130 A/m² there was not a definite trend and in some experiments
<table>
<thead>
<tr>
<th>Anodic Current Density $\text{A/m}^2$</th>
<th>Weight Changes g</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Still Bath</td>
<td>Ultrasonic Bath</td>
</tr>
<tr>
<td></td>
<td>Anodic Wt. loss</td>
<td>Cathodic Wt. gain</td>
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<td>30</td>
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<tr>
<td></td>
<td>-.3876$^4$</td>
<td>.2694*</td>
</tr>
</tbody>
</table>

* Burned or Powdery deposit

The weight of copper from the still bath was higher and in other cases lower. At 195 A/m² and above, the deposits from the ultrasonic bath were heavier than those from the still bath. In the preliminary work, the ultrasonic agitation of the solution increased the total weight of copper deposited at all current densities.
Almost all the deposits plated with a current density of 290 A/m² and above from the still bath were burned or powdery in appearance, whereas those from the ultrasonically agitated solution did not appear powdery. This means that the maximum, or limiting current density which can be used to produce good quality deposits under these conditions is between 240 and 290 A/m² in the still bath, but is above 385 A/m² with ultrasonic agitation.

Conclusion

It may be concluded that:

(1) the anodic current efficiency was higher than the cathodic value at, and above, a current density of 130 A/m² but occasionally was lower at current densities below 130 A/m²;

(2) ultrasonic agitation usually increased the anodic current efficiency;

(3) ultrasonic agitation decreased the cathodic current efficiency below 130 A/m² but usually increased it above 130 A/m²;

(4) ultrasonic agitation improved the quality of the deposits produced at current densities of 290 and 385 A/m² by preventing burning, i.e. the limiting current density was increased.

6.2.6. Effect of Benzotriazole in the Plating Bath

Introduction

This work was done after that described in section 6.2.5 with the object of comparing the effect on the current efficiency of adding benzotriazole to both a still and an ultrasonically agitated solution. The experiment was performed at room temperature (20°C) with several different current densities and the plating time was chosen to give approximately the same weight changes for each current. Four Haring-Blum cells were used and connected in series, two of the cells containing still solutions and two immersed in an ultrasonic tank. The electrodes were prepared by the method described in section 2.3.6.

Results

These are given in Table 6.2.6.
<table>
<thead>
<tr>
<th>Bath</th>
<th>Electrode</th>
<th>Weight changes g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Current Density A/m²</td>
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<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Still</td>
<td>Anode</td>
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<tr>
<td></td>
<td>Cathode</td>
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<tr>
<td>Still+</td>
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<td>-.3334</td>
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<td>Benzo</td>
<td>Cathode</td>
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<tr>
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<td>Anode</td>
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<td>Ultrasonic+</td>
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<tr>
<td>Ultrasonic+</td>
<td>Cathode</td>
<td>.3128</td>
</tr>
</tbody>
</table>

* Burned or powdery deposits

Table 6.2.6.

Discussion

Because the four cells which were used at one current density were connected in series, it was possible to compare the effect produced on the change in electrode weight by ultrasonic vibrations and/or the addition of benzo| to the solution for a particular current density. The results were not suitable for plotting in graphical form of Weight Change v. Current Density, because the amounts of copper deposited or dissolved at different current densities were not comparable, since a different quantity of electricity was used for each run.

The results for the still and ultrasonically agitated baths confirm the conclusions in the previous section 6.2.5., so are not discussed further. The presence of 0.12 g/l benzo| produced brighter deposits from both the still and the agitated baths; the appearance of these coatings has been described and illustrated by photographs in Chapter 5.

In the still bath, the addition of benzo| had very little effect, except for the cathodic process in the experiment with a current density of 385 A/m². In this cell, it gave a large increase in the weight of copper plated, because the deposit was not as powdery as that from the corresponding plain solution, although it was slightly burned. Therefore, it appears that the presence of benzo| in this cell increased both the cathodic current efficiency and also the limiting current density.
In the ultrasonically vibrated solutions, the benzotriazole reduced the anodic current efficiency at low current densities. This may be due to the formation of a surface film of greenish appearance on the anode, which probably would slow down the dissolution process. At higher current densities, with a much faster rate of production of copper ions, this film was less apparent. The presence of benzotriazole had very little effect on the weight gains of the cathodes.

**Conclusion**

In all the plating solutions without benzotriazole, the anodic current efficiency was higher than the cathodic current efficiency.

The use of ultrasonic vibrations in the plain bath:

1. increased the anodic current efficiency;
2. decreased the cathodic current efficiency at current densities below 130 A/m² but increased it at 130 A/m² and above;
3. prevented the formation of powdery deposits at a current density of 385 A/m².

These conclusions are similar to those in section 6.2.5.

The addition of benzotriazole to a still solution:

1. gave a brighter deposit;
2. tended to increase the anodic current efficiency slightly;
3. had little effect on the cathodic current efficiency, except for that at 385 A/m² which showed a large increase.

This increase at 385 A/m² corresponded to a slight improvement in the quality of the deposit which was less powdery than that from the plain bath, i.e. the limiting current density was raised to a small extent.

Benzotriazole in an ultrasonically agitated bath:

1. gave a brighter deposit;
2. significantly reduced the anodic current efficiency at current densities up to 130 A/m², but had less effect at the higher values;
3. had no overall effect on the cathodic current efficiency.
6.3. Metal Distribution Ratio and Throwing Power

6.3.1. Introduction

In section 6.2, it has been shown that the current efficiency and the relative deposit thickness depend upon many plating variables. This part of the work was designed to investigate how these same factors affect the distribution of the copper over irregularly shaped cathodes. The Haring-Blum cell which has been described in section 2.4.2. was used in these experiments, with two cathodes placed on opposite sides of a perforated anode at distances of 2.5 x 10^-1 m, and 1.25 x 10^-1 m.

6.3.2. Effect of Current Density and Ultrasonic Agitation

Introduction

Because both the metal distribution ratio and the throwing power of a solution are related to the ratio of the weight gains of the two cathodes, their values do not depend upon the absolute weight changes. This means that the results from cells through which different quantities of electricity were passed can be directly compared. This enables the separate effects of current density and ultrasonic vibrations to be determined, if the other plating factors remain constant. However, the throwing power may depend upon the deposit thickness, so that the quantity of electricity passed through the cells was kept as constant as possible.

Three Haring-Blum cells were used and connected in series for convenience and speed. Two similar runs were carried out at each current density; in the first, two still solutions and one ultrasonically agitated solution were used, whereas in the second, two ultrasonically agitated solutions and one still solution were used. All the results are given, because small differences in the weights of copper deposited on each electrode, while making only a slight variation in the metal distribution ratio, have a large effect on the throwing power. The weight changes of the anode and cathodes were recorded at room temperature (20°C) and have been used in the determination of the current efficiencies (section 6.2.5.); the preparation of these has been described in section 2.3.6.

Results

These are given in Table 6.3.2. and plotted in a graph, Fig. 6.3.2.
<table>
<thead>
<tr>
<th>Average Current Density A/m²</th>
<th>Agitation of Bath</th>
<th>Cathode Weight Gain g C₁</th>
<th>C₂</th>
<th>Metal Distribution C₁/C₂</th>
<th>Throwing Power %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
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<td>4.240</td>
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<td>.0960</td>
<td>3.434</td>
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<td>Ultrasonic</td>
<td>.3542</td>
<td>.0805</td>
<td>4.400</td>
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<td>4.542</td>
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<td>.2236**</td>
<td>.0812</td>
<td>2.754</td>
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<td>.3030*</td>
<td>.0927</td>
<td>3.269</td>
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<td>.3408</td>
<td>.0730</td>
<td>4.448</td>
<td>4.32</td>
</tr>
</tbody>
</table>

* Powdery deposit  ** Some deposit was lost before the specimen was weighed.
FIG. 6.3.2. EFFECT OF CURRENT DENSITY AND AGITATION ON THROWING POWER AND METAL DISTRIBUTION RATE.

- Still Bath
- Ultrasonically Agitated Bath
Discussion

The variation in the metal distribution ratio and the throwing power with current density is shown in the table and graph, for both the still and the ultrasonically agitated solutions. The values for the throwing power are in good agreement with those in the preliminary work (see section 3.4.). The current density given is an average value, being the current divided by the electrode area, although the cathode surface closer to the anode has a much higher current density than the one further away. The equation relating the throwing power, $T$, with the metal distribution ratio, $M$,

$$T = \frac{P - M}{P + M - 2} = \frac{5 - M}{3 + M}$$

where $P$ = primary current distribution, which is 5 in these experiments, shows that the throwing power increases as the metal distribution ratio decreases. Therefore, the changes in the throwing power only are discussed.

In the still bath, the throwing power at first decreased and then started to increase with the current density, the minimum value being about 12% at 150 A/m². At current densities greater than 195 A/m², the cathode closer to the anode, i.e. that with the higher current, had a powdery or burned deposit. This has been related to a low current efficiency, and for at least one electrode which gave a very high value for the throwing power, some copper powder was lost during the washing and drying process.

The throwing power of the ultrasonically agitated solutions was lower than that of the still bath, for all the current densities used. This is in agreement with the results in the preliminary work (section 3.4.). With these solutions, the throwing power decreased as the current density rose, until a steady value was reached above about 290 A/m². No burned deposits were produced from ultrasonically vibrated solutions, even at the higher currents used. This was probably due to the fact that these vibrations reduced the cathodic concentration polarization and enabled the formation of good deposits at high current densities which would otherwise have given burned deposits from still solutions.

These results are in reasonable agreement with those of Haring and Blum, who found that the throwing power decreased with an increase in both the
current density and solution agitation. The decrease in throwing power with increasing current density has also been observed by other workers.\textsuperscript{259}

**Conclusion**

The throwing power of the acid copper sulphate plating solution:

1. decreased and then increased with current density in the still bath;
2. was always lower for the ultrasonically agitated solution than for the still one;
3. decreased with the current density in the ultrasonically vibrated bath over the whole range studied.

The effects on the metal distribution ratio were the reverse of the above trends.

6.3.3. **Effect of Electrolyte Temperature**

**Introduction**

This section describes the work carried out on the effect on the metal distribution ratio and throwing power of varying the solution temperature at a current density equivalent to 195 A/m\textsuperscript{2}. The first results were obtained using four Haring-Blum cells connected in series containing still solutions at different temperatures.

Several problems arose with this arrangement. Firstly, it was difficult to obtain and maintain a constant elevated solution temperature. The reason for this was that, when the cells were immersed in constant temperature water baths, the material from which they were constructed, namely perspex or polymethylmethacrylate, was a poor heat conductor, so that the electrolyte did not quickly attain or hold the required temperature. A second difficulty was that some of the cells leaked when raised to 60°C or higher. These problems were partially overcome by using just one cell at a time, so that the exact solution temperature could be recorded before, during and after the run, and the average value was used. The final difficulty was that at high temperatures rapid evaporation occurred which resulted in a decrease in the volume and an increase in the concentration of the solution, as well as an increase in the current density (a constant current was passed between a gradually reducing area of immersed electrodes). This was rectified by using a cover on the cell, so that the steam condensed on the cover and returned into the plating bath.
Results

These are given in Table 6.3.3, and plotted in a graph, Fig. 6.3.3.

<table>
<thead>
<tr>
<th>Average Solution Temperature °C</th>
<th>Cathodic Weight Gain g</th>
<th>Metal Distribution Ratio C1/C2</th>
<th>Throwing Power %</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.3916</td>
<td>3.327</td>
<td>26.44</td>
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<tr>
<td>7</td>
<td>0.3000</td>
<td>3.250</td>
<td>28.00</td>
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<tr>
<td>10</td>
<td>0.3248</td>
<td>3.759</td>
<td>18.35</td>
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<td>15</td>
<td>0.3376</td>
<td>3.897</td>
<td>16.00</td>
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<tr>
<td>20</td>
<td>0.3160</td>
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</tr>
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<td>-9.09</td>
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<tr>
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<td>0.3186</td>
<td>5.619</td>
<td>-7.18</td>
</tr>
</tbody>
</table>

Table 6.3.3.

Discussion

The results show that the metal distribution ratio of a still solution increased and the throwing power decreased, as the bath temperature rose. At temperatures of 47°C and above, the metal distribution ratio rose above 5 and, therefore, the throwing power became negative. This may be due to the fact that the ions were more mobile at higher temperatures, causing less concentration polarization, so that more copper could be plated on to the cathode closer to the anode, resulting in a higher metal distribution ratio and a lower throwing power.

These observations agree with those of Haring and Blum, who found that the metal ratio increased from 4.53 at 21°C to 4.89 at 45°C with a cell of different dimensions from that used in these experiments.

Conclusion

The general trend is for the metal distribution ratio to increase and the throwing power of a still solution to decrease, as the electrolyte temperature is raised.
FIG. 6.3.3. EFFECT OF BATH TEMPERATURE ON THROWING POWER AND METAL DISTRIBUTION RATIO.
6.3.4. **Effect of Benzotriazole in the Plating Bath**

**Introduction**

This series of experiments was designed to investigate the effect on the metal distribution ratio and the throwing power of adding 0.12 g/l benzotriazole to both a still and an ultrasonically vibrated solution at room temperature, 20°C.

The procedure and operating conditions used have already been described in section 6.2.6., which studied the effect of benzotriazole on the anodic and cathodic current efficiencies by using the weight loss of the anode and the total weight gain of the cathodes obtained in this section of the work. The results given record the weight of copper deposited on to both cathodes and from these values the metal distribution ratio and throwing power were calculated.

**Results**

These are given in Table 6.3.4. and plotted in a graph, Fig. 6.3.4.

**Discussion**

The values of the metal distribution ratio and the throwing power at different current densities are given in tabular and graphical form, and show the effect of benzotriazole in both the still and ultrasonically agitated solutions. The graphs of both the Metal Distribution Ratio and the Throwing Power v. Current Density for the still and vibrated baths are similar to those obtained in section 6.3.2.

The main difference produced by the addition of 0.12 g/l benzotriazole was that at lower current densities the metal distribution ratio rose, so lowering the throwing power of both baths. This was achieved by increasing the weight of copper plated on to the closer cathode and reducing that on the distant cathode. One explanation of these weight changes is that benzotriazole probably produces proportionally more polarization at low current densities than at higher values. If this happened, then the cathode further from the anode would be more polarized than the other one, and the lower current density would deposit less copper. This in turn would increase the current density on the nearer cathode and give more deposition. As the current density of the whole cell increased, the polarization would decrease, resulting in a less pronounced effect.
FIG. 6.3.4. EFFECT OF BENZOTRIAZONE AND AGITATION ON THROWING POWER AND METAL DISTRIBUTION RATIO.
<table>
<thead>
<tr>
<th>Plating Bath</th>
<th>Average Current Density ( A/m^2 )</th>
<th>Cathode Weight Gain g</th>
<th>Metal Distr. Ratio ( C_1/C_2 )</th>
<th>Throwing Power %</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>( C_1 )</td>
<td>( C_2 )</td>
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<tr>
<td>Still</td>
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<td>.0795</td>
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</tbody>
</table>

* Burned or powdery deposit

°Bath containing 0.12 g/l benzotriazole

Table 6.3.4.

**Conclusion**

The presence of 0.12 g/l benzotriazole in the plating solution:

1. produced a less powdery deposit from the still bath with a current density of 385 \( A/m^2 \);
(2) reduced the throwing power in both the still and ultrasonically agitated baths at current densities of 30, 65 and 130 A/m²;

(3) increased the throwing power in all other circumstances.
6.4. Grain Size of Electrodeposits

6.4.1. Introduction

In the literature survey a strong correlation has been reported between the grain size and both the hardness and the internal stress of electrodeposits. Because many of the plating variables which affect these properties are interdependent, it was decided that, when investigating the effects of a given parameter, all the other conditions would be kept constant. Therefore, the composition of the plating bath was changed only to study the change in the grain size produced by purification. The values given for the 'grain size' are the mean intercept lengths which are easy to measure accurately and for equiaxed grains are related to the grain size in the A.S.T.M. Standard Designation E 112-63. The method of measurement using a Quantimmet television screen or a Vickers Projection Microscope has been described in section 2.4.4.

6.4.2. Effect of Bath Temperature and Current Density

Introduction

This work was planned to study the effect on the grain size of varying the bath temperature with a fixed current density. The experiment was repeated at current densities of 55, 110, 215, 430 and 645 A/m². The deposits produced were also used for the measurement of the microhardness, which necessitated the use of coatings about 5 x 10⁻⁵ m thick. The details of the experimental technique were as described in section 2.4.4. The grain size of a few deposits from a bath containing 0.119 g/l benzotriazole were determined with the Vickers Projection Microscope at a magnification of x 4,000.

Results

These are given for deposits from the plain bath in Table 6.4.2. and plotted in a graph, Fig. 6.4.2.

The grain size of several deposits from the bath containing 0.12 g/l benzotrizole were measured on the Stereoscan and found to be between 0.1 and 1.0 x 10⁻⁶ m.

Discussion

The results have been given in a table and also in graphical form, Fig. 6.4.2., to illustrate that the grain size is very dependent upon both the bath
FIG. 6.4.2. EFFECT OF BATH TEMPERATURE AND CURRENT DENSITY ON GRAIN SIZE.
Bath Temperature °C | Grain Size 10^-6m at Current Density A/m²
--- | --- | --- | --- | --- | ---
0 | 8.5 | 2 | 4.0 | 1.0* | 0.7*
23 | 10 | 11.5 | 12 | 7.6 | 2.4
40 | 15.8 | 15 | 11 | 12 | 7.8
60 | 16 | 17 | 16 | 15 | 9.2
80 | 20 | 18 | 22 | 16 | 9.2

* Burned or powdery deposits

Table 6.4.2.

Because the values of both the bath temperature and current density have been used on modules, it is possible to compare the effect of varying the bath temperature at different current densities and vice versa. An increase in the bath temperature, at a fixed current density, raised the grain size of the resulting deposit. As the current density rose, at a fixed bath temperature, the grain size tended to decrease. Thus, the smallest grain size was produced at low temperatures and high current densities, while the coarsest grained deposits formed at the highest temperatures and lowest current densities. The surface topography of these deposits has been discussed in section 5.3.

The grain size was measured for several copper deposits plated from a bath containing 0.119 g/l benzotriazole. However, because these were so small, approximately 10^-7m, it was not possible to study any variation in their size which was close to the limit of resolution of the Vickers Projection Microscope.

**Conclusion**

The grain size of copper deposits plated from the plain bath:

1. generally increased as the solution temperature rose;
2. tended to decrease with an increase in the current density.

The grain size of the deposits from a bath containing 0.119 g/l benzotriazole was much smaller and it was not possible, with the instruments used, to measure any variation in it.
6.4.3. Effect of Solution Agitation

Introduction

This section compares the grain size of copper deposits plated from still, stirred and ultrasonically agitated baths, which were connected in series at the required current density. The still bath was placed on anti-vibration padding and the stirring was produced by immersed magnets. The ultrasonic vibrations were produced by immersing the plating cell in an ultrasonic tank, the temperature of which was kept constant by the use of cold water flowing through a copper cooling coil. All the cells were used at room temperature, which was 23°C, and the experiment was repeated at several current densities. Thick deposits were again used because they were needed for hardness measurements.

Results

<table>
<thead>
<tr>
<th>Agitation of Standard Bath</th>
<th>Grain Size $10^{-6}$ m at Current Density $A/m^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td>Still</td>
<td>50</td>
</tr>
<tr>
<td>Stirred</td>
<td>18</td>
</tr>
<tr>
<td>Ultrasonically vibrated</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 6.4.3.

Discussion

At most of the current densities used, the grain size decreased with the solution agitation, those from the ultrasonic bath being the finest and those from the still bath the coarsest. For each bath the grain size decreased as the current density increased. These findings are in agreement with those of Butts and DeNora, who formulated several rules which state that the grain size decreases with (1) an increase in the current density and (2) an increase in the agitation.

Conclusions

The grain size of copper deposits:

(1) decreased as the current density increased;

(2) tended to decrease as the solution agitation increased.
6.4.4. **Effect of Solution Purification**

**Introduction**

The effect of purifying the plating solution on the resulting grain size of deposits was investigated. A series of experiments was conducted at different current densities with a standard bath and a purified standard bath which were connected in series and magnetically stirred. The purification treatment was that described in section 2.3.2. Thick deposits were produced and also used for the hardness measurements in section 6.5.4.

**Results**

<table>
<thead>
<tr>
<th>Plating Solution</th>
<th>Grain Size $10^{-6}$m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at</td>
</tr>
<tr>
<td></td>
<td>Current Density A/m²</td>
</tr>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>215</td>
</tr>
<tr>
<td></td>
<td>430</td>
</tr>
<tr>
<td>Standard Bath</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
</tr>
<tr>
<td>Purified Standard Bath</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>

Table 6.4.4.

**Discussion**

The purification of the plating solution had very little effect on the grain size of the copper deposits. The difference at each current density was within the experimental error.

**Conclusion**

Purification of the plating solution had virtually no effect on the grain size of the deposits.
6.5. Microhardness of Copper Electrodeposits

6.5.1. Introduction

Chronologically the work on the microhardness of the deposits from the plain bath followed immediately after the determination of the grain size, because the same surfaces were used for both sets of experiments. It was concluded from the preliminary results, sections 3.5. and 3.6., that the hardness of copper plated from the plain bath depended upon the solution purity and concentration of copper sulphate in the solution, the bath temperature, current density and electrolyte agitation. The effect of some of these variables is studied with deposits from the plain bath and from a bath to which 0.119 g/l of benzotriazole had been added just before plating. Each value reported was an average of at least seven measurements with an accuracy of ±10 HV, the readings being taken immediately after the completion of plating to minimize any self annealing of softening.

6.5.2. Effect of Bath Temperature and Current Density

Introduction

The production of the deposits from the stirred plain bath has been described elsewhere, 5.4.2. One set of deposits from the stirred bath containing 0.119 g/l benzotriazole was plated over a range of temperatures from 0 to 95°C at 215 A/m² and another set at a fixed temperature (23°C), and with a variation in the current density used.

Results

These are given in Tables 6.5.2.(a), (b) and (c) and plotted in graphs, Fig. 6.5.2.(a), (b), (c) and (d).

Plain Deposits

<table>
<thead>
<tr>
<th>Bath Temperature °C</th>
<th>Hardness HV at Current Density A/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td>23</td>
<td>85</td>
</tr>
<tr>
<td>40</td>
<td>77</td>
</tr>
<tr>
<td>60</td>
<td>71</td>
</tr>
<tr>
<td>80</td>
<td>70</td>
</tr>
</tbody>
</table>

*Deposits were slightly powdery
Fig 6.5.2. (a) EFFECT OF BATH TEMPERATURE ON HARDNESS.
FIG. 6.5.2(b) EFFECT OF CURRENT DENSITY ON HARDNESS.

Current Density  A/m²

Hardness  HV
FIG. 6.5.2. (c) EFFECT OF BATH TEMPERATURE AND BENZOTRIAZOLE ON HARDNESS

○—○ Plain Bath  ×—× Bath with 0.119g/l Benzotriazole
FIG. 6.5.2. (d) EFFECT OF CURRENT DENSITY AND BENZOTRIAZONE ON HARDNESS

○—○ Plain Bath ×—× Bath with 0.119g/l Benzotriazole
Deposits from Bath containing 0.119 g/l Benzotriazole

<table>
<thead>
<tr>
<th>Hardness of deposits HV plated with 215 A/m²</th>
<th>Bath Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>253</td>
</tr>
</tbody>
</table>

Table 6.5.2.(b)

<table>
<thead>
<tr>
<th>Hardness of deposits HV plated at 23°C</th>
<th>Current Density A/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>201</td>
</tr>
</tbody>
</table>

Table 6.5.2.(c)

Discussion

The effect on the microhardness of deposits from the plain bath of varying the bath temperature and the current density is shown in Fig. 6.5.2.(a) and (b) respectively. At a fixed current density, the hardness of the deposits decreased as the bath temperature increased, with the greatest change at the highest current. With a constant bath temperature the hardness increased with the current density, the maximum effect being at the lowest temperature. These results are in good agreement with those in the preliminary work (section 3.5.4. and 3.5.5.). These changes in the microhardness may be correlated with the variations on the grain size, section 5.4., or be due to modifications in the surface topography, 5.3.

The presence of benzotriazole in the solution increased the hardness of the deposits very considerably. The graph in Fig. 6.5.2.(c) shows the variation in the hardness produced by changes in the bath temperature: the values for the plain deposit are also included as a comparison. The hardness of these deposits dropped from a high value (HV 253) at 23°C to a relatively low value (HV 101) at 95°C. This suggests that the presence of the benzotriazole has much less effect on the hardness at higher bath temperatures. Fig. 6.5.2.(d) shows the effect of the current density on the hardness of deposits from the bath with benzotriazole, again the values for the plain bath are included for a comparison. These results are in good agreement with those in the preliminary sections 3.6.3. and 3.6.4. The hardness of deposits containing benzotriazole increased rapidly with the current density with a maximum effect at the lower current densities.
Conclusion

The microhardness of deposits from the baths both without and with benzotriazole:

(1) decreased with a rise in the bath temperature;
(2) increased with an increase in the current density.

The deposits from the bath containing benzotriazole were very much harder than the ones from the plain bath.

6.5.3. Effect of Solution Agitation

Introduction

In this section a comparison was made of the hardness of deposits plated from still, magnetically stirred and ultrasonically vibrated solutions. Two solutions, a plain one and another containing 0.119 g/l benzotriazole, were used at room temperature, which was 23°C. The hardness was measured on the thick deposits from the plain bath which were used for the grain size determinations in section 6.4.3. A similar set of deposits from the bath containing 0.119 g/l benzotriazole were produced under the same plating conditions.

Results

These are given in Table 6.5.3 and plotted in a graph, Fig. 6.5.3.

<table>
<thead>
<tr>
<th>Plating Solution</th>
<th>Agitation</th>
<th>Hardness HV at Current Density A/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>Standard</td>
<td>Still</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>Stirred</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>Ultrasonic agitation</td>
<td>81</td>
</tr>
<tr>
<td>Standard + 0.119 g/l</td>
<td>Still</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>Stirred</td>
<td>201</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>Ultrasonic agitation</td>
<td>209</td>
</tr>
</tbody>
</table>

Table 6.5.3.
FIG. 6.5.3. EFFECT OF SOLUTION AGITATION ON HARDNESS

△○ Plain Bath  △○○ Bath with 0.119g/l Benzotriazole
Discussion

The values obtained and recorded above for the stirred bath in this experiment are not identical with those given in the results in section 6.5.2. They are, however, within the accuracy of ±10 HV suggested in 6.5.1., and some of the difference may be due to slight variations in what are nominally the same plating conditions.

The deposits from the ultrasonically vibrated baths were the hardest and those from the still bath were the softest. This applies to both the solutions without and with benzotriazole and at all the current densities used. As in the previous experiment, the hardness of the deposit increased with the current density and was much harder if the bath contained benzotriazole. The hardness values of deposits from both the solutions under different conditions of agitation are in good agreement with those in the preliminary work (sections 3.5.6. and 3.6.5.).

Conclusion

The microhardness of copper deposits from the baths both without and with benzotriazole:

(1) was a maximum from the ultrasonically vibrated bath and a minimum from the still bath;

(2) increased with an increase in the current density.

The deposits from the bath containing benzotriazole were very much harder than those from the plain bath.

6.5.4. Effect of Solution Purification

Introduction

The purification of the plating solutions was found in the preliminary results 3.5. and 3.6. to reduce the hardness of the deposits produced at one current density (215 A/m²). It was, therefore, decided to investigate this effect and repeat the previous experiments at several different current densities. Results were also obtained for the effect of purifying the standard solution prior to the addition of benzotriazole. The purification treatment followed that described in the experimental procedure in section 2.3.2. The deposits were plated from solutions at room temperature, 23°C.
Results

These are given in Table 6.5.4. and plotted in a graph, Fig. 6.5.4.

<table>
<thead>
<tr>
<th>Plating Solution</th>
<th>Hardness HV at Current Density A/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td>Standard</td>
<td>77</td>
</tr>
<tr>
<td>Standard purified</td>
<td>60</td>
</tr>
<tr>
<td>Standard with 0.119 g/l Benzotriazole</td>
<td>201</td>
</tr>
<tr>
<td>Standard purified with 0.119 g/l Benzotriazole</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 6.5.4.

Discussion

From the above results it can be seen that the purification treatment given to the plating solutions reduced the hardness of the deposits. These values are in good agreement with those in the preliminary work (sections 3.5.1. and 3.6.1.). The change was small at the low current densities, being 22% in the plain bath and only 5% in the bath with benzotriazole at 55 A/m², but was very much larger at the highest current density, being 35% in the plain bath and 21% in the bath with benzotriazole at 430 A/m².

Conclusion

In both the baths without and with benzotriazole, purification of the standard plating solution decreased the hardness of the resulting deposit at all the current densities used.

6.5.5. Effect of Concentration of Benzotriazole

Introduction

In the preliminary work, it was shown that the hardness of copper deposits increased with the concentration of benzotriazole in the bath from which they were plated. However, the hardness values reported in section 3.6.2. are probably too low, because the small volumes (150 mls) of solution which were used contained only very low weights of benzotriazole which could easily have been codeposited before the completion of plating. This means that the hardness of the copper surface was not related to the initial concentration of benzotriazole.
FIG. 6.5.4. EFFECT OF SOLUTION PURIFICATION ON HARDNESS.
To overcome this inaccuracy, much larger volumes of solution were used, containing correspondingly higher weights of benzotriazole. The plating cells, with one litre of solution, were connected in series and the appropriate amount of addition agent added just before the start of deposition, to minimize any ageing of the benzotriazole in the solution. The solution temperature was 23°C and the current density 260 A/m².

Results

These are given in Table 6.5.5. and plotted in a graph, Fig. 6.5.5.

<table>
<thead>
<tr>
<th>Concentration of Benzotriazole</th>
<th>0</th>
<th>0.0005</th>
<th>0.001</th>
<th>0.005</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness of Deposits HV</td>
<td>93</td>
<td>110</td>
<td>140</td>
<td>203</td>
<td>231</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration</th>
<th>0.05</th>
<th>0.119</th>
<th>0.2</th>
<th>0.3</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>262</td>
<td>275*</td>
<td>295*</td>
<td>258*</td>
<td>211**</td>
<td>124**</td>
</tr>
</tbody>
</table>

* Peeled after end of plating
** Peeled during plating

Table 6.5.5.

Discussion

The graph shows that the hardness increased with the concentration of benzotriazole in the plating up to a maximum of HV 295 with 0.2 g/l. These results, which are much higher than those in the preliminary work (sections 3.6.6.), show a trend which is similar to that found by Kendall, who used benzotriazole in very pure plating solutions and obtained lower hardness values. Other addition agents, including Rochelle salt and thiourea, have been found to affect the hardness of electrodeposits in a similar manner.

The decrease in the hardness of the coatings from the baths containing high concentrations of benzotriazole was accompanied by peeling of the deposit. This peeling is probably a result of the combined effect of a high tensile internal stress and poor adhesion to the substrate. This explanation is consistent with the preliminary results in which it was shown that the use of benzotriazole in the solution has a marked effect on the internal stress, and also it is known that the adsorption of benzotriazole on a surface prior to plating reduces the adhesion of the coating. One result of this peeling would be to relieve partially the internal stress and probably to reduce the hardness of the coating.
FIG. 6.5. EFFECT OF CONCENTRATION OF BENZOTRIAZOLE ON HARDNESS.

- Brightest Deposit
- Cracked Deposit

Benzotriazole Concentration (g/l)

23°C 213 A/m² 1 hr.
The concentration of benzotriazole in the plating bath also had an effect on the surface appearance of the deposits. The brightest deposit, which also had the highest hardness, was obtained with a concentration of 0.2 g/l. From more concentrated solutions, the coatings peeled and were darker, being a brown/purple colour. Very low additions gave matt deposits which became brighter with a concentration of 0.05 g/l.

Conclusion

The hardness of the deposits depended upon the concentration of benzotriazole in the bath. It increased with the amounts of addition up to 0.2 g/l (which was also the brightest surface), but above this value cracked deposits were produced and the hardness was reduced.

6.5.6. Effect of Ageing the Benzotriazole Solution

Introduction

In the preliminary work (section 3.6.7.), it was found that the ageing or storage of a solution containing benzotriazole prior to its use had a significant effect on the external stress of the resulting deposits. For this work, a fresh plating solution was made and 0.119 g/l benzotriazole was added to it. A litre of solution was immediately used at a temperature of 23°C, with a current density of 215 A/m², and the hardness of the plated copper was measured. This experiment was repeated after storing the solution for increasing time intervals up to 29 days.

Results

<table>
<thead>
<tr>
<th>Storage Time prior to plating, days</th>
<th>0</th>
<th>0.17</th>
<th>0.5</th>
<th>5.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness of deposit HV</td>
<td>253</td>
<td>256</td>
<td>274</td>
<td>308</td>
</tr>
<tr>
<td>Storage Time</td>
<td>24</td>
<td>22</td>
<td>26</td>
<td>29</td>
</tr>
<tr>
<td>Hardness</td>
<td>309</td>
<td>307</td>
<td>310</td>
<td>310</td>
</tr>
</tbody>
</table>

Table 6.5.6.

Discussion

From the graph, Fig. 6.5.6., it can be seen that the hardness increased with storage until a steady value was reached after about 5.6 days. Because the hardness increased under the same plating conditions, it is probable that the benzotriazole was affected by storage and that the modified form had a
Fig 6.5.6. EFFECT OF AGEING THE BENZOTRIAZOLE SOLUTION ON HARDNESS.
greater effect on the hardness than the original substance. A similar effect has been observed with both refined and commercial purity sulphanated anthracene and discussed in section 1.3.5.

Conclusion

The hardness of copper deposits from the plating solution containing benzotriazole increased with the storage time of the bath prior to deposition reaching a steady value after six days.

6.5.7. Effect of Benzotriazole on the Structure and Hardness

Introduction

In the preliminary work, section 3.6.6., it was observed that low values were obtained when a small volume of plating solution containing a certain concentration of benzotriazole was used for hardness determinations. In this experiment, a small volume of 200 mls of electrolyte with 0.12 g/l benzotriazole was used and the cross-sectional structure of the resulting deposit was examined. A series of hardness measurements was made at different regions on the cross-sectioned surface and these were compared with the structure.

Results

Fig. 6.5.7. shows a photograph of the cross-section of the deposit after it had been polished and etched in alcoholic ferric chloride. The hardness of different areas in the surface is indicated below the photograph.

Discussion

The first copper deposited on to the substrate from the solution containing 0.12 g/l benzotriazole had a layered or banded structure, which has been observed with other similar coatings. However, the concentration of benzotriazole in the bath decreased as the plating time increased, due to the codeposition of cuprous benzotriazole. Thus after about an hour the bands in the plated copper became less distinct. After a further period of plating, the structure of the deposited copper had changed from a layered to a plain appearance, typical of the coatings from solutions with a lower concentration of benzotriazole.

The hardness of the banded deposit close to the copper substrate was about HV 257 to 244, but decreased to about HV 192 for the plain unbanded copper plated from the solution depleted in benzotriazole. Thus, the structure and
Plain Deposit  Banded Deposit  Copper Substrate

192  239  244  257

Hardness Values  HV

FIG. 6.5.7.  INFLUENCE OF BENZOTRIAzoLE ON THE STRUCTURE AND HARDNESS OF COPPER ELECTRODEPOSITS

Magnification  x  2,000
the hardness of copper depend upon the actual concentration of benzotriazole in the plating bath.

However, no variation in either of these properties was observed in copper deposited from a bath containing one litre of solution under the conditions used in the work in this chapter. Furthermore, no change was observed in deposits from the plain bath, which did not materially alter during deposition, because the anodic and cathodic current efficiencies were similar.

Conclusion

The structure and the hardness of copper deposited from a small volume of plating solution containing benzotriazole vary with the thickness of the deposit.
6.6. Internal Stress in Electrodeposits

6.6.1. Introduction

It was concluded from the preliminary results, sections 3.7 and 3.8, that the internal stress in deposits from the bath without any addition was always tensile, and from the bath with benzotriazole the stress could be either tensile or compressive. The magnitude of the stress depended upon the thickness of the deposit, the concentration of copper sulphate in the solution, the temperature of the bath and the current density. For the deposits from the solutions containing benzotriazole, there were two additional factors, which are both time dependent, namely the period of storage of the solution prior to plating and the change in stress with time after the completion of plating. As stated in the preliminary section, the deposit thickness and the plating conditions were recorded for each experiment, because they affect the stress value.

The main error in the stress measurements was due to the poor reproducibility of the contractometer. The sensitivity of the instrument depended upon the spirals used and the thickness of the deposits and, under the conditions used in Section 6.6.2., it was \( \pm 1^\circ \), equivalent to \( \pm 1.0 \text{ MN/m}^2 \). The effect of raising the temperature of the helix was investigated, using a bath of distilled water and watching for any deflection. None was observed below 40°C and a maximum of \( 3^\circ \) occurred at 90°C, (equivalent to a compressive stress of about 3.1 MN/m\(^2\)), which was produced by the different thermal coefficients of the copper and nickel coatings and the stainless steel helix. Any change in the stress which was greater than \( \pm 2.1 \text{ MN/m}^2 \) at room temperature and outside the range 1.0 to 5.2 MN/m\(^2\) (compressive) at 90°C was considered significant and the result of variations in the plating conditions.

6.6.2. Effect of the Concentration of Copper Sulphate in the Bath

Introduction

The first part of this work covered the effect of varying the copper sulphate concentration on the stress in deposits from an ordinary bath without any additions, and the second part the stress in deposits from a solution containing 0.119 g/l benzotriazole as studied in the preliminary work, sections 3.7.2. and 3.8.2. In both cases a constant concentration of sulphuric acid (49 g/l) was used and the solutions were slowly magnetically stirred. Because all the results were obtained with one spiral contractometer, each stress
determination was made separately, under carefully controlled conditions. A current density of 215 A/m² was used for 15 minutes, which produced a coating thickness of 7 x 10⁻⁶ m and this was checked by weighing and calculations. The baths were all used at room temperature which was 21 ± 2°C for the first part, and 25 ± 2°C for the second part of the work.

Results

These are given in Tables 6.6.2.(a) and (b) and plotted in a graph, Fig. 6.6.2.(a).

Standard Bath

<table>
<thead>
<tr>
<th>Concentration of Copper Sulphate CuSO₄·5H₂O g/l</th>
<th>Contractometer Deflection degrees</th>
<th>Tensile Stress MN/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>4.75</td>
<td>12.4</td>
</tr>
<tr>
<td>93</td>
<td>3.75</td>
<td>9.65</td>
</tr>
<tr>
<td>140</td>
<td>3</td>
<td>7.93</td>
</tr>
<tr>
<td>186</td>
<td>3</td>
<td>7.93</td>
</tr>
<tr>
<td>233</td>
<td>2.75</td>
<td>7.24</td>
</tr>
<tr>
<td>280</td>
<td>2.25</td>
<td>5.86</td>
</tr>
<tr>
<td>327</td>
<td>2</td>
<td>5.17</td>
</tr>
</tbody>
</table>

Bath Temperature 21 ± 2°C
Current Density 215 A/m²
Deposit Thickness 7 x 10⁻⁶ m

Table 6.6.2.(a)

Discussion

All the deposits from the bath without benzotriazole had a dull matt appearance and good adhesion to the helix of the contractometer. The tensile stress, which was relatively low, decreased with an increase in the concentration of copper sulphate in the solution. This change in the stress appears to follow a logarithmic law, as shown in Fig. 6.6.2.(b).

The stress in the deposits from the bath containing benzotriazole increased in a tensile direction as the concentration of copper sulphate increased, from very low values (20.1 MN/m² at 8 g/l) to a maximum stress value of 53.8 MN/m² at 32 g/l. At higher concentrations, the tensile stress was reduced to zero at about 60 g/l, and then the stress became oppressive, reaching a steady value of about 52.8 MN/m² with a concentration of 100 g/l copper sulphate. The
FIG. 6.6.2(a) EFFECT OF CONCENTRATION OF COPPER SULPHATE ON INTERNAL STRESS

- Plain Bath
- Bath with 0.119 g/l
- Benzotriazole
- Equilibrium stress
- Cracked deposit
- After 900 seconds
FIG. 6.6.2 (b) LOG STRESS v CONCENTRATION COPPER SULPHATE.
Bath containing 0.119 g/l Benzotriazole

<table>
<thead>
<tr>
<th>Concentration of Copper Sulphate CuSO₄·5H₂O g/l</th>
<th>Contractometer Deflection degrees</th>
<th>Stress MN/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>8*</td>
<td>20.1T</td>
</tr>
<tr>
<td>16</td>
<td>10*</td>
<td>26.2T</td>
</tr>
<tr>
<td>24</td>
<td>10.75</td>
<td>28.0T</td>
</tr>
<tr>
<td>32</td>
<td>20.5</td>
<td>53.8T</td>
</tr>
<tr>
<td>47</td>
<td>10.5x</td>
<td>27.3T</td>
</tr>
<tr>
<td>59</td>
<td>11²</td>
<td>28.7T</td>
</tr>
<tr>
<td>70</td>
<td>-14.5</td>
<td>37.9C</td>
</tr>
<tr>
<td>78</td>
<td>-16.25</td>
<td>43.1C</td>
</tr>
<tr>
<td>93</td>
<td>-20</td>
<td>52.8C</td>
</tr>
<tr>
<td>140</td>
<td>-17.5**</td>
<td>45.5C</td>
</tr>
<tr>
<td>186</td>
<td>-20</td>
<td>52.8C</td>
</tr>
<tr>
<td>233</td>
<td>-12.5**</td>
<td>32.8C</td>
</tr>
<tr>
<td>280</td>
<td>-21</td>
<td>54.9C</td>
</tr>
<tr>
<td>327</td>
<td>-13**</td>
<td>34.2C</td>
</tr>
</tbody>
</table>

Bath Temperature 25 ± 2°C
Current Density 215 A/m²
Deposit Thickness 7 x 10⁻⁶ m

*Hydrogen evolved during plating
XInitial deflection negative (compressive stress) which then became positive (tensile stress)
**Rucked deposits
T Tensile Stress
C Compressive Stress

Table 6.6.2.(b)

Coatings from the two baths containing benzotriazole with the lowest concentration of copper sulphate had a matt or powdery appearance and the codeposition of hydrogen was observed. This agrees with the work of Prall who noted hydrogen evolution during plating from a bath containing 20 g/l copper sulphate. From the solutions containing larger weights of copper sulphate, the deposits were fairly bright and adherent, except those from baths with more than 200 g/l which were slightly discoloured and showed some ruckling. This wrinkling in the highly compressively stressed coatings
probably resulted in some stress relief. These stress values for deposits from both plating solutions are in good agreement with those in the preliminary work (sections 3.7.2. and 3.8.2.).

Conclusion

It may be concluded that the stress in deposits from the plain bath was always tensile and decreased as the concentration of copper sulphate increased. The addition of benzotriazole produced deposits with a high tensile stress at low concentrations of copper sulphate and a high compressive stress at high concentrations.

6.6.3. Effect of Bath Temperature

Introduction

In this section, the effect on the internal stress in deposits produced by varying the plating bath temperature is studied. The standard bath, without any additions, was used in the first set of experiments with a current density of 260 A/m². The plating solution containing 0.119 g/l benzotriazole was used in the second part of this work with a current density of 260 A/m², and in the third part with 1,040 A/m². The experiments were repeated with a higher current density to determine whether the shape of the curve of Stress v. Bath Temperature Density was the same at 1,040 A/m², as at 260 A/m².

Three spiral contractometers were used in this work and each instrument was calibrated, prior to plating the spiral to be used in that particular stress measurement. Because the different instruments may not have identical calibration curves, not all the deflections in the table are comparable. However, each deflection can be converted to an equivalent weight by using the appropriate calibration curve. Therefore, in the results the deflections and the equivalent weights are both listed. The plating time was 30 minutes at a current density of 260 A/m² with the standard bath; for the bath containing benzotriazole, the times were 15 minutes at a current density of 260 A/m², and 3½ minutes at 1,040 A/m². The thicker deposits were used in the case of the standard bath, because the contractometer deflections were very small after 15 minutes, but were higher after 30 minutes, so the experimental error was reduced.

Results

These are given in Tables 6.6.3.(a), (b) and (c) and plotted in a graph, Fig. 6.6.3.
FIG. 6.6.3 EFFECT OF BATH TEMPERATURE AND BENZOTRIAZOLE ON INTERNAL STRESS.

- □-□ 260A/m² Plain Bath
- ▲ Cracked Deposit (260A/m²)
- □-□ 1040A/in² Bath with 0.119g/l Benzotriazole
Standard Bath: current density 260 A/m²

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>3</th>
<th>8</th>
<th>15</th>
<th>19</th>
<th>20</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection degrees</td>
<td>34</td>
<td>27</td>
<td>10</td>
<td>7.5</td>
<td>7</td>
<td>5.5</td>
</tr>
<tr>
<td>Equivalent Weight g.</td>
<td>10.6</td>
<td>9.0</td>
<td>3.15</td>
<td>2.5</td>
<td>2.2</td>
<td>1.70</td>
</tr>
<tr>
<td>Tensile Stress* MN/m²</td>
<td>38.6</td>
<td>30.7</td>
<td>11.4</td>
<td>8.27</td>
<td>7.93</td>
<td>6.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>33</th>
<th>38</th>
<th>52</th>
<th>54</th>
<th>64</th>
<th>78</th>
<th>98</th>
</tr>
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<tbody>
<tr>
<td>Deflection</td>
<td>5.25</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Equivalent Weight</td>
<td>1.35</td>
<td>1.25</td>
<td>0.65</td>
<td>0.65</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Tensile Stress</td>
<td>4.83</td>
<td>4.14</td>
<td>2.07</td>
<td>2.07</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Deposit Thickness 8.5 x 10⁻⁶ m

* Tensile Stress calculated for Deposit Thickness 8.5 x 10⁻⁶ m

Table 6.6.3.(a)

Bath containing 0.119 g/l Benzotriazole: current density 260 A/m²

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>-2</th>
<th>0.5</th>
<th>6</th>
<th>8</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection degrees</td>
<td>+58</td>
<td>+44**</td>
<td>+67</td>
<td>+54</td>
<td>+22.5**</td>
</tr>
<tr>
<td>Equivalent Weight g</td>
<td>18.1</td>
<td>14.1</td>
<td>16.9</td>
<td>16.9</td>
<td>7.35</td>
</tr>
<tr>
<td>Stress* MN/m²</td>
<td>123T</td>
<td>100T</td>
<td>115T</td>
<td>115T</td>
<td>50.3T</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>17</th>
<th>20</th>
<th>20.7</th>
<th>22</th>
<th>24.5</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>+33</td>
<td>+26</td>
<td>-12</td>
<td>+17.5</td>
<td>-6</td>
<td>-43</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>8.7</td>
<td>3.1</td>
<td>4.6</td>
<td>1.8</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>68.3T</td>
<td>59.3T</td>
<td>21.4C</td>
<td>30.7T</td>
<td>12.4C</td>
<td>92.5C</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>37.5°C</th>
<th>44</th>
<th>54.5</th>
<th>60</th>
<th>66</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>-55°C</td>
<td>-60.5</td>
<td>-45.5</td>
<td>-43</td>
<td>-1.5</td>
<td>-5</td>
<td></td>
</tr>
<tr>
<td>113°C</td>
<td>17.8</td>
<td>13.8</td>
<td>14.95</td>
<td>3.45</td>
<td>10.0°C</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.6.3.(b)
Bath containing 0.119 g/1 Benzotriazole: current density 1,040 A/m²

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>5</th>
<th>10.5</th>
<th>15.5</th>
<th>22</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection degrees</td>
<td>+11.5**</td>
<td>+21**</td>
<td>+8.3**</td>
<td>+60</td>
<td>+66</td>
</tr>
<tr>
<td>Equivalent Weight g</td>
<td>2.55</td>
<td>3.55</td>
<td>12.55</td>
<td>16.0</td>
<td>16.9</td>
</tr>
<tr>
<td>Stress* MN/m²</td>
<td>17.2T</td>
<td>24.1T</td>
<td>85.5T</td>
<td>109T</td>
<td>115T</td>
</tr>
<tr>
<td>Deposit Thickness</td>
<td>4.25 x 10⁻⁶ m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Stress Calculated for Deposit Thickness 4.25 x 10⁻⁶ m
** Cracked Deposit
T Tensile Stress
C Compressive Stress

Table 6.6.3.(c)

Discussion

Three different curves are shown, one for the standard bath with a current density of 260 A/m² and two for the solution containing benzotriazole with current densities of 260 A/m² and 1,040 A/m². The equivalent weights for the deposits from the two different baths cannot be compared, because they apply to deposits of different thickness.

In the copper deposits from the plain bath, the tensile stress decreased as the temperature of the plating solution increased. The decrease was very marked at the lower temperatures, but was only slight at the higher temperatures. This relationship appears to approximately obey a logarithmic law with a gradient that is similar to that found by Kushner for the stress in nickel deposited from the sulphamate bath at different temperatures. All these coatings had a matt appearance with good adhesion to the substrate metal and no peeling was observed.

For deposits from the bath containing benzotriazole, the shape of the curves in Fig. 6.6.3.(b) and (c) was more complex than for the standard bath. At the low solution temperatures, the stress in the coatings was tensile and very high (about 123 MN/m² at -2°C). For deposition at these low temperatures
with a current density of 1,040 A/m², the deposits were so stressed that they usually peeled from the substrate. This peeling reduced the tensile stress in the coatings, so that the values measured were much lower than those which would have been observed, without the stress relief produced by the peeling. The first stress measurements at the higher current density were too low because they were for cracked coatings, so that two determinations were made for the bath at 22°C, this being the first deposit which did not peel. At the higher temperatures, the stress in the copper plated from the electrolyte containing benzotriazole was compressive with a maximum value of about 121 MN/m² at 44°C with 260 A/m², and 62.7 MN/m² at 60°C with 1,040 A/m². The stress then decreased to very low values at about 80°C at both current densities. All these deposits were much brighter than those from the standard bath.

The changes in the stress deposits plated at different temperatures are in good agreement with those found in the preliminary work (sections 3.7.3. and 3.8.3.) and are discussed, together with those from the other sections on the stress determinations, in the discussion chapter.

Conclusions

The tensile stress in deposits from the plain bath, with a current density of 260 A/m², was found to decrease as the temperature of the bath increased. In deposits from the solution containing benzotriazole with a current density of 260 A/m², the stress was high and compressive at intermediate temperatures (30-50°C) and finally became very low at 80°C. An increase in the current density moved the whole curve in a tensile direction at a higher temperature.

6.6.4. Effect of Current Density

Introduction

This section covers the effect on the internal stress produced in deposits by varying the current density used to plate the copper. In the first part, the standard bath without any addition was used with the solution temperature controlled at 22°C. In the remaining parts, the results refer to a bath containing 0.119 g/l benzotriazole, with electrolyte temperatures of 22°C and 31°C. The work was carried out at the higher temperature to indicate whether the shape of the curve of Stress v. Current Density was the same at 31°C as at 22°C.
As in the previous section, three spiral contractometers were used and the deflections and equivalent weights were listed. The plating time was varied and depended upon the current density, being that which give the same deposit thickness of $8.5 \times 10^{-6}$ m from the plain bath and $4.25 \times 10^{-6}$ m from the bath with benzotriazole, i.e. 30 minutes at 260 A/m$^2$ with the plain bath and 15 minutes with the bath containing benzotriazole.

Results

These are given in Tables 6.6.4.(a), (b) and (c) and plotted in a graph, Fig. 6.6.4.

Standard Bath at 22°C

<table>
<thead>
<tr>
<th>Current Density A/m$^2$</th>
<th>25</th>
<th>130</th>
<th>260</th>
<th>520</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection degrees</td>
<td>1.5</td>
<td>1.5</td>
<td>6.25</td>
<td>11.25</td>
</tr>
<tr>
<td>Equivalent Weight g</td>
<td>.45</td>
<td>.45</td>
<td>1.7</td>
<td>3.4</td>
</tr>
<tr>
<td>Tensile Stress* MN/m$^2$</td>
<td>1.72</td>
<td>1.72</td>
<td>6.21</td>
<td>12.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>65</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection degrees</td>
<td>-25.5</td>
<td>-34</td>
</tr>
<tr>
<td>Equivalent Weight g</td>
<td>6.5</td>
<td>8.2</td>
</tr>
<tr>
<td>Stress* MN/m$^2$</td>
<td>43.4C</td>
<td>55.8C</td>
</tr>
</tbody>
</table>

Deposit Thickness = $8.5 \times 10^{-6}$ m

* Tensile Stress calculated for Deposit Thickness $8.5 \times 10^{-6}$ m

Table 6.6.4.(a)

Bath containing 0.119 g/l Benzotriazole at 22°C

<table>
<thead>
<tr>
<th>Current Density A/m$^2$</th>
<th>65</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection degrees</td>
<td>-25.5</td>
<td>-34</td>
</tr>
<tr>
<td>Equivalent Weight g</td>
<td>6.5</td>
<td>8.1</td>
</tr>
<tr>
<td>Stress* MN/m$^2$</td>
<td>43.4C</td>
<td>55.2C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>260</th>
<th>390</th>
<th>520</th>
<th>650</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>34.5</td>
<td>49</td>
<td>54</td>
<td>58.5</td>
</tr>
<tr>
<td></td>
<td>9.3</td>
<td>12.2</td>
<td>14.6</td>
<td>14.95</td>
</tr>
<tr>
<td></td>
<td>64.1T</td>
<td>83.1T</td>
<td>99.3T</td>
<td>102T</td>
</tr>
<tr>
<td></td>
<td>104T</td>
<td>89.6T</td>
<td>106T</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>780</th>
<th>1,040</th>
<th>1,300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65</td>
<td>60</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>6.6</td>
<td>16.9</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>113T</td>
<td>115T</td>
<td>117T</td>
</tr>
</tbody>
</table>

Table 6.6.4.(b)
FIG. 6.4. EFFECT OF CURRENT DENSITY AND BENZOTRIAZOLE ON INTERNAL STRESS

- 22°C Plain Bath
- 22°C Bath with 0.119 g/l

Cracked Deposit

Stress (MN/m²) vs. Current Density (A/m²)
Discussion

The variation in the internal stress in the deposits produced by changing the current density used in the plating is shown in Fig. 6.6.4. The equivalent weights in the two different baths cannot be compared, because they apply to deposits of different thickness. A tensile stress was observed in all the coatings from the standard bath without any additions. The stress increased from a very low value of 1.72 MN/m² at 25 A/m² to a higher value of 26.2 MN/m² at 1,300 A/m² with a solution temperature of 22°C. All the deposits had a matt appearance with good adhesion and no peeling.

In the deposits from the solution containing benzotriazole, a compressive stress was produced at the low current densities, the maximum values being 55.8 MN/m² at 22°C with 130 A/m² and 97.5 MN/m² at 31°C with 260 A/m². As the current density was increased the compressive stress was reduced and became zero at about 230 A/m² at 22°C and about 520 A/m² at 31°C. At higher current densities, the stress became tensile and, from the graph, appeared to reach a constant value of about 117 MN/m² at 22°C and 103 MN/m² at 31°C. Several of the stress determinations were repeated, particularly when high values were obtained or cracking occurred in the coating. These duplicate values also indicate the reproducibility of the stress values.
The compressively stressed deposits did not peel, whereas those with high
tensile stresses did. All the deposits from the bath containing benzotriazole
were brighter and had a smaller grain size than those from the standard bath.
A change in the stress was observed after the plating current had been
switched off and this stress after-effect is discussed in a separate section.
The changes in the stress in deposits plated at different current densities
are in good agreement with those found in the preliminary work (sections
3.7.4. and 3.8.4.) and a discussion of the significance of these stress
results appears in Chapter 7.

Conclusion
All the deposits from the standard bath without any additions were matt in
appearance and the internal stress was tensile, increasing with the current
density. The deposits plated from a solution containing benzotriazole had
a compressive stress at low current densities and a tensile stress at high
current densities.

6.6.5. Effect of Ageing the Plating Solution

Introduction
From the preliminary results (see section 3.8.5.) it was concluded that the
stress in the copper plated from a solution containing 0.119 g/l benzotriazole
became more tensile, as the storage time of the solution increased. A
similar change has been observed with deposits from a copper plating solution
containing naphtalene disulphonic acid.
The results in this part of the work were obtained with the modified
Hoar-Arrowsmith apparatus. With this instrument the electromagnetic force
which was required to restore the cathodic strip to its original position
was measured. This electromagnetic force was then converted to an equivalent
weight, using the non-linear calibration curve. A tensile stress is indicated
by a restoring force on one side of the cathodic stress and is given a
positive sign, a force on the opposite side is compressive and has a negative
sign.

A fresh plating solution was prepared and the standard amount of benzotriazole
(0.119 g/l) was added. The cathode strip, mounted in the clamp, was then
introduced into the solution, the current was switched on after an immersion
time of five minutes, and readings were taken every minute, for a quarter of an hour. This experiment was repeated with different immersion times up to sixty hours.

The experiment was repeated using two plain solutions, one which had been freshly prepared and the other which had been stored for sixty hours.

Results

These are given for the solutions containing benzotriazole in Table 6.6.5® and plotted in a graph, Fig. 6.6.5®. There was no significant difference in the stress values of the deposits from the plain solutions.

<table>
<thead>
<tr>
<th>Plating Time m</th>
<th>Restoring Force</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ageing Time</td>
</tr>
<tr>
<td></td>
<td>60 hr</td>
</tr>
<tr>
<td></td>
<td>m amps</td>
</tr>
<tr>
<td>1</td>
<td>-24</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>47</td>
</tr>
<tr>
<td>6</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>62</td>
</tr>
<tr>
<td>8</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>73</td>
</tr>
<tr>
<td>10</td>
<td>77</td>
</tr>
<tr>
<td>11</td>
<td>82</td>
</tr>
<tr>
<td>12</td>
<td>86</td>
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<td>13</td>
<td>91</td>
</tr>
<tr>
<td>14</td>
<td>95</td>
</tr>
<tr>
<td>15</td>
<td>100</td>
</tr>
</tbody>
</table>

Deposit Thickness $7 \times 10^{-6}$ m

Current Density 215 A/m$^2$

Bath Temperature 20°C

Table 6.6.5®.
FIG. 6.6.5. EFFECT OF AGEING THE BENZOTRIAZOLE SOLUTION ON THE RESTORING FORCE.
Discussion

In all the deposits which were produced after plating for one minute, the stress was compressive. This quickly changed to a tensile value in the deposits from the solutions which had been stored for 17 and 60 hours, but took much longer in that stored for only half an hour; the stress remained compressive in the deposit from the bath stored for five minutes. The overall effect of ageing the solution was to increase the tensile stress. The factors which are responsible for this change are probably those mentioned in the discussion on the variations in the microhardness produced by ageing the benzotriazole solution (sections 1.3.5. and 6.5.6.).

Conclusion

The general effect of ageing on storing the benzotriazole solutions was to change the stress in a tensile direction. Ageing the plain solution had no effect on the stress in the deposits.

6.6.6. **Effect of Ageing the Deposit or the Stress After-Effect**

Introduction

In the preliminary results (see section 3.8.6.) it was reported that the stress in deposits plated from a bath containing benzotriazole changed after the current had been switched off. No such change was observed in any deposits from the standard bath without any addition.

This section reports on the stress changes which occurred in the deposits plated from the solution containing 0.119 g/l benzotriazole and having different concentrations of copper sulphate, the experimental procedure being that which was described in section 6.6.2. These concentrations were chosen because they represent a range from tensile to compressive stress.

The equilibrium stress was the constant value of the stress, which was obtained after the current had been switched off, normally within a period of fifteen minutes after the end of plating, with the spiral still in the electrolyte. To illustrate how the stress changed with time, two graphs were produced in which the contractometer deflection was plotted against the deposit thickness, the plating time and the stress after-effect time (Figs. 6.6.6.(b) and (c)).

Results

These have been given in Table 6.6.6. and plotted in graphs, Figs. 6.6.2., 6.6.6.(a),(b) and (c).
FIG. 6.6.8 (a) EFFECT OF CONCENTRATION OF COPPER SULPHATE ON STRESS AFTER EFFECT

- Bath Composition g/l CuSO₄ 5H₂O

× Cracked Deposit
**FIG. 6.6.6 (b) EFFECT OF DEPOSIT THICKNESS AND TIME ON CONTRACTOMETER DEFLECTION**

Bath contained 47 g/l CuSO₄

- x Plain Bath
- o Bath with 0.119 g/l Benzotriazole
FIG. 6.6.6 (c) EFFECT OF DEPOSIT THICKNESS AND TIME ON CONTRACTOMETER DEFLECTION

Bath contained 14.0 g/1 CuSO₄ 5H₂O

× Plain Bath  ○ Bath with 0.110g/1 Benzotriazole
Concentration of CuSO$_4$$\cdot$5H$_2$O g/l Initial Stress after plating for 15 mins. MN/m$^2$ Equilibrium Stress MN/m$^2$ Stress After-Effect Change in a Tensile Direction MN/m$^2$ % of Initial Stress

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Initial Stress</th>
<th>Equilibrium Stress</th>
<th>Stress After-Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$$\cdot$5H$_2$O g/l</td>
<td>after plating for 15 mins. MN/m$^2$</td>
<td>MN/m$^2$</td>
<td>Change in a Tensile Direction MN/m$^2$</td>
</tr>
<tr>
<td>8</td>
<td>20.1T</td>
<td>23.4T</td>
<td>3.3</td>
</tr>
<tr>
<td>16</td>
<td>26.2T</td>
<td>31.4T</td>
<td>5.2</td>
</tr>
<tr>
<td>24</td>
<td>28.0T</td>
<td>45.5T</td>
<td>17.5</td>
</tr>
<tr>
<td>32</td>
<td>53.8T</td>
<td>62.1T</td>
<td>8.3</td>
</tr>
<tr>
<td>47</td>
<td>27.3T</td>
<td>41.4T</td>
<td>14.1</td>
</tr>
<tr>
<td>59</td>
<td>28.7T</td>
<td>44.1T</td>
<td>15.4</td>
</tr>
<tr>
<td>70</td>
<td>37.9C</td>
<td>26.9C</td>
<td>11.0</td>
</tr>
<tr>
<td>78</td>
<td>43.1C</td>
<td>22.7C</td>
<td>20.4</td>
</tr>
<tr>
<td>93</td>
<td>52.8C</td>
<td>25.2C</td>
<td>17.6</td>
</tr>
<tr>
<td>140</td>
<td>45.5C*</td>
<td>35.2C</td>
<td>10.3</td>
</tr>
<tr>
<td>186</td>
<td>52.8C</td>
<td>32.8C</td>
<td>20.0</td>
</tr>
<tr>
<td>233</td>
<td>32.8C*</td>
<td>13.1C</td>
<td>19.7</td>
</tr>
<tr>
<td>280</td>
<td>54.9C</td>
<td>34.2C</td>
<td>20.7</td>
</tr>
<tr>
<td>327</td>
<td>34.2C</td>
<td>19.7C</td>
<td>14.5</td>
</tr>
</tbody>
</table>

T Tensile Stress
C Compressive Stress
* Ruckled Deposits

Table 6.6.6.

Discussion

Some of the results in this section have already been plotted in the form of a graph in Fig. 6.6.2. in which the initial stress, after plating for fifteen minutes, together with the equilibrium stress were plotted against the concentration of copper sulphate in the solution. The actual stress after-effect, i.e. the difference between the above stresses, is shown in Fig. 6.6.6.(a).

In every deposit with a tensile initial stress the value increased after the completion of plating, and this is shown in the table as a positive stress after-effect. For deposits which had a compressive initial stress, this decreased after plating and is shown as a positive stress after-effect in a tensile direction. This change in the stress in a tensile direction is in agreement with the observations of other workers $^{125, 184, 138, 191}$ and has been observed in nickel, chromium lead and zinc as well as in copper.
Kushner found that the stress after-effect was much higher in deposits from plating solutions which contained addition agents than from plain baths. The stress after-effect is also illustrated in two other graphs, Figs. 6.6.6.(b) and (c), which show the change in the stress during and after plating from both a standard solution without any additions, and from one containing benzotriazole. The stress in the deposit from a solution containing 47 g/l copper sulphate and benzotriazole, Fig. 6.6.6.(b), was compressive at first, then became tensile and the stress after-effect showed an increase in this tensile stress. A compressively stressed deposit was obtained from a solution containing 140 g/l copper sulphate and benzotriazole, Fig. 6.6.6.(c) and this compressive stress decreased, so becoming more tensile in nature.

Conclusion

The stress after-effect, or change in the stress after the current had been switched off, was not observed in deposits from the standard bath, but only in deposits from the solution containing benzotriazole. The value of the stress after-effect appeared to be related to the concentration of the copper sulphate on the plating bath and not to the initial stress. In every case, a tensile stress increased and a compressive stress decreased after the end of plating.

6.6.7. Effect of the Thickness of the Deposit

Introduction

The internal stress has been observed by many workers to change with the thickness of the deposit. In each of the sections in this chapter a continuous series of deflections have been taken at regular intervals of time, so that the variation of the stress with thickness could be calculated.

The results given below were obtained for deposits from solutions containing 0.119 g/l benzotriazole in earlier sections of this chapter. Those from part 6.6.3. illustrate the effect of varying the bath temperature on the contractometer deflection v. plating time or deposit thickness curves. A similar set of readings was produced for variations with current density from part 6.6.4. The variations of the internal stress with the thickness of the coating is also illustrated by two graphs, Figs. 6.6.6.(b) and (c) used in the work on the stress after-effect.
Results

These are given in Tables 6.6.7*(a) and (b) and plotted in graphs, Figs. 6.6.7*(a) and (b).

<table>
<thead>
<tr>
<th>Deposit Thickness (approx) (x 10^{-5} m)</th>
<th>Contractometer Deflection in degrees at Bath Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-2</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
</tr>
<tr>
<td>18</td>
<td>17.5</td>
</tr>
<tr>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>24</td>
<td>27.5</td>
</tr>
<tr>
<td>27</td>
<td>32</td>
</tr>
<tr>
<td>30</td>
<td>36</td>
</tr>
<tr>
<td>33</td>
<td>40.5</td>
</tr>
<tr>
<td>36</td>
<td>45</td>
</tr>
<tr>
<td>39</td>
<td>49</td>
</tr>
<tr>
<td>42</td>
<td>55</td>
</tr>
<tr>
<td>45</td>
<td>58</td>
</tr>
</tbody>
</table>

Table 6.6.7*(a)

Discussion

It can be seen from the graphs in Figs. 6.6.7*(a) and (b) that the deflection of the spiral of the contractometer, and, hence, the value of the stress which is calculated from it, depends upon the thickness of the deposit. The mean internal stress \((Sm)\) on the coating can be calculated from the deflection \((D)\) at any deposit thickness \((t)\) from the equation:

\[
Sm = \frac{2KD}{p\cdot h \cdot t}
\]

where

- \(p\) = pitch of helix
- \(h\) = thickness of the material of the helix
- \(K\) = deflection constant of the helix per unit torque.

As the lines representing the Spiral Deflection v. Deposit Thickness at a particular bath temperature (Fig. 6.6.7*(a)) or current density (Fig. 6.6.7*(b)) do not show any maximum or minimum, it follows that the mean stress varies regularly with the thickness of the coating.
FIG. 6.6.7. (a) EFFECT OF DEPOSIT THICKNESS ON CONTRACTOMETER DEFLECTION AT DIFFERENT BATH TEMPERATURES.
FIG. 6.6.7. (b) EFFECT OF DEPOSIT THICKNESS ON CONTRACTOMETER DEFLECTION AT DIFFERENT CURRENT DENSITIES.
Table 6.6.7*(b)

The instantaneous stress gives information about the nature of the stress on the top layer of the coating. This instantaneous stress ($S_i$) can be calculated from a graph of the mean stress ($S_m$) v. deposit thickness ($t$) by using the equation:

$$S_i = S_m + t \frac{d}{dt} S_m$$

where $\frac{d}{dt} S_m$ = the gradient of the line of $S_m$ v. $t$ at a deposit thickness $t$.

Thus, the change in gradient of the mean stress (or Contractometer Deflection) v. Thickness curve from a negative to a positive value, as shown in Fig. 6.6.6.(c), has a marked effect on the instantaneous stress. In this particular deposit,
the initial mean stress was compressive and then layers of copper with a tensile stress were plated on top of the compressive stress, until the mean stress became tensile, at a deposit thickness of about $3.5 \times 10^{-6}$m.

Conclusion

The mean internal stress varied with the deposit thickness and in certain deposits (not shown) it changed from compressive to tensile. If is, therefore, necessary to use the same thickness of coating when comparing the effect of different variables on the internal stress.

6.6.8. Effect of Concentration of Benzotriazole

Introduction

The internal stress in deposits plated from solutions containing various concentrations of benzotriazole was measured. To minimize any variations in the strength of the addition agent in the electrolyte, which has been discussed previously in section 6.5.5., a litre of fresh solution was made for each determination. The current density used was 215 A/m$^2$ and the temperature of the bath $24 \pm 2^\circ$C, the deposit thickness being standardized at $4.30 \times 10^{-6}$m.

Results

These are given in Table 6.6.8. and plotted in a graph, Fig. 6.6.8.

<table>
<thead>
<tr>
<th>Concentration of Benzotriazole g/l</th>
<th>0</th>
<th>0.02</th>
<th>0.03</th>
<th>0.04</th>
<th>0.06</th>
<th>0.08</th>
<th>0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection, degrees</td>
<td>7</td>
<td>11</td>
<td>24</td>
<td>9.5</td>
<td>16</td>
<td>7</td>
<td>-9.5</td>
</tr>
<tr>
<td>Equivalent Weight g</td>
<td>.9</td>
<td>3.1</td>
<td>3.0</td>
<td>1.9</td>
<td>2.8</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Stress MN/m$^2$</td>
<td>6.2T</td>
<td>21T</td>
<td>20T</td>
<td>13T</td>
<td>19T</td>
<td>4.2T</td>
<td>5.6C</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>-17</td>
<td>-12</td>
<td>-50</td>
<td>-40</td>
<td>-61</td>
<td>-39</td>
<td>-29</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>3.0</td>
<td>3.0</td>
<td>3.6</td>
<td>3.8</td>
<td>5.1</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>17C</td>
<td>20C</td>
<td>20C</td>
<td>25C</td>
<td>26C</td>
<td>35C</td>
<td>38C</td>
</tr>
</tbody>
</table>

Table 6.6.8.

Discussion

With small additions of benzotriazole, the internal stress was tensile with a maximum value of about $20$ MN/m$^2$ at 0.02 and 0.03 g/l. With concentrations above 0.03 g/l the tensile stress decreased, became zero at about 0.1 g/l, and then a compressive stress was formed which rose with the amount of benzotriazole in the solution.
Bath Temperature 23 ± 2°  Deposit Thickness 430 x 10⁻⁶ m
Current Density 215 A/m²

FIG. 6.6.8. EFFECT OF CONCENTRATION OF BENZOTRIAZOLE ON INTERNAL STRESS
It can be seen from Fig. 6.6.8. that the shape of this curve is similar to those obtained for other addition agents. When studying the deposition of copper, Vagramyan et al\textsuperscript{225} and also Khonikevich and Fedot'ev\textsuperscript{210} produced this type of relationship for different concentrations of thiourea, while Fedot'ev and Kruglova\textsuperscript{209} did the same for Rochelle salt. Sulphonated naphthalene behaved in this manner, when used in a nickel plating bath\textsuperscript{229}.

Conclusion

Very low concentrations of benzotriazole in the plating bath produced tensile stresses and with more than about 0.1 g/l compressive stresses are formed and increase in magnitude up to 1.0 g/l under the plating conditions used in this experiment.

6.6.9. Effect of Ultrasonic Agitation of the Plating Solution

Introduction

The internal stress in deposits plated from a plain, ultrasonically agitated solution were compared with those from a still bath and a magnetically stirred bath. In the first section the stress was measured at different deposit thicknesses up to $15 \times 10^{-6}$ m for copper plated from a magnetically stirred bath and an ultrasonically agitated bath. In the former, the rate of stirring was sufficient to minimize any concentration or temperature effects and to avoid excessive aeration of the solution.

The second part of the work consisted of a series of stress measurements of deposits from a still and an ultrasonically agitated solution. The experiments were performed over a range of current densities and the stresses calculated at a deposit thickness of $1 \times 10^{-5}$ m.

Results

These are given in Tables 6.6.9.(a) and (b) and plotted in graphs, Fig. 6.6.9.(a) and (b).

Magnetically Stirred Bath

<table>
<thead>
<tr>
<th>Deposit Thickness x $10^{-6}$ m</th>
<th>2.5</th>
<th>3</th>
<th>3.5</th>
<th>4.8</th>
<th>6.0</th>
<th>6.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Stress MN/m\textsuperscript{2}</td>
<td>59.3</td>
<td>53.5</td>
<td>45.6</td>
<td>34.8</td>
<td>30.1</td>
<td>27.0</td>
</tr>
</tbody>
</table>

| Thickness | 7.0 | 7.5 | 10.0 | 12.3 | 15.0 |
| Stress    | 24.5 | 24.1 | 21.7 | 20.7 | 19.3 |
Internal Stress (Tensile) \( \text{MN/m}^2 \)

Deposit Thickness \( (x10^{-6} \text{ m}) \)

\( \triangle \) Magnetically Stirred Bath  
\( \times \) Ultrasonically Agitated Bath  
Bath Temperature 17°C  
Current Density 215 A/m²

FIG. 6.9. (a) EFFECT OF SOLUTION AGITATION ON INTERNAL STRESS 
IN COPPER ELECTRODEPOSITS AT DIFFERENT THICKNESSES
Internal Stress (Tensile) MN/m$^2$

$0 \quad 200 \quad 400 \quad 600 \quad 800$

Current Density A/m$^2$

© Still Bath
× Ultrasonically Agitated Bath

Bath Temperature 18°C
Deposit Thickness $1 \times 10^5$ m

FIG. 6.6.9. (b) EFFECT OF SOLUTION AGITATION ON INTERNAL STRESS IN COPPER ELECTRODEPOSITS AT DIFFERENT CURRENT DENSITIES


Ultrasonically Agitated Bath

<table>
<thead>
<tr>
<th>Deposit Thickness x 10^{-6} m</th>
<th>1.0</th>
<th>1.7</th>
<th>2.2</th>
<th>3.0</th>
<th>3.5</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Stress MN/m^2</td>
<td>60.0</td>
<td>45.1</td>
<td>42.5</td>
<td>30.9</td>
<td>26.6</td>
<td>20.8</td>
</tr>
<tr>
<td>Thickness</td>
<td>6.0</td>
<td>7.5</td>
<td>10.8</td>
<td>13.1</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>Stress</td>
<td>19.6</td>
<td>17.9</td>
<td>15.2</td>
<td>13.5</td>
<td>12.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.6.9.(a)

<table>
<thead>
<tr>
<th>Current density A/m^2</th>
<th>300</th>
<th>520</th>
<th>630</th>
<th>780</th>
<th>930</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Stress Still Bath</td>
<td>3.3</td>
<td>5.5</td>
<td>8.3</td>
<td>12.4</td>
<td>17.8</td>
</tr>
<tr>
<td>Stress Ultrasonically Agitated Bath</td>
<td>2.9</td>
<td>4.5</td>
<td>5.8</td>
<td>8.3</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Table 6.6.9.(b)

Discussion

It can be clearly seen from the graphs 6.6.9.(a), that, under the plating conditions used, the internal stress was always tensile, lower in deposits from the ultrasonically agitated solution than in those from the stirred bath, at all the deposit thicknesses used. The tensile stress in nickel deposits from a Watts bath have been found to decrease in a similar manner with increasing deposit thickness, when a comparison was made between ultrasonically agitated and magnetically stirred solutions\(^7\)\(^8\), 298. It is interesting to note that the compressive stress in zinc deposits from a sulphate bath were also decreased when the results of an ultrasonically agitated bath was compared with a still bath\(^7\)\(^8\), 298. Graph 6.6.9.(b) shows that the tensile stress in deposits from an ultrasonically agitated solution were lower than those from a still bath, at all the current densities used under the plating conditions chosen.

The stress also decreased with the deposit thickness and increased with the current density; thus is in good agreement with the results of other workers.

Conclusion

The tensile stress on copper deposits was found to:

1. decrease with the deposit thickness;
2. increase with the current density;
3. be lower in deposits from an ultrasonically agitated solution than those from a magnetically stirred or a still solution.
6.6.10. A Comparison of the Hardnesses and Internal Stresses produced by Triazole, Benzotriazole and Naphthotriazole

Introduction

In this section, a comparison is made of the effects produced by the use of triazole, benzotriazole and naphthotriazole as addition agents, in the acid copper plating bath. These compounds were chosen so that the influence of the number of benzene rings in a substance could be determined by comparing triazole with benzotriazole (a triazole ring attached to a benzene ring) and naphthotriazole (a triazole ring connected to two benzene rings); the corresponding anthacene compound is cancogenic, so was not used. All the measurements were made with the same molar concentration (10^-3 M) of each substance.

Both the hardness and the internal stress were determined for the plain bath and with each addition agent. The plating cells were used at room temperature (18 ± 2°C), with a current density of 260 A/m² and magnetic stirring, the addition being made just before the current was switched on.

Results

Hardness

<table>
<thead>
<tr>
<th>Plating Bath</th>
<th>Hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain bath</td>
<td>92</td>
</tr>
<tr>
<td>Bath with 10^-3 M Triazole</td>
<td>156</td>
</tr>
<tr>
<td>Bath with 10^-3 M Benzotriazole</td>
<td>264</td>
</tr>
<tr>
<td>Bath with 10^-3 M Naphthotriazole</td>
<td>287</td>
</tr>
</tbody>
</table>

Table 6.6.10.(a)

Internal Stress

<table>
<thead>
<tr>
<th>Plating Bath</th>
<th>Stress MN/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain bath</td>
<td>10.3 T</td>
</tr>
<tr>
<td>Bath with 10^-3 M Triazole</td>
<td>10.1 C</td>
</tr>
<tr>
<td>Bath with 10^-3 M Benzotriazole</td>
<td>57.9 T</td>
</tr>
<tr>
<td>Bath with 10^-3 M Naphthotriazole</td>
<td>77.2 T</td>
</tr>
</tbody>
</table>

T = Tensile Stress
C = Compressive Stress

Table 6.6.10.(b)
Discussion

The hardness of the deposit increased with the molecular size of the addition agent, for a given molar concentration in the plating bath. This change was from HV 92 for the plain deposit up to HV 287 for copper plated from a solution containing naphthotriazole. If the same molecular concentration of inhibitor were codeposited with the copper, this would account for the increase in hardness being greatest with the largest molecular size giving the maximum blocking effect for dislocation movement.

The effect of triazole in the plating solution was to produce a compressive stress, whereas the stress in the deposit from the plain bath was tensile. Increasing the molecular size of the addition agent raised the stress in a tensile direction to 57.9 MN/m$^2$ with benzotriazole and 77.2 MN/m$^2$ with naphthotriazole. These stress changes are in good agreement with the results reported by Tsareva et al. who found that acetic acid ($\text{CH}_3\text{COOH}$) lowered the tensile stress, propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) increased the tensile stress and valeric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$) produced an even higher tensile stress in copper deposits from the acid sulphate bath. Unfortunately, this appears to be the only reference in the literature survey which covers the effect of varying the size of the addition agent on either the hardness or the internal stress in electrodeposited metals.

Conclusion

The hardness of a deposit from the plain bath was HV 92 and this increased with the molecular size of the addition agent in the order triazole HV 156, benzotriazole HV 264 and naphthotriazole HV 287.

The stress of a deposit from the plain bath was 10.3 MN/m$^2$ (tensile) and this changed to 10.1 MN/m$^2$ (compressive) with an addition of triazole, 57.9 MN/m$^2$ (tensile) with benzotriazole and 77.2 MN/m$^2$ with naphthotriazole.
7. DISCUSSION

7.1. Introduction

In the first part of this chapter a brief summary is made of the present state of knowledge concerning the role of benzotriazole as a corrosion inhibitor for copper and also as an addition agent in the copper sulphate-sulphuric acid plating bath, so that the results obtained in the present work can then be considered and related to the existing theories. This information is subsequently used to extend and/or modify those theories and, finally, suggestions are made for future work which could clarify the outstanding problems in these fields.

7.2. Benzotriazole as a Corrosion Inhibitor for Copper

The practical applications of benzotriazole as an inhibitor for copper and copper alloys have received much attention recently. However, much of the reported work has been fragmentary and concerned with particular aspects, such as lacquers and antifreezes. The theoretical studies have mainly concentrated on polarization curves, impedance measurements and ellipsometric investigations. The polarization work was for copper immersed in sodium chloride solutions and indicated that benzotriazole assisted in the passivation of copper and the inhibition of one of the cathodic reactions, namely the hydrogen evolution process. The impedance and ellipsometric studies confirmed the formation of a surface film, (variously quoted as about 50 Å or 400 Å to 5,000 Å), which is considered to give protection and to be produced by the chemisorption of benzotriazole on to the copper surface.

Therefore, to be able to connect the fragmentary data a systematic study had to be carried out to ascertain:

(A) the physical properties of benzotriazole in water;

(B) the chemical properties of benzotriazole as they influence the corrosion rate of immersed copper;

(C) the effect of the pretreatment of copper in a solution of benzotriazole on the corrosion and oxidation rates.

It is intended now to summarize briefly the outcome of the present study and then to discuss the significance of the results in greater detail.
7.2.1. Physical Properties of Benzotriazole in Water

It has been shown in this work that benzotriazole:

(1) increases its solubility in water with temperature from 1.01 w% v at 1°C to 19.7 w% v at 97°C (section 4.2);

(2) existed as a white crystalline powder below about 40°C, when in excess in a saturated aqueous solution, and as a brown liquid above this temperature (section 4.2);

(3) had only a slight effect on the pH and conductivity of water, decreasing the former and increasing the latter (section 4.3).

The results listed in the solubility data in Fig. 4.2 confirm the values obtained by other workers \(^{19,21,22}\), but the present results are more comprehensive, since they cover a larger range of temperatures. The transformation in the excess benzotriazole, in a saturated solution, from a white powder at temperatures up to about 40°C to a brown liquid in water above this temperature, produces the expected change in the shape of the solubility curve previously reported by Tadashi \(^{19}\), but not by other authors. At temperatures as low as 1°C, the solubility data appear to justify the use of an addition of up to 1 w% v of benzotriazole in order to obtain a good inhibitor efficiency in many of the aqueous solutions used in this work and also in antifreezes \(^{23}\). The data also show the maximum concentration which can be dissolved in water to combat corrosion at a particular temperature; however, the solubility is higher in acidic solutions \(^{21,22}\), so these data do not apply to the work with the plating solutions.

There are two different theories regarding the nature of dissolved benzotriazole in water; one considers it to be present as a molecule and the other in an ionized form. The decrease produced by benzotriazole in the pH of deionized, distilled and tap water, which was observed in section 4.3, confirms the previously reported results of Tadashi \(^{19}\), which suggested that benzotriazole formed weakly acidic solutions in water. He proposed that benzotriazole ionized in water according to the equation;

\[
C_6H_4N_2\text{NH} \rightleftharpoons C_6H_4N_2\text{N}^- + H^+
\]

The production of the hydrogen ion, indicated in the above equation, would account for the decrease in the pH, while the formation of an anion and a cation from a neutral molecule would also explain the increase in the conductivity reported in all three waters in section 4.3. Therefore, the present results appear to disprove the theory of Fagel and Ewing \(^{18}\), which
was that benzotriazole existed in neutral and mildly acidic solutions as a neutral molecule, since this would affect neither the pH nor the conductivity of these solutions.

Because the addition of benzotriazole to waters reduces the pH and raises the conductivity, both of which would tend to increase the rate of corrosion, the effectiveness of benzotriazole as an inhibitor cannot be the result of changes in the pH and conductivity of aqueous solutions. Hence its action, as a corrosion inhibitor, must depend upon some other mechanism.

7.2.2. Chemical Properties of Benzotriazole used as a Corrosion Inhibitor

It has been shown in this work that benzotriazole:

1) was an effective inhibitor for many acidic, neutral and alkaline solutions, but ineffective in complexing and oxidizing solutions (section 4.4);

2) became more efficient as the concentration of the inhibitor increased, except in complexing and oxidizing solutions (section 4.5);

3) gave increasing protection in sulphuric acid as the pH was increased (section 4.6);

4) acted as a weak buffer in acidic, neutral and alkaline solutions (section 4.8);

5) prevented dezincification of 70/30 brass in many solutions; in some cases reducing the rate of corrosion of brass to a lower value than that obtained for copper (section 4.9);

6) reduced both the corrosion of copper and the subsequent pitting of aluminium foil immersed in the same water (section 4.13);

7) was a better corrosion inhibitor and more effective in imparting stain resistance to copper than triazole and as good as, but cheaper than, naphthotriazole (sections 4.10 and 4.11);

As shown in the literature survey (section 1.1.5), benzotriazole is generally considered to inhibit the corrosion of copper by the formation of a thin, chemically bonded complex on the metal surface. Furthermore, this complex, cuprous benzotriazole is thought to reinforce the protection afforded by the naturally occurring oxide film on the surface of copper, particularly at defects and other points of weakness. Thus, Evans suggested that the inhibition in chloride solutions was due to the production of basic copper chloride which interacted with the benzotriazole to form a "blocking
substance. The mechanism of inhibition has been widely studied and attributed to the polarization of the anodic and/or cathodic processes. Benzotriazole is also considered to inhibit the corrosion of steel immersed in acidic solutions, by the formation of a surface film that reduces the rate of the anodic and/or cathodic reaction.

A protective film of benzotriazole may be formed on copper by three general methods: either by adding benzotriazole to the aqueous solution containing the copper or by immersing the copper in a hot solution of benzotriazole followed by rinsing or by exposing the metal to benzotriazole vapour at room temperature. There is some doubt about the actual thickness of the surface film produced by these methods, but the majority of workers consider it to be about 50Å.

In this work, as can be seen from the summary of chemical properties, the use of 0.1 g/l benzotriazole produced a marked reduction in the rate of corrosion of copper immersed in many acidic, neutral and alkaline solutions. However, in some complexing and oxidizing solutions (ammonia, ferric chloride and hydrogen peroxide) in which copper is not stable, benzotriazole did not give inhibition, presumably because no protective oxide film was present to be reinforced; this observation confirms the work in ammoniacal solutions of Cotton and Scholes.

If one assumes that corrosion is concentrated at areas where the surface film is defective, then it follows that, with higher concentrations of benzotriazole in the solution, the size of the uncovered areas must be reduced due to the increased adsorption. Thus, it appears that with a low concentration of benzotriazole (0.12 g/l) a considerable area is already covered and a relatively high degree of corrosion inhibition is achieved. Although the addition of more inhibitor may thicken the existing film or be adsorbed on unprotected areas, the consequent increase in protection is proportionally less. With a concentration of 0.5 g/l in many solutions, the greater part of the surface can be assumed to be covered with the adsorbed film, giving a high degree of protection (about 97% for phosphoric acid), and a further addition of 0.5 g/l gives a very small increase in the inhibition (to about 98% for phosphoric acid). A similar trend has been observed by West with tolythiourea and steel, and by Sathianandhan et al. who used benzotriazole in 0.1 N acids to reduce the corrosion of mild steel. It is interesting to note that, in this work with copper, a 100% increase in the concentration of benzotriazole increased the protection by only 1%. One possible explanation for this is that, if the adsorption on the surface is not uniform and the extra benzotriazole is preferentially attracted to the peaks because of
easier diffusion, then the area of the recesses remaining uncovered and the consequent rate of corrosion are only slightly reduced.

In the present work, it was shown that the rate of corrosion of copper decreased and the inhibitor efficiency of benzotriazole increased with a rise in the pH of a sulphuric acid solution (section 4.6). It can be seen from the Pourbaix Diagram for Copper-Water (Fig. 7.2.1) that the thermodynamic stability of the oxide film on copper decreased as the pH was reduced.

Fig. 7.2.1. Pourbaix Diagram for Copper and Water.
Thus, if benzotriazole acts by reinforcing this oxide film, it would have a very small effect in the strongly acidic solutions where the film is very unstable, but the efficiency would increase with the pH. On the other hand, if one assumes that the active form of the inhibitor is the \( \text{C}_6\text{H}_4\text{N}_2\text{N}^- \) ion, then it would follow that at the lower values of pH there would be less of this form present, due to ion mass action, and consequently less protection against corrosion in the acidic solutions.

The above experiments are confirmed by the results from the experiments in section 4.6, in which the efficiency increased from 36% at a pH = -1 to 98% at a pH = 1 and 100% at a pH = 1.91, where the oxide-benzotriazole film gave complete protection. At a pH = 3, the oxide film alone was satisfactory, without the additional inhibition which would result from the formation of an adsorbed film of benzotriazole.

From this work, it appears that benzotriazole was responsible for the lower change in pH which occurred during the corrosion of copper in a wide selection of acidic, neutral and alkaline solutions. This fact appears not to have been discussed in the literature, but can be deduced from a data sheet on anti-freezes. The figures given were obtained with the Ford glassware test, according to the British Standard 3152 for antifreeze, and showed that the pH changed from 7.9 to 7.7 in a plain solution but remained at 7.8 with 0.2 w% benzotriazole, when the solution was agitated with air; with no solution agitation the change was from 7.9 to 7.5 and, with benzotriazole, from 7.9 to 7.6. Thus, benzotriazole acts as a weak buffer during the corrosion of copper and may have the same effect as borax which is widely used as a buffer in proprietary corrosion inhibitors.

Tadashi suggested that benzotriazole existed in water in an ionic form as \( \text{C}_6\text{H}_4\text{N}_2\text{N}^- \). The addition of acid or hydrogen ions to this solution may give deionization according to the equation:

\[
\text{C}_6\text{H}_4\text{N}_2\text{N}^- + \text{H}^+ \rightarrow \text{C}_6\text{H}_4\text{N}_2\text{NH}.
\]

The addition of hydroxyl ions may result in the formation of water in the following manner:

\[
\text{C}_6\text{H}_4\text{N}_2\text{N}^- + \text{H}^+ + \text{OH}^- \rightarrow \text{C}_6\text{H}_4\text{N}_2\text{N}^- + \text{H}_2\text{O}.
\]

Hence the addition of acids or alkalies can be buffered as indicated.

It has also been observed in this study and elsewhere that benzotriazole prevented the dezincification of 70/30 brass in some solutions. There are two theories that have been proposed to explain this dezincification: one considers that the dissolution of the copper and the zinc together in the
brass is followed by the redeposition of the copper, while the zinc ions remain in the solution, whereas the other theory assumes the selective dissolution of the zinc. Both these mechanisms lead finally to a solution containing zinc ions and a copper rich surface.

Benzotriazole is thought to reinforce the copper oxide film on the copper in the surface of the brass so that, if the first mechanism applies, there is a reduction in the dissolution of the copper and consequently a decrease in the corrosion of the brass. Also, because the benzotriazole molecule is large in comparison with the copper ion in the surface film, it may shield the zinc next to the copper on which it is adsorbed. If the second mechanism applies, this shielding would reduce the rate of dissolution of zinc from the surface and decrease the rate of dezincification. Therefore, theoretically benzotriazole can inhibit dezincification of brass whichever mechanism applies.

In the comparison of the inhibitive properties for copper, (sections 4.10 and 4.11) there was very little overall difference between benzotriazole and naphthotriazole, both of which were much better than triazole. These results are in agreement with those of Cotton and Scholes who found that:

(1) "triazole showed very little or no inhibitive properties";

(2) "naphthotriazole behaved in a similar manner to benzotriazole".

The only other references found in the literature on the corrosion inhibition of naphthotriazole concerned the patented use of benzotriazole or naphthotriazole in detergents, to prevent the surface staining of copper. However, no quantitative data appeared in any of these publications.

It may be concluded from the present results that benzotriazole and naphthotriazole are both adsorbed on to the surface and form protective films on copper and behave in a similar manner. The probable reason for the greater interest in benzotriazole is that it is much cheaper than naphthotriazole (currently £2.25 for 100 g compared with £45.6 for 100 g).

An addition of 0.12 g/l benzotriazole to either tap or distilled water was found to be effective in reducing the rate of corrosion of copper and the subsequent pitting of aluminium foil immersed in the same water. This work confirms previous observations that benzotriazole inhibits the corrosion of copper-aluminium couples. It can be argued that, because benzotriazole reduces the rate of attack of copper, it follows that it also decreases the detrimental effects that can be produced by the ions formed during corrosion.
As a consequence of this, it should prevent the pitting of aluminium, which is caused by the formation of local active-passive cells, at areas where copper ions are deposited on to the immersed aluminium foil.

7.2.3. The Effect of the Pretreatment of Copper with Benzotriazole

It has been shown in this work that benzotriazole:

(1) produced a protective film on copper dipped in benzotriazole solutions, but these films were normally not as effective in resisting corrosion as those obtained when the inhibitor was added to the test solutions; however, the relative protection due to the film was much better for the dipped specimens than that obtained when benzotriazole was added to some complexing and oxidizing solutions (section 4.7);

(2) was better than triazole and naphthotriazole in forming a corrosion resistant film on copper (section 4.12);

(3) formed, during a pretreatment dip, a film more resistant to corrosion and reduced the subsequent pitting of aluminium immersed in the same tap water to a greater extent than obtained by adding 0.12 g/l benzotriazole to the water (section 4.13);

(4) gave some protection against oxidation in air, at temperatures below about 350°C, to copper which had been pretreated in a hot aqueous solution of benzotriazole (section 4.14).

Tests have been carried out in this work to compare and contrast the different behaviour of benzotriazole as an inhibitor when applied as a film or in a solution, and these show that the pretreatment of copper by immersion in a hot aqueous solution of benzotriazole increased the resistance to corrosion. This process did not produce as much inhibition as the addition of 0.12 g/l benzotriazole in several solutions and, in a few solutions, even appeared to increase the corrosion (section 4.7). However, the dipped copper was much better at resisting corrosion than the coating obtained when an addition of 0.12 g/l benzotriazole was made to solutions of ammonia, ammonium chloride and ferric chloride, and there was also a decrease in the pitting of aluminium, immersed with the copper, in tap water.

It is generally agreed that this pretreatment reinforces the existing oxide film on the copper and improves the corrosion resistance. However, it is not clear why the pretreatment has sometimes been found to increase the rate of corrosion of copper. In this work, it was discovered that a pretreatment consisting of immersion for five minutes in a 0.25% benzotriazole solution at
60°C gave irreproducible results (section 4.13), and sometimes increased the corrosion rate, while another pretreatment of thirty minutes immersion in a 5% solution at 80°C appeared to give very much better resistance to corrosion. It was considered that the shorter process probably produced an incomplete copper benzotriazole film which could give a combination of active and passive regions on the surface and accelerate the rate of corrosion: this effect can be compared with that produced by the use of an insufficient quantity of an anodic inhibitor. The longer process was thought to increase the adsorption and to form a more continuous and protective film of benzotriazole which gave a high degree of corrosion inhibition. The fact that, during the pretreatment, the copper was immersed at a higher temperature for a longer time, means that a thicker oxide film would be expected to form, because the growth process is usually considered to be controlled by the diffusion of oxygen to the surface. Therefore, the treatment in a 5% solution for thirty minutes at 80°C results in a very much more protective film.

The copper benzotriazole film on the surface of dipped copper gave a higher degree of protection when immersed in solutions of ammonia, ammonium chloride, and ferric chloride, than that afforded by the addition of 0.12 g/l benzotriazole to the solutions. Thus, it appears that, once the protective film has been formed, it can resist corrosion even in some complexing and oxidizing solutions, in which the addition of benzotriazole to the solution itself has been shown to be ineffective. Therefore, it is clear that, once the benzotriazole has been adsorbed on to the copper surface, it is not easily affected by these solutions even though benzotriazole dissolved in these solutions appears to act as a poor inhibitor.

It is interesting to note that the surface film produced by dipping also reduced the rate of oxidation of copper at temperatures up to about 350°C. This observation confirms the work of Cotton and Scholes [43], who unfortunately did not give any quantitative data, and is interesting in the light of the fact that the copper benzotriazole complexes have been found to be thermally stable only up to about 250°C.

It can be concluded that the bond between the copper surface and the benzotriazole must be quite strong, because it withstands attack in aggressive solutions and also is stable at high temperatures in air. These observations are consistent with the view that benzotriazole is chemically and not physically adsorbed on to the surface of the copper.
7.3. Effect of Benzotriazole on the Nucleation, Surface and Structure of Copper Electrodeposits

It was observed in chapter 5 that the appearance of the copper deposits depended upon the plating conditions and the solution used. In the first part of this section, the effects of these variables are discussed for deposits from the plain bath and, in the second, for deposits from the bath containing benzotriazole. Because of the widespread nature of the experimental work, it is intended now to summarize briefly the outcome of the present study and then to discuss the significance of these results in greater detail.

7.3.1. Deposits from the Plain Solution

It has been shown in this work that copper plated from the bath containing no addition agent:

(1) grew from flat sided nuclei with straight edges, which appeared to be single crystals (sections 5.2 and 5.4);

(2) was coarsely grained when high bath temperatures and low current densities were used, and finely grained with low bath temperatures and high current densities (section 5.3);

(3) was slightly powdery when produced at low temperatures and high current densities (section 5.3);

(4) had a very smooth surface when the solution was ultrasonically agitated as compared with deposits from still or magnetically stirred solutions (section 5.4);

(5) improved in quality, i.e. was less powdery, and the surface became smoother as the solution agitation increased (section 5.5).

Nucleation of Deposits

This work on the copper plated at a current density of 215 A/m², showed isolated growth centres and crystals that were bounded by facets with definite crystallographic indices, which confirms the results of Pick and others. The actual shape and distribution of these nuclei is known to depend upon the orientation of the basis metal and the current density. In the present study the nuclei had various forms because they were growing on different grains in a polycrystalline cathode; they were assumed to continue to grow and then to merge, appearing as grains and grain boundaries where the cross-section was viewed (see Fig. 5.2.(f)). The current density is important because it controls the rate of deposition of the ions. If it is low, a high
rate of surface diffusion can occur to the most favourable crystallographic sites on the polycrystalline cathode and a relatively low degree of nucleation occurs with the formation of crystals with regular facets. This is shown in Fig. 5.4(b), for which a current density of 20 A/m² was used, resulting in the growth mechanism being controlled by crystallographic considerations. However, with the higher current density of 215 A/m² there is less opportunity for surface diffusion and a more irregular surface is produced, as shown in Figs. 5.4 and 5.8 ((a) and (b)), in which the growth mechanism is under diffusion control.

Effect of Ionic Mobility on the Surface Appearance

The mobility of the copper ions in the solution and on the cathodic surface probably controls the rate of nucleation, the surface appearance, the grain size and the hardness of the deposits. In order to investigate this effect, copper was plated over a range of five bath temperatures and five current densities and the surface of each of the resulting deposits was photographed (Fig. 5.3).

It is well established that the mobility of the copper ions increases as the solution temperature is raised. This enables an easier migration of ions to and from the cathodic surface and reduces the cathodic polarization which, together with the improved surface diffusion, allows depositing ions to move into suitable sites for nucleation and also for the continued growth of nuclei. Because the ions are more mobile at higher solution temperatures, one would expect fewer nuclei to be formed and larger grains to be produced. At lower temperatures, with less ionic mobility, smaller grains would be formed. As already mentioned above, there is less opportunity for ionic movement at the cathodic surface when high current densities and, therefore, high deposition rates occur, and this must result in more nuclei and a smaller grain size. One consequence of a very fine grain size is that the surface of the deposit would appear to be smoother, brighter and more uniform than that obtained with a coarse grained deposit. Fig. 5.3 shows clearly the validity of this argument, where large grain sizes result from high temperatures and low current densities, thus giving the experimental evidence for the effect of the mobility of the ions on the surface of the deposits.

Effect of Solution Agitation on the Surface Appearance

Agitation of the plating solution can be considered to have several effects:
(1) to increase the ionic movement in the solution;
(2) to reduce the concentration polarization at the cathodic surface;
(3) to encourage the movement of impurities to the cathodic surface;
(4) to increase the passivity of the cathode.

The first two of these effects would normally increase the mobility of the copper ions on the cathode surface, reduce nucleation, increase the grain size and give a coarse surface. However, since the foreign particles at the surface can act as nuclei, an increase in the agitation raises the number of these particles and should lead to a grain size. At the same time, agitation of the solution can also encourage the formation of an oxide film on the surface of the cathode, due to the greater supply of oxygen, and thus increase the passivity of the surface and also the rate of nucleation, because of the large number of oxide particles. From Fig. 5.4, it is clear that ultrasonic vibration of the solution assists nucleation and the formation of a smoother surface and, therefore, effects (3) and (4) are consider to predominate over effects (1) and (2) under these experimental conditions. It is worth noting that, under other experimental conditions, solution agitation has been observed to increase the grain size, so it can be assumed that in these cases effects (1) and (2) must have been more predominant than (3) and (4). The fact that solution agitation improved the quality of the powdery deposits from the plain bath (see Fig. 5.5) suggests that the increased mobility of the copper ions and the reduced cathodic polarization appear to be the important factors. Thus, it could be argued that if more copper ions can reach the cathodic surface, there is less possibility of the formation of hydrogen gas and/or the production of powdery deposits, both of which have been previously observed in plating from still solutions containing very low concentrations of copper sulphate (section 6.2.2).

Formation of Powdery Deposits

Powdery copper deposits were sometimes produced in this work while studying the cathodic current efficiency (sections 6.2.2 and 6.2.4), throwing power (section 6.3.2 and 6.3.4) and surface appearance (section 5.3). It is interesting to note that in most of these cases hydrogen evolution was also observed and the use of ultrasonic agitation of the solution improved the quality of the deposit by reducing the powdery nature.

It is a known fact that the use of high current densities may produce powdery deposits. The upper current density limit for the deposition of good
deposits is considered to be the value at which the rate of copper ion
discharge exceeds the rate of diffusion of the ions to the cathodic surface.
It is given by the following form of the Nernst Equation:

\[ i = \frac{\Delta C \cdot D \cdot nF}{\delta} \]

where \( i \) = current density

\( \Delta C \) = the copper ion concentration difference across the diffusion
layer of thickness \( \delta \)

\( D \) = diffusion coefficient

\( nF \) = Faradaic discharge constants.

The maximum value of \( \Delta C \) occurs when the copper ion concentration at the
surface is zero and the current density then reaches its limiting value
denoted by \( i_L \). According to this theory powdery deposits start to form when
the current density has a value of 0.4 \( i_L \) to 0.7 \( i_L \) depending upon the
plating conditions \(^{80,299}\) (in particular the flow rate of the solution).

Let us now consider the factors in the above equation which could affect
the value of the limiting current density. At low solution temperatures,
the mobility or diffusion of the copper ions is low, the concentration at
the cathodic surface is probably very small and the diffusion layer thick­
ness is relatively high, so that the overall effect is a slow diffusion of
ions to the cathode surface leading to a low limiting current density. This
could explain the formation of the powdery copper deposits at a solution
temperature of 3°C with a current density of 215 A/m\(^2\).

In baths containing 10 g/l and 40 g/l copper sulphate there is probably a
low concentration gradient across the double layer. Thus, with these weak
solutions, the rate of diffusion of copper ions to the cathode is low and,
therefore, the limiting current density is low, so that powdery deposits are
formed at a current density of 215 A/m\(^2\).

It is notable that ultrasonic agitation of the solution prevented the
formation of powdery deposits which were produced from still solutions at
current densities of 290 A/m\(^2\) and 385 A/m\(^2\). Ultrasonic vibrations are
considered to reduce the thickness of the diffusion layer (see literature
review 1.3.6), so increasing the diffusion of ions to the cathode and
raising the limiting current density. The addition of benzotriazole to
the plating solution had very little effect on the critical current density
and formation of powdery deposits (see 6.2.2 and 6.3.4); this confirms the
results obtained by Gabe and Robinson 80.

Therefore, by considering the Nernst Equation and the rates of ionic discharge and diffusion to the cathodic surface, the production of powdery deposits can be explained at low solution temperatures and from baths containing low concentrations of copper sulphate. The beneficial effect of ultrasonic agitation of the solution can also be understood from this theory.

The physical production of the powdery copper deposits may be linked to the codeposition of hydrogen which was observed in section 6.2.2. Thus, nascent hydrogen on the surface of the cathode may be considered to react with the depositing cupric or cuprous ions and to reduce them to a finely divided copper powder according to the equations:

\[ \text{Cu}^{2+} + 2\text{H}^- \rightarrow \text{Cu} + 2\text{H}^+ \]
\[ \text{Cu}^+ + \text{H}^- \rightarrow \text{Cu}^0 + \text{H}^+ \]

This copper could then either remain as a fine powder or be oxidized by dissolved oxygen in the bath to give oxides. In both cases a dark, powdery appearance would be produced on the cathode.

Another possible explanation is that copper is plated in the form of dendritic, nodular or tree-like growths 299. In this theory the deposits are considered to grow outwards from the surface and through the double layer formed on the surface by the depletion of copper ions in the electrolyte. Thus, deposition can occur directly from the bulk solution on to the dendrites where there is a much higher concentration of copper ions, so that the discharge process is not limited by diffusion of the ions through the double layer. A coating formed by this mechanism would be mechanically weak and would appear as a powdery growth on the surface; this theory is supported by the powdery dendritic growth shown in Fig. 5.3(a).

7.3.2. Deposits from Solutions Containing Benzotriazole

In this section it is intended first to briefly summarize the results obtained and then to compare and contrast them with those for the pure deposits. It has been shown in this work that copper plated from solutions containing benzotriazole:

(1) grew from reniform, i.e. kidney shaped nuclei (section 5.2);

(2) was much brighter, smoother and more highly stressed than that from the plain bath (section 5.5);
(3) appeared to consist of truncated crystals when low concentrations of benzotriazole were used and had a nodular growth when there was more than about 0.01 g/l benzotriazole in the solution (section 5.6);

(4) had poor adhesion if more than 0.2 g/l benzotriazole was used and showed a layered structure with concentrations above about 0.12 g/l and usually a banded structure below this value (section 5.7);

(5) had a smoother and brighter surface, consisting of small nodules, than the deposits from the plain bath which were matt and consisted of flat faced, angular crystals (section 5.8);

(6) produced broadening of X-ray lines, with a lattice parameter almost the same as that of pure copper (section 5.9).

Let us now consider in turn the significance of these conclusions.

Nucleation of Deposits

The effect of addition agents on the nucleation and growth of electrodeposits has been reviewed in section 1.2.6. The addition agent or surface active substance is considered to be adsorbed on to the surface of the cathode before deposition and also on to the surface of the growing crystals, thus preventing epitaxial growth, modifying the shape of the crystals and changing the structure and properties of the coating.\cite{126,137,141,145}

The effect of 0.119 g/l benzotriazole on the nucleation of copper plated under normal conditions is found to act in the above manner. An adsorbed film of benzotriazole is thought to be formed over the whole of the copper cathode and this prevents epitaxial growth, i.e. the "basis orientated reproduction growth" (in the Fischer classification).\cite{126} This film may weaken the adhesion of the deposit to the substrate and this property has been patented for the production of electroformed articles.\cite{166} For deposition to take place, discharge of copper ions must occur on top of this benzotriazole surface layer and probably does so at positions where the film is weak, giving an "unorientated dispersion type" of growth (Fischer's classification).\cite{125} and a nodular growth could be expected to form. However, if there is a high residual concentration of benzotriazole in the plating solution, as reported in section 5.2 when 0.119 g/l benzotriazole was used, an adsorbed film may occur again on these nodules and then growth continues at random points on the hemispherical surface. Hence, the formation of reniform nuclei shown in Fig. 5.2 can be considered to be due to the continual process of nodular growth followed by surface adsorption and more nodular growth on the existing nodules.
The classical theory of deposition of solutions containing surface active agents suggests that the initial adsorption occurs preferentially on the growth peaks, resulting in the inhibition of ionic discharge at these areas, and then further adsorption and inhibition occur at other areas. This is supported by the observation of Beacon and Riley, who used radio-tracers to show that the inclusion content of an addition agent is higher at the peaks than in the valleys of the deposit. As unhindered deposition occurs in the recesses and not on the prominences, a level surface is formed, and this theory of levelling has been developed from the work of Foulke and Kardos and also Watson and Edwards.

The adsorption of benzotriazole, from solutions containing different concentrations, on to the growing copper surfaces is now considered in the light of the above theory. This levelling action is indicated in the cross-sections of the coatings in Fig. 5.5, which show that the deposits from a bath containing 0.12 g/l benzotriazole are very smooth and consist of a layer structure with the lamellae parallel to the substrate. The smoothness of the surface also produces reflective coatings, as shown in Fig. 5.8, in which the brightness appears to be related to the smoothness.

Let us now consider the structure of the copper plated from solutions containing different concentrations of benzotriazole (see Fig. 5.7). During deposition the current was switched off three times, for periods of one, five and a further five minutes, to encourage adsorption and banding. It is generally thought that the degree of adsorption on a surface in a solution depends upon the concentration of the surface active agent and the time of immersion. If a sufficient concentration of adsorbed material were attracted to this surface it would produce banding in this coating. This banding would be visible when the cross-section of the deposit is viewed and the lines formed should be parallel to the original surface of the substrate, if uniform deposition occurs, the strength of the bonds depending upon the extent of adsorption.

It can be seen from the photographs, Fig. 5.7((b), (c) and (d)), that there was insufficient adsorption to produce any banding in the solutions containing low concentrations of benzotriazole during the period of one minute when the current was switched off. However, when the period of adsorption was increased to five minutes, bands did appear in the deposits from the solutions containing 0.005 and 0.01 g/l benzotriazole. This adsorption must have decreased the remaining concentration to a level that was insufficient to give banding when
the current was switched off for the second period of five minutes. With concentrations above 0.05 g/l benzotriazole, banding occurred during all the breaks in plating, as is to be expected because much higher concentrations of additive were present in the bath. The adsorption can also be seen to have reduced the adhesion, during both the five minute breaks, in the deposits from the solutions containing 0.2 and 0.3 g/l benzotriazole.

A different, but allied, phenomenon is often found in the structure of bright electrodeposits. This is the codeposition of the addition agent in coarse or fine layers in the deposit and has been observed by Prall 71 and Kendall 68 in bright copper deposits from solutions containing benzotriazole, by Raub 142 in bright nickel deposits containing formalin and also with thiourea, and in silver with cyanide. Many theories have been proposed to explain this phenomenon of layering in deposits, including the supersaturation and delayed precipitation of the addition agent in the cathodic double layer. Another view is that in the diffusion layer at the cathode a critical concentration of the discharging ion and the addition agent has to be attained before each band is formed during deposition. In both mechanisms, the concentration of benzotriazole in the double layer decreases after the band has been formed and copper alone is then deposited. The thickness and distribution of these bands depend upon the concentration of addition agent in the solution and the plating conditions. It is not possible from observations in this work to decide which of the above suggestions applies in the formation of bands in the copper deposits from the solution containing benzotriazole, because either could be used to explain the decrease in density of the bands in a deposit from a solution in which the concentration of benzotriazole decreased during plating (see Figs. 5.7(f) and 6.5.7).

Surface Appearance of Deposits

Let us now consider, in the light of the above classical theory, the effect of benzotriazole in the solution on the surface appearance of the copper deposits, which should be influenced by the concentration of benzotriazole. Because benzotriazole is known to be chemisorbed on to copper surfaces, it is probable that the surface film formed on cathodic areas would hinder further electrodeposition at these areas. With low concentrations of benzotriazole (0.0001 g/l to 0.005 g/l), it can be argued that there is only partial coverage of the cathode and the additive is probably preferentially adsorbed on to the most prominent areas of the cathode, which are the pyramidal peaks, and there would be little or no adsorption at the recessed areas. Thus, if discharge at these peak sites is effectively blocked by adsorption, the depositing ions must discharge at other points on the sides of the pyramids. This means that growth is encouraged in a lateral, rather than a vertical direction, which
results in the production of flat platelets growing sideways until they meet. It would follow that this formation of flat topped crystals is encouraged by the presence of relatively large concentrations of benzotriazole in the solution and thus an increased adsorption, which indeed can be seen in Fig. 5.6 (1)(b) to (e) giving weight to the validity of the above assumptions.

It appears from the present experimental work that, with concentrations of 0.01 g/l benzotriazole and above, the shape of the growing particles became nodular and very different from the truncated pyramids obtained with lower additions. At these higher concentrations, it is probable that the surface is completely covered with adsorbed material which prevents epitaxial or "basis orientated" growth. This adsorbed surface layer effectively blocks the growth of the existing crystals and, for further discharge, nucleation of new crystallites must occur over the new surface. The new growth appears to be randomly orientated, or according to Fischer the "unorientated dispersion" type of growth. The size of the nodules again seems to be a function of the benzotriazole concentration and was very small at the lower concentrations but increased to a steady size with additions of 0.12, 0.2 and 0.3 g/l.

The copper deposits plated from solutions containing 0.12, 0.2 and 0.3 g/l benzotriazole were all very bright, which is probably due to the fact that the nodules on the surface were much flatter than those on the deposit from the solution containing 0.05 g/l, which were smaller and more irregular. At higher concentrations the surface became less bright and was covered with particles or precipitates which stopped light being reflected. It is not clear, without further work, why this type of surface should be produced. However, it is probable that any addition to the copper sulphate bath which promotes this type of nodular growth would lead to bright deposits, provided that surface precipitates did not form.

**X-Ray Analysis**

X-ray diffraction techniques have been used to indicate the grain size and the stress in electrodeposited metals and to investigate the effect of addition agents in the plating solution. In this work it was considered that the X-ray powder and backreflection methods could be used to examine the deposits from the plain bath and also from the bath containing 0.119 g/l benzotriazole, so that a comparison could be made between the photographs produced.
The deposits containing codeposited cuprous benzotriazolate gave diffuse X-ray diffraction lines in both the powder and the back reflection methods. It is generally considered that the formation of diffuse lines can be ascribed to several effects including:

(1) a very small grain size;
(2) a high internal stress;
(3) the heterogeneous distribution of a second phase.

Although the powdery deposits produced from the plain solution using a high current density had a fine grain size, the X-ray diffraction lines were quite sharp, so that this small grain size does not appear to result in line broadening. Because the dendritic shape of the crystals indicates growth under equilibrium conditions, these deposits are not considered to have a high stress, so the sharp X-ray lines observed can be considered to confirm the low stress.

The deposits from the bath containing 0.119 g/l benzotriazole gave broad X-ray lines that could be due to effects (1), (2) and (3). The work described in section 6.4.2 indicated that the deposits had a very fine grain size (mean intercept length 0.1 to 1.0 × 10⁻⁶ m) which could be expected to produce the diffuseness. However, according to Barrett and others, line broadening occurs only if the grain or particle size is less than about 10⁻⁶ m so this explanation is no longer considered. The deposits have been shown to have a high internal stress of the order of 50 MN/m² (see section 6.6.3) and this may be responsible for the line broadening. It is considered that the presence of cuprous benzotriazolate in the copper deposits can give lattice distortion and a widening of the X-ray lines, if it is in a heterogeneous state. Alternatively, if it is present as a solid solution or in another homogeneous form, it can produce a change in the lattice parameter. The fact that the benzotriazole appeared to be incorporated as layers in the deposit from the bath containing 0.119 g/l benzotriazole (see Fig. 5.7) means that it was not present in a homogeneous state, so that it should not produce any change in the lattice parameter. It can be seen from the X-ray photographs in Fig. 5.9 that no such change was produced. The line broadening with these deposits is, therefore, considered to be due to the presence of a high stress and/or the codeposited cuprous benzotriazolate.

In order to determine the cause of the line broadening in the deposits containing benzotriazole, a comparison was made between the X-ray pictures for these deposits before and after annealing in a vacuum for 3 hours at
300°C. The annealing temperature of 300°C was chosen because the differential thermal analysis work indicated that the copper benzotriazole complex was stable at this temperature. The observed reduction in the line diffuseness is considered to be due to neither an increase in the grain size, (because grain growth is not thought to occur at a temperature as low as 300°C and the grain size was initially too large \(^{295}\)), nor to a change in the codeposited cuprous benzotriazolate (effect (2)). Therefore, the decrease in line broadening is thought to be produced by a reduction in the internal stress in the deposits (effect (3)) and the residual diffuseness could be due to the codeposited benzotriazole.

The relief of internal stress in copper electrodeposits by a heat treatment at 300°C for three hours has been investigated experimentally. The deflection in a narrow cathode strip, plated on only one side with copper, was found to decrease during heating, so confirming the reduction in the stress found in the X-ray work (effect (3)).
7.4 Effect of Benzotriazole on some Properties of the Solution and Deposits

The presence of benzotriazole in the plating bath has been shown to increase the hardness and to change the stress of deposits, the actual magnitude of these changes being controlled by the composition of the bath and the plating conditions. Prior to this work the effect of these variables had not been determined systematically, as can be seen from the literature section 1.2.7.

In this discussion the effects of the various plating conditions on the properties of the solutions and the deposits from the plain bath are considered. The effect of the benzotriazole on the structure of the coating has already been investigated and discussed in section 7.3 and the modifications to the properties of the deposits are now discussed in the light of these new results.

7.4.1 Properties of the Plating Solution

Let us first consider the properties of the plain plating solution and then compare them with those of the solution containing benzotriazole. It has been established that during electrolysis, changes in the concentration of the bath and/or the production of hydrogen gas may have a direct bearing on the current efficiencies and both these effects have been studied because they may also affect the hardness and stress of the deposits. The throwing power of the plating solutions was measured under various experimental conditions, because it has a practical significance in the production of uniformly thick coatings in commercial plating.

Current Efficiency

In this work the current efficiency has been found to vary with the plating conditions and any theory regarding the physical nature of the deposits must account for the following observed facts. The cathodic current efficiency increased and then became steady as the concentration of copper sulphate was raised to 100 g/l (section 6.2.2) and also as the current density was raised to 215 A/m² at bath temperatures of 11°C, 27°C and 55°C (section 6.2.3). However, it increased steadily at a temperature of 77°C (section 6.2.3) but decreased at 3°C (section 6.2.4) as the current density was raised. It is worth noting that hydrogen was evolved during plating from the baths containing 10 g/l and 40 g/l copper sulphate (section 6.2.2) and powdery deposits were formed in solutions at 3°C with current densities of 215 A/m² and 430 A/m² (section 6.2.4). Ultrasonic agitation of the solution increased the limiting current density, decreased the
cathodic current efficiency at current densities below 130 A/m² and increased it above 130 A/m² (section 6.2.5). The cathodic current efficiency was low at low solution temperatures with current densities of 110, 215 and 430 A/m² (section 6.2.4), whereas the anodic current efficiency changed very little with variations in the copper sulphate concentration, except with 240 g/l when it was much lower (section 6.2.2).

Let us now consider these points in greater detail and see whether they conform to the known theories. There are two main reasons why the current efficiency is important and may affect the properties of the deposits. Firstly, a change in the concentration of copper ions in the plating solution does occur, if the anodic and cathodic current efficiencies are not the same, and this may modify the properties and, secondly, the production of hydrogen gas which often occurs with a low cathodic current efficiency may produce poor quality deposits as already discussed in section 7.3.1.

The change in the concentration of copper ions is usually undesirable, because some properties of the electrodeposits depend upon the bath composition and are difficult to control. Thus, if the copper sulphate concentration drops to about 70 g/l it leads to the production of poor quality powdery deposits. Hence, the regular addition of copper sulphate to the bath may be necessary to maintain the composition. The production of hydrogen gas may also encourage the formation of powdery deposits and, if the gas enters the lattice of either the copper or the substrate, it is considered that it can create internal stresses in the coating. However, the results shown in section 6.2.2 indicate that both these effects are minimized if the bath contains about 125 g/l copper sulphate and, therefore, they confirm the observation of Shreir and Smith²⁶² that a bath with 125 g/l copper sulphate gave the most reproducible results.

In cases where the cathodic current efficiency is less than 100% there must be some alternative reaction to:

\[
\text{Cu}^{2+} + 2e \rightarrow \text{Cu} \quad (1)
\]

Several other cathodic reactions can be postulated including:

\[
2\text{H}^+ + 2e \rightarrow \text{H}_2 \quad (2)
\]

\[
\text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^+ \quad (3)
\]

\[
\text{Cu}^{2+} + e \rightarrow \text{Cu}^+ \quad (4)
\]

\[
X \cdot \text{Cu} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}_x \overset{\text{H}_2\text{SO}_4}{\text{H}_2\text{SO}_4} \rightarrow \text{Cu}^{2+} \quad (5)
\]

At very low concentrations of copper sulphate, hydrogen evolution was
observed (section 6.2.2), so it can be presumed that under these conditions reactions (1) and (2) occurred simultaneously. As the concentration of copper ions was raised, reaction (1) became relatively much more probable and the evolution of hydrogen (2) decreased. The other conditions that favoured a low cathodic current efficiency were a low current density and a low solution temperature (sections 6.2.3 and 6.2.4). With current densities of 2.5 A/m² and 430 A/m², at a temperature of 3°C, powdery deposits were produced but no hydrogen evolution was actually observed, although it may have occurred since the solubility of hydrogen in the solution is higher and the rate of production of hydrogen is lower, as the temperature is decreased. It is difficult to ascertain which of the four reactions is responsible for the decrease in the current efficiency, because both cuprous and cupric ions are present and their relative concentrations depend upon the electrolyte conditions. However, all three reactions (3) to (5) may occur, but are not considered now because they probably do not influence the properties of the deposits in the same manner as the evolution of hydrogen (2).

The concentration of copper ions in the solutions containing low amounts of copper sulphate increased during the experiments because the anodic current efficiency was much higher than the cathodic current efficiency. Therefore, as plating proceeded, the concentration of copper ions, and consequently the cathodic current efficiency, increased. The low anodic current efficiency of the bath containing 240 g/l copper sulphate had little relative effect on the high concentration of copper ions during the period of these experiments.

At high current densities and low bath temperatures powdery copper deposits were produced and hydrogen was evolved (section 6.2.4). These deposits were of a poor quality and were produced only when the limiting current density was exceeded. Ultrasonic agitation of the plating solution increased the limiting current density and prevented the evolution of hydrogen (section 6.2.5), probably by reducing the cathodic double layer and consequently lowering the concentration polarization. Because the formation of powdery deposits has already been discussed in Section 7.3.1, it is not considered here. The main conclusions arising from this work, relevant in the electroplating of copper, are that hydrogen gas may be evolved during deposition, poor quality powdery deposits can be formed above the limiting current density and changes do occur in the concentration of the copper sulphate in the plating bath, under those conditions where the anodic and cathodic current efficiencies are different. This last
effect is usually only significant if the plating solution contains a very low concentration of copper sulphate, but is not important in the present work because plating occurred for a short time only and, therefore, produced very little change in the overall concentration of the electrolyte.

**Throwing Power**

Let us now consider the work on the throwing power of the copper sulphate-sulphuric acid plating bath and its dependence upon the plating conditions. The main changes which have been observed and will be discussed are that the throwing power was higher for still solutions than for ultrasonically agitated solutions (sections 6.3.2 and 6.3.4), decreased as the current density was raised in the ultrasonic bath (sections 6.3.2 and 6.3.4) and decreased as the temperature of the still bath was raised (section 6.3.3). However, for still solutions, the throwing power decreased at first, and then increased, as the current density was raised, with powdery deposits being formed at current densities of 290 A/m² and above (sections 6.3.2 and 6.3.4).

These results confirmed those found in the literature review (section 1.3.7) where polarization and current efficiency effects were used to account for these changes. It is considered that one effect of raising the current density in the Haring-Blum cell was to increase the concentration polarization, particularly at the cathode nearer to the anode; this higher polarization should result in more deposition at the other cathode, lower the metal distribution ratio and increase the throwing power. This was found to occur in both the still and the ultrasonically agitated solutions. Because ultrasonic agitation of solutions is known to reduce the concentration polarization, it can be used to produce good quality deposits at high current densities when powdery deposits are normally formed. Therefore, under these conditions ultrasonic agitation should raise the cathodic current efficiency and lower the throwing power, as indeed was observed in this work.

Because an increase in the bath temperature increases the ionic mobility and reduces the polarization, it should produce a decrease in the throwing power of a plating solution. In this work the throwing power has been found to decrease considerably with an increase in the solution temperature. This supports the above theory and confirms the results of Haring and Blum.

It may be concluded that, to produce good quality copper deposits in commercial plating, the best conditions for a high throwing power from the plain bath are a low current density and a low solution temperature;
unfortunately these conditions are not of commercial interest because of the slow rate of deposition.

**Effect of Benzotriazole on the Current Efficiency and Throwing Power**

In this work an addition of 0.12 g/l benzotriazole to the plating solution has been found to modify both the cathodic current efficiency and the throwing power and these effects are now discussed together.

In comparison with the plain bath, the presence of benzotriazole gave brighter deposits (section 6.2.2 and 6.2.6) and raised the limiting current density in the still bath (sections 6.2.6 and 6.3.4). It had virtually no effect on the cathodic current efficiency as

(1) the copper sulphate concentration was raised (except for the decrease with 10 g/l, see section 6.2.2), and

(2) as the current density was raised in the still and ultrasonically agitated solutions (except for an increase at 385 A/m$^2$, see section 6.2.6). However, benzotriazole lowered the throwing power at current densities up to 130 A/m$^2$ and increased it above 130 A/m$^2$ in both the still and ultrasonically agitated solutions (section 6.3.4).

As regards this part of the research no comparison can be made with previous results because there appears to be no published data on the effect of benzotriazole on either the cathodic current efficiency or the throwing power of this acid copper sulphate plating bath. The preferential adsorption of benzotriazole on the peaks of the cathode, where the current density is a maximum, has already been discussed (section 7.3) in relation to the production of level and bright deposits. On a macroscale, rather than a microscale, this adsorption should lead to more deposition on low current density surfaces and less on the high current density areas. This indeed is observed in section 6.3.4 with current densities above 130 A/m$^2$ and is manifest in a reduced metal distribution ratio and a higher throwing power than obtained with the plain bath. However, at relatively low current densities, this preferential adsorption probably does not occur to the same extent and other effects can become more important, such as the formation of the copper-benzotriazole complex which reduces the activity of the copper ions$^{79}$. Thus, at low current densities, the rate of deposition is slower and more formation of the complex can occur, resulting in less deposition and a lower throwing power, as found in section 6.3.4. The production of the complex reduces the concentration of copper ions and can account for the decrease in the cathodic current efficiency that is particularly noticeable in the solution containing only 10 g/l copper sulphate. At higher
concentrations the relative effect of the complex in reducing the concentration of copper ions appears to be insignificant.

7.4.2 Properties of the Copper Deposits from the Plain Bath

The values of the grain size, hardness and internal stress of the deposits from the plain bath have been carefully and systematically measured in this work, so that they could be analysed and examined for any relationship between the properties. It is intended to summarize and then discuss the results.

Grain Size

The grain size of copper electrodeposits was affected by the plating variables and increased as the bath temperature was raised (section 6.4.2), as the current density was lowered (sections 6.4.2 and 6.4.3) and as the solution agitation decreased (section 6.4.3). The grain size was not affected by purification of the solution (section 6.4.4).

Let us now consider how these results can be explained in terms of the existing theories.

From the literature survey on the grain size of electrod eposited metals (sections 1.3.1 and 1.3.2), it can be seen that the changes produced by variations in the bath temperature, current density and solution agitation appear to confirm the results of Butts and DeNora Nicol.

It is generally considered that nucleation and grain growth depend upon the mobility and concentration of the depositing ions (as discussed in section 7.3). Thus, as the bath temperature is raised, the mobility should increase and therefore the depositing ions become more able to move to existing nuclei and larger grains should form. As the current density is increased more ions should be deposited per unit area, resulting in less surface diffusion so that more nuclei would be formed and a smaller grain size should result. Agitation of the solution is thought to increase passivity of the cathode and may accelerate the delivery of foreign particles that can then act as nuclei on the surface, and both these factors should reduce the grain size of the deposit as concluded in section 7.3. It is interesting to note that the grain size does not appear to depend upon the purification which was carried out on the solutions: thus, the nucleation appears to be independent of the impurities removed by boiling, hydrogen peroxide, activated charcoal, filtration of pre-electrolysis.

Hardness

The hardness of copper deposits was affected by the plating variables and
increased with a reduction in the solution temperature (section 6.5.2), with an increase in both the current density (sections 6.5.2 and 6.5.3) and the solution agitation (section 6.5.3) and with an increase in the concentration of impurities (section 6.5.4).

From the literature on the hardness of electrodeposited metals (see sections 1.3.4 and 1.3.5), it appears that the theories proposed to explain the high hardness of deposits are based upon the effects produced by the lattice distortion caused by either occluded hydrogen \(^{138,179,185,231}\), or metallic oxides, or hydroxides, or surface active agents and other foreign matter \(^{179,184,226,227}\) and also the effect of a small grain size \(^{138,170,171,179,155}\). The hardness values obtained are in good agreement with those reported in the published literature (Tables 1.3.4 (a) and (b)). The results on the hardness of copper deposits from the plain bath suggest that the most probable of these theories is the one based on the grain size effect. Thus, factors which increased the grain size decreased the hardness and vice versa, so that raising the bath temperature, lowering the current density and increasing the solution agitation all produced a large grain size and a low hardness. However, Raub and Muller thought that a high hardness should not necessarily be ascribed to a small grain size, but that the factors which produce a small grain size can also give hard deposits, e.g. the presence of impurities may increase both the nucleation and the hardness. Since the results in this work show that purification decreased the hardness but did not affect the grain size, it follows that the grain size effect cannot be solely responsible for the hardness and that other factors such as the presence of impurities may also have a significant effect.

In order to investigate the quantitative relationship between the hardness of the copper deposits from the plain bath and the grain size, these parameters were plotted (Fig. 7.4(a)) and two curves with hyperbolic shape were obtained. The values were also plotted according to the:

1. Hall-Petch equation \(^{173}\) (Fig. 7.4(b));
2. Semi-logarithmic equation \(^{186}\) (Fig. 7.4(c)) and a computer was used to evaluate and draw the lines by applying the method of least squares. Although the semi-logarithmic equation appears to represent the relationship over the whole range slightly better than the Hall-Petch equation, it is proposed to discuss the latter, because the former gives only a mathematical relationship.

It is interesting to note that the Petch Equation has been applied to electrodeposited metals although it was originally produced for annealed
FIG. 7.4(a) DEPENDENCE OF HARDNESS ON GRAIN SIZE AT DIFFERENT CURRENT DENSITIES AND BATH TEMPERATURES.
FIG. 7.4(b) VARIATION OF HARDNESS WITH GRAIN SIZE
ACCORDING TO PETCH EQUATION \(H = H_0 + k_H d^{-1/2}\)
FIG. 7.4(c) VARIATION OF HARDNESS WITH GRAIN SIZE ACCORDING TO SEMI-LOGARITHMIC EQUATION $H = A + B \log_{10} d$. 
steel in a stress-free condition. However, in this work, the relationship appears to be obeyed only approximately because there is no straight line which can be drawn to give a good fit for all the points in Fig. 7.4(b). The deviation from the straight line may be due to the fact that the internal stress is high in deposits with a small grain size, whereas in deposits with a large grain size, the stress is very low.

It may be concluded that the main factors which affect the hardness of the electrodeposited copper from the plain acidic sulphate bath are the grain size effect, (or factors which affect the grain size), and the codeposition of impurities from the plating solution.

Internal Stress

The internal stress of copper deposited from the plain bath was always tensile in nature and depended upon the plating conditions. The tensile stress was found to decrease with an increase in the concentration of copper sulphate in the bath (section 6.2.2), the temperature of the solution (section 6.6.3), the solution agitation (section 6.6.9) and purification (section 3.7.1). The stress also increased as the current density was raised (section 6.6.4), but it was not affected by ageing either the solution (section 6.6.5) or the deposit (6.6.6), and it varied with the deposit thickness (section 6.6.7).

The various theories that have been proposed to explain the cause of the internal stress in electrodeposited metals have been discussed in section 1.3.3. It is generally agreed that the stressed condition results from a small volume change that may occur during, or soon after, the deposition, and an internal stress results if this volume change is restrained by the basis metal or the preceding layers of the deposit.

The chief problem in explaining the cause of the volume change in the deposit is to decide the cause of the initial unstable form of the deposited metal. There are many suggestions which may account for this unstable state and these include the existence of non-equilibrium conditions during deposition, the co-deposition of hydrogen or hydrides, the process of joining together isolated plated particles to form denser solids and the incorporation of foreign substances in a metastable form in the deposit. There are also theoretical reasons for the existence of this unstable state and these include the excess energy theory involving deposition at high local temperatures and the formation of lattice defects.

The stress values in deposits from the plain bath were always relatively
low and tensile in nature and were of the same magnitude as those given elsewhere. The results appear to confirm the previously reported correlation between a relatively high stress and deposition under non-equilibrium conditions. Thus, plating from a bath with a low concentration of copper sulphate, at a low solution temperature, a high current density and with a low solution agitation can be considered to occur under non-equilibrium conditions (with a high polarization) which are likely to produce a strained lattice.

The stress values obtained in this work do not appear to support the theory that the evolution of hydrogen during deposition can produce copper deposits with a high stress. Thus, the low cathodic current efficiency and evolution of hydrogen in solutions containing low concentrations of copper sulphate, reported in section 6.2.2, do not lead to a high stress in deposits (section 6.6.2). Similarly, other plating conditions that resulted in a low cathodic current efficiency do not correspond to those producing highly stressed deposits.

Deposition under non-equilibrium conditions, such as low temperatures and high current densities, may be considered to result in a smaller grain size with more lattice defects and perhaps a higher concentration of isolated plated particles and codeposited foreign matter than deposition under equilibrium conditions. No information about the excess energy theory can be obtained from the present results.

The fact that ageing the solution did not affect the stress in the deposits (section 6.6.5) indicates that there is no significant change in the plating solution during storage. The stress in the deposit from the plain bath did not change after the completion of plating (section 6.6.6). This suggests that the copper deposits were stable at the end of the plating and could not have changed significantly in volume, nor given off any gas or dissolved and been redeposited, all of which have been suggested to explain the stress after-effect (already discussed in Section 1.3.5). The fact that the stress varies with the deposit thickness (section 6.6.7) confirms previous work and may be due to the fact that the metal ions are being deposited on a cathodic surface which is continuously being deformed by bending.

The decrease in the tensile stress observed with purification of the plating solution (section 6.6.10) would tend to support the theory that the codeposition of impurities or foreign substances from the plating solution can increase the internal stress. However, the relative concentration and
nature of these impurities is important, because it is known that addition agents can increase the stress in either a tensile or a compressive direction.

These results do appear to confirm the previously observed relationship between a high tensile stress and a low grain size\textsuperscript{179-182} or factors which produce a small grain size.

7.4.3 Properties of the Copper Deposits from the Bath containing Benzotriazole

The object of this section is to compare and contrast the results obtained for deposits from the plain bath with those from one containing benzotriazole, produced under the same plating variables. The values of the grain size, hardness and internal stress of deposits from the bath containing 0.119 g/l (0.001M) benzotriazole have been carefully measured and examined for any relationship between the properties. It is now intended to summarize and then discuss the results.

**Grain Size**

The grain size of copper electrodeposits from the bath containing 0.119 g/l benzotriazole was very small, the mean intercept lengths being between 0.1 and 1 microns (section 6.4.2).

Let us consider the significance of the fact that the grain size of the deposits from the baths containing benzotriazole was found to be very small compared with deposits from the plain bath. This grain refinement has been observed previously with the use of many other addition agents\textsuperscript{96,126} and benzotriazole may be considered to act in the classical manner as described for other addition agents by Fischer\textsuperscript{126} and Vermilyea\textsuperscript{96}. Thus, benzotriazole appears to have two main effects:

(1) as it is adsorbed on the comparatively coarse grained copper substrate, it prevents epitaxial growth which would give a deposit with a large grain size;

(2) since it is adsorbed at the active nucleation sites with the lowest energy on the surface it raises the cathodic polarization and encourages deposition to occur at higher potentials with a faster nucleation rate.

Both these effects tend to decrease the grain size of the deposits, as was reported in the work with benzotriazole in section 6.4.2.

**Hardness**

The hardness of copper deposited from the bath containing benzotriazole was affected by the plating variables. In general, the deposits became harder with an increase in the current density (sections 6.5.2 and 6.5.3),
solution agitation (section 6.5.3), concentration of benzotriazole (section 6.5.5), storage time of solution (section 6.5.6) and with addition agents, the hardness increasing in the order triazole, benzotriazole, and naphthotriazole (section 6.6.10). On the other hand, the deposits became softer with an increase in the bath temperature (section 6.5.2), solution purification (section 6.5.4), the deposit thickness when a small volume of solution was used (section 6.5.7) and with time after the end of plating (section 3.6.6).

It is notable that the factors which increased the hardness of deposits from the plain bath have also been found to increase the hardness of deposits from the bath containing benzotriazole and in some cases to a greater extent. The actual increase in the hardness appears to rise with the concentration of benzotriazole in the solution up to a maximum which depends upon the plating conditions (sections 6.5.5 and 6.5.7). Since Prall has shown that the amount of benzotriazole codeposited with the copper increases with the concentration in the plating solution, it could be assumed that the hardness of the deposits increases as the concentration of benzotriazole in the coating increases. This fact is also in agreement with the theory that the hardness of a coating is controlled, to some extent, by the presence of codeposited foreign matter. It is interesting to observe that the storage of the benzotriazole solution prior to plating may allow oxidation to occur and this oxidized form of benzotriazole produces a greater hardness than the pure form, thus implying that the actual form of the included matter affects the hardness (section 6.5.6). The fact that naphthotriazole has been shown to give harder deposits and triazole softer deposits than benzotriazole (section 6.6.10) appears to confirm the theory that the hardness also depends upon the chain length of the additive.

The variation in the hardness of the plain deposits has been thought to result from the effect of the grain size, (and factors which affect the grain size, such as the deposition under non-equilibrium conditions), and the codeposition of impurities which together can account for the hardness range of about HV 70 to 160. However, it is worth noting that the deposits from the bath containing benzotriazole had a hardness of HV 310, and even HV 350 has been measured. These values are extremely high for copper but are of the same order as those reported elsewhere for other addition agents (Table 1.3.4(c)). In this case the increase in hardness caused by the benzotriazole appears to be due to the conjoint effect of:

1. a very fine grain size,
(2) the codeposition of cuprous benzotriazole in the deposit.

The former, with a relatively large volume of grain boundaries, would be expected to produce a high resistance to dislocation movement and slip. The latter effect is thought to cause dispersion hardening and distortion of the crystal lattice of the deposit.

In this work, there appears to be no evidence to support the other theories that have been proposed to explain the high hardness of deposits, including those involving the production of hydrogen, metallic oxides or hydroxides. However, these factors are probably very important in the deposition of metals such as nickel and chromium, in which the cathodic current efficiency can be very low.

The fact that there appears to be a maximum hardness for the copper deposits, above which cracking occurs, is of considerable commercial importance and it has been shown that the maximum value depends upon the plating conditions, such as the concentration of benzotriazole and the temperature of the bath. It also suggests that it is not possible to increase the concentration of codeposited cuprous benzotriazolate above a certain value and this means that there is a limit to the corrosion resistance produced by benzotriazole in the coatings, which, unfortunately, is not sufficiently high to give a significant improvement in performance.

It is interesting to note that, with the deposits plated from the bath containing benzotriazole, the hardness decreased (section 3.6.6) and the stress increased in a tensile direction (section 6.6.6), after the end of plating. Neither of these effects was observed in deposits from the plain bath, so it is assumed that these changes in the properties are produced by the same effect and linked to the codeposited benzotriazole.

These changes in properties of electrodeposits have been widely observed and theories to explain them have been discussed in the literature review (section 1.3.5). Because the hardness of plated copper decreased during storage of air, the electrolyte theory of Kushner is not valid in this work. The production of an internal stress in the copper deposited in this work does not appear to be related to the codeposition of hydrogen, so the theory of Nishihara et al is not applicable. Therefore, the remaining possible explanations include those of Vagramyan and Tsareva, who suggested the diffusion of surface atoms, Polukarov and Kuznetsov, who proposed an ordering or similar process in the lattice and Hoar and Arrowsmith, who suggested the change or movement of dislocations in the deposit.

Both the decrease in the hardness and the increase in the tensile stress
(or decrease in the compressive stress) could be explained by a reduction in the concentration of the codeposited benzotriazole (see sections 6.5.5 and 6.6.8). However, it is improbable that the codeposited cuprous benzotriazolate could diffuse out the deposit, but it may become less effective if it decomposes, is involved in some ordering process or if the distribution of the dislocations associated with it changes. By mechanisms such as these the hardness can be reduced and the stress increased in a tensile direction.

**Internal Stress**

The internal stress in copper deposited from the bath containing benzotriazole was affected to a considerable extent by the plating values. Thus, the stress could be tensile or compressive in nature and could change from one form to the other as the experimental conditions were altered. A change from a tensile to a compressive stress was observed in deposits when the concentration of copper sulphate in the solution was increased (section 6.6.2), when the bath temperature was raised (section 6.6.3) and when the concentration of benzotriazole in the plating solution was increased (section 6.6.8). However, a change in the opposite direction, from a compressive to a tensile stress, occurred as the current density was raised (section 6.6.4). In most cases the stress became more tensile as the solution was aged prior to plating (section 6.6.5), and always changed in a tensile direction after the completion of plating (section 6.6.6). It is interesting to note that the tensile stress in deposits from the plain bath became compressive when triazole was added to the bath, but with benzotriazole the tensile stress increased and became still higher when naphthotriazole was used (section 6.6.10).

The presence of benzotriazole in the plating bath has been shown to have a profound effect on the internal stress of the deposits which may be compressive or tensile in nature. Generally, it appears that factors which decrease the tensile stress in deposits from the plain bath, such as an increase in the concentration of copper sulphate, an increase in the bath temperature and a decrease in the current density, also reduce the tensile stress and may produce a compressive stress in deposits from the bath containing benzotriazole.

In the section on the cathodic current efficiency, the amount of hydrogen evolved from baths containing benzotriazole decreased as the concentration of copper sulphate in the bath increased (see section 6.2.2). Over the same concentration range of copper sulphate, the tensile stress in the deposits at first increased and then decreased. This suggests that the evolution of hydrogen was not a main factor in the production of the tensile
stress in these deposits.

Let us now consider the effect on the stress produced by varying the concentration of benzotriazole in the solution. It would be interesting to be able to correlate the concentration of benzotriazole in the plating solution with the amount of benzotriazole in the deposit and also the magnitude and sign of the resulting stress. Since Prall has shown that there is no direct relationship between the concentrations of benzotriazole in the solution and in the deposit, it is intended to attempt to correlate these concentrations separately with the internal stress.

It can be seen (Fig. 6.6.8) that, as the concentration of benzotriazole was raised, the tensile stress increased at first, then decreased to zero became compressive and then increased again gradually, in almost exactly the same manner as observed by Fedot'ev and Pzin who studied the influence of Rochelle salt in a copper plating bath and sodium naphthalene disulphonate in a nickel plating solution. This suggests that the benzotriazole and other addition agents can act in two different ways, depending upon their concentration. Thus, at low concentrations a tensile stress is increased, while a compressive stress is produced with larger additions. From these results it appears that with low concentrations of benzotriazole the main physical effect is the formation of a deposit with a finer grain size which has been associated with a higher tensile stress both in deposits from the plain bath (section 7.4.2) and in the literature. The formation of high compressive stresses in deposits plated from solutions containing high concentrations of benzotriazole is consistent with work done with other addition agents. The mechanisms suggested to account for the production of compressive stresses include the preferential adsorption of the molecules at surface vacancies, giving arrays of dislocations with a negative sign, or the action of the addition agent as a wedge, particularly at grain boundaries, putting a compressive force on the grains. Thus, in the light of these theories and the present work, one can visualize that, as the concentration of benzotriazole increased, the addition agent may be considered to produce a fine grained deposit and raise the tensile stress; then, at higher concentrations, to penetrate into the grain boundaries and weaken the tensile stresses and produced compressive stresses which increase with the concentration.

An attempt it now made to correlate the magnitude and sign of the stress with inclusion content of benzotriazole in the copper deposit, as determined by Prall and Shreir. In the experiment to study the effect of the concentration of benzotriazole in the solution, in which all the plating
conditions were fixed, there was a definite relationship between a high incorporation of benzotriazole and a high compressive stress. However, the results under different experimental conditions do not show a similar effect, as indicated by the fact that an inclusion content of about 5 mg benzotriazole/1 g copper deposit corresponds to a tensile stress of about 50 MN/m², when plated from a solution containing 30 g/l copper sulphate (see Fig. 6.2.2.(a)), and to a compressive stress of about 5 MN/m² when a temperature of 75°C is used (see Fig. 6.6.3). Therefore, it can be concluded that the concentration of included benzotriazole in the deposit is not the only factor which determines the internal stress.

The experiments, in which only one variable, such as the current density or temperature, was changed, are now discussed in relation to the concentration of incorporated benzotriazole and the corresponding stress. As the concentration of copper sulphate was raised (see section 6.6.2(a)), the benzotriazole inclusion increased and then decreased, while the tensile stress also increased and decreased before becoming compressive: this change in the stress has also been noted by Prall. Hence, under these conditions a high benzotriazole content in the deposit coincided with a high tensile stress. However, the bath temperature was raised (see section 6.6.3), the benzotriazole concentration in the deposits decreased and then increased while the stress was tensile, became compressive, reached a maximum and then fell to almost zero. Therefore, in this experiment a high concentration of benzotriazole corresponded to a high tensile stress (at low temperatures) and also to a low compressive stress (at high temperatures), while the maximum compressive stress occurred with the lowest benzotriazole content.

In another experiment, as the current density was raised (see section 6.6.4), the amount of benzotriazole in the deposit decreased gradually and the corresponding compressive stress decreased and became tensile. Hence the maximum benzotriazole content corresponded to the maximum compressive stress. It follows that in the experiments in which only one variable was changed at a time, there was no overall correlation between the concentration of codeposited benzotriazole in the deposit and the magnitude and sign of the corresponding internal stress, suggesting that some other factor must be predominant.

It may be concluded that, irrespective of the amount of codeposited benzotriazole, the factors that produce conditions tending to give a strain free lattice and a larger grain size in deposits from the plain bath, e.g. a high concentration of copper sulphate, a high bath temperature and a low current density, also favour the production of a compressive stress.
in deposits from the bath containing 0.119 g/l benzotriazole. The conditions producing a more strained lattice and a smaller grain size in deposits from the plain bath, e.g. a low concentration of copper sulphate, a low bath temperature and a high current density, give a high tensile stress in deposits from the bath containing 0.119 g/l benzotriazole. However, if all the plating variables are fixed and only the concentration of benzotriazole is changed, there is a general correlation between a low quantity of codeposited inhibitor and a tensile stress and between a high quantity and a compressive stress.
7.5 **FINAL DISCUSSION**

The scope of the present work can be subdivided into two main sections. In the first (Chapter 4), benzotriazole has been studied from the point of view of its corrosion inhibiting properties with regard to copper, and to a much smaller extent brass. The second part describes a study of the use of benzotriazole as an addition agent in the acid copper sulphate plating bath and has involved a consideration of its effects on the structure of the deposits (Chapter 5) and on the properties of both the solution and the deposits (Chapter 6).

In the light of the present work benzotriazole is considered to be strongly adsorbed on to the surface of copper, when the copper is immersed in an aqueous solution of benzotriazole. Once formed this surface film produces good corrosion inhibition when immersed in corrosive solutions, in aggressive atmospheres and in air, at temperatures up to 350°C. This benzotriazole film is also formed on the electrodes in the copper plating solution containing benzotriazole as an addition agent; it can result in both poor adhesion between the cathode and the copper deposit and poor cohesion within the coating, particularly if the current is switched off and then on again during plating. It has been shown that, when 0.0001 g/l to 0.0005 g/l benzotriazole is used in the bath, preferential adsorption occurs at the higher current density areas on the growing crystals, which has the effect of inhibiting further growth, so encouraging deposition in the recesses and other areas of lower current density; the result of this is to raise the microthrowing power and produce the beneficial effect of a more level surface. With higher concentrations of benzotriazole adsorption appears to occur over the whole cathode surface and subsequently deposits form on top of this film giving a bright and nodular type of growth. When a cross-section is examined, these deposits have a banded or layered appearance with parallel banding probably consisting of copper rich and benzotriazole rich layers. The presence of the benzotriazole in the deposit has been shown in this research to have a marked effect on the physical properties of the copper coating by decreasing the grain size, raising the hardness and changing the internal stress. The actual magnitude of these properties of the deposits depend upon the concentration of the benzotriazole in the solution, the composition of the solution and the plating conditions, such as bath temperature, current density and solution agitation.
7.6 CONCLUSIONS

The present research on corrosion inhibition has shown that:

1. Benzotriazole is an effective inhibitor (with an efficiency of over 90% when 1g/l is used) for copper and brass in many acidic, neutral and alkaline solutions, but is not satisfactory for solutions containing oxidizing and complexing agents;

2. Benzotriazole is slightly better than naphthotriazole and much better than triazole as an inhibitor in preventing immersed corrosion and atmospheric tarnishing of copper;

3. Benzotriazole appears to act as a weak buffer during corrosion of copper in many aqueous solutions;

4. A very stable surface film is formed between copper and benzotriazole, which is probably produced by chemisorption, and this film imparts increased resistance to corrosion in many environments.

The work on electrodeposition from the copper sulphate sulphuric acid plating bath has established that:

1. There is a correlation between a small grain size, a high hardness and a high tensile stress, or the factors which control these properties, in copper electrodeposits;

2. The ultrasonic agitation of the plating solution increases the limiting current density, reduces the cathodic current efficiency at low current densities and increases it at high current densities, lowers the throwing power, increases the hardness and reduces the stress in electrodeposits;

3. The formation of hydrogen gas does not appear to produce a tensile stress in copper deposits.

The study of electrodeposition from the plating bath containing benzotriazole has shown that:

1. Benzotriazole changes the nucleation process;

2. A highly reflective coating can be produced when specific plating conditions are used;

3. Benzotriazole reduces the adhesion of the coating to the cathode and also the cohesion in the deposit;

4. The surface topography, structure and brightness of the deposit depend upon the concentration of benzotriazole in the bath;
5. Benzotriazole decreases the grain size, increases the hardness and modifies the stress in the deposits, compared with those from the plain bath;

6. Plating conditions which produce a high tensile stress in deposits from the plain bath favour the formation of higher tensile stress in deposits from the bath containing benzotriazole, whereas conditions which give a low tensile stress in deposits from the plain bath tend to give compressive stress when benzotriazole is present;

7. As the concentration of benzotriazole in the bath increases, the deposits become harder and then crack, while the tensile stress initially increases, then decreases, becomes compressive and finally increases steadily;

8. The concentration of cuprous benzotriazolate in the copper deposit is not the major factor in determining the magnitude and sign of the internal stress;

9. Ageing or storage of the solution prior to plating increases the hardness and makes the stress in the deposits more tensile;

10. Ageing the deposit after plating decreases the hardness but changes the stress in a tensile direction;

11. The molecular size of the addition agent increases the stress in a tensile direction and also raises the hardness in the order triazole, benzotriazole and naphthotriazole.

Furthermore, benzotriazole appears to possess most of the properties of addition agents suggested by Brown in 'The Encyclopedia of Electrochemistry'.
7.7 RECOMMENDATIONS FOR FURTHER WORK

The following suggestions should prove useful in elucidating the mechanisms of benzotriazole when used as a corrosion inhibitor and also as an addition agent.

1. The determination of the form of benzotriazole in an aqueous solution and the mechanism and capacity of the buffering action during the corrosion of copper.

2. The determination of the corrosion efficiency and stability of benzotriazole in aqueous solutions as a function of temperature.


4. The use of Surface Electron Spectroscopy (ESCA) to study the bonding at the copper-benzotriazole surface and to confirm that it is due to chemisorption.

5. The use of the Geoscan to examine the bands in the structure exposed by cross-sectioning the layered deposit for nitrogen or carbon peaks.

6. The use of the electron microscope to measure the dislocation density in very hard deposits, in an attempt to correlate the dislocation density with the hardness.

7. The investigation of another addition agent to be used with benzotriazole, to facilitate the production of good quality, bright coatings which are not brittle; this could be done in the same manner as in nickel plating, where one addition agent gives a bright, brittle coating but is used jointly with another which has the effect of reducing the stress and the brittleness to acceptable levels.
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STRESS IN COPPER ELECTRODEPOSITS MADE WITH BENZOTRIAZOLE AS ADDITION AGENT*

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Abstract—The effect of M/1000 benzotriazole in an acid copper sulphate bath has been investigated. Measurements of the internal stress and the microhardness in copper electrodeposits were taken. The deposits were bright and had a high internal tensile stress and a higher microhardness than that obtained with other addition agents. An ageing effect and a stress after-effect were also observed.


INTRODUCTION

The use of benzotriazole C_6H_4-NH-N=N as a specific inhibitor for the corrosion of copper and copper-based alloys is well known. It can be used as an addition agent to acid copper sulphate plating baths to give fully bright coherent copper electrodeposits. It was one of the first examples of a known corrosion inhibitor to be deliberately introduced into an electrodeposition; Prall found it was deposited in the form of cuprous benzotriazolate. This codeposition was studied further because inclusions in an electrodeposit normally decrease the corrosion resistance.

Measurements were made of the internal stress and the microhardness of copper deposits with and without benzotriazole as an addition agent to the plating bath. The internal stress in an electrodeposit is important because it may affect the corrosion, fatigue and corrosion fatigue properties of the basis metal. It may cause deformation of the article plated, which is important in electroforming, and also peeling of the deposit if the adhesion is poor.

EXPERIMENTAL TECHNIQUE

Analar chemicals were used, for 0.5 M copper sulphate, 0.5 M sulphuric acid solutions, with and without 0.001 M benzotriazole (0.119 g/l). The solutions were magnetically stirred at room temperature. The cd was 20 A/f².

Stress measurements were made using the Brenner-Senderoff contractometer with the modifications suggested by Fry and Morris. The stainless steel helix was coated with nickel and copper from a cyanide bath to provide a base with good adhesion for the copper deposit from the acid bath. This instrument measured the stress on a continuously bending cathode. Measurements of the stress were also

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taken using a modified form of the Hoar-Arrowsmith apparatus. The cathode used was a platinum-10% iridium alloy strip flashed with copper from the cyanide bath. This gave stress measurements for deposits on a cathode which was prevented from moving by an applied electromagnetic force. The microhardness of the deposits was measured with a G.K.N. Microhardness Tester.

**RESULTS**

*Stress and microhardness*

Figures 1 and 2 show deposit thickness plotted against the restoring force, measured with the contractometer and the modified Hoar-Arrowsmith apparatus. These graphs show that the stress is tensile in both deposits and that in the deposit with benzotriazole is more than twice as high as that in the pure deposit. Kushner has measured the stress in a pure copper deposit from a copper sulphate bath using his Stresometer and found a stress, at a thickness of $5.6 \times 10^{-4}$ in, of 2510 psi. The present stress values for pure copper deposits measured by the different techniques were 2720 psi with the Hoar-Arrowsmith null method, 2800 psi with the contractometer on a moving helix and 2510 psi on a clamped disk in the Stresometer, which show good agreement.

![Graph 1](image1.png)

**Fig. 1. Stress measured by Brenner-Senderoff contractometer.**

![Graph 2](image2.png)

**Fig. 2. Stress measured by Hoar-Arrowsmith null method.**

The presence of benzotriazole also increased the tensile stress in plating solutions made from commercial salts.

Figure 3 shows that, in some cases, the initial stress in deposits with benzotriazole
Stress in copper electrodeposits made with benzotriazole

is compressive and changes to a tensile value; this effect has also been observed in chromium deposits on nickel.\textsuperscript{24,25} This change from compression to tension is influenced by certain variables including the pretreatment of the cathode and the time period between the immersion of the cathode in the fresh benzotriazole solution and the actual deposition. Thus the effect of the benzotriazole on the resultant stress in the copper deposits changes as the time of immersion increases. A similar ageing effect has also been observed by Vagramyan and Petrova\textsuperscript{26} with a copper sulphate solution containing naphthalene disulphonic acid: a freshly prepared solution gave lower internal stresses than those from a solution which had been stored for a year. The proposed explanation for this was that the addition agent oxidized during the storage and the oxidation products were more active than the original additive. Benzotriazole may behave in a similar manner.

The stress in the electrodeposit containing benzotriazole continued to increase after the current had been switched off; this is known as the stress after-effect. With the pure copper deposit there was no such increase but with benzotriazole the stress increased by about 900 psi, as shown in Fig. 4. Kushner\textsuperscript{22} has measured the stress after-effect and found that it varied from a decrease of 9 to 17\% in the compressive

![Diagram](image_url)

**Fig. 3.** Effect on stress of immersion time prior to plating.

![Diagram](image_url)

**Fig. 4.** Stress after-effect.
stresses in copper deposits from a solution containing thiourea, to an increase of 2 to 7% in the tensile stresses in nickel deposits.

The deposits with benzotriazole appeared to be harder and more brittle than the pure deposit, as shown in Fig. 5. Very thick deposits were produced on a copper foil base and the average of five microhardness values was 102 V.H.N. for pure copper and 374 V.H.N. for the deposit with benzotriazole: other workers quote similar values for pure copper deposits of 100 V.H.N., 60 to 100 V.H.N. and 51 to 80 V.H.N.

**X-ray examination**

Back-reflexion photographs were taken using filtered copper radiation and an 'Astbury'-type exposure mask used on the front side of the cassette. Figure 6 shows the {331} and {420} diffraction lines of the copper foil base F, the pure copper deposit A and the copper deposit containing benzotriazole B. Powder photographs were also taken to give accurate values for the three lattice parameters. The lattice parameter of the copper foil base was 3.629 Å (higher than the value normally quoted for pure copper, 3.6147 Å, which suggests impurities in the foil) and the value for the pure copper deposit was 3.613 Å. The parameter for the deposit containing benzotriazole appears to be smaller than that for the pure deposit, but could not be measured because of the diffuseness of the X-ray diffraction lines.

The pure deposit and the foil both gave sharp lines with the high angle doublets clearly resolved, indicating a low or zero stress. However the deposit with benzotriazole produced slightly displaced diffuse lines: this could be due to a small grain size and/or a stressed condition and/or codeposited cuprous benzotriazolate. The deposits were compared under a microscope, Fig. 7. Although the crystallographic appearance of these is different, the deposit with benzotriazole did not appear to have a smaller grain size than the pure deposit, so that small grain size was not the cause of the line diffuseness.

Prall, using a similar solution, found the ratio of the weight of benzotriazole included in the deposit to the weight of copper deposited was 0.0023:1. He also found that the cuprous benzotriazolate was included in the deposit as a layered structure and not as a solid solution; this is confirmed by Fig. 8 which shows this layered deposit. Hence this addition would not give the displacement of the X-ray lines observed. Therefore the broadening and the displacement of the X-ray diffraction lines are attributed to the stress in the deposit. The addition agent could give a separate pattern of X-ray lines but, with such a small quantity present, it is not likely that these lines would be seen on the photograph.

The line displacement is probably due to a homogeneous elastic deformation which causes all the interplanar spacings to change by a similar amount and so the lattice parameter is also changed. This first-order stress can be measured by mechanical methods. The line broadening is due to heterogeneous plastic deformation which varies between different grains and the diffuseness is due to the superimposition of many lines with different displacements; this second-order stress cannot be measured by mechanical methods.

**DISCUSSION**

An addition of 0.119 g/l of benzotriazole to acid copper sulphate baths has been shown to give hard copper electrodeposits, 374 V.H.N., harder than those produced by
Fig. 5. Copper electrodeposits (a) without and (b) with benzotriazole. ×4 (original).

Fig. 6. Back reflection X-ray photograph. F, foil; A, pure deposit; B, deposit with benzotriazole.
Fig. 7. Copper electrodeposit (a) without and (b) with benzotriazole. ×500 (original).

Fig. 8. Copper electrodeposit with benzotriazole. Cross section ×500 (original).
Stress in copper electrodeposits made with benzotriazole

other copper plating baths, eg fluoborate 40 to 75 V.H.N., pyrophosphate 160–190 V.H.N., cyanide 100 to 160 V.H.N. and cyanide with periodic reversal 150–220 V.H.N. Other addition agents may be used with various sulphate baths to increase the deposit hardness, eg naphthalene disulphonic acid (0.5 g/l of the sodium salt) 160 V.H.N.,26 sugar (20 g/l) 146 V.H.N.,26 gelatine (0.01 g/l) 134 V.H.N.,30 thiourea (0.015 g/l) 248 to (0.2 g/l) 340 V.H.N., citric acid (2.34%) 275 to 299 V.H.N.30 and tartaric acid (1.24%) 195 to 278 V.H.N.30

The internal stress in the deposits, produced under the present experimental conditions, is tensile and fairly high, 6200–7200 psi. Typical stress values for deposits from other copper plating baths include cyanide 5800–14,700 psi, pyrophosphate 10,000 psi (compressive); fluoborate is similar to sulphate, 0–3000 psi. However the stress depends upon many variables, eg bath composition, cd, temperature, addition agents etc; these variables may change the sign of the stress. Prall found that by changing the concentration of copper sulphate from 60 g/l to 190 g/l, in a bath containing 0.5 M sulphuric acid and 0.001 M benzotriazole, the stress changed from tensile to compressive. Tsareva et al. observed that when the cd was increased above about 42 A/ft² the stress in a copper deposit from a sulphate bath containing 0.6 g/l of thiourea changed from compressive to tensile. Vagramyan and Petrova found a change in the stress from tensile to compressive when the concentration of thiourea was increased to above 0.26 g/l in an acid copper sulphate bath.

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STRESS IN COPPER ELECTRODEPOSITS 
FROM THE SULPHATE BATH*

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Abstract—The effect of different concentrations of copper sulphate in the acidic copper sulphate 
bath on the internal stress and hardness of the resulting deposits has been investigated. The use of 
benzotriazole, as an addition agent to this bath has also been studied. The internal tensile stress 
decreases as the concentration of copper sulphate in the bath is increased, and for solutions con­ 
taining benzotriazole a change from tensile to compressive stress is found. 

Résumé—Etude de l'effet de différentes concentrations en sulfate de cuivre dans un bain acide de 
sulfate de cuivre sur la tension interne et la dureté des dépôts formés. L'utilisation du benzotriazole, 
comme agent additif dans ce bain a aussi été examinée. La tension interne de contrainte décroît 
quand la concentration en sulfate de cuivre dans le bain augmente et pour des solutions contenant du 
benzotriazole la contrainte de tension se transforme en contrainte de compression. 

Zusammenfassung—Der Einfluss der Kupfersulfatkonzentration in sauren Kupfersulfatbädern auf 
die innern Spannungen und die Härte der abgeschiedenen Niederschläge wurde untersucht. Zudem 
wurde die Verwendung von Benzotriazol als Zusatzstoff in diesen Bädern untersucht. Die interne 
Zugspannung nimmt mit steigender Kupfersulfatkonzentration in der Lösung ab, bei Verwendung 
von Benzotriazol findet ein Übergang von Zug- zu Druckspannung statt. 

INTRODUCTION 
The internal stress in an electrodeposit depends upon many variables, including 
the bath composition, pH, temperature and cd. Lamb and Valentine\(^1\) showed that, 
for copper deposits from the copper sulphate-sulphuric acid bath, the tensile internal 
stress increased with cd, and decreased with increase in the bath temperature. When 
the solution composition was changed, the evidence was conflicting. Graham and 
Lloyd\(^2\) found a decrease in the stress in the copper deposit from the cyanide bath with 
increasing concentration. The concentration effect has also been studied for other 
metals. In zinc deposits\(^3\) a decrease in compressive stress has been found from the 
zinc sulphate bath with increase of concentration, and for cobalt\(^4\) an increase followed 
by a decrease. Martin\(^5\) found no appreciable effect in nickel deposits and Brenner 
et al\(^6\) found a very small effect from the nickel chloride bath. 

EXPERIMENTAL TECHNIQUE 
Commercial purity chemicals were used and all plating solutions contained 
49 g/l (0.5 M) sulphuric acid. Magnetic stirring was used in all cases to allow mixing 
of the solution and to reduce polarization but was sufficiently slow to prevent aeration. 
The solutions were at room temperature and 20 A/ft\(^2\) was passed for 15 min, which 
produced a deposit thickness of about 3 \(\times\) 10\(^{-4}\) in. An addition of 0.001 M benzotriazole \((\text{C}_6\text{H}_4\text{NHN}:\text{N})\) was made to the bath: this has been shown to improve the 
appearance of the resulting deposits and also to improve the corrosion resistance of 
the resulting copper deposit.\(^7,8\) 

* Manuscript received 31 October 1968.
Current efficiencies were investigated by weighing the anode and cathode before and after plating, for different copper sulphate concentrations both with and without benzotriazole. A steady current equivalent to about 20 A/ft², was passed for 15 min through a series of cells.

The hardness of the electrodeposits was measured with a G.K.N. Microhardness Tester. This required thick deposits, produced by plating for 3 h.

Internal stress was measured with a Brenner-Senderoff Spiral Contractometer with the modifications of Fry and Morris. The change in the stress during plating and after the current had been switched off (the stress “after effect”) was measured.

**RESULTS**

**Current efficiency**

The cathodic current efficiency of the more concentrated solutions (150 g/l and over) was ca 96-100%. At lower concentrations of copper sulphate (10 to 50 g/l) hydrogen was evolved and a lower current efficiency resulted. Benzotriazole in solutions with low copper sulphate concentration gave a further reduction in the current efficiency.

**Hardness**

The hardness of the copper deposits depended on the concentration of copper sulphate. Benzotriazole increased the hardness significantly, whereas stirring gave a slight decrease. The appearance of these deposits is shown in Fig. 1.

<table>
<thead>
<tr>
<th>Concentration CuSO₄·5H₂O g/l</th>
<th>Average Hardness VPN(unstirred)</th>
<th>“Pure” deposit Unstirred</th>
<th>Deposit with benzotriazole Unstirred</th>
<th>Stirred</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>(powdery)</td>
<td>207</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>104</td>
<td>303</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>58</td>
<td>237</td>
<td>224</td>
<td></td>
</tr>
</tbody>
</table>

**Stress**

All the deposits from solutions without benzotriazole had a dull matt appearance and good adhesion to the helix. The stress decreased with increase in the concentration of copper sulphate, Fig. 2. No stress “after effect” was observed.

The stress in deposits from the bath containing benzotriazole increased in the tensile direction at low copper sulphate concentrations and reached a maximum at about 47 g/l CuSO₄·5H₂O; it then decreased and became compressive, reaching a steady value at about 140 g/l, Fig. 3.

The stress changed in the tensile direction after the current had been switched off in all deposits containing benzotriazole. This “after effect” reached a constant value at about 160 g/l of CuSO₄·5H₂O, Fig. 4. The variation of the spiral deflection with the deposit thickness and the “after effect” are shown in typical curves, Figs. 5 and 6, with and without benzotriazole.

**DISCUSSION**

**Current efficiency**

The production and adsorption of hydrogen has been found to increase the hardness and also the internal stress of the electrodeposit. The normal deposition
Fig. 1. Copper electrodeposits. a—Pure deposit, 140 g/l CuSO₄·5H₂O, b—47 g/l + benzotriazole, c—140 g/l + benzotriazole, d—280 g/l + benzotriazole.
Fig. 7. Copper electrodeposits with benzotriazole. Cross section (a) ×160, (b) ×800.
Stress in copper electrodeposits from the sulphate bath

Process may be affected by the presence of hydrogen and, at very low concentrations of copper sulphate, spongy deposits may form.

**Hardness**

The presence of benzotriazole, a corrosion inhibitor for copper, increased the microhardness of copper deposits but not to the same extent as previously observed with Analar solutions. This increase in the hardness is probably due to the codeposition of cuprous benzotriazolate with the copper. A layered structure is formed Fig. 7, and inclusions increase the hardness by restricting the movement of dislocations. The solution that was magnetically stirred gave deposits with a slightly lower hardness than the unstirred: this could be due to more even deposition and a better deposit, which would favour a lower hardness.
The hardest deposit had the maximum reflectivity and the softest deposit had the lowest, Fig. 1.

**Internal stress**

The decrease in the internal stress in “pure” deposits with an increase in the concentration of copper sulphate appeared to follow a logarithmic law, Fig. 8. The stress values were lower than those produced in thicker deposits from Analar solutions. This reduction in the tensile stress when impurities are present has been observed in copper-plating solutions by Lyzlov and Samartsev. Hoar and Arrowsmith have suggested that tensile stress in a deposit is caused by
Surface vacant sites which give an array of edge dislocations of similar orientation. Impurity molecules, which are adsorbed on the growing surface, give edge dislocations of the opposite sign, or cause grain boundaries, both of which create compressive stresses.

At low concentrations of copper sulphate, in the solution containing benzotriazole the deposits had a high tensile stress, and the current efficiency was lower than the normal value of 96-100%. This tensile stress could therefore be due to the presence of hydrogen in the metal lattice. The hydrogen, which is codeposited with the metal, causes a lattice expansion: when the hydrogen diffuses away the lattice contracts and a tensile stress results. This theory has been proposed for many electrodeposits including nickel, chromium, iron and cobalt.

At higher concentrations of copper sulphate, with benzotriazole the stress becomes compressive. This change in the type of internal stress with an increase in the copper sulphate concentration was also observed by Prall. The production of compressive stress can be explained by the adsorption of the benzotriazole during plating.

Benzotriazole in copper sulphate solutions shows an ageing effect, i.e. its effect depends upon the immersion time prior to plating: a similar effect has been observed for naphthalene disulphonic acid in copper sulphate solutions. The benzotriazole solutions used in these experiments were freshly made and plating was started immediately, so a maximum compressive tendency should be present.

A change in the internal stress after plating had ceased was observed only in deposits from baths containing benzotriazole. This stress “after effect” changed the stress in a tensile direction in all cases, i.e. a tensile stress increased and a compressive stress decreased, Fig. 3. This effect has also been observed for electrodeposited nickel, chromium, and zinc. Kushner using a copper sulphate bath containing thiourea found the change in the stress increased as the compressive stress increased. In this work the stress “after effect” was found to increase as the stress became more compressive.
compressive with the copper sulphate concentration, Fig. 3; the values obtained were larger than those previously observed.

Kushner has suggested that the "after effect" may be due to dissolution and redeposition which occurs after the current has been switched off. The solution in the diffusion zone close to the metal surface is depleted in copper ions compared with the bulk composition of the bath and so a concentration cell is formed. Hence the recessed areas and grain boundaries become anodic and areas proud of the surface are in the bulk solution and become cathodic. Kushner associates the adsorption of impurity molecules with grain boundaries and compressive stress and so dissolution of these areas, together with foreign matter, reduces the compressive stress. This reduction increases as the compressive stress increases and is lower in deposits with tensile stress which have lower impurity concentrations.

Acknowledgements—The authors wish to thank Professor M. B. Waldron for his interest and for the provision of research facilities at the University of Surrey.

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Stress in copper electrodeposits from the sulphate bath

SHORT COMMUNICATION

THE EFFECT OF BENZOTRIAZOLE ON THE HARDNESS
OF COPPER ELECTRODEPOSITS*

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INTRODUCTION

It has been widely reported that the hardness of copper deposits from the acid sulphate plating bath increases with current density\(^1,2\) and ultrasonic vibrations\(^3\) and decreases with the bath temperature\(^1,2,4\) and purification.\(^4\) This paper reports on the effect of these variables on the hardness of copper deposits from a bath containing benzotriazole.

The presence of addition agents in a plating solution normally increases the hardness of deposits, eg with an addition of 0.10 g/l of gelatine,\(^5\) the hardness changes are 99–215 VHN and 150–305 VHN at 18.6 A/ft\(^2\) and 92.9 A/ft\(^2\) respectively, while for thiourea\(^6\) they are from 100 (no addition) to 248 VHN (0.015 g/l) and 270 VHN (0.2 g/l). As the concentration of the addition agent increases, the hardness rises and may reach a maximum value, eg thiourea\(^7\) gives 340 VHN with 0.2 g/l and 300 VHN with 0.7 g/l depending upon experimental conditions, and Rochelle salt\(^8\) gives 263 VHN with 0.02 g/l. The hardness increases with cd\(^5\) from 99 (18.6 A/ft\(^2\)) to 150 VHN (92.9 A/ft\(^2\)) and decreases with increase of temperature from 215 (25°C) to 140 VHN (50°C).

The addition of benzotriazole to the acid sulphate bath has been found to give bright coherent deposits.\(^9–13\) These deposits are harder and more stressed than those from the plain bath and tend to crack.\(^10–14\) Kendall,\(^12\) using a purified bath, found that hardness increased with concentrations of benzotriazole to a maximum value of 207 VHN with 0.06 g/l at 25°C: the brightest deposit was produced with an addition of 0.24 g/l.

The grain refining of the surface and the production of a banded structure have been observed on cross-sections of deposits with benzotriazole.\(^9–12\) An ageing effect, ie a change in the stress depending on the time of immersion or storage of the solution, has been observed in several copper baths containing naphthalene disulphonic acid,\(^15\) thiourea,\(^16\) and benzotriazole:\(^10\) the effect of ageing on the hardness of the last-mentioned compound has not previously been investigated. A self-annealing effect, ie a reduction of the hardness of a deposit with time at room temperature, has been observed\(^17\) in a fall from 225 to 145 VHN in 100 days with copper from a bath containing β-naphthoquinoline.\(^18\)

EXPERIMENTAL TECHNIQUE

General grade chemicals were used for the bath with 0.5 M copper sulphate (125 g/l CuSO\(_4\)-5H\(_2\)O) and 0.5 M sulphuric acid (49 g/l), both with and without * Manuscript received 10 August 1970.
benzotriazole. Purification of the solution consisted of refluxing with hydrogen peroxide (10 ml of 100 vol%), the addition of activated charcoal (20 g/l) and again refluxing and stirring, filtration with glass wool and pre-electrolysis with Analar copper anodes for several hours. One litre of solution was used for each run with slow magnetic stirring. Unless otherwise stated, 0.119 g/l benzotriazole was added to the plating bath immediately before each experiment to minimize the ageing effect. The cathodes used were 0.1 in. thick to provide a firm base for the hardness measurements, and the plating time and cd were adjusted to give a deposit thickness of approximately $2 \times 10^{-8}$ in.

Measurements were taken on an Akashi microhardness tester with a 50-g load so the indentation depth was less than 5 per cent of the total deposit thickness; readings were taken immediately after plating to minimize any stress relief. The values given are an average of at least 7 readings, which were taken on the central region of the cathode before and after lightly polishing the surface. Others were taken on the mounted cross-section of the deposit.

A maximum of six cells were connected in series with a fixed cd and a variable bath temperature. Ultrasonic vibrations were produced by immersing the plating cells in an ultrasonic tank and cold water was passed through copper coils to prevent the temperature rising: the other baths were either magnetically stirred or were damped by standing in an anti-vibration padding. The ageing effect was studied by making a large volume of solution containing 0.119 g/l benzotriazole: this was sealed, stored and used at different time intervals up to 30 days.

**RESULTS**

**Appearance**

The surfaces of the specimens plated under different conditions of solution agitation, both with and without benzotriazole, are shown in Fig. 1. The plain deposits had a matt surface, whereas most of those with benzotriazole were bright, and cracked during, or soon after, plating. Ultrasonic vibration improved the surface of the deposit by reducing the powdery area and decreasing the extent of cracking. The microstructure of the deposits (Fig. 2) showed that the specimens plated with ultrasonic vibrations had the finest structure. The grain sizes of deposits from the plain bath varied from 30 to 0.7 μm and those from the bath containing benzotriazole were much smaller, less than 0.1 μm.

The cross-sections of the deposits (Fig. 3) from the plain bath show that, as the degree of agitation was increased from still to ultrasonic, the surface smoothness improved. The deposits with benzotriazole had a very different appearance and the degree of layering increased with agitation.

**Hardness**

The hardness of the deposits from the plain stirred bath decreased with the bath temperature from 110 at 0°C to 75 VHN at 80°C (Fig. 4) and increased with the cd from 77 for 5 A/ft² to 141 VHN for 60 A/ft² (Fig. 5). Ultrasonic vibrations increased the hardness Fig. 5 (still 120, stirred 141 and ultrasonics 161 VHN, for 60 A/ft² at 23°C) and purification reduced it from 130–84 VHN for 40 A/ft² at 23°C (Fig. 6). Deposits with a high hardness had a small grain size and *vice versa*.
Fig. 1. Effect of electrolyte motion on the deposit surface.
23°C. Magnification ×2/7.
Fig. 2. Effect of electrolyte motion on the microstructure.
20 A/ft², 23°C. Magnification × 80.
Fig. 3. Cross-sectional microstructure of copper deposits. 40 A/ft², 23°C. Magnification × 250.

Fig. 8. Surface of deposit from stirred bath with 1 g/l benzotriazole. 40 A/ft², 23°C. Magnification × 80.
Fig. 4. Effect of temperature on microhardness of copper electrodeposits.
- No BTA, × with BTA.

Fig. 5. Effect of benzotriazole on microhardness of copper electrodeposits.
△ ○ No BTA, ▲ • with BTA.
These plating variables had a more marked effect on the hardness of deposits from the bath containing benzotriazole. The hardness decreased with increase of temperature from 253 at 22°C to 101 VHN at 95°C, and increased with increase of cd from 201 for 5 A/ft² to 265 VHN for 60 A/ft². Ultrasonic vibration increased the hardness (still 251, stirred 265 and ultrasonics 310 VHN) and purification lowered the hardness from 260 to 205 VHN.

As the concentration of benzotriazole was increased, the hardness of the deposits rose rapidly at first, from 86 VHN (no addition) to 120 VHN (5 × 10⁻⁴ g/l) and to 203 VHN (5 × 10⁻³ g/l), and reached a maximum of about 295 VHN with 0.2 g/l (Fig. 7). No cracking or peeling was observed during or after plating with concentrations up to 0.05 g/l; with additions of 0.119 g/l and 0.2 g/l peeling occurred after plating, and with above 0.2 g/l cracking occurred during plating. The brightest deposits were produced with concentrations of 0.2 g/l and at higher values the surface became darker (Fig. 8).

The effect of benzotriazole depends upon the time between the addition being made and the commencement of plating. The hardness increased to a maximum value (about 310 VHN) after keeping the solution for about 14 days; further storage did not change the hardness (Fig. 9). The hardness of some deposits was very high immediately after plating (384 VHN) but fell quickly to about 300 VHN, which was the recorded value; this process has been called self-annealing.

![Figure 6: Effect of electrolyte purity on microhardness of copper electrodeposits.](image)
DISCUSSION

Appearance

The ultrasonic vibrations produced smoother and finer surfaces than those from a still or a stirred bath; a similar effect has been previously observed for copper deposits.\(^5\) These vibrations also reduced the area of powdery or burned surface. This is achieved by lowering the activation polarization and also the thickness of the cathode layer, so increasing the limiting cd, other workers using a similar bath have found a 3- to 8-fold increase\(^19,20\) in this cd.

The layered structure produced from the stirred or ultrasonic bath containing benzotriazole is clearly shown and has been recorded previously.\(^9-12\) However, the deposit from the still bath showed banding in some regions but not in others (as in the photograph). Prall,\(^21\) by switching the current on and off, induced banding in a
solution containing very little benzotriazole, which otherwise produced no banding. When the current was off, and no deposition occurred, a surface film formed, which affected subsequent deposit growth. This benzotriazole surface complex produced a weak bond between the deposit and the substrate and has been used to facilitate the stripping of deposits used in the production of foils, starting sheets and electro-formed articles.\textsuperscript{22}

The brightening effect of benzotriazole is illustrated in Fig. 1 with 0.12 g/l but as the concentration is increased the surface becomes darker with large nodules (Fig. 8). Prall\textsuperscript{21} analysed the deposits and found that a dark surface was produced under normal conditions if the deposit contained more than a certain amount of benzotriazole (a ratio of additive to copper of about 0.003), \textit{i.e.} from solutions containing more than 0.24 g/l. However, with agitation of the solution or the cathode, bright deposits could be obtained with an inclusion ratio of up to 0.0077. Ultrasonics can therefore be used to produce bright deposits with a higher benzotriazole content than those from a stirred bath (see Fig. 2).

Ultrasonics have also increased the intensity of the layers in the deposit and in certain areas of the cross-section there were no layers near the surface. This suggests that the rate of deposition of cuprous benzotriazolate had increased, resulting in the premature depletion of benzotriazole in the plating bath. Miller and Kuss\textsuperscript{23} have suggested that the use of intense agitation encourages the inclusion of foreign matter into the deposit, so the premature depletion of benzotriazole reported above agrees with their theory.

**Hardness**

The hardness values for plain copper deposits given in this paper are in good agreement with those recorded in the literature.\textsuperscript{18,24} Changes in the hardness with variation in the plating conditions similar to those described above have been reported previously; thus the hardness increases with increase of $c_d$,\textsuperscript{1,5} ultrasonic vibration\textsuperscript{9} and impurities,\textsuperscript{4} and decreases slightly with increase of bath temperature.\textsuperscript{1,25} All these plating variables, except for purification, change the grain size of the deposits and a correlation has been suggested between a high hardness and a small grain size.\textsuperscript{26-28}

The hardness of deposits from a bath containing benzotriazole has not been widely studied but it is known that hard, bright, brittle deposits are produced.\textsuperscript{14,21} Some of the deposits from this unpurified bath were very hard (384 VHN) immediately after plating, but quickly became softer (about 300 VHN). This drop explains the slight variations in the values given in this paper as well as the high value of 374 VHN previously recorded,\textsuperscript{19} which was taken before softening occurred.

Changes with time after plating had stopped have been observed in the internal stress and electrical resistance of deposits as well as in the hardness. The microstresses in bright copper from some baths have completely disappeared in 10 days\textsuperscript{29} and, in sulphate baths with benzotriazole, tensile stresses increased and compressive stresses decreased.\textsuperscript{10,11} Deposits from a sulphate bath containing gelatine or thiourea showed a reduction in both the electrical resistance and the compressive stress.\textsuperscript{16} The hardness of silver deposits has been found to fall by 50 per cent\textsuperscript{30} and in another case, from 105-90 to 65-50 VHN.\textsuperscript{31} The microstructure, microhardness and electrical resistance of iron deposits\textsuperscript{32} all changed with time.
The high internal stress, electrical resistance and hardness of deposits and the subsequent decrease in those properties have been widely studied. For many metals the co-deposition of hydrogen has been suggested as the cause of high internal stress and hardness, eg iron, nickel, chromium and zinc. The adsorption of hydrogen during the plating of copper from the sulphate bath is not normally proposed as the reason for the internal stress, because the current efficiency is almost 100 per cent, but this is the conclusion from some work by Nishihara et al. The changes in the above properties according to this theory are explained by the diffusion of hydrogen out of the lattice and the formation of a less strained structure.

Another explanation of these changes is that the co-deposition of impurities or addition agents creates a distorted lattice and impedes the movement of dislocations. The disintegration of co-deposited material and ordering processes which can take place in the distorted lattice may also account for these property changes. The co-deposition of cuprous benzotriazole in copper deposits has been established by Prall and Shreir and layers of this compound are shown in Fig. 3. This is probably one of the causes of the high hardness, and also the high internal stress, which has been recorded previously. The very fine grain size, less than 0.1 \( \mu m \), also increases the hardness of the benzotriazole deposits by reducing the movement of dislocations.

The increase in hardness of deposits with the storage of the benzotriazole solution prior to plating is probably due to chemical processes (oxidation) affecting the benzotriazole in the solution. A similar effect has been observed with the internal stress from this bath and also from the sulphate baths containing naphthalene disulphonic acid and thiourea.

The effect of increasing the concentration of benzotriazole in the plating solution to 0.24 g/l is known to increase the amount included in the deposit. It is reasonable to expect the hardness of the deposit to increase with the amount of cuprous benzotriazole co-deposited. A maximum value of the hardness is obtained with 0.2 g/l, which also gives the brightest deposit. The reduction in hardness with higher concentrations could be due to the fact that peeling of the deposits occurred during plating, so giving stress relief and a reduction in hardness. Another possible explanation is that at 0.2 g/l a very fine deposit is produced, which gives a maximum resistance to slip and, together with dispersion hardening due to co-deposited cuprous benzotriazole, gives this peak hardness. At lower concentrations a coarser deposit is produced with a lower hardness while with higher amounts the fine deposit is retained, so that no further hardness occurs. The copper complex in the plating bath has been analysed and found to be cuprous benzotriazole below 0.25 g/l and cupric benzotriazole at about 0.25 g/l, so this change could also affect the co-deposition and hardness of the deposits.

Ultrasonic vibrations have produced copper deposits with a finer crystal size and containing more benzotriazole than deposits from the stirred bath. Both these factors increase the deposit hardness by impeding the movement of dislocations. Because these vibrations also raise the limiting cd, give smoother and finer surfaces and reduce the internal stress and the brittleness, it is recommended that ultrasonics should be used to produce smooth, hard copper deposits.

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The use of benzotriazole as a corrosion inhibitor for copper

. Walker

Benzotriazole is a specific corrosion inhibitor for copper and copper alloys. It is now widely used in industry to reduce the corrosion of these alloys under both atmospheric and immersed conditions. Corrosion of copper may produce a face stain or tarnish, pitting of surfaces of pipes or protec tion pitting of other metals, such as aluminium, which are contact with dissolved copper in the water. Benzotriazole has been used to reduce these forms of attack and the methods by which it is applied are discussed in this paper.

Atmospheric inhibition

In atmospheric conditions it generally develops a protective surface layer of corrosion products which reduce subsequent attack. Thus copper roofs become green patina which is protective and has an aspening appearance. However, there are particular applications in which a corrosive coating or tarnish is detrimental as decorative finishes for domestic or ornamental purposes.

Techniques which can be used to prevent the tarnishing of copper in air have been listed in a recent paper by jagopalan and Aravamudan:

1. packaging in materials that are impervious to gaseous, liquid and solid pollutants
2. application of a transparent lacquer
3. formation of a tarnish resistant surface film by dipping in a suitable electrolyte or by electrolytic treatment
4. purification of the air to remove hydrogen sulphide
5. addition of a tarnish resistant metal followed by the selective oxidation of the alloying element (often aluminium).

Benzotriazole has been used in the first three of these techniques to prevent the atmospheric tarnishing of copper and copper-based alloys. It has also been used as an additive to water and other liquids to prevent corrosion.

The vapour from benzotriazole stops the discoloration of copper surfaces which are in close proximity. The inhibitor is contained in impregnated packaging which is the object of several patents. One patent uses 5 - 10% benzotriazole in a paper, plastic film or metal foil together with suitable inhibitors for ferrous metals; another uses a solution of 0.5 - 1% benzotriazole to impregnate wrapping material, so inhibiting the corrosion of copper and copper alloys. Cotton found that interleaving paper impregnated with about 2% wt inhibitor was good for the storage and purification of the air to remove hydrogen sulphide. Benzotriazole withstands staining when exposed to 0.25% salt mist for 24 hours or to 0.1% sulphur dioxide for 5 days. This vapour treatment is particularly suitable for components which cannot be wetted e.g. electrical equipment. It is also suitable for application to brass surfaces, which are then able to resist attack for more than 14 days in an outdoor industrial atmosphere where the untreated surfaces tarnish.

Copper and its alloys are widely used for architectural metalwork. However, when it is used for exterior surfaces it loses the natural colour and tarnishes or stains. Much work has therefore been carried out to find a transparent coating which is durable over a long period in outdoor atmospheric conditions and stops this discolouration. This resulted in the formulation of Incralac which contains a small but essential addition of benzotriazole to inhibit the corrosion of copper and copper alloys. This acrylic lacquer prevents any perceptible change in the colour of the copper or its alloys over a period of two or three years and has been widely used since it became commercially available in Britain on 1 June 1964. Because it can be applied easily and reduces the regular maintenance required it has been used for architectural bronze including tin bronze and wrought brasses as well as nickel silver and silver bronze on doors, nameplates, plaques, window frames, pillars and building facades, its uses are more fully described elsewhere.

Incralac has also been found to be a suitable coating for copper, brass, nickel silver and bronze test samples exposed to alpine conditions for 18 months. It has been used as an addition to paint, lacquer, ink and in a coating and this use is subject to patents. An acrylic varnish containing benzotriazole has been successful in protecting copper used for electrical purposes for more than 5 years.

One limitation of Incralac is that the acrylic coating is rather soft: this has resulted in the production of a harder lacquer based on polyurethane containing 1.5% wt of benzotriazole with an ultra violet absorber to stop the coating yellowing, making the lacquer very suitable for finger plates and handrails. When subjected to a humid atmosphere and salt spray a copper panel covered with a polyurethane lacquer without any inhibitor tarnished at a scratch in the coating after two days, whereas a similar coating with benzotriazole was unattacked after four weeks.

The dipping of copper into a hot aqueous or organic solution of benzotriazole has been found to form a protective layer on the surface. Cotton and Scholes have suggested that a suitable treatment is to dip the article for at least two minutes into a 0.25% aqueous solution at 60°C and then allow it to air dry. This has been applied satisfactorily to large scale industrial processes for brass strip, which then resisted staining for 11 days in an outdoor industrial atmosphere. This process of preventing tarnishing has been the subject of several patents. The pitting of copper and copper alloy surfaces in domestic water systems has also been
prevented by the treatment of the surfaces with the vapour or an aqueous solution of benzotriazole.22

**Immersed corrosion**

However, by far the greatest use of benzotriazole is as an inhibitor in cooling or heating systems, anti-freezes and other solutions. Many waters produce an initial dissolution from new copper pipes for a few weeks, at the end of which a protective film is formed which prevents further attack. There are, however, certain very aggressive waters which can produce pitting of domestic water pipes in less than a year but these are, fortunately, unusual. The mechanisms of pitting and dissolution of copper in different fresh waters have been widely investigated.23-26 One of the most important aspects in the corrosion of copper is the detrimental effect of copper ions in water, one indication of dissolution is given by the staining of sanitary fittings with a bluish-green colour. Waters which dissolve copper are called cuprosolvent and their importance is illustrated by the fact that the presence of as little as 0.1 parts per million of dissolved copper27 in water can produce a breakdown of passivity and pitting in aluminium. The copper ions are deposited, by a replacement reaction, on to the surface of the aluminium and form numerous small local action cathodes, which produce accelerated corrosion of the aluminium.28 Therefore, it is potentially dangerous to connect copper and aluminium together in a water system or to run water through or over copper, if subsequently it comes into contact with aluminium e.g. water from copper roofing may cause pitting if it runs into aluminium guttering or pipes. Aluminium kettles have been completely pierced by pitting corrosion caused by the action of copper dissolved from water pipes.29 Pitting of zinc,30 galvanized steel, iron and steel31 may occur by a similar process. The presence of copper ions in aqueous solutions may have a detrimental effect in textile, soap and food processing equipment, where the products may be contaminated. The copper may also act as a catalyst in the deterioration of chemical compounds; for example in the oxidation and breakdown of anti-freezes. Chemical degradation of rubber by copper is also important in certain systems containing rubber hoses, and rubber hot water bottles have been known to perish in six weeks.29

**Immersed inhibition**

Benzotriazole, which is very stable, is soluble in both hot and cold conditions and does not suffer from the formation of insoluble compounds by oxidation. This makes it very suitable for both heating and cooling systems as well as anti-freezes.22

In enclosed water systems it has been found to form a highly insoluble complex on the surface of copper. This compound, under suitable conditions, can prevent the movement of copper ions into a solution and also the ingress of other substances which may cause the copper to tarnish. Thus it inhibits the corrosion of other metals formerly caused by contact with the dissolved copper as discussed above.

There are many patents for the use of benzotriazole together with other inhibitors to reduce the corrosion of metals used in automobile cooling systems: these include copper, iron, zinc, aluminium, lead and alloys of these metals.32-38 From 0.4% to 1% of copper ions in benzotriazole has been included in anti-freeze solutions40-42 to inhibit corrosion. Other patents involve the use of benzotriazole salts or substituted compounds44-46 for similar purposes. The use of 0.05-2% wt benzotriazole, preferably 0.25% wt in hydraulic fluids containing glycol ether, has been found to prevent the deleterious action on rubber and metal parts in the hydraulic systems of automobiles.47

The corrosion of copper in distilled water has been reduced from 400µg/l to 27 µg/l by the addition of 100 ppm benzotriazole.48 This inhibition is important in closed circuit, water cooled stators (used in the power industry), because the solved copper increases the conductivity of the water; if the increase is too great excessive energy losses or even flovers may occur in conductors and heat exchange equipment because high voltages are used (6-8kV). Thus the use benzotriazole to reduce the rate of increase of ionic concentration due to copper pick-up removes the necessity for continuous purification, lengthens the periods between flushings and enables a considerable capital saving to be made because a demineralizer is no longer required.49

The inhibition of detergents to prevent the corrosion, nish or discoloration of metals and machinery has been studied.54-56 Thus in a particular detergent the corrosivity of copper has been reduced from the range 3.1—1 g/in/hr, at 40—100°C respectively, to 0.2-0.4 g/in/hr by 0.1% benzotriazole.54 A similar addition of benzotriazole has been found to stop the discoloration of copper and brass in copper-benzotriazole compounds have been found to very considerably reduce the corrosion of brass strip in a Tide solution as indicated:— with no inhibitor the corrosion rate 0.0865 in/year, with 0.1 g/l copper bis-benzotriazole it was reduced to 0.0035 in/year, which was reduced to 0.0003 in/year by the addition of 0.025 g/l of nickel bis-benzotriazole. It has been added to the chemical coolant used in the machining of uranium to eliminate the corrosion of copper in the circulation system and bearings.52

The radiolytic corrosion of copper in irradiated cooling water circuits for proton accelerators has been found to be different from the normal corrosion in demineralized water. In these conditions benzotriazole was found to be the best inhibitor tested. The recommended method for protecting was given as the passivation of the copper with a solution containing 0.2 to 0.25% benzotriazole followed by the addition of the water with an addition of 200—500 ppm benzotriazole.54

**Inhibition of brass**

The dezincification and corrosion of brass is inhibited by the presence of benzotriazole in the liquid.50,55,56 Dezincification which results in regions of brass being replaced by a porous mass of copper, has been described as the dissolution of copper and zinc followed by the deposition of the copper ions.56 Insoluble copper-benzotriazole compound which forms on the surface inhibits the dissolution of the copper and thus reduces the corrosion of the brass as indicated.56

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Corrosion rate-10^{-3} g/dm^2/day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 NaCl</td>
</tr>
<tr>
<td></td>
<td>Without</td>
</tr>
<tr>
<td>α-cast</td>
<td>-2.2</td>
</tr>
<tr>
<td>(α+β) cast</td>
<td>-1.7</td>
</tr>
<tr>
<td>β-cast</td>
<td>-1.7</td>
</tr>
<tr>
<td>(α+β) deformed</td>
<td>-22</td>
</tr>
</tbody>
</table>

Cotton5 has found that the inhibitor controls the stress corrosion of brass in an atmosphere of moist 0.1% sulphur dioxide: an untreated specimen cracked in 3 days whereas treated one was satisfactory after 43 days.

**Inhibition of copper in contact with steel**

When two dissimilar metals with different corrosion potentials are metallically joined together and immersed, this no metal becomes the cathode and stimulates the corrosion of the other, the anode. Thus when copper and steel, whi
The supporting mast of Scheveningen’s radio tower is protected with a DD formulation.

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From Johannesburg to Anchorage, Alaska, expensive machinery, equipment, ridges, buildings, and loading installations are at risk from corrosion. Very often conventional paints are just not suitable for their protection. DD finishes, he polyurethane coating systems based on the Bayer raw materials ®Desmodur and ®Desmophen, are different.

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After only 1½ years the mast supporting radio Scheveningen’s transmitters had been attacked by fine salt crystals. Realizing that salt-containing deposits and temperature fluctuations would only be withstand by a really reliable protective material, Radio Scheveningen decided to have the mast treated with a specially formulated DD finish. In the five years which have passed since the finish was applied the mast has hardly suffered at all.

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Wherever the problems of corrosion are taken seriously DD finishes are being used ever-increasingly thanks to their outstanding physical and mechanical properties — and to the fact that they can be tailored to suit the application concerned. Use the coupon to request detailed information.

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Please send us detailed information about DD surface coating systems.

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We have the following technical problem, which we would like to solve with a DD finish:

Advice on this problem would be appreciated from our paint suppliers, who are

Messrs.

Polyurethane lacquer
have a large potential difference, are connected together the steel corrodes. One important example of this galvanic coupling is the joining of copper and steel pipes in domestic water systems.

The corrosion of ferrous metals in systems with other metals and alloys has been inhibited by a mixture of sodium nitrite, sodium borate and benzotriazole. A similar mixture has been found to reduce the corrosion of iron in contact with copper by a factor of 100 when benzotriazole was added, the effect of this addition (5mg/l) was enhanced if polyphosphates were present. It is well known that the corrosion of steel is inhibited by the presence of amines. However, these have been found to increase the corrosion of any copper present. This has led to the study of the joint effect of amines and benzotriazole on the inhibition of both steel and copper when immersed together in distilled water. As the concentration of the amine compound was increased, the corrosion rate of the copper was found to increase, while that of the steel decreased. The combined effect on the rate of corrosion of copper of different concentrations of amines and benzotriazole is shown below:

<table>
<thead>
<tr>
<th>Inhibitors concentration m.mols/l Corrosion rate g/m²/day</th>
<th>Amine</th>
<th>Benzotriazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x Ethylenediamine</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1.50</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>2.90</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>0.06</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

| 10°                                                       | 0     | 0.8           |
| 10                                                        | 1     | 0             |

This shows that the simultaneous corrosion of copper and steel can be prevented by using a suitable mixture of benzotriazole and an amine.

In a solution of 0.5 NaOH and 1.0 N (NH₄)₂SO₄ the presence of steel coupled to copper has been found to increase the corrosion rate of the copper by a factor of 4 to 5. The addition of benzotriazole has decreased the attack on the copper alone by 95% and, when in contact with steel, by 98.99%. Similar reductions (96 and 97%) were found in copper in contact with steel in 3% ammonia solution. T benzotriazole did not stimulate the corrosion of ferrous metals.

The corrosion of copper alone and also in contact with steel has been investigated in a solution of 0.5 NH₄Cl a 0.025 N NH₄Cl as well as 1.0 N H₂SO₄ and 0.0 N (NH₄)₂SO₄. An addition of 0.01 M solution of benzotriazole reduced the corrosion of the copper by a factor of 10 in the first solution, but was less effective in the second. Steel alone or in contact with copper, was well protected by 0.001 M solution of benzotriazole. The protective action of benzotriazole has also been investigated for copper and ferrous metals in neutral and acidic media as indicated below. The corrosion of steel and gray cast iron was reduced by factor of 8 to 10-fold by the use of a 1% addition to distill water over a 30 day test. In a 2 normal solution of hydrochloric acid the corrosion of copper was lowered by a factor of 5.5. Tests were also carried out in a buffer solution containing benzotriazole and its sodium salt at pH 7.5: the protective concentrations of this mixture were 0.5% for gray cast iron 0.2% for steel, 0.6% for steel in contact with copper, 0.1 for Ni-Resists and 0.001% for copper.

**Inhibition of other metals and alloys**

Benzotriazole has been found to inhibit the corrosion of steel and cast iron. Steel is protected by 0.01% benzotriazole and the corrosion rate in water has been reduced fr 0.0543 to 0.0054 g/m²/hr. An improvement has been found if a mixture of benzotriazole and its sodium salt are used and at a pH of 7-8 a solution almost completely stops corrosion. At a pH=8 complete inhibition was obtained with 0.2% inhibitor mixture for mild steel and with 0.5% for gray cast iron. This sodium salt has been found to reduce the corrosion of copper in neutral solutions and hydrochloric acid as well as that of steel and gray cast iron in neutral conditions but it was not effective for ferrous metals in acid or neutral solutions. The effect of water soluble organic sulphides the inhibition of benzotriazole for iron has been investigated by Nakagawa et al who found protection was increased for iron in neutral solutions but the corrosion increased in aci conditions.

Cadmium and cadmium alloys treated with a solution 0.01—2% wt benzotriazole in water or industrial methylol spirits at 65° for 5 minutes did not tarnish in 24 hours an atmosphere containing 10 ppm hydrogen sulphide where an untreated sample stained in 2—4 hours. The tarnish resistance of cadmium as well as copper surfaces has been improved by immersion or spraying with a 0.1—5% solution in alcohol or wrapping in a paper impregnated with benzotriazole. The use of benzotriazole and its derivatives (which have been claimed to give a marked improvement) have been used to inhibit tarnish on silver. Benzotriazole in a wax has been found to give good protection to chromium plated car h caps.

**Other uses**

The inclusion of benzotriazole in greases and oils to inhibit corrosion of copper, silver and steel surfaces has been patented. The addition of 0.2 to 2% of a solution alkylated benzotriazole to an ester based lubricating oil has been found to be effective: 0.05 to 5% wt benzotriazole h also been used in similar oil and prevented the formation of a light brown stain on copper at 200°C, this was also go for all surfaces. The inclusion of 0.02—0.06% has been found to make organosiloxane grease less corrosive to copper and steel. When more than 0.5% wt benzotriazole was mix with thickened lubricating greases, rust was inhibited and t grease passed the ASTM D 1743—60T test: if less than 0.5
The addition of benzotriazole to plating solutions to produce bright electrodeposits has been investigated for zinc in a cyanide free alkaline bath and for copper from the sulphate bath. In copper deposits it has been found that an inhibitor was used. The rapid tarnishing of soft copper surfaces which have been treated with benzotriazole and then washed in aqueous and organic reagents still retained the inhibitive properties when the surface is exposed to tarnishing conditions. The formation of a passive film which is more difficult to describe and it appears that the benzotriazole strongly bonded to the metal and probably forms a chemically bonded layer on the surface. The thickness of this type of film has been shown by ellipsometry to be less than 50Å thick if an insufficient surface material can be obtained for a detailed eminal analysis.

Because it is impossible to make sufficient compound by a reaction of benzotriazole with copper, Cotton has proposed large quantities of copper benzotriazole complexes in reactions of ionic solutions and he studied the properties of these compounds. Both the cuprous and cupric derivatives formed precipitates which were insoluble in water and many organic liquids.  They were also thermally stable, the cuprous compound began to decompose at about 250°C and the cupric compound at about 200°C.  He investigated the portance of the nitrogen and hydrogen atoms in the benzotriazole ring by comparing compounds in which different substitutions have been made. Benzotriazole, indazole, benzdazole, indole and methyl benzotriazole.  Of these benzotriazole and indazole prevented staining of treated copper exposed to salt spray and only the former retained this resistance when washed with chloroform or other organic solvents.  This suggested that for stain resistance a compound should be capable of forming insoluble complexes with copper ions.  These studies also showed that all of these compounds benzotriazole appeared to be the best inhibitor.

The strong bond which forms between benzotriazole and copper surfaces suggests it is similar to the chemical combination which occurs in the insoluble complexes with copper ions. From the above studies Cotton considered that the hydrogen and two nitrogen atoms are required for the bonding between copper and benzotriazole. Infra red spectroscopic data indicated that cuprous benzotriazole was polymeric so a linear structure was suggested. In this structure the copper was bonded using sp orbitals with a covalent link formed by the replacement of the hydrogen atom from the N-H group and a co-ordinate bond with a lone pair of electrons from one of the nitrogen atoms. A chain is therefore built up of alternating benzotriazole molecules and copper atoms. The bonding in the cupric complexes (of which there are at least two) is more difficult to describe and it appears necessary to include chlorine, oxygen and water to fit the existing data. The structure of these compounds has not been established although it is known from infra red measurements that they are polymeric. The presence of a polymeric type of material is also supported by the low solubility and good thermal stability of these compounds as well as by crystallographic data. Further substitutions have been made in the benzene ring of benzotriazole but unmodified benzotriazole appeared to give the best inhibitive properties.

The mechanism of inhibition of the benzotriazole is probably due to the reinforcement of the copper oxide which is normally present on the surface of the metal. Electrochemical techniques have been widely used to study this inhibition. Dugdale and Cotton found that benzotriazole prevented the staining of copper by forming a complex on the surface of the metal: this complex acts mainly as a cathodic inhibitor but also as a physical barrier on the surface. In contact with the copper this surface film shows rectifying properties opposing the anodic current but not the cathodic current. Cotton and Giles decided that benzotriazole slightly suppressed the oxygen reduction process at the cathode but the main inhibition was due to the formation of a passive film which reduced the dissolution of copper at the anode so it was concluded that the main protection was afforded by anodic inhibition.

Results
Corrosion tests have been conducted in both atmospheric and immersed environments to confirm the inhibitive properties of benzotriazole for copper. Specimens of copper foil dipped in an aqueous solution of 1% wt benzotriazole at 60°C for 5 minutes were compared with untreated copper in different atmospheres. The time before staining or tarnishing was first observed in salt spray, sulphur dioxide and rural atmospheres was considerably increased by the treatment with the benzotriazole solution. The addition of 0.12 g/l of this inhibitor to stirred N/10 solutions of different chemicals in distilled water has been investigated. The rate of corrosion of copper was reduced by this amount of inhibitor in all the solutions tested except ferric chloride in which an increase was observed. Those which showed significant reduction included acetic, hydrochloric, nitric and sulphuric acids, ammonium chloride and sodium.
chloride and solutions containing dissolved carbon dioxide and sulphuric dioxide. The immersed copper surfaces in many of these solutions were badly tarnished whereas with the inhibitor this tarnishing was prevented in sodium chloride and sodium sulphate, acetic acid, ammonium chloride and carbon dioxide. Fig. 1 shows the marked difference in corrosion behaviour between copper immersed in ammonium chloride solution (a) without and (b) with benzo triazole. With no inhibitor the solution was cloudy and the specimens stained but with benzo triazole the solution was clear and the copper clean. In Fig. 2 the staining of copper specimens is shown for three different solutions: no staining was observed with benzo triazole.

As mentioned in a previous section on immersed corrosion the presence of dissolved copper ions may produce pitting of aluminium surfaces. A section of an aluminium kettle used with water containing dissolved copper which perforated in about 18 months is shown in Fig. 3. This is also illustrated in Fig. 4 which shows a pitted aluminium foil specimen which was immersed together with copper foil in distilled water for only two days: the copper foil showed no visual sign of corrosion and only a very slight loss in weight.

Discussion

The corrosion tests indicate the extensive range of inhibition which can be obtained for copper surfaces by the use of benzo triazole. However, it may be necessary to ascertain the correct concentration of inhibitor required to give protection because if insufficient is used the corrosion rate may be increased in certain conditions. This occurs with many anodic inhibitors and is in agreement with Cotton and Giles who found that benzo triazole acts mainly as an anodic inhibitor.

The rapid pitting of the aluminium foil is an example of the potential danger of waters containing dissolved copper coming into contact with other metals. The use of benzo triazole can be considered to be the prevention of staining of atmospheric and immersed surfaces; the reduction of the rate of corrosion of immersed copper surfaces and the avoidance of the detrimental effects of dissolved copper ions in the water. These effects include the corrosion of other metal surfaces, the degradation of rubber surfaces and the catalytic deterioration of chemical compounds as well as the contamination or discoloration of any products in manufacturing processes.
ANTICORROSION 15

Callordes Industriels Francais S.A., French Pat. 1,442,210, 10 June, 1968.


Metals 1967 2 (15) 32.


I.C.I. Ltd., British Pat. 975,115, 6 May, 1964 (addition to 907,793).


M. Knaack Schering A-G, German Pat. 1,243,488.


R. Walker, Plating, to be published.


International Congress on Anti-Corrosion Coatings

On 22-23 October this year, an international congress on "New Trends in Anti-Corrosion Coatings" will be held in Milan, Italy. It is being sponsored by Colorificio Italiano Max Meyer, an Italian paint and varnish manufacturing concern.

The congress has been organized on an international scale, with respect to speakers and delegates, in order to evaluate the different atmospheric conditions that determine corrosion rates and to study the protection methods adopted by the leading countries in the field of technology.

The programme, at the time of writing, includes papers on the following subjects, of the country of origin being given in brackets:

Economic aspects of metal corrosion (Czechoslovakia).

Process and corrosion forms: steel and light alloy protection (France).

Surface preparation (U.S.A.)

Advanced application methods (Sweden).

Zinc-rich anti-corrosion primers (Italy).

Protection of pipelines, sea-lines, pressure water pipes and dams (Italy).

Paint systems for the chemical and petrochemical industries. Comparison between conventional and long-lasting paint systems (U.K./U.S.A.).

The closing date for registration is 10 October and full details can be obtained from the Secretariat at Via Visconti Venosta 7, 20122 Milan, Italy.
Talking corrosion...

So once again corrosion makes the front pages. The navy is apparently in trouble because detonators on torpedoes have corroded either unexpectedly or because somebody forgot that action has to be taken to keep corrosion at bay. It is odd that every two years or so there is a major news item in the national press blaming corrosion for some costly trouble. Why do we never see an item praising anti-corrosion? Perhaps they do exist but if they do they must be tucked away in the middle pages somewhere as we never see them. Mind you the national press has our sympathies. We receive a lot of paper in our office each week and a majority of it tells us how wonderful such and such a product or material has been in solving a specific corrosion problem. When we do get one that says that something has failed it is a red letter day.

Some years ago, when we could afford the entry fee and the time, we were wandering around the Boat Show when we encountered a wooden hulled vessel fitted with magnesium anodes. We were solemnly told by the salesman that the anodes would not need replacement for a long time as they had been well painted. The trouble was that we were uncertain as to whether or not there might have been something in this—the marine boys seem to have a habit of coming up with the unexpected in a very practical way.

What brought this to mind was a report that a Round Britain Sailing Race ketch, The Ocean Spirit, built by moulding in glass fibre (that seems amazing enough in itself) needed over 5,000 bolts and screws of stainless steel and silicon bronze. Obviously no matter how anti-corrosive is the hull it won't do the job properly unless all the bits fixed to it are fixed with anti-corrosive fasteners. That we understand (think of fixing plastic guttering) but 5,000 special fasteners and, in addition, a claim by the builders that this is less than is required on traditionally built ketches of this size. We've already mentioned in this month's commentary the idea of the need to make fasteners non-corrodible and now we hear of this. The message is, of course, that with fasteners in such material being available then some of the designers' excuses no longer hold water (we hope that the ketch does.)

We suppose that it could be loosely said that the level of our success in anti-corrosion can be judged by the value of scrap steel in the country. We are always interested in useless bits of information and on the scrap steel front we find that although there is talk of raising ferrous scrap steel prices from about £12 a ton in this country we are still way below £20 plus a ton on the Continent and in America and Japan. Apparently exports of scrap steel are virtually banned because of the home industrial demand (a period of stagnating industry?) which is running at over 8 million tons per year. Are we being conceited when we say that if a few of us in anti-corrosion were to pack up tomorrow then the country's export figures would soar by the addition of a this scrap steel. We wonder.

We've just laid our hands on another material corrosion performance chart (Polypenco Chemical Resistance Chart showing the performance of six specific materials in some 200 different liquids. Whilst we are great believers in the method of information presentation we use them only as a guide to possible material utilization. This we have shown by including a certain amount of such data in our Data Guides. The trouble is, though, that there seems to be an infinity of materials and an infinity of liquids producing in consequence, an infinity (How much is infinity squared, of corrosion charts. We collect them but even so, by th famous engineers' law, the particular liquid/material combination we want is never covered.

One difficulty we have found with these wall charts is actual wall space. We've been giving serious thought to preparing a special corrosion performance wallpaper for corrosion experts' offices. Anybody interested? It would be in vinyl, of course.

Our job is to talk corrosion: whether in the form of the column or in the more formal form of the lecture type discussion is unimportant. We use words to explain happenings and things and, if we're any good at our job, we can put out a sentence without the reader being aware that when he is reading is rubbish or, far more important, we can condense a mass of information into, we hope, a pithy sentence. In doing the latter we find that we must be idiomatic. When we are doing this we sometimes stop and look back at ourselves (it's a harrowing experience). Try doing this yourself and look into the terminology that you use there is no other way of corrosion charts. We collect them but even so, by the famous engineers' law, the particular liquid/material combination we want is never covered.

Our latest gem is '...the carefully controlled application of manually operated non-dynamic means of a resistive skin to the surface of a ferrous substrate'. How complicated can slapping on a coat of paint become? (believe it or not, this phrase was written by an Englishman)
he Effect of Benzotriazole on the Stress in Copper Electrodeposits

R. Walker

ABSTRACT

The internal stress in copper electrodeposited from a copper sulfate-sulfuric acid bath was measured at different solution temperatures and current densities. The tensile stress was found to decrease from 3.9 kg/mm² (5600 psi) at 3°C to 0.07 kg/mm² (100 psi) at 90°C. An increase in the current density raised the tensile stress from 0.18 kg/mm² (250 psi) at 0.26 A/dm² to 2.6 kg/mm² (3700 psi) at 13 A/dm². These results are in general agreement with other published work.

Stress measurements were also made with deposits from a similar bath containing an addition of M/1000 benzotriazole. This modified bath produced copper with a bright surface whereas the bath without this addition gave dull or mat deposits. The presence of the benzotriazole also had a very marked effect on the internal stress. At low bath temperatures high tensile stresses were observed (about 12.6 kg/mm², 18,000 psi) at −2°C and as the temperature increased the stress decreased and became compressive. This compressive stress increased to a maximum, about 12.6 kg/mm² at 2.6 A/dm², and then decreased to almost zero at 90°C. At low current densities high compressive stresses were observed: 9.1 kg/mm² (13,000 psi) at 2.6 A/dm² and 31°C, and 4.9 kg/mm² (7000 psi) at 12 A/dm² at 22°C. As the current density increased the compressive stress decreased and became tensile, reaching values of 10.5 kg/mm² (15,000 psi) at 31°C and 11.9 kg/mm² (17,000 psi) at 22°C at 13 A/dm². Prior to this work the highest compressive stress observed with deposits containing benzotriazole was only 5.2 kg/mm² (7500 psi).

Both the bath temperature and the current density had a marked effect on the grain size of the deposits. It was noted that a deposit with a low stress had a large grain size and a high stress occurred with a small grain size.

The presence of a high tensile stress may cause a deposit to peel (if the adhesion is poor), produce deformation of a thin substrate or cause the deposit to crack. This deformation of a thin substrate or deposit is particularly harmful in electroforming processes and cracking of the coating may decrease the corrosion resistance. A high tensile stress reduces the fatigue, corrosion fatigue and stress corrosion properties of a plated article whereas a compressive stress is normally beneficial. Further details of the properties affected and methods of controlling the internal stress have been described elsewhere.

LITERATURE REVIEW

Because the stress in a deposit depends upon the experimental plating conditions, many of which are interdependent, the literature appears conflicting and comparisons are difficult to make. However, it is possible to obtain a general indication of the variation in the internal stress due to changes in the bath temperature and current density.

Normally, an increase in the bath temperature reduces the tensile stress in a deposit. For metals plated with a high tensile stress this reduction may be considerable; for iron deposits from the sulfate-chloride bath, the tensile stress was reduced from 41 kg/mm² (59,000 psi) at 61°C to 22 kg/mm² (31,000 psi) at 80°C; and for hard nickel, the values were 20 kg/mm² (28,500 psi) at 30°C, 16 kg/mm² (22,800 psi) at 50°C and 12 kg/mm² (17,100 psi) at 70°C. However, for copper deposits the tensile stress was much lower than these values and, as the bath temperature increased, the tensile stress has been observed to decrease and become compressive in some cases. This reduction with increase in temperature was measured by Lamb and Valentine who obtained the following values: with a current density of 4 A/dm² the stress was 2.9 kg/mm² at 20°C, 1.5 kg/mm² at 30°C and 0.13 kg/mm² at 45°C (4200, 2200 and 200 psi); and at 2 A/dm² the corre-
the 504 (based on 5 cm (2 in.) squares) thickness readings were as shown in Table VI after the selective chemical milling. The nominal spread could be reduced to a variation of ±25 μm (1 mil) by masking off the five low spots (ignoring one high spot) and chemically milling 25 μm (1 mil) from the remainder of the surface. This part would then meet the weight requirements with plenty to spare; in fact, it would have met the weight requirement without this additional operation as there were more 0.068 readings than the 0.070 in. readings combined.

**Production Part Chemical Milling**
The tank cones and domes are chemically milled in the same position at all times. This does not give an opportunity to correct the taper induced by the etchant by inverting the part 180° between etchant immersion cycles. For example, a 117 cm (46 in.) diameter dome which has an initial thickness variation of 178 μm (7 mil) would at times have a thickness variation of approximately 500 μm (20 mil) after it was chemically milled in the standard etchant solution. The thickness variation was relatively unchanged when it was chemically milled in the nitric-hydrofluoric acid solution. Thus, the amount of selective chemical milling may be reduced on this type of part even though the weight tolerance was reduced by 60 per cent.

**DISCUSSIONS**

Etchant activity in general is extremely reproducible from part to part and from day to day at the same etchant temperature. However, several factors were determined to influence the etch rate. They were:

Metal parts less than 0.5 mm (20 mil) thick will at times chemically mill at an extremely slow rate—this is because thin metal parts do not retain sufficient heat to maintain good etch rate; and the wetting agent must be maintained at a sufficient level to insure proper wetting of the metal surface—if the surface is not wet properly, it will become passive in the etchant solution.

**CONCLUSIONS**

Nitric-hydrofluoric acid etchant meets all the design requirements for a slow titanium etchant that will give a form etch rate over the surface being chemically mill-milling. Tests indicate that there will be no problem with hydro pickup in this etchant. This etchant should be used for titanium selective chemical milling and some of the major metal removal steps on the cones and domes.

**ACKNOWLEDGMENT**

The work of Vern VonVihl on the development of an improved method of analysis for the nitric-hydrofluoric acid system helped to expedite the development of this etchant.

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Discussions of this paper are invited for publication in future issue of Plating.

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**MEET THE AUTHOR**

David M. Shuford graduated from North Carolina State School of Engineering in 1951 and received an MS in chemical engineering from the University of Florida in 1957. He was employed by the Sandia Corporation from 1957 to 1960 as a staff member working in electrochemistry. From 1960 to 1969, he was employed by the Martin Marietta Corporation's Denver Division as head of the Advanced Manufacturing Chemical Laboratory with responsibilities in the areas of chemical milling, metal cleaning and finishing, electroplating, flame spraying, corrosion and contamination control. He has been with the LTV Aerospace Corporation and LTV Research Center for the past year doing materials research on carbon-carbon composites and high modulus composite structures.
sponding figures were 10 kg/mm², 0.17 kg/mm² and a compressive stress of 0.22 kg/mm² at 45°C (1500, 250 and -300 psi).

For most metals, an increase in the current density increases the stress in a tensile direction at a given thickness of deposit. For deposits with a high tensile stress, a significant increase is found: in iron deposits from the sulfate-chloride bath, the change was from 27 kg/mm² (39,000 psi) at 5 A/dm² to 59 kg/mm² (84,000 psi) at 20 A/dm². In nickel coatings from the sulfamate bath, the compressive stress decreased from 5700 psi with 4 A/dm² to 1420 psi with 10 A/dm². In copper deposits, an increase in the tensile stress has been found by Nishihara and Tsuda, Lyzlov and Samartsev (2.2 kg/mm² at 0.5 A/dm² to 6 kg/mm² at 4.5 A/dm²) and Vagramyan and Petrova (2.3 kg/mm² at 1 A/dm² to 5 kg/mm² at 2 A/dm²). Lamb and Valentine observed a change from a compressive stress of 0.07 kg/mm² at 0.5 A/dm² to a tensile stress of 1.3 kg/mm² at 2.0 A/dm² and 2.7 kg/mm² 4.0 A/dm².

EXPERIMENTAL

The stress measurements were made with the Brenner-Senderoff Spiral Contractometer with the modifications suggested by Fry and Morris. The spirals, which are the cathodes in this instrument, required careful preparation to ensure good adhesion of the deposit to the stainless steel substrate. These helices were degreased in acetone in an ultrasonic bath and etched in concentrated hydrochloric acid. They were then plated with nickel from the Wood's bath at 60°C with 1 A for 1 min, thoroughly washed and plated with copper from the cyanide bath for 2 min at the same temperature and current and again thoroughly washed. This procedure was found to produce a lustrous copper surface. If this bright surface was not obtained, the preparation process was repeated because reproducible stress measurements could only be obtained from identical substrate surface conditions. After a satisfactory pretreatment, the spirals were calibrated in the usual manner and then ready for plating with the acid copper bath.

The composition of the bath was 125 g/l commercial grade copper sulfate (CuSO₄·5H₂O) and 49 g/l commercial grade sulfuric acid in distilled water. The plating tank was a beaker which was lined with a freshly-etched cylindrical copper foil anode. This arrangement gave a uniform deposit of copper on the outer surface of the helix but virtually no deposit on the inner surface. The plating time was 30 min with 1 A (equivalent to 2.6 A/dm²) which produced a deposit thickness of about 8.5 μm (0.3 mil). At different current densities, the plating time was that which gave the same deposit thickness (e.g., 10 min at 3 A). The plating bath was magnetically stirred to allow mixing of the solution which reduced any temperature gradients as well as the polarization but was sufficiently slow to prevent aeration. The plating bath was immersed in a water bath and the temperature controlled to ± 2°C.

The deflection of the dial, produced by the stress in the deposit on the spiral, was recorded every minute with a current of 1 A or at the equivalent thickness (every 20 sec with 3 A). This gave a continuous record of the variation of the deflection with the deposit thickness. The stress was calculated for each experiment after deposition for 0.5 A-hr and this value was used in the graphs.

The experiments were repeated with a similar plating solution to which had been added 0.119 g/l benzotriazole (M/1000). This addition was made to the bath just prior to deposition because an ageing effect has been observed with benzotriazole and the timing of the addition affected the stress. The procedure was the same as for the pure bath (without the addition) but the plating time was 15 min and readings were taken every 0.5 min or at the equivalent thickness.

A qualitative assessment of the grain size was made using flat copper cathodes which were plated under the same conditions of temperature and current density as the spirals. These cathodes were then mounted in Bakelite, polished, etched and examined under the microscope.

RESULTS

Effect of Bath Temperature

Bath Without Addition Agents

In the copper deposits from the plain bath, the tensile stress decreased as the temperature of the plating solution increased, Fig. 1. This decrease in the stress was very marked at low bath temperatures: from 3.9 kg/mm² (5600 psi) at 3°C to 1.2 kg/mm² (1700 psi) at 15°C; but at higher temperatures, only a slight change was observed: from 0.5 kg/mm² (700 psi) at 35°C to almost zero at 98°C. All the deposits had a mat appearance (Fig. 2) with good adhesion to the basis metal, and no peeling was observed. The grain size of the deposits increased with the bath temperature.

Bath Containing Benzotriazole

For deposits from the bath containing benzotriazole, the change in the stress with bath temperature is shown in Fig. 3; it was more complex than for the bath without benzotriazole. A high tensile stress, about 12.5 kg/mm² (18,000 psi), was
observed in deposits plated at a current density of 2.6 A/dm² and a bath temperature about 0°C. For deposition at this temperature at a current density of 10.4 A/dm², the deposits were so stressed that they usually peeled from the substrate at temperatures below 20°C, as shown in Fig. 4. This peeling reduced the tensile stress in the deposits so that the values obtained were much lower than those which would have been observed without the stress relief produced by the peeling.

As the bath temperature increased, the tensile stress decreased to zero at about 23°C at 2.6 A/dm² and about 43°C at 10.4 A/dm². With a further increase in the temperature, a compressive stress was observed with a maximum value of about 12.5 kg/mm² (18,000 psi) at 44°C and 2.6 A/dm² and about 6.3 kg/mm² (900 psi) at 60°C and 10.4 A/dm². The stress then decreased to very low values at about 80°C. No peeling occurred in deposits with a high compressive stress. All the deposits from the bath containing benzotriazole had a brighter appearance with a grain size which was different from those from the bath without benzotriazole.

A stress after-effect, which has been observed elsewhere,⁴ was observed with the deposits from the bath containing benzotriazole. This effect involved a change in the stress, after the current had been switched off, which increased in a tensile direction, i.e., a tensile stress increased and a compressive stress decreased.

**Effect of Current Density**

**Bath Without Addition Agents**

In all deposits from the plain bath, a tensile stress was observed at a solution temperature of 22°C. The stress increased with the current density from a low value of about 0.18 kg/mm² (250 psi) at about 0.26 A/dm² to 2.6 kg/mm² (3800 psi) at 13.0 A/dm², as shown in Fig. 5. The deposits were matte (Fig. 3) with good adhesion, and no peeling occurred. The grain size of the deposits decreased as the current density increased.

**Bath Containing Benzotriazole**

The changes in the stress with current density for deposits from the bath containing benzotriazole are shown in Fig. 6. At low current densities a compressive stress occurred which increased to a maximum value of about 5.6 kg/mm² (8000 psi) at 22°C and 1.3 A/dm² and about 9 kg/mm² (13,000 psi) at 31°C and 2.6 A/dm². As the current density increased, the stress decreased to zero at about 2.3 A/dm² at 22°C, and about 5.2 A/dm² at 31°C. A tensile stress was produced at higher current densities; this appeared to approach a constant value of about 12 kg/mm² (17,000 psi) at 22°C and 10.5 kg/mm² (15,000 psi) at 31°C and 13.0 A/dm².

The deposits with a compressive stress did not peel but some deposits with a high tensile stress showed peeling, as shown in Fig. 4. The deposits appeared brighter with a different grain size from those from the bath without benzotriazole. A stress after-effect was again observed.
The stress which was greater than ±0.2 kg/mm² (300 psi) was considered significant and produced by changes in the bath temperature or current density. Any change in the bath temperature was important because it affected the resulting internal stress. This is called the ageing effect and the tensile stress in the deposit has been found to increase with the time period between the addition and the commencement of plating. In this series of experiments, the addition was made immediately before plating to reduce to a minimum any tensile stress resulting from this ageing effect. A similar change in the stress with naphthalene disulfonic acid in the copper sulfate plating bath has been observed by Vagramyan and Petrova.

To obtain reproducible stress measurements, it was essential to plate the spirals with a fine bright copper surface from the cyanide bath prior to deposition with the acid copper electrolyte. The importance of the surface condition has been extensively studied and Kushner found it had a marked effect on the stress in thin deposits but a negligible effect at a thickness of 7.6 μm (0.3 mil). The surface cleanliness (including the presence of any oxide film) also has a significant influence on the adhesion of a deposit, and if this was poor, peeling often resulted.

The main error in the stress measurements was due to the reproducibility of the contractometer. The sensitivity of the instrument depended upon the spirals used and was 1°, equivalent to a stress of about 0.1 kg/mm² (150 psi). The effect of raising the temperature of the helix was investigated using a bath of distilled water and observing any deflection. No deflection was observed below 40°C, and a maximum of 3° at 90°C which was produced by the different thermal coefficients of the copper and nickel coatings and the stainless steel helix. This deflection of 3° was equivalent to a compressive stress of about 0.3 kg/mm² (450 psi). Any change in the stress which was greater than 0.2 kg/mm² (300 psi) at room temperature and outside the range 0.1 to 0.5 kg/mm² (150 to 750 psi) (compressive) was considered significant and produced by changes in the bath temperature or current density.

Discussion of Stress Results

The presence of an internal stress in an electrodeposited deposit is thought to be due to an expansion or contraction of the deposit during, or soon after, the deposition process. The depositing layer may be formed with a volume which differs from that of the basis layer and then be elastically deformed to fit the basis. Another explanation is that the depositing layer fits the basis metal layer and then expands or contracts after deposition. The current density, bath temperature and other plating variables affect the condition of the deposit and the internal stress.

Pure Deposits

The decrease in the tensile stress from a high value at a low bath temperature to a low stress at a high temperature is in general agreement with other observations. The relationship between stress and temperature with a current density of 2.6 A/dm² appears to obey a logarithmic law, Fig. 7 (the deviation at high temperatures can be ignored because there is a large experimental error with low stress values) rather than the inverse relationship found by Lamb and Valentine. Further work is planned to determine if this logarithmic law is obeyed at other current densities using the copper sulfate-sulfuric acid bath. An increase in temperature in the grain size of the deposits was also found, which agrees with other published results.

The increase in the tensile stress with an increase in the current density was of the same order as that observed by other workers. The grain size decreases with the current density and this has been correlated elsewhere with increased hardness, tensile strength and ductility.

Several theories have been proposed to explain the effect of the bath temperature and the current density on the internal stress on an electrodeposited deposit. Several workers have noticed the correlation, found in this work, between a small grain size and a high tensile stress. Kushner observed that the grain size has a definite effect on stress and Mahla found an inverse relationship between the stress and grain size. Subramanian et al suggested that the grain size and internal stress are the result of some common factor rather than the grain size influencing the stress. Work is now being done to study this correlation between grain size and internal stress in copper deposits using no addition in the plating bath.

Deposits with Benzotriazole

The addition of benzotriazole to the plating bath has a marked effect on the internal stress. At low temperatures or high current densities, a high tensile stress, about 12.6 kg/mm², is produced: these conditions in the plain bath gave deposits with a maximum tensile stress of about 2.8 to 3.5 kg/mm². At bath temperatures about 40–50°C or low current densities the plain bath produced deposits with a low tensile stress and the bath containing benzotriazole gave deposits with the high compressive stress of about 12.6 kg/mm². At high temperatures, above 55°C in the plain bath and 80°C in the bath containing benzotriazole, the stress was very low. Thus the effect of benzotriazole on the internal stress is related to both the bath temperature and the cathodic current density.

The change in the stress with increasing deposit thickness has been discussed in general by Kushner and in copper deposits with and without benzotriazole in other papers. Several of the deposits with a high tensile stress peeled away from the basis and the deposit curled as shown in Fig. 4. This reduces the tensile stress in the deposit and is indicated during deposition by a sudden decrease in the deflection of the contractometer. Compressive stresses did not produce peeling.

The effect of addition agents in a plating bath on the internal stress in deposits has been widely studied. Knödler suggested that the addition was incorporated into the deposit...
in a hydrated state and then became dehydrated, so producing a stress due to the volume change. Foreign substances may prevent deposition on certain sites so that vacancies form; the distribution of these vacancies can produce compressive or tensile stress as proposed by Hoar and Arrowsmith. Another suggestion was due to Kendrick who proposed that interstitials could form on foreign molecules in the deposit and produce an extra plane of atoms and an internal stress. Popereka, in his dislocation-sorption theory, explained that a compressive stress was produced by the trapping of foreign particles in the intercrystalline spaces in the deposit. A tensile stress was caused by the adsorption of foreign matter which affected the dislocation density and produced a change in the surface of the growing crystals.

Benzotriazole is known to be codeposited with copper as cuprous benzotriazolate and, therefore, it may alter the stress by any of the above mechanisms. It also has a significant effect on the grain size of copper deposits which may influence the internal stress as suggested for pure deposits.

**CONCLUSION**

In this work it has again been found that copper deposits plated from a bath containing benzotriazole have a brighter appearance than those without the addition. The stress in these electrodeposits has been found to vary with both the bath temperature and the current density. Using the results in this paper, it should be possible to adjust the bath temperature and current density, either with or without the addition of benzotriazole, to control and predict more accurately the stress in the copper deposits. The data may be useful in determining the plating conditions to prevent the peeling of the deposits away from the substrate and so improve commercial practice.

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Microhardness, Grain Size and Topography of Copper Electrodeposits

R. Walker* and R. C. Benn**

ABSTRACT

The effect of varying the bath temperature, current density and solution agitation on copper deposits from the copper sulfate-sulfuric acid bath has been studied. Conditions which favored smooth deposits were low temperatures and high current densities and the application of ultrasonic agitation to the plating solution. These conditions, together with the impurities present in the unpurified bath, produced hard deposits (160 VHN). The mean intercept length was used as a measure of the grain size, on polished and etched surfaces, and was found to increase with temperature and decrease with current density. A Petch and a semilogarithmic relationship showed reasonable correlation between the microhardness with the mean intercept length.

This paper is a continuation of an earlier work previously published in This Journal.1 It reports on the effect of varying the bath temperature and current density on the microhardness, grain size† and surface appearance whereas the earlier article concerned the effect on the internal stress in copper deposits plated from a similar bath.

Photographs show the influence of both the temperature and current density on the surface appearance of the deposits. A comparison is made between the hardness of deposits from a still bath and those from a stirred and an ultrasonically-agitated bath. The microhardness is correlated with the grain size using both a Petch-type and a semilogarithmic relationship.

LITERATURE REVIEW

It is well-known2 that coarse-grained copper deposits are obtained from the acid sulfate bath at low current densities and room or elevated temperatures. These deposits have a low hardness and a tensile strength comparable with annealed wrought copper. At lower temperatures and higher current densities, a finer deposit is produced which is harder and stronger than the coarser deposit. Much fundamental work on the understanding of the nucleation and growth of copper deposits has been reported at the CITCE Conference on Electrodeposition in Vienna 1959.24

The microhardness of electrodeposited metals is usually much higher than that of fully-annealed metals and is frequently higher than that of the work-hardened metal.3 The factors which affect the hardness of deposited copper are of practical importance because there is a wide application for hard plated copper,4 e.g., injection molds and press tools for plastics, electrodes for welding, electrical components. The hardness of a coating depends mainly upon the structure and composition of the deposit, but for thin coatings it is also affected by the metal substrate. The principal factors which control the structure are the plating conditions, such as bath composition and purity, pH, addition agents, temperature, current density and agitation of the cathode or electrolyte. The variation for copper plated form an acid sulfate bath without addition agents is from 41 to 189 VHN; Lamb and Valentine using purified solutions found the range from 46 to 88 KHN.

An increase in the current density normally increases the hardness of many plated metals. For iron, this change with current density has been found to be from 210 (5 A/dm²) to 480 KHN (20 A/dm²) and with another bath 300 (1 A/dm²) to 570 VHN (4 A/dm²); higher values have been obtained for chromium 600 (30 A/dm²) to 900 VHN (60 A/dm²).6 For copper, smaller effects have been found under different plating conditions of 99 (2 A/dm²) to 150 VHN (10 A/dm²) of 115 (1 A/dm²) to 137 VHN (5 A/dm²) and 105 (2 A/dm²) to 160 VHN (10 A/dm²).7 Grain refining has been observed as the current density increased and Butts and DeNora8 found that a change from 1 to 7 A/dm² reduced the grain size by a factor of three. Graham9 reported that high current densities resulted in grain refinement but also promoted modules and tree growth.

The hardness of deposits usually falls with a rise in the temperature of the plating solution.2,6,8 For chromium this drop in hardness with temperature is from 700 (50°C) to 380 VHN (85°C); for iron it may be from 500 (20°C) to 250 (40°C) or 250 (20°C) to 190 VHN (40°C) depending upon the plating bath. For copper deposits, the decrease is much smaller and has been recorded as 59 (20°C), 58 (30°C) and 47 KHN (40°C) and 51 (15°C) to 47 VHN (26°C).10 Some workers11 have reported that the hardness increases and then decreases: 48 (20°C), 52 (30°C) and 41 VHN (58°C) with a current density of 1 A/dm² and 53 (20°C), 80 (30°C) and 57 VHN (58°C) with 7 A/dm².

Another factor which may have a pronounced effect on the hardness is agitation. A still bath has been found to give softer copper deposits (75 VHN) than a stirred bath (95 VHN) or one subjected to ultrasonic vibrations (111 VHN).11 Several workers12,17 have noted the correlation between a small grain size and a high tensile stress in copper deposits which is associated with an increased hardness.5,7,10,15 Variations in the concentration of copper sulfate in the plating bath affect the hardness14 with values of 104 VHN with 140 g/l and 58 with 280 g/l CuSO₄·5H₂O although other workers13 found no appreciable effect. The hardness increases slightly with the concentration of the sulfurous acid.7

EXPERIMENTAL

The composition of the plating bath was 125 g/l copper sulfate (CuSO₄·5H₂O) and 49 g/l sulfuric acid (both general grade reagents) in distilled water. To investigate the effect of impurities, a quantity of this solution was purified. Hydrogen peroxide (10 ml/l of 100 vol) was added to the solution.
ON THE OTHER HAND, ELECTRODEPOSITION OF ALLOYS FROM THICK LAYERS OF HIGH VISCOSITY SOLUTIONS (APPROXIMATELY 40,000 CENTIPOISES) AS IS DONE IN BARREL PLATING, GIVES RESULTS THAT ARE VERY SIMILAR TO RESULTS OBTAINED IN AQUEOUS SOLUTIONS (FIG. 7).

This indicates that in thick layers in these systems the major bulk of the ions is supplied in both cases by regular diffusion processes.

CONCLUSION

These studies indicate that in thin layers of plating baths metal is plated primarily from the ions trapped in the thin layer. On increasing the thickness of the plating bath, an increasing number of ions are supplied by diffusion from the bulk of the solution. One can, by plating from thin layers until the electrode is polarized, plate alloys with the same composition as the bath. If one plates beyond the point of polarization in the region where hydrogen is codeposited, one often obtains powdery non-adherent deposits.

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MEET THE AUTHORS

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**JAMES V. JOHNSON** obtained a BS in chemistry at Baylor University in 1969. While at Baylor, he was a member of the Student Affiliate Chapter of the American Chemical Society, as well as a member of Phi Mu Alpha, national fraternity for men in music. He is now employed as a process engineer at Texas Instruments in Dallas, working with plating process in the printed circuit board group of the firm's government products division. He is a member of the American Chemical Society.

**DR. KENNETH W. WARREN** is employed as a senior chemist with the Bellaire Research Laboratory of Texaco, Inc., at Bellaire, Texas. He was graduated from Baylor University in 1968 with a PhD in physical chemistry. His research interests include the electrochemistry of viscous systems and clay surface chemistry.
which was then refluxed for 40 min after the evolution of oxygen had ceased: activated charcoal (20 g/l) was added and the solution refluxed and stirred for about 30 min and then filtered with glass wool. A pre-electrolysis followed using Analar copper anodes with a current density of 2.2 A/dm² for several hours.

About one liter of fresh solution was used for each run and it was magnetically stirred slowly; this avoided aeration, but permitted solution mixing and reduced the temperature gradients. The cathodes were 2.5 mm thick to provide a firm base for hardness measurements, and lacquered to give an exposed area of 42.5 cm². The anodes were general grade copper sheet of the same area. All the electrodes were degreased with acetone, cleaned in nitric acid and rinsed in distilled water. The anode-cathode separation distance was 7 cm with the magnetic stirrer placed midway at a fixed distance below the electrodes. Immediately after plating, the cathodes were removed from the bath, rinsed in distilled water and dried.

Hardness measurements were made with the Akashi micro-hardness tester with a 50 g load. An annealed, polished copper plate was used as a standard to check the accuracy and setting of the instrument. For all experiments, the plating time and current density were adjusted to give the constant deposit thickness of about 50 μm, so ensuring the absence of any errors arising from the variation of hardness with thickness.7 The depth of indentation of the 50 g load was found to be less than 6% per cent of the total deposit thickness so the hardness of the substrate did not affect the measurements.20 Readings were taken on the as-plated and highly polished surfaces in the central region of the cathode and on some transverse sections but no appreciable difference was detected. Each recorded value is an average of at least seven measurements and is given to an accuracy of ± 10 VHN.

Up to six cells were connected in series for each run and the current density fixed (± 2 per cent) with temperature as the variable (± 3°). To determine the effect of electrolyte motion the still baths stood on anti-vibration padding and stirring was by immersed magnets; ultrasonic vibration was produced by immersing the plating baths in water in an ultrasonic tank, the temperature of which was kept constant by the use of cold water flowing through a copper cooling coil.

The electrodeposits were polished with a fine metal polish ‘doped’ with ammonia and then electropolished in phosphoric acid to remove the Beilby layer. A piece of mild steel flashed with nickel and plated with copper to the same thickness showed no signs of the substrate after electropolishing for 20 min. A grain boundary etch of ammonium hydroxide (50 ml), hydrogen peroxide (20 ml of 30 vol) and water (50 ml) was used. The intercept method was used to measure the grain size using a Quantimet television screen for large grains and a Vickers Projection Microscope with oil immersion (quoted magnification up to 4,000 x) for finer grains. By superimposing a straight-edged linear scale on the screen, the number of grain boundary intercepts was determined over the largest possible scale length, 300 mm on the Quantimet and 150 mm on the Vickers. All the measurements were confined to the central region of each cathode and the average taken from transverse, longitudinal and diagonal orientations of the scale. Twin boundaries were not included as grain boundaries. Some back reflection X-ray photographs were taken on the plated copper surface and the {331} and {420} diffraction lines examined.

RESULTS AND DISCUSSION

Because many plating variables are interdependent, it was necessary when investigating the effects of a given variable to keep all the other plating conditions constant. The composition of the plating bath was changed only to study the effect of purification on the hardness of the deposits.

MAY, 1971

Fig. 1. Effect of temperature and current density on the surface topography of copper deposits. Original magnification 320X.
Bath Temperature

In general, the deposits produced at high temperatures had a coarser, more uniform crystal structure (Fig. 1) with a larger grain size (Fig. 3) than at lower temperatures. These deposits are classified as "shiny and crystalline" and the pyramidal habit appears to be octahedral but is really non-planar as reported by Hardesty. The decrease in hardness with increasing temperature is illustrated in Fig. 4: the highest decrease occurred with the highest current density.

The bath temperature affects the diffusion reaction velocity, the polarization and the relative rates of nucleus formation and crystal growth. The ions are more mobile at higher temperatures, which favors equilibrium deposition and the formation of large grains with a low free energy. This is probably the reason for the production of large grains at high temperatures and small grains at low temperatures.

Electrolyte Motion

The surface appearance (Fig. 5) and cross sections (Fig. 6) of deposits from still, stirred and ultrasonic baths show a very marked difference. The deposits from the still and stirred baths had a powdery burned appearance with 4.3 A/dm² at 23°C, whereas from the ultrasonic bath the coating was satisfactory with 6.5 A/dm² at 23°C. The dependence of both the hardness and grain size on the current density and the degree of agitation is indicated in Fig. 7.

Ultrasonic vibrations have been used in copper plating to increase the limiting current density and the hardness, as well as to give grain refinement. These vibrations reduce the activation polarization and also the thickness of the cathodic double layer so increasing the limiting current density. These increases in the limiting current density, the microhardness, and also the grain refining have been observed previously for copper plating.

Purity

The purification treatment which removed some of the impurities from the plating solutions gave no significant change in the grain size but reduced the hardness of the deposits (Fig. 8) by about 20 VHN. These values are in good agreement with those obtained by others, using a similarly purified plating bath.

Hardness

In all this work there appears a strong correlation between a high hardness and a small grain size, or factors which produce a small grain size. This has been previously observed and many theories proposed to explain the relationship. Macnaughton and Hothersall suggested that the hardness was connected with the grain size and, for a given grain size, differences in the hardness could be due to different packing within the crystal lattice. Arkharov explained that a very small grain size produced many grain boundaries which...
blocked slip planes along which deformation of the crystals would normally occur. Other workers suggested that an increased hardness could result from a similar blocking effect caused by the adsorption of hydrogen\textsuperscript{35} and other foreign matter in the deposit such as impurities and addition agents.\textsuperscript{36-38} Hofer and Hintermann\textsuperscript{39} found that three factors seemed to influence the microhardness of copper deposits: the fineness of the grain, the dislocation density and the pinning of the dislocations by impurities; deposits with the smallest grain size and the highest strains had the highest hardness value.

The effect of impurities found in this work, namely, the increase in hardness without an accompanying alteration in grain size, suggests that the change in the hardness was due to the codeposition of these impurities which causes a distortion in the lattice of the deposited metal so impeding dislocation movement in the deposit.\textsuperscript{2} Miller and Kuss\textsuperscript{27} have indicated that intense agitation, such as ultrasonic vibration, favors the inclusion of foreign matter into the deposit so increasing the hardness. This confirms and explains the change in the hardness of 20 VHN produced by ultrasonics and reported above.

**Grain Size**

A change in the current density and also in the bath temperature caused a marked effect on the grain size (Fig. 3). Figure 9 shows the relationship between the grain size and

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**Fig. 5.** Surface topography of copper deposits. 4.3 A/dm\textsuperscript{2}, 23C. a) Still bath, b) Stirred bath, c) Ultrasonic bath. Original magnification 320 X.

**Fig. 6.** Cross-sectional microstructure of copper deposits. 4.3 A/dm\textsuperscript{2}, 23C. a) Still bath, b) Stirred bath, c) Ultrasonic bath. Original magnifications on the left, 200X on the right, 1000X.

**Fig. 7.** Effect of electrolyte motion on microhardness and grain sizes at different current densities.
microhardness for all the experiments with both the purified and unpurified stirred baths; a high deposit hardness is shown to correspond with a small grain size.

A thick deposit was used to ensure complete elimination of any epitaxial effect on the hardness and grain size measurements. Preliminary investigations were successfully made with mild steel plate flash-coated with nickel and copper-plated to give a 50 μm (2 mil) deposit; this ensures that surface polishing did not reduce the deposit thickness below acceptable limits5, 7, 20 (the nickel coating acted as a base marker).

There have been several attempts to relate the grain size of a metal with its mechanical properties.41-43 One of these, the Hall-Petch equation,42 relates the grain size 'd' with the hardness 'H' of a metal

\[ H = H_0 + K_H d^{-1/2} \]

The term \( H_0 \) is the value characteristic of dislocation blocking (related to the friction stress43) and \( K_H \) takes account of the penetrability of the boundaries to moving dislocations (related to the number of available slip systems). The equation has been found applicable to several polycrystalline, pyrometallurgical materials44 and also for electrodeposited iron.45 Other work46 has shown that a semilogarithmic equation may be used to connect the grain size 'd' with hardness 'H' by:

\[ H = a + b \log d \]

(a and b are constants)

This has been found satisfactory for pure pyrometallurgical iron46 and the data reported for nickel deposits appear to obey this equation,47 which, however, does not have any theoretical basis.

The grain size and hardness values reported in this paper have been plotted and a computer used to draw the lines using the method of least squares and are slightly better represented by the semilogarithmic relationship (Fig. 10) than by the Petch equation (Fig. 11). For deposits from the pure bath the \( H_0 \) term, in the Petch equation, has a lower value than with the unpurified bath which suggests that the co-deposited impurity increases dislocation blocking.

Although much work has been carried out on the relationship between the grain size and hardness of as-cast and heat-treated metals, the results in this paper indicate that these equations also apply to electrodeposited metals which have a much smaller grain size and increased hardness.

**X-Ray Analysis**

All the X-ray photographs of the copper deposits showed resolved doublets for the \{331\} and \{420\} diffraction lines which suggests that the deposits had a low or zero microstress because a high stress gives diffuse lines. Plated copper specimens with a large grain size gave spotty rings whereas those with a fine grain size produced continuous uniform rings.
CONCLUSION

The results in this work show that the microhardness of copper deposits from an acid sulfate bath increases with current density (with a maximum effect at low temperatures) and decreases with bath temperature (the maximum effect being at high current densities). Both these factors affect the surface topography and also the grain size, the finest structure being obtained with a high current density and low temperature. Ultrasonically-agitated plating baths give a harder deposit with a finer grain size than those from a magnetically-stirred or still bath. Purification of the bath decreases the hardness by about 20 VHN but does not significantly alter the grain size. The hardness and grain size values have been analyzed using the Petch equation, but a better correlation was found using a semilogarithmic relationship. Some indication of preferred orientation was observed in deposits from low current density and high temperature baths.

ACKNOWLEDGMENTS

We thank Professor M. B. Waldron for his interest and for the provision of research facilities at the University of Surrey.

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Discussions of this paper are invited for publication in a future issue of Plating.
Recovery of Mixed Rinse Water by Means of Ion Exchange

J. F. Zievers and C. J. Novotny*

Recent American and British literature on recovering plating rinse waters for re-use by means of ion exchange generally discusses two methods: (a) treatment of combined rinse waters after “self neutralization” \(^{1, 2}\) and (b) elimination of cyanide or chromium-bearing rinse waters by either separate treatment or destruction, and recovery of acid and alkaline rinse water by means of ion exchange.\(^{3, 4, 5}\)

Technical literature, especially from other areas in Europe, reveals a tendency toward the direct application of ion exchange to mixed rinse waters regardless of their content.\(^{6, 7}\) Full-scale applications of this European technique have been made in selected plants in the U.S.A. and also tested on laboratory scale.\(^{1, 2}\) It has generally been found that when rinse waters containing both cyanide and hexavalent chromium are treated by conventional ion exchange techniques, the resultant water returned for rinsing will contain 6 to 15 ppm of cyanide or chromium.\(^{8, 9}\) The presence of these quantities of cyanide can result in release of hydrocyanic acid, which, of course, is toxic.\(^{10}\) However, modifications of the plating process and rinse treatment techniques can eliminate potential health hazards and make direct treatment of combined rinses by ion exchange a useful and economic tool.

This paper discusses first a method of setting up for rinse water recirculation; it then explores successively three alternative equipment “answers” to the same problem. These answers are considered in order of increasing desirability. Equipment and chemical costs indicated are the actual costs at time of writing (June, 1970). It is shown that a carefully chosen combination of modern ion exchange techniques can reduce the cost of recovered water by about 25 per cent.

For illustration, it is helpful to discuss a hypothetical plant, of which the details relevant to this discussion are shown in Table I.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>HYPOTHETICAL PLATING PLANT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water—310 ppm TDS**</td>
<td>Recirculated water quality—30 μmhos/cm</td>
</tr>
<tr>
<td>Recirculated water rate—150 gpm (U.S.) minimum</td>
<td>Effluent requirement (Max permitted to sewer), ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>Ni</td>
</tr>
<tr>
<td>Cr (total)</td>
<td>Cr (total)</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe</td>
<td>CN (free)</td>
</tr>
<tr>
<td>2.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>Cl</td>
</tr>
<tr>
<td>0.1</td>
<td>6.5-9.0</td>
</tr>
<tr>
<td>Zn</td>
<td>Fe</td>
</tr>
<tr>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Ca</td>
<td>Cl</td>
</tr>
<tr>
<td>0.5</td>
<td>6.5-9.0</td>
</tr>
<tr>
<td>Mg</td>
<td>Cl</td>
</tr>
<tr>
<td>0.5</td>
<td>6.5-9.0</td>
</tr>
<tr>
<td>K</td>
<td>Cl</td>
</tr>
<tr>
<td>0.5</td>
<td>6.5-9.0</td>
</tr>
<tr>
<td>Na</td>
<td>Cl</td>
</tr>
<tr>
<td>0.5</td>
<td>6.5-9.0</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>Total suspended solids</td>
</tr>
<tr>
<td>30 jumho/cm</td>
<td>30 jumho/cm</td>
</tr>
</tbody>
</table>

- Equipment: Automatic machines, hoist lines, hand lines, rack and barrel (oblique, rotated above bath during dwell time).
- Work: 16 hr day; plating on steel and brass, 50% rack; 660 ft²/hr zinc; 165 ft²/hr chromium on steel, 30% instrument housing, 20% typical solid handles.
- Raw water—310 ppm TDS**
- Recirculated water quality—30 μmhos/cm
- Recirculated water rate—150 gpm (U.S.) minimum
- Effluent requirement (Max permitted to sewer), ppm
- Cu | Ni
- Cr (total) | Cr (total) | Cr (total) | Cr (total) | Cr (total)
- 2.0 | 1.0 | 0.5 | 0.5 | 0.5
- Fe | CN (free) | Ni | TSS | Cd
- 2.0 | 0.1 | 3.0 | 30 | 3.0
- Mn | Cl
- 0.1 | 6.5-9.0
- Zn | Fe
- 3.0 | 3.0
- Ca | Cl
- 0.5 | 6.5-9.0
- Mg | Cl
- 0.5 | 6.5-9.0
- K | Cl
- 0.5 | 6.5-9.0
- Na | Cl
- 0.5 | 6.5-9.0
- Total dissolved solids
- Total suspended solids

Setting up—First Possibility

With such a hypothetical plant, where the plant operators were planning for detoxification and neutralization of effluent for disposal to sewer only, experience indicates that the total rinse flows are approximately 150 gpm, with an average increase (net over raw water content), in total dissolved salts of 200 ppm. Dumps (if equalized over the work day), will average approximately 1 gpm of cyanide and highly alkaline materials at a concentration of approximately 100,000 ppm total dissolved solids and 1 gpm of hexavalent chromium plus acid at a concentration of 100,000 ppm total dissolved solids.

Estimated direct chemical costs and direct chemical costs plus amortization of equipment have been adequately set forth in earlier papers, for such a detoxification and neutralization plan.

At the total rinse flow of 150 gpm cited, experience shows that rinsing would be considered “adequate.” Experience has shown that if the rinse rate were doubled to 300 gpm the total contaminant in the rinse water would increase by about 4 per cent. In other words, doubling the rinse rate will produce a relatively low increase in total contaminant, but will produce excellent rinsing quality with all of the previously reported benefits.\(^9\) If the rinse rate were doubled, the contaminant level would be 4 per cent more than one-half of what it was. This would give a flow of 300 gpm with a contaminant level of 108 ppm total dissolved salts.

Contamination from the dumps, and hence the cost of treating for detoxification and neutralization of those dumps, would remain the same as it would be in a total destruction plant.\(^4, 5\)

Setting up—Second Possibility

Consider a plant where dumps are destroyed and rinses are recirculated. If a doubled (300 gpm) rinse rate is passed through a demineralizer station, excellent rinse water will be produced. During the demineralization cycle, the cation resin will remove trivalent chromium along with other cations present. The anion resin will capture cyanide and hexavalent chromium as well as other anions present.

Safe waste treatment of the anion regenerant will first require chlorination at the existing high pH of that regenerant, followed by depressing the pH from about 10 to about 3 to reduce the hexavalent chromium to the trivalent state by treatment with a reducing agent such as sulfur dioxide. The pH must again be raised to the tolerable limits, which in this hypothetical case would be at least 6.5. This will produce a very high chemical cost for treatment of the ion exchange regenerant effluent. It should also be remembered that even the benefit of normally being able to self-neutralize the cation resin and the anion resin regenerant effluents by mixing them does not pertain here: when they are finally in a condition where they can be mixed, they are both at a very low pH.

Setting up—Third Possibility

The situation described could be avoided by having two separate demineralization stations, e.g., one to handle only chromium-bearing rinses and one to handle all other rinses. This will reduce the cost for waste treatment of the regenerant effluent, because the volume of hexavalent chromium bearing anion effluent on the anion half of the chromium demineralizer loop would be much smaller. The problem of depressing the pH still exists, but it would be much smaller. The capital cost for two demineralizer stations as opposed to
Engineering Aspects of Internal Stress in Electrodeposits

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A number of factors may influence the internal stress present in an electrodeposit, and this in turn may affect the chemical and mechanical properties of the plated product. From a production aspect, an understanding of the effects and of possible methods of reducing any detrimental ones is of the greatest importance.

The problems associated with the internal stress in an electrodeposited metal have troubled the plating industry for many years. Although two electroplated coatings may have a similar appearance, their mechanical and chemical properties may be completely different due to the different internal stresses which are present in the deposits. Thus the fatigue strength of a steel plated with nickel may be decreased by as much as 40% or increased by 10%; the corrosion protection afforded to brass articles by chromium deposits may vary by a factor of four. Electrodeposition is used to produce different coatings for a variety of purposes and consequently the deposit thicknesses will vary and this influences the stresses present. For example in the following two extreme cases, gold or chromium deposits for decoration may have a thickness of about 0-00001 in., whereas hard nickel for the building up of worn machine parts may be 0-5 in. or more.

Because of the extensive application of electroplating to a wide range of products a large number of different metals are used to meet particular requirements. Some of the following properties may be necessary to produce satisfactory coatings in the metal finishing industry:

1. mechanical (wear surfaces) e.g. Cr, Ni, Rh.
2. conductive (switch gear) e.g. Au, Ni, Rh, Cu, Pd, Sn.
3. protective (‘tin’ cans) e.g. Sn, Zn, Cd.
4. reflective (mirrors) e.g. Cr, Rh, Ag.
5. decorative (cutlery) e.g. Ag, Au, Rh, Pt, Ni, Cr.
6. joining (solderability) e.g. Sn, Cd.

In electroforming and electrotyping copper and nickel deposits are used and in the building up of worn or overmachined parts coatings of nickel, chromium or iron are applied.

The internal stress in a deposited coating is the force per unit area acting in a direction parallel to the plated surface. The electroplated metal may shrink during or soon after plating and this produces tensile stress or the deposit may expand resulting in compressive stress. If only one side of a thin metal strip is plated a tensile stress causes the strip to bend towards the deposit whereas a compressive stress bends the strip away from the deposit. The tensile stress in a nickel deposit from the deposit (Fig. 1) and if the base is dissolved the deposit bends to a greater extent (Fig. 2).

The magnitude of this internal stress in a deposit depends upon many factors including the plating conditions and varies from very high tensile values of about 200,000 lb./sq. in. for chromium and rhodium to low compressive values of about 4,000 lb./sq. in. for lead and zinc: in electrodeposited tin-nickel alloys the stress varies from 36,000 lb./sq. in. tensile to 40,000 lb./sq. in. compressive. Kushner has shown an apparent correlation between a high tensile stress and a high melting point. A few typical values are given for some commonly plated metals.

Stresses in Electrodeposits

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress Range (in 1,000 lb./sq. in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodium</td>
<td>100-300</td>
</tr>
<tr>
<td>Chromium</td>
<td>50-250</td>
</tr>
<tr>
<td>Palladium</td>
<td>50-100</td>
</tr>
<tr>
<td>Cobalt</td>
<td>15-90</td>
</tr>
<tr>
<td>Nickel</td>
<td>6-65</td>
</tr>
<tr>
<td>Manganese</td>
<td>5-6</td>
</tr>
<tr>
<td>Gold</td>
<td>1-10</td>
</tr>
</tbody>
</table>

Indium, bismuth and tin are also deposited with a compressive stress, while gallium and antimony deposits may have a compressive or tensile stress.

**Measurement of Internal Stress**

The internal stress in a deposit can be measured by several methods, the majority of which depend upon the bent strip technique. This involves plating a metal on one side of a thin metal strip (the other side is usually lacquered to prevent deposition) and measuring the resulting deflection which is caused by the internal stress in the deposit. The fundamental principles and equations used to calculate the internal stress from this deflection are compared by Gabe and West. The strip may be held rigidly during plating in which case the stress value obtained is relevant to deposition on thin objects or in electroforming.

If the extent of bending of the strip during plating can be measured, then a continuous record of the variation of the stress with deposit thickness can be calculated. Brenner and Senderoff increased the accuracy of this method by using a long strip in the form of a helix which twists during plating; this Spiral Contractometer (Fig. 3) is produced commercially and is widely used in industry and research. The upper end of the helix is
clamped and the movement of the lower end is magnified by a system of gears and is indicated on a dial. Another form of the bent strip method was designed by Hoar and Arrowsmith. They used a null method and measured the restoring force required to prevent the strip from moving during the deposition of a stressed deposit. Both these methods have been modified to increase the sensitivity.

The original method of plating a stressed deposit on a silvered glass thermometer bulb and measuring the change in the level of the mercury, as used by Mills in 1877, has been modified by Kushner. This Stresometer consists of a metal disc firmly clamped on to a shallow chamber containing a measuring fluid. As plating occurs this thin disc distorts and changes the volume of the vessel; the stress is calculated from this volume change which is measured by the variation in height of the liquid in a capillary tube attached to the vessel.

Other methods of measuring the stress include the use of X-rays and the calculation of the stress from the resultant line broadening; this is non-destructive but rather complicated and consequently is used for research purposes only. Magnetic and strain gauge techniques have also been used.

**Properties Affected**

The presence of a high stress in an electrodeposited coating may be detrimental to the coating or to the basis metal; this is particularly so if the stress is high and tensile.

If a metal is plated in a highly stressed condition and the adhesion to the substrate is poor the coating may peel away from the substrate. Figs. 4 and 5 show identical Watts nickel deposits on a brass sheet base; the peeling in Fig. 5 is due to bad adhesion caused by poor surface cleaning. This is important in the plating of non-conducting articles, e.g., plastic badges, mouldings and name plates. With good adhesion a deposit with a tensile stress may crack and so relieve the internal stress; deposit cracking and peeling is shown in Fig. 6. This spontaneous cracking has been observed in coatings of chromium, iridium, palladium and rhodium and is utilised in the production of microcracked chromium deposits. Deposits with a compressive stress do not have this tendency to crack but may peel. The porosity of a deposit has been found to increase with the internal tensile stress and so the corrosion protection afforded to the basis metal may be decreased.

Electroforming, the manufacture of articles by electrodeposition, is frequently used in the fabrication of components where special requirements are needed, e.g., high accuracy, surface finish, hardness and extreme thinness or detailed reproduction. A high tensile or compressive internal stress causes deformation of the article (Figs. 1 and 2) when it is removed from the mandrel (which may be aluminium, plastic, wax etc.). This loss of dimensional accuracy is extremely important in the production of waveguides, printed circuits and gramophone record matrices. In the printing industry, use is made of deposits which should be fairly hard to give mechanical strength and have a low stress to reduce any tendency to distortion for electrotyping, photogravure and lithography: in 1950 over 2,500 tons of copper were used in making electrotypes which had a value of over £25 million.

The presence of a high internal stress in a deposit normally makes the metal more reactive (or anodic) than a stress-free deposit because of the higher internal energy and therefore thermodynamically it is more liable to corrode. Also any distortion due to the stress may produce surface active sites, e.g., steps or kinks which increase the surface reactivity. Krijil and Melse have used calorimetric methods to show that the dissolution rate of a bright, highly-stressed nickel deposit is about three times that of a matt deposit. This fact is utilised...
in the production of double layer or duplex nickel coatings which consist of a bright nickel layer, with a high stress, superimposed on a semi-bright nickel underlayer, with a lower stress. When corrosion occurs the bright coating, which is anodic, is preferentially attacked and the semi-bright coating, which is cathodic, is protected. This undercoat therefore prevents both corrosion of the basis steel and discoloration of the nickel plate. The double layer gives about twice the corrosion protection of a single layer of bright nickel of equal thickness.

If the deposit has a high tensile stress it may crack as mentioned above (Figs. 5 and 6). The corrosion at cracks such as this has been studied by Hoar and Shreir. This is not very important from a corrosion aspect if the coating is anodic to the basis material to which it gives protection, e.g. zinc or cadmium on steel. However, if the coating is cathodic, these cracks may increase attack on the anodic basis metal, e.g. nickel and chromium on steel. The extent of this corrosion depends upon the corrosive environment and may be stimulated in immersed conditions, but not normally in the atmosphere. It is often difficult to maintain a crack-free chromium deposit because the coating is highly stressed and may
crack on impact during service. A micromachined chromium deposit is used which spreads the corrosion of the substrate over a large area and reduces the tendency for deep pitting. A coating with about 2,000 cracks per linear inch is desirable and gives an improvement in the corrosion behaviour over the conventional chromium deposit of about 300-400%.

The fatigue strength of a steel object coated with a metal with a high tensile stress may be considerably reduced. The effect of chromium plating steel has been widely studied and it has been found that the fatigue strength is normally reduced by between 10% and 40%, but may be as high as 80% of the variation depending upon the plating conditions and the stress. Williams and Hammond have related the percentage change in the fatigue limit (L) with the internal stress (I) in t.s.i. and the fatigue limit (F) for chromium deposits on steel by

\[ L = 50 - 3I - 2F. \]

Hence a tensile stress in the coating is detrimental but a compressive stress is beneficial. A zinc deposit with a compressive stress has been found to increase the fatigue strength by up to 10%.

The corrosion-fatigue behaviour (the conjoint action of corrosion and fatigue) of a steel is also affected by a stressed deposit. Nickel and cadmium coatings are plated with a low compressive stress which increases the dry fatigue limit (see above), and both are employed to give sacrificial cathodic protection against corrosion to steel. Hence, these are used to give corrosion-fatigue protection to steel. A zinc deposit has been found to increase the corrosion-fatigue strength of steel in a 3% salt spray test from 3.5 tons/sq. in. to 21.4 tons/sq. in. in the drawn state and from 4.0 tons/sq. in. to 14.7 tons/sq. in. in the normalised condition; cadmium plating on the same steel altered the corrosion-fatigue strength to 18.9 tons/sq. in. and 13.7 tons/sq. in., respectively. In fresh water, using a different steel, the values changed from 9 tons/sq. in. to 22 tons/sq. in. with a zinc deposit and to 20.5 tons/sq. in. with a cadmium deposit. Nickel and chromium deposits, which are cathodic to steel, also give added protection to steel in fresh water and improvements of 50% and 100%, respectively, have been obtained.

The presence of an electrodeposited coating with a high tensile stress reduces the stress-corrosion life of the article: the life of a 5% chromium steel was reduced by about 300% with a nickel deposit with a tensile stress. However, electrodeposits of nickel-cadmium with a lower stress have been found to increase the time to failure of the same steel by stress cracking from 1.5-3 days to 363 days in a marine atmosphere from 4-20 days to more than 420 days in a semi-industrial atmosphere. The protection conferred by different deposited metallic coatings on the stress-corrosion behaviour of brass has been studied by Laub who found considerable improvements in some cases. He tested thirteen deposits (including alloy and multilayer systems) and found the best protection was given by heat treated nickel layers or a nickel-silver system but a lead deposit was also good. Stress-corrosion has never been found if the total stress (in the article and coating) is compressive.

The presence of internal tensile stress in a deposit may be used to advantage in certain circumstances. In the production of electrodeposited magnetic films the internal stress causes preferred directions of easy magnetisation. Such has proposed that to maintain satisfactory production (i.e. no cracking in the plate) for nickel plating baths the ratio of the tensile stress and the ductility should be kept within certain limits (these vary with the plating bath and for one bright bath the values given were less than 1,000 for the ratio and with the stress below 10,000 lb./sq. in. and ductility about 8). Methods of Reducing the Detrimental Effects of Stress

The different methods of reducing the stress of a deposit on a particular substrate include varying the composition of the plating bath, the control of the operating conditions and the subsequent treatment, and these may be used separately or together.

The internal stress in a deposit varies with the deposit thickness; initially it is usually high in thin coatings and decreases to a limiting value in thick films: in nickel deposits from the bromide bath the stress is 29,000 lb./sq. in. at 1 x 10^-1 in. and the limiting value is 11,000 lb./sq. in. The effect of the composition of the plating bath is very important. Thus the Watts bath is used extensively to produce nickel deposits because it is economical although it may give deposits with a high tensile stress (5,000 to 41,000 lb./sq. in.). Special baths may be used to produce deposits with a low tensile or compressive stress; for example the nickel sulphamate bath gives deposits with a compressive stress (6,000 to 0.000 lb./sq. in.) whereas the Watts bath gives deposits with a high tensile stress (21,000 to 30,000 lb./sq. in.). Kushner has compared the effect of different anions in the nickel plating bath and lists them in order of the limiting value of the internal tensile stress: sulphamate (8,500 lb./sq. in.), bromide (11,000 lb./sq. in.), fluoborate (17,000 lb./sq. in.), sulphate (22,800 lb./sq. in.) and chloride (33,000 lb./sq. in.). For copper deposits typical stress values are 8,000 lb./sq. in. (tensile) for the cyanide bath and 0-3,000 lb./sq. in. (tensile) for the sulphate bath; the pyro sulphate bath gives compressive stresses. However, these special baths are usually more expensive than the usual baths and so are not normally used unless a high stress is very undesirable.

If circumstances do not permit the composition of the bath to be changed, then the operating conditions should be carefully considered. The effect of the bath temperature is very important and normally, as the temperature of the bath is raised, the tensile stress decreases. For copper deposits from the cyanide bath the tensile stress values have been found to be 11,500 lb./sq. in. after plating at 55° C., 8,700 lb./sq. in. at 70° C. and 5,800 lb./sq. in. at about 80° C.; for hard nickel deposits the figures are 28,500 lb./sq. in. at 30° C., 22,800 lb./sq. in. at 50° C. and 17,100 lb./sq. in. at 70° C. A minimum stress has been reported for nickel coatings at 55° C. for the Watts bath and 43° C. for the sulphamate bath. The effect of varying the current density depends upon the particular bath, however, the tensile stress often increases with the current density e.g. for copper cyanide at 20 A./sq. ft. the stress is 8,700 lb./sq. in. and at 40 A./sq. ft. it is 14,700 lb./sq. in. It has been found that the current efficiency is related to the resulting stress and so the current density which gives the lowest tensile stress may be that corresponding to the maximum current efficiency; this would reduce the production of hydrogen and so reduce any tendency to hydrogen embrittlement or internal stress due to the incorporation of hydrogen in the deposit.

Variations in the concentrations of the constituents in the bath also affect the internal stress. The structure of an
electrodeposit depends upon the pH of the plating bath. This is particularly true of nickel deposits and the oxygen and hydrogen content of the deposit increase rapidly above a pH of about 5. The tensile stress also increases noticeably at a similar pH and the stress values are 25,000 lb./sq. in. at pH = 5, 43,000 lb./sq. in. at pH = 5.5 and 60,000 lb./sq. in. at pH = 5.7. Increasing the concentration of chromic acid in a conventional bath decreases the internal stress in the chromium deposit.

As the copper concentration in the Rochelle cyanide bath increases the tensile stress decreases, e.g. 9,700 lb./sq. in. with 2-5 oz./gal., 8,700 lb./sq. in. with 4 oz./gal. and 6,800 lb./sq. in. with 5 oz./gal. In a Watts bath the tensile stress increases linearly with chloride content rising from 17,000 lb./sq. in. in a 2N nickel bath in steps of 7,000 lb./sq. in. for every 0-5 N addition of nickel chloride up to 46,000 lb./sq. in.; a similar effect occurs in the nickel sulphamate bath.

Addition agents are commonly used in plating baths to reduce pitting and to give bright and level deposits. The addition agents used in bright nickel baths often considerably increase the tensile stress and corrosion rate of a deposit, hence the frequent use of stress reducing addition agents. However, in copper plating baths the use of benzotriazole, which is codeposited with the copper, increases the tensile stress and gives a bright coating with a high residual oxygen content. Naphthalene sulphonates (1,3,6-; 1,5-; 2,7- and 2-) produce compressive stress in nickel deposits from the Watts bath (even, in some cases, when only a 0.003M solution is used). Saccharin and p-toluenesulphonamide are also used to reduce the tensile stress in nickel baths. Impurities in a plating bath are also important. Marti has studied the effect of foreign ions in a nickel sulphamate bath and found that to change the stress by 1,000 lb./sq. in. (normally the stress is increased) concentrations of as little as 5 p.p.m. of phosphate or nitrate or as much as 300 p.p.m. of iron or 1,000 p.p.m. sulphate are required.

Another method of reducing internal stress is the periodic reversal of the plating current or the superimposition of alternating current on direct current. Thus, reductions have been observed in the stress in copper deposits from the acidic bath from 1,750 lb./sq. in. to 1,290 lb./sq. in. and in silver deposits from the cyanide bath from 2,100 lb./sq. in. to 1,500 lb./sq. in. Kendrick found that using an all chloride bath direct current gave dark deposits with low ductility and high tensile stress (56,000 lb./sq. in.) whereas with superimposed alternating current he obtained soft ductile deposits with a lower tensile stress (17,000 lb./sq. in.). Other metals which show a reduced tensile stress with superimposed alternating current include chromium, iron and cobalt. The extent of the change in the stress depends upon the frequency of the alternating current, the ratio of the direct to alternating current and the current density. The plating of nickel in an ultrasonic field has been found to improve the ductility and adhesion, increase the hardness and decrease the internal stress of the deposit. The stress was less than half when plated under normal conditions, the reason suggested was that the ultrasonic field encourages the molecular hydrogen on the nickel surface to form bubbles which are shaken off and so the hydrogen does not penetrate into the metal. In contrast with normal conditions, as the temperature of the bath increases so does the stress in the deposit produced in the ultrasonic field.

A post plate heat treatment may be used to reduce the internal stress. The introduction of hydrogen into the lattice during plating may give a stress of up to 10,000 lb./sq. in.; if this hydrogen is removed and there is no external force the stress is completely removed without damage to the lattice. Hence with nickel and chromium coatings, which are permeable to hydrogen, a short bake at about 200°C will remove the hydrogen and so reduce the stress and any tendency for hydrogen embrittlement. However, with zinc and cadmium coatings, which are relatively impermeable to hydrogen, a much longer time is required for the baking (about 24 hours) at 200°C. An alternative method is to deposit a very thin coating of zinc or cadmium and then to bake it for a very short time. This thin coating allows the hydrogen to diffuse outwards but on subsequent plating it acts as a barrier against the inward diffusion of more hydrogen. A heat treatment of between 5 and 16 hours at 1600°C in hydrogen has been used to produce ductile, recrystallised chromium electro-forms with both the cracks and the stress removed.

The use of a soft silver undercoat which allows some stress relief by plastic deformation when coated with highly stressed rhodium has been proposed by Reid. Similarly a layer of lead or tin between a nickel deposit and a steel base has been shown to prevent cracks in the nickel spreading into the steel under fatigue conditions.

**Conclusion**

In this paper it has been shown that the internal stress in an electrodeposit has an important effect on the final performance of the finished article. This aspect of plating has not always been sufficiently considered by the metals engineer. From a production aspect an understanding of the properties affected by internal stress in a deposit and possible methods to reduce any detrimental effects is vital in the manufacture of satisfactory coatings. Therefore for control purposes, wherever the magnitude of the internal stress is important, regular stress measurements during plating should be made.

At present the cause of the internal stress is not fully understood although many theories have been proposed. These theories are discussed in recent reviews which include detailed descriptions of the measurement and significance of internal stress in electrodeposited metallic coatings.

**Acknowledgment**

The author wishes to thank Professor M. B. Waldron and Dr. J. Mackowiak of the Metallurgy and Materials Department, University of Surrey, for helpful suggestions.

**REFERENCES**

Changes Increase Production and Improve Quality

The six finishing stands and run-out conveyor of the narrow hot strip mill.

The recent completion of two extremely complex engineering feats has added to the product range and increased the competitive power of the Whitehead Works at Newport, Monmouthshire. The modernisation at Whiteheads (a member of the East Moors and Whitehead Division of the British Steel Corporation, South Wales Group) involved the building of a new narrow hot strip mill at a cost of £2 million, together with the amalgamation of two bar mills and various ancillary work involving a further total of £350,000.

The new strip mill, capable of finishing speeds varying from 1,200–3,600 ft./min., according to gauge, replaces one installed in 1920. Its highly sophisticated tension control enables it to produce strip of very consistent quality with excellent surface characteristics. It also covers a wider range of widths (2 in. to 8 in.) and gauges (0-040 to 0-250 in.) than the old mill and can provide heavier coils.

The bar mill conversion means that instead of concentrating largely on rolling cut lengths of reinforcing bars for the construction industry, Whitehead’s are now producing forging quality bars and bars for the manufacture of nuts and bolts. Eventually they will be able to supply also bars, hexagons and flats for bright drawing.

Major users of narrow strip produced on the new hot mill are the tube manufacturers but the car industry also takes large quantities for the production of suspension units, wheels, exhaust systems, starter motors, lamp reflectors and many other essential parts. Whitehead’s also supply material for a variety of household articles, such as washing machines, refrigerators, TV sets and even lipstick cases.

The new mill was designed by Schloemann, A.G., of West Germany, and manufactured in Great Britain by Wellman Machines, Ltd. It is built along the line of the old mill and phasing new units with the old as installation proceeded, presented engineers and production personnel with many problems, all of which were overcome with negligible interruption to production. The bar mill operation also needed intricate planning, since sections of the old No. 1 mill had to be incorporated into No. 3 mill with the minimum of lost production time.

Mill Descriptions

The new narrow strip mill has been designed to meet the call for strict limits on tolerances by the installation of twelve horizontal stands which are divided equally in the roughing and finishing sections. There are also two vertical stands which are capable of heavy reduction in sizing of slabs and billets.

Two edging mills complete the complement of roll stands and are used for light control to help maintain the essential tolerances now required with hot strip. To further guarantee the strict rolling limits, an Exatest width gauge has been fitted to give a continuous indication of the coil width.

Red hot bars, half an inch in diameter, being coiled on the pouring reels.
PLATING in an ultrasonic field has been found to produce electrodeposits with improved physical and mechanical properties. Using ultrasonics, an increase has been observed in the brightness, hardness, and adhesion of deposits as well as a decrease in the grain size, internal stress and porosity. A higher current density can be used during plating with ultrasonics than under normal conditions and this decreases the deposition time required to produce a specific thickness. The use of an ultrasonic field during plating is particularly beneficial if hydrogen is produced in deposition, because it reduces the tendency for atomic hydrogen to enter the metal and give hydrogen embrittlement of the plated article.

Since the observation by Young and Kersten(1) in 1936 of ripples in electrodeposits produced in an ultrasonic field, little work has been done until fairly recently. The effect has been studied extensively in the U.S.S.R., but it is difficult to assess the work because many of the papers published have not yet been translated into English.

This paper reviews some of the literature on ultrasonic plating. It reports on the results of a comparison, which has been made by the authors, of the properties of deposits from this type of bath with those obtained from a static and a stirred acid copper-sulphate plating bath.

In the majority of the literature it has been assumed that the main effect of an ultrasonic field is similar to that of intense mechanical mixing. These vibrations produce a more uniform composition in the electrolyte than can be obtained by any other method of mixing used in electrodeposition(2). Ultrasonic vibration has also been found to achieve a more uniform deposit than can be produced by mechanical mixing of the plating solution.

Current density

For many metals, a much higher current density can be used when plating in an ultrasonically irradiated bath than in a static or mechanically agitated bath(3-4). The reason for this increase is that an ultrasonic field reduces the polarization of the solution at the metal surface and makes the layer of electrolyte adjacent to the electrode more uniform. Because the polarization is reduced, the total voltage required for the process is also reduced; this has been described for copper plating from the cyanide bath(5).

The effect of different electrolyte conditions on the anodic current density which can be used in copper plating wire has been investigated by Luk’yanov and Pavlov(6). They found that for a stationary electrolyte the maximum current density was 15 A/dm², which increased to 50 A/dm² when the solution was mixed mechanically; in an electrolyte vibrating at a frequency of 100Hz, the current density was 75 A/dm², and this increased to 125 A/dm² when an ultrasonic field was used. This last form of mixing permitted the plating time to be reduced by a factor of about 8 compared with the static solution.

The extent of the increase in the highest current density which can be used in an ultrasonic field compared with ordinary conditions, depends upon the particular plating bath. This has been studied for the deposition of many metals including chromium(7-9), silver(10), gold(11), and cadmium(12). For zinc plating, the increase in the current density has been widely studied(12-17) and given as 2(14), 5(15), and 7(16) fold for different baths. An increase of 25-fold has been recorded for nickel from acid baths(13) and 15-fold for the nickel cyanide bath(14). Copper deposition from an ultrasonic bath has been studied(16) and increases of two or three-fold found for ammonia electrolytes(23), eight-fold(24) and 20 to 30-fold(14) for cyanide baths. For the acid copper bath, the increase depends upon the bath composition; as follows: with 200 g/l copper sulphate and 60 g/l sulphuric acid(24) the increase was from 5 A/dm² to 16 A/dm²; and with 250 g/l and 75 A/dm² to 125 A/dm². Good deposits(25) have been produced from the sulphate bath with a current density of 140 A/dm² whereas spongy coatings are produced under ordinary plating conditions.

The extent of the possible increase in the current density depends upon the intensity of the ultrasonic field and the electrolyte temperature. As the intensity increases from 0.05 to 1.0 W/m² x 10⁻⁴ at 20°C, the plating rate increases by factors of 1.85 and 4.12 compared with ordinary conditions(24). These increases are indicated at different temperatures: they are 2.8 and 5.92 at 10°C, and 2.61 and 6.28 at 35°C, and 3.72 and 7.36 at 50°C.

The use of an ultrasonic field is beneficial because, due to the decrease in the polarization, it is possible to plate from electrolytes with much lower concentrations of salts than normally used. Good quality deposits of nickel(21-27) and copper(6-27) have been obtained from very dilute solutions. This improvement may be due to the electrical conductivity of electrolytes, this increasing when they are subject to an ultrasonic field(29), or may result from the elimination of dissolved gases from the
plated foam...

BY nickel plating a plastic foam, Dunlop have developed a material which is finding applications in such diverse fields as sound absorption in high-temperature environments, in flame arrestors and as catalyst supporters. An important use for the material is as a burner, especially for natural gas, where conventional burners present flame stability problems. The new burner employs two \( \frac{1}{2} \)in thick plates of this material, supported by a bottom plate and a gallery, into which the gas is fed at low velocity; here it mixes with air, giving a stable, short blue flame over the whole surface of the matrix, which measures 5in by 5\( \frac{1}{2} \)in. In the average domestic appliance, a heat release of 1500—1800 Btu/in\(^2\) per hour is obtained, with a complete absence of noise although rates of up to 7100 Btu/in\(^2\) per hour can be reached with higher gas pressures. It will operate in any attitude.

Basically, the idea of a porous matrix as a burner is not new, although making it of metal in this way is an innovation. For some years, Maywick Appliances Ltd. has been producing a luminous wall furnace, in which the gas is burned at the face of a porous ceramic through which it passes.

A recent installation at the Research Centre of the Tubes and Pipes Division, British Steel Corporation, Corby, has two firing walls, each measuring 32in by 20in, with a steplessly variable heating input capacity of 20 000—80 000 Btu/ft\(^2\) per hour. It is claimed that the heating and cooling times for this furnace are exceptionally rapid. In particular, cooling twenty times faster than with electric furnaces is obtainable by switching off the fuel supply and blowing air only through the firing surfaces. The heating is also said to be particularly uniform.

how the French do it...

Our French contemporary, Galvano, has just carried out a survey of the interests of its 2650 readers. A questionnaire was sent out to them, and a response of 41.6% was obtained.

It appears that almost half the readership is about equally divided between jobbing platers and supply houses, and that each copy is read by an average of 4.3 persons.

The importance of the advertising is significant, 69.4% of readers saying that they turn to the advertisement pages when they have a technical equipment problem, and that generally the information available there meets the needs of 81.4% of them. Finally, the natural frugality of the French shows itself in the fact that they don't throw their journals away as soon as they have finished with them: 87.5% of subscribers keep their copies of Galvano for an average of no less than six years.

mutual benefit...

An indirect consequence of recent interest in British plating supply houses by American companies is, oddly enough, a much closer integration of the industry in this country with Europe. This should make things a bit easier when (and if) we join the Common Market.

The reason for this is that whereas British companies hitherto worked through agents on the Continent (with all the problems which this entails), American companies, for the most part, conduct their business on a group basis with a single European headquarters. The companies concerned therefore act as a European consortium, often highly autonomous, with a great deal of freedom of action.

The result is that customers everywhere get better service, and the pooling of research results is also of great benefit to customers as a whole. It also eliminates the curious situations which arose from time to time when agents could be in competition with their principals in the export field, for a variety of reasons.

cobalt...

One of the results of the nickel shortage may well be that cobalt could become a permanent feature of the plating scene, either on its own or as an alloy with nickel. In this country nickel-cobalt alloy plating was fairly extensively used shortly after World War II, because it happens to be an essential constituent of the cobalt-formate process—one of the first bright-plating methods to be put into successful commercial production in this country. The mechanism whereby formates brighten nickel-cobalt alloys, but do not brighten nickel deposits alone, has, incidentally, never been satisfactorily explained. By the time the interest of research workers had been aroused, the process was superseded by the organic bright nickels.

Cobalt is substantially dearer than nickel, but one of the consequences of the shortage of the latter metal is that cobalt became cheaper than the free market price of nickel. Hence, the interest in replacing nickel, part at any rate, with cobalt. A number of proprietary nickel/cobalt alloy processes has

Continued on page 106
Plating from solutions of simple salts without the addition of the buffers or compounds which are normally used to increase the conductivity and, with ultrasonics, good deposits can be obtained from a solution of nickel sulphate.

**Throwing power**

The ability to plate a uniformly thick deposit over an irregular surface depends upon the throwing power. When uniform corrosion occurs, the life of a plated article increases with the coating thickness and perforation of the deposit occurs at areas with the thinnest deposit. From a practical aspect, it is necessary to specify the important functioning areas of a plated article and to ensure that these areas are well covered. However, it is economically wasteful to produce an article with too thick a deposit, so control of the metal distribution over the whole surface is very important.

Plating in an ultrasonic field has been found to produce a more uniform concentration of electrolyte at the cathodic surface and to improve the throwing power of copper(3,19), zinc(2,2,3), nickel(3,5,2,2,3), cadmium(2,2,3), chromium(3,2,4,2,3,5), and tin(2,2,3). However, some workers have observed no difference in zinc(19), nickel(3,3,3,4), and chromium(3,4), and in some cases the throwing power is even reduced(3,7). More uniform or smoother deposits of copper(3,8,4,3,0), nickel(3,3,3,4), cadmium(2,8,4,1), zinc(19,3,3,4,2), silver(2,8), gold(3,3) and chromium(4,1,4,3) have been produced in an ultrasonic field.

**Current efficiency**

The current efficiency is the percentage of the total current usefully employed in the cathodic deposition or anodic dissolution of a metal. If the current efficiency is less than 100%, some of the current is used in detrimental secondary reactions such as the co-deposition of hydrogen at the cathode. The effect of plating in an ultrasonic field has been found to increase the cathodic current efficiency in the plating of copper(4,2), chromium(7,3), gold(10), nickel(2,3) and zinc(11,12). An increase from 14% to 23% has been found for chromium deposits at certain field intensities.

The current efficiency has been shown to depend upon the current density for copper plating from the pyrophosphate bath (4,0). The variation in the current efficiency compared with an intensively mechanically agitated bath, is indicated below:

<table>
<thead>
<tr>
<th>Current density</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>7</th>
<th>9 A/dm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current efficiency</td>
<td>99.5</td>
<td>97.5</td>
<td>95</td>
<td>90</td>
<td>65%</td>
</tr>
<tr>
<td>Current density</td>
<td>12</td>
<td>16</td>
<td>20</td>
<td>22</td>
<td>24 A/dm²</td>
</tr>
<tr>
<td>Current efficiency</td>
<td>97</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>90%</td>
</tr>
</tbody>
</table>

 intensively agitated
ultrasonics

The quality of the deposits was improved by ultrasonics: the deposits at 7 and 9 A/dm², with mechanical agitation, were dark and powdery whereas those at a much higher value of 20 A/dm² with ultrasonics were smooth and bright, at 22 A/dm² they were smooth and matt and at 24 A/dm² rough and the maximum current density by a factor of 4.5.

Ultrasonics has been found to increase the current efficiency during the deposition of cadmium(4,2) and has also completely eliminated the hydrogen embrittlement produced during this process. An increase in the anodic current efficiency has also been observed(4,8), but breaking up of a nickel anode(3,1) may occur as indicated by the nickel powder which collects at the bottom of the plating tank. Passive anodes(4,8), which do not corrode in a stationary solution, dissolve in the same solution when subject to ultrasonic vibration and this eliminates the need to use depassivators.

**Physical and mechanical properties**

Ultrasonic vibration of a plating bath decrease polarization (2,2,4) at the anodic and cathodic surfaces. This effect at the cathode should produce a larger grain size but, in fact, a smaller grain size has been observed for nickel(2,2,3,5), chromium(2,2,3,5) and zinc(12,4,4,3). This reduction in the grain size may have a considerable effect on the microhardness, brightness, porosity and internal stress of the deposits. A brighter, finer-grained deposit has been produced in many instances (6,7,5). However, the grain size depends upon the frequency and intensity of the ultrasonic vibration, and in copper deposits a larger grain size has been observed(5,2) when a frequency greater than 330 kHz was used.

**Microhardness**

The hardness of electrodeposited metals exceeds that of metals obtained by other methods. The hardness is further increased for many metals, including gold(11,5,5), silver(5,7), copper(2,4,0,3,5), cadmium(1,2), zinc(1,2), and chromium(2,8,4,1) with the use of ultrasonics. Large increases have been observed for deposits of nickel(5,8) from 215 to 310 VPN, and also from 260 to 400 VPN, and for chromium(2,2,2) from 740 to 920 VPN. The wear resistance of iron deposits has been found to be much higher for deposits from an ultrasonic field than for ordinary deposits.

A slight increase occurred in the hardness of cadmium(5,1) and chromium(6,0), although other workers found no change for copper(1,2,9), nickel(3,3) and chromium(3,6,5) and, in at least one instance, the hardness decreased(6,9).

Macnaughton and Hothersall(14) have suggested that the hardness of electrodeposits is connected with their grain size; the finer the grain size the greater the hardness. For one grain size, differences in the hardness may be due to a different packing of atoms in the crystal lattice. Miller and Kuss(2,9) thought that the intense agitation of the electrolyte produced by the ultrasonic vibration favoured the inclusion of more foreign materials in the deposit, thus increasing the hardness.

**Internal stress**

The internal stress in an electrodeposit is the force per unit area acting in a direction parallel to the plated surface. The stress may be tensile or com-
A high tensile stress is normally detrimental to the properties of the plated article and practical methods which can be used to reduce this stress to a low tensile or compressive value are important. The measurement and importance of internal stress have been covered elsewhere.

The application of ultrasonic vibrations reduces the internal tensile stress in nickel deposits. Deposits were produced with a low stress and good adhesion, whereas coatings from the ordinary bath had a high stress and cracked or peeled away from the substrate, which had a poor appearance and low corrosion resistance.

One proposed cause of internal stress in electro-deposits is the incorporation of atomic hydrogen in the deposit or substrate. This hydrogen is produced during the deposition of metals with a current efficiency of less than 100%, and the presence of hydrogen has been shown to produce a stress of up to 10,000 lbf/in². The production of gaseous hydrogen from atomic hydrogen at the cathodic surface is assisted by ultrasonic vibrations, which lower the potential at which the gas is liberated. This decreases the tendency for atomic hydrogen to be incorporated in the metal and reduces the internal stress of the deposit.

Other properties

The porosity of coatings produced with ultrasonic vibrations has been found to decrease in copper, nickel, and zinc, while the latter has also been plated in a non-porous form. Ultrasonic vibration reduces the porosity in nickel deposits from 130 to 58 pores/cm² at a thickness of 3 microns, from 10 to 4 pores/cm² at 10 microns, and from 3 pores/cm² to pore-free at 15 microns. With copper deposits the reduction is even greater, from 460 to 74 pores/cm² at 15 microns. This reduction in the porosity of a cathodic coating tends to increase as the porosity decreases.

The adhesion of a coating may be related to the internal stress and a high tensile stress can cause peeling or cracking of a deposit. Work on copper plating has shown that the use of ultrasonic vibrations increases the adhesion of the deposit.

The brightness of deposits has been found to increase with ultrasonic vibrations in nickel, chromium, copper, zinc, and cadmium. Deposits of other metals, including iron and cobalt, are also brighter and in nickel deposits there is a three-fold increase in the reflectivity. This change in brightness may be due to the fact that the discharging ions, in an ultrasonic field, approach the cathode from an angle which depends upon the vibration. Another explana-

Fig. 1. Surface of deposit from static bath (x20).

Fig. 2. Surface of deposit from stirred bath (x20).

Fig. 3. Surface of deposit from bath with ultrasonic field (x20).
which had previously been plated with nickel (from METAL FINISHING JOURNAL APRIL 1970 103 copper was deposited on to a stainless-steel spiral has been fully described elsewhere (6 3  7 6  7 7 ). The weighed again and the formula of Field(7 5 ) was used for an hour, so that the depth of the indentation used efficiency was compared for the same three solutions of the total thickness. The hardness of the substrate weighed with a GKN micro-hardness testing machine. Thick deposits were produced by plating using cells in series. The micro-hardness of copper deposits was measured with a GKN micro-hardness testing machine. Thick deposits were produced by plating for an hour, so that the depth of the indentation used in the measurement of the hardness was less than 6% of the total thickness. The hardness of the substrate copper was also measured to check the validity of the results obtained. The internal stress was measured with a Brenner Senderoff spiral contractometer, the use of which has been fully described elsewhere (63 76 77 ). The copper was deposited on to a stainless-steel spiral which had previously been plated with nickel (from the ordinary plating bath). In most of the experimental work, a comparison was made between a stagnant, a magnetically stirred, and an ultrasonically agitated solution. The plating cells were arranged in series with identical electrodes, so that the current density, plating time and deposit thickness were the same in each case.

RESULTS

Appearance

The deposit from the bath with ultrasonic vibration had a smoother and brighter surface with a finer grain size than those without vibration. This is illustrated in figures 1, 2 and 3 which show the surface of deposits from the still, stirred and ultrasonic baths, respectively.

Throwing power

The throwing power of the still, stirred and ultrasonic baths was measured with a range of current density from 1.3 to 2.6 A/dm$^2$. For all the range of current density there was very little difference in the throwing power of the three baths.

Current efficiency

The weight of copper deposited at the cathode or dissolved at the anode was determined for the three baths. The weight change for both the cathode and anode in the still bath was higher than in the ultrasonic bath, but less than in the stirred bath. In all baths, the anodic current efficiency was greater than the cathodic, the maximum difference being 3%. The ultrasonic bath had the highest cathodic current efficiency, but was only 0.15% and 0.1% above those for the still and the stirred baths, respectively.

Maximum current density

The photographs, figures 4, 5, and 6, show copper deposits from the three baths at a current density of 2.16 A/dm$^2$. The deposit from the still bath was non-coherent, dark and powdery with a 'burned' appearance. The one from the stirred solution showed some burned deposit, but was better than that from the still bath. A good deposit was produced from the ultrasonic bath at 2.16 A/dm$^2$ and also with a current density of 4.32 A/dm$^2$.

Internal stress

In all the copper deposits plated at different current densities, the stress in the deposit produced in an ultrasonic bath was lower than that in a stirred solution — in some cases the reduction was as high as 50%. In both baths, the stress at a given deposit-thickness increased with the current density. Typical stress values for deposits of thickness about 0.4 x 10^{-4} in (1.0 x 10^{-5} cm) are given below:

<table>
<thead>
<tr>
<th>C. density A/dm$^2$</th>
<th>Stress lbf/in$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.13</td>
<td>stirred bath 710 1130 1160 1440</td>
</tr>
<tr>
<td>6.26</td>
<td>ultrasonic bath 540 630 810 1030</td>
</tr>
<tr>
<td>7.78</td>
<td></td>
</tr>
<tr>
<td>9.28</td>
<td></td>
</tr>
</tbody>
</table>

Microhardness

The hardest copper deposits were obtained from the ultrasonic bath; the stirred solution gave harder deposits than the still solution.
Fig. 4. Copper deposit from static bath at 2.16 A/dm².

Fig. 5. Copper deposit from stirred bath at 2.16 A/dm².

Fig. 6. Copper deposit from ultrasonic bath at 2.16 A/dm².

Fig. 7. Effect of agitation—static—on microstructure (x200).

Fig. 8. Effect of agitation—stirred—on microstructure (x200).

Fig. 9. Effect of agitation—ultrasonic—on microstructure (x200).
The authors wish to thank Professor M. B. Waldron for his interest and for the provision of facilities at the University of Surrey.

Acknowledgement

The effect of the bath condition on the grain size was very marked. As shown in the microphotographs, figures 7, 8 and 9, the still bath produced columnar grains, the stirred bath fewer columnar grains and the ultrasonic bath gave equiaxed grains.

DISCUSSION

This paper reports on the effect of using ultrasonic vibrations during the plating of copper from the copper sulphate-sulphuric acid bath. This type of agitation has been shown to produce deposits with a brighter appearance and better properties than those obtained from a stirred or still bath.

The maximum or critical current density which can be used to produce good deposits, without a 'burned' appearance, was found to be at least twice as high with ultrasonic vibrations as with a stirred solution. This means that the plating time required to produce a deposit with a specified thickness can be reduced by a factor of at least two, if ultrasonic vibrations are used.

The grain size of deposits from an ultrasonic plating bath is smaller than from stirred or still solutions. This produces an increase in the microhardness of the deposits which is beneficial for mechanical properties, e.g., wear and load-bearing surfaces; it also reduces the internal tensile stress in electrodeposits. This is advantageous because a decrease in the tensile stress reduces the tendency of a deposit to peel away from the substrate or for the deposit to crack, both of which may increase the corrosion rate of the plated article. A decrease in the tensile stress improves the stress corrosion, fatigue and corrosion-fatigue properties of the finished product.

The literature review surveys the other improved properties which are obtained by using ultrasonics, such as lower porosity, reduced hydrogen embrittlement and better adhesion. The current efficiency and throwing power may also be improved in certain plating baths. Another advantage is in the electro-deposition of alloys (40 76 79) in which ultrasonic vibration affects the cathodic polarization and, consequently, the composition of the alloy deposit.

It is for these reasons that, even though the cost of the equipment is considerable, the use of ultrasonic vibration is being used to an ever-increasing extent in the electrodeposition of metals (1 16 40 81).

Grain Size

Although a similar order was found for nickel deposits plated in figures 7, 8 and 9, the still bath produced columnar grains, the stirred bath fewer columnar grains and the ultrasonic bath gave equiaxed grains.
now been introduced commercially. Although the price of cobalt has risen sharply since the renewal of interest in it, prices have been kept down by the release of about two million pounds a month from the American stockpile—the U.S. Government appears to have a surplus.

Accelerated tests indicate that cobalt/nickel alloy coatings behave quite satisfactorily, particularly under microcracked or microporous chromium, but there is little or no experience of their performance in extended service. Cobalt is, however, not recommended for the semi-bright undercoat of a duplex nickel system. It is also known that from the ductility and levelling points of view, cobalt-nickel alloy deposits are better than bright nickel; cobalt alone is inferior to either. Perhaps the ductility of the alloy has something to do with its musical properties; a well-known manufacturer of steel bicycle bells found it inadvisable to change from a bright cobalt-nickel deposit to a straight nickel process because the tone of the ring was found to be much inferior!

Cobalt can be used in anode form, or as broken cathode sheet in titanium baskets, and must be adequately bagged. Additions can be in the form of cobalt chloride or sulphate; the cobalt plates out faster than nickel.

An alternative approach to the problem of the nickel shortage is to replace it with 50% of copper in conjunction with microcracked or microporous chromium, since performance tests indicate that very good results are obtainable in this way.

There is no indication, incidentally, that nickel will be in great surplus even when the new deposits are exploited. The reason is that there are quite a few potential applications for the metal which are only being held back because of the present shortage.

Intergalva 70: galvanized steel in the seventies

GALVANIZING cuts maintenance, cuts costs. This is the theme of a special exhibition organised by Zinc Development Association, on the Third Floor of the Building Centre, Store Street, London W.C.1., from 15 April to 1 May. It forms part of a comprehensive programme of events arranged under the banner of Intergalva 70 — the second International Galvanizing Year.

The exhibition is open to the public each day from 9.30 a.m. to 5 p.m., Mondays to Fridays. Special displays include photographs of unusual and newly developed major uses—covering road furniture, transport, building, bridges, communications and power — together with cost-comparison charts and a range of publications about the process, fabrication techniques, finishing and applications. A representative selection of galvanized products will be exhibited and technical staff will be available to answer questions.