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MOLYBDATE-BASED PASSIVATION TREATMENTS
FOR TIN, TINPLATE AND ZINC

by

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A thesis submitted in fulfilment of the regulations for
the award of the degree of
Doctor of Philosophy
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September 1986

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To my parents . . . .
ABSTRACT

The level of toxicity of chromate conversion coating solutions has led to a search for alternatives. Molybdate has been considered, being a relatively non-toxic analogue from group (VIA) of the periodic table. The ability of molybdate to perform as an inhibitor in aerated conditions is well-reported, although its application in conversion coatings is less widely documented.

The experimental work reported in this thesis was to a large extent based on potentiodynamic polarisation which is considered a powerful tool for evaluating potential coating solutions. The cathodic polarisation characteristics of zinc in group (VIA) oxy-anion solutions has been studied quantitatively. The effect of temperature, pH and aeration has been examined. The film-forming ability of molybdate-based solutions such as molybdate-orthophosphoric acid (MP), molybdate-orthophosphoric acid-nitrate and molybdate-orthophosphate has been examined with respect to a tin, tinplate or zinc substrate. Films were formed electrochemically (anodically and cathodically) or by a simple immersion technique. The performance of such coatings has been studied using classical corrosion tests such as sulphide stain and salt spray.

The cathodic reduction characteristics of molybdate solutions have also been examined in detail with respect to possible lower valency films being produced (possibly as a result of molybdate's complex electrochemistry) on tinplate, zinc and platinum metal surfaces.

Experimental results have indicated that simple, relatively dilute, molybdate solutions at pH 3 are capable of imparting good staining resistance to tinplate in sulphide stain tests. However, other mixed systems have proved less successful, only molybdate-orthophosphoric acid providing acceptable protection on tin foil. Simple immersion techniques in dilute, pH 5 molybdate solutions have provided moderate protection on zinc in 24-hour salt spray tests.

Inflections exhibited on cathodic polarisation curves of tinplate in simple molybdate solutions have been attributed to a physical degradation of the coating as opposed to a reduction step.
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ABBREVIATIONS, SYMBOLS AND TERMINOLOGY

AZC - Ammonium zirconium carbonate
BZT - Benzotriazole
c.d. - Current density
E° - Standard electrode potential
\( \Delta E_p \) - Magnitude of anodic passive region in terms of potential
Epp - Primary passive potential
EPMA - Electron probe microanalyser
ESCA - Electron spectroscopy for chemical analysis
HE - Hydrogen evolution
HEDP - 1-hydroxyethylidene-1, 1-diphosphonic acid
\( i_{\text{crit}} \) - Critical current
\( i_{\text{pass}} \) - Passive current
ITRI - International tin research institute
MBT - Mercaptobenzothiazole
MP - Molybdate-orthophosphoric acid
SCE - Saturated calomel electrode
SEM - Scanning electron microscope
TFS - Tin free steel

**Inflections on Cathodic Polarisation Curves Nomenclature:**
The term inflection was applied to arrests on the polarisation curve i.e.
These inflections were termed as "strong" when there was an actual reduction in current or "shallow" when there was a steady current (rather than a fall), followed by an increase, as shown below:
CHAPTER 1
INTRODUCTION

1.1 HISTORICAL

The process of producing a conversion coating covers several well-known solution treatments for metals, thereby imparting an acceptable degree of protection in relatively mild atmospheres. The most common coating systems are probably chromate and phosphate, although anodising is also recognised by many as another form of conversion coating. The process by which such a coating is applied to a metallic surface can be considered in essence as a controlled corrosion of the metal substrate yielding a protective film firmly bonded to it. Hence, the process "converts" the metal from an "active" state to a "passive" one whereby metallic dissolution is diminished. The conversion coating treatment usually forms one element of a protective system. On its own it can only provide protection against relatively mild atmospheres e.g. household interiors. More usually a conversion coated article benefits from subsequent organic treatments, e.g. paint finishes on phosphated steel and lacquers on chromated tinplate, or oiling or waxing.

The first real evidence of the application of phosphate conversion coatings appeared in the nineteenth century when iron corsets were pre-treated by plunging them red hot into phosphoric acid. Indeed phosphating at its simplest involves the immersion of a metal surface into hot, dilute, phosphoric acid. Industrial phosphating can be considered to have grown from the patented Coslettizing process which included zinc phosphate; thicker coatings were formed using dihydrogen phosphate (Parkerizing) and accelerators such as copper or nitrate (Bonderizing) were later added to solutions to reduce process times.

Whereas phosphating is limited mainly to ferrous metals and zinc (and to a much lesser extent Cd and Al), chromate coatings are applied to a much wider range e.g. Al, Cu, Zn, Sn and Mg. Of these zinc, tin and aluminium are probably the main recipients of this type of coating.
chromating process was first applied to magnesium in 1924 and is now extensively used on items such as galvanised strip and castings and tinplate. Processing methods range from a slow immersion treatment in chromic acid, which has the virtues of simplicity and low cost, to specific treatments such as "Protecta-tin" (hot alkaline sodium chromate and hydroxide) and the MBV process (Modified Bauer-Vogel process for aluminium based on an alkaline sodium chromate solution).

1.2 TIN AND ZINC COATED PRODUCTS

The two major metal surfaces under consideration for this work are tin and zinc. The vast majority of metallic tin production is in the form of tinplate. Tinplate can be considered as light gauge, cold-reduced, low carbon steel (in either sheet or strip form) coated with commercially pure tin. It therefore combines the strength and potential formability of steel with the corrosion resistance and inherent solderability of tin. The thickness of the steel ranges between 0.15 to 0.5 mm whilst the tin, if electrolytically deposited, can differ in thickness (typically 2.8 to 15 g/m²) depending on the service conditions it is likely to face i.e. thinner coating for exterior of cans, thicker for interior. The corrosion resistance of the tin surface can be further enhanced with a suitable passivation treatment and/or lacquer coating. Unpassivated tinplate has also a thin oil film on the tin oxide as illustrated in Figure 1.

The origins of tinplate can be traced back in history to the tinning of hammered iron sheet in Bavaria in the fourteenth century. The process spread across Europe and by 1720 hot-rolled iron sheets were being tinned in Wales and the Forest of Dean. Steel was substituted for iron and by the 1930s cold-rolled steel strip was being electrotinned on a commercial scale in Germany. Today tinplate is being produced in some thirty-seven countries.

Tinplate is now mainly produced by electroplating as opposed to the older, more expensive hot-dipping process. The acid sulphate electroplating solution is the most widely used. The uncoiled steel
strip enters a series of vertical tanks for electrolytic cleaning and pickling. The strip is then passed through the plating tanks at speeds as high as 600 m/min. The electrolyte consists, in the foremost process, of a solution of stannous tin in phenolsulphonic acid, together with addition agents which inhibit the oxidation of tin (II) to tin (IV) and promote wetting and smooth, even deposits. The normal operating temperature is 40°-50°C. After electroplating, flow melting takes place in which the tin deposit is fused to create a bright surface finish. Flow melting also causes an iron-tin alloy layer to form comprising of a broken, uneven band of FeSn₂ adjacent to the steel. An optimum form and thickness of this intermetallic enhances the bonding of the tin to the steel substrate, increases the corrosion resistance of the product and improves its solderability. Following flow melting, a passivation process can be carried out, usually in sodium dichromate or chromic acid solutions, to further improve the corrosion resisting abilities of the tinplate. Finally a very light oil film, usually dioctyl sebacate or acetyl tributyl citrate, is applied electrostatically.

Other electroplating solutions include the chloride-fluoride solution, which was developed by Weirton Steel Co and Wean Engineering in the USA for the 'Halogen' process. Here the electrolyte is stannous chloride and alkaline ammonium fluorides. The fluoborate process, which is operated by Rasselstein AG in West Germany, is the other common solution in use. The alkaline stannate process was formerly applied but is little used today.

The tin coating at 1-5 µm thickness is not of course continuous but contains a number of microscopic pores. These can be divided into two groups - those which traverse both the tin and alloy layer and those which extend through only the former layer, known as "potential pores". The purity of the tin is normally above 99.8% and has in essence the chemical and physical properties of cast tin. Thus under normal aerobic conditions when tin is coupled to iron the former will become the cathode resulting in rapid iron dissolution. However, in certain foodstuffs (e.g. citrate, tartrate etc) the stannous ions are complexed, and, under certain typical anaerobic conditions, a polarity reversal can occur.
whereby the tin becomes anodic and thus protects the iron substrate.\textsuperscript{2,13}

Zinc finds widespread use as a material for castings, particularly die cast, and in the protective coating of steel. This ability to confer corrosion protection to steel stems from the formation, in aqueous solutions, of an electrolytic cell in which zinc becomes the anode and steel the cathode. Therefore, at scratches and surface abrasions, zinc can sacrificially protect the substrate steel and limit "rusting". Zinc can however also protect in a second manner by means of a slow corroding barrier coating. In moist air zinc corrodes, mainly as basic zinc carbonate, which is partially protective and hence reduces the rate of metallic dissolution of the underlying steel. Polarity reversal of the zinc-steel couple occurs at elevated temperatures (>60°C) in normal supply waters and generally limits the extent of its usefulness for water storage tanks.

There are many methods of application of a zinc coating. Hot dip galvanising is probably one of the oldest, pre-cleaned steel sheet being fluxed and immersed into a bath of molten zinc (450°C). By this method a fairly constant coating thickness can be obtained. The reaction between the iron substrate and the molten zinc produces several iron-zinc alloys, however the surface of the article is predominantly pure zinc\textsuperscript{14,15}. Sprayed zinc coatings have also been utilised for many years. Here the bond between the zinc and substrate is purely mechanical and although the coating is porous, its protectiveness is assured by the sacrificial nature of the zinc\textsuperscript{15}. The use of electrogalvanising (i.e. zinc electroplating) is also widespread. This process leads to fine, smooth finishes where surface tolerances are important (e.g. instrument parts, bolt threads etc). There are basically four types of plating solution i.e. high cyanide, low cyanide, cyanide free (zincate) and acid (chloride or sulphate). The cyanide solutions are probably the most widely used, although their high toxicity is a major drawback, and because of this the acid sulphate solution has received widespread application\textsuperscript{14,16}. Other methods of applying zinc or zinc-rich coatings include sherardising, in which articles are tumbled in a heated barrel containing zinc dust, and the application of zinc-rich paints which are able to confer sacrificial
protection to steel substrates in a similar manner to their wholly metallic zinc counterparts.

The production of an unsightly zinc carbonate corrosion product ("white rusting") on both zinc coatings and cast products has led to the requirement of a passivation treatment to stem this phenomenon. In this respect chromate type coatings have been successfully applied to zinc surfaces, exposed to relatively mild atmospheres, for many years.14-17

1.3 THE POSSIBLE REPLACEMENT OF CHROMATES AS PROMOTERS OF CONVERSION COATINGS

The use of chromates as passivating oxidants is widespread, particularly as conversion coatings on the aforementioned metals (i.e. tin and zinc). Their performance, in the mild atmospheres for which they were designed to endure, is quite acceptable. However, the inherently toxic nature of chromate processing solutions (based on Cr(VI)) is a major drawback, particularly with increasing concern of the environmental effects of effluent disposal. Thus there are strong grounds for a non-toxic alternative to chromate-based solutions.

Molybdates have, for many years, been regarded as efficient inhibitors in aerated conditions, particularly in cooling water systems. They have the major advantage of a low or negligible degree of toxicity, a prominent feature of any system which is to successfully replace chromate. The application of molybdates for conversion coating processes is not widely reported, however, their possible application in this field warrants further investigation.

This project has examined the suitability of molybdate as a passivating agent for tin and zinc metal surfaces. Potentiodynamic polarisation has been utilised as the major investigative technique for examining the film-forming abilities of several molybdate-based systems. Once optimum conditions for suitable formulations had been chosen, coated zinc, tin foil and tinplate samples were assessed by their performance in appropriate corrosion tests. For zinc, a twenty-four hour salt spray
test\textsuperscript{18} was applied and for tin foil and tinplate a thirty minute sulphide stain test. Corroded samples were assessed visually and, in the case of the tin foil and tinplate, selected stained specimens were tested coulometrically as an indication of the amount of sulphide staining present.

Electron microscopy, EPMA (electron probe microanalysis) and ESCA (Electron Spectroscopy for Chemical Analysis) were techniques applied to examine the microstructure and nature of the surface of passivated samples. The ability of molybdate films to undergo one or a series of reduction processes during cathodic polarisation was also investigated using tinplate, zinc and platinum cathodes. This phenomenon was highlighted in earlier investigations at Loughborough\textsuperscript{19,20,42} and has also been reported by other authors\textsuperscript{21-25}. 
CHAPTER 2
CHROMATE PASSIVATION COATINGS

2.1 HISTORICAL

Chromate conversion coatings were first applied to metallic substrates when magnesium was coated in this manner in 1924\(^7\). These early solutions were only used on a small scale and it was not until the period between 1924-1936 that patents were taken out on specific metal treatments e.g. the Cronak process for zinc and cadmium\(^{26}\). This treatment solution was based on dichromate and sulphuric acid and produced coatings of slightly opalescent, yellow or brown. During the second world war advancements in colouration were made with the production of olive-green (drab) coatings which had the added advantage of greater corrosion resistance when compared to their earlier counterparts. A greater range of coloured coatings became available following the discovery of suitable dyeing agents which could be applied to the olive-green chromate finishes. These older treatments for zinc and cadmium are widely used today, although further refinements have occurred with the application of electrolytic treatments as opposed to the older, more simple, immersion processes. In later years chromate coatings have been applied to a wide range of metals but particularly to tin (e.g. the "Protecta-Tin" process),\(^{27,28}\) zinc and aluminium.

Thus it can be seen that the real advance in the science of chromating was initiated during the second world war due to the requirement of additional corrosion protection for military equipment destined for use in hot, humid theatres of action. After the cessation of hostilities in 1945, many producers continued with chromate coatings on various articles resulting in steady improvement up until the present day. However, due to the high toxicity of processing solutions a gradual but definite increase in potential alternative systems has developed, with interest being shown in trivalent chromium (Cr III) solutions\(^{29,30}\) and those based on molybdate (see Section 3.4).
2.2 THE CHEMISTRY AND ELECTROCHEMISTRY OF CHROMATE COATINGS

2.2.1 Introduction

The term "chromating" applies to a series of solution treatments, usually based on chromate or dichromate, from which, either chemically or electrochemically, a protective film is imparted to a metallic substrate. The use of chromates as passivating-type inhibitors, particularly in circulating water systems, is well-known. This ability to reduce corrosion at a metal surface has therefore been successfully extended to atmospheric conditions, the conversion coating in essence acting as a reservoir of soluble chromate. The chromate film enhances the performance of metals with an already high intrinsic corrosion resistance i.e. cadmium, copper and some aluminium-based materials. However, where less corrosion resistant metals and alloys are concerned chromate coatings can only be considered as a pre-treatment prior to the application of a more protective (e.g. paint) coating.

The four main advantages of applying chromate conversion coatings can now be summarised:

1. An increase in corrosion resistance of the coated metal substrate leading in many cases to a prolongation of the first appearance of corrosion sites.
2. A decrease in the susceptibility of the metal substrate to finger-marking and staining.
3. An increase in the adhesion of subsequent organic finishes.
4. The ability, in many cases, to obtain a chromate finish which increases the aesthetics of the metal surface.

The methods of applying chromate coatings can be broadly divided into two clear groups:

1. Chemical, where articles are submerged in solutions containing chromates, dichromates etc. This being an essentially inexpensive process.
2. Electrochemical, which also involves the immersion in a suitable solution but in addition has the imposition of an external current.

Irrespective of the mode of application the types of chromate coating can be divided into two groups, i.e. those which are deposited onto clean metal surfaces and are by themselves considered as sufficient protection, and, secondly, those which are used to supplement other coatings e.g. the sealing of an anodic oxide or phosphate coating.\(^7,15\)

2.2.2 Mechanism of Formation

The chromate conversion coating is formed by the direct reaction between hexavalent chromium (Cr(VI)) in the treatment solution and the metal substrate:

\[
M + M^{2+} + 2e
\]

It is generally agreed that this anodic metal dissolution step involves the simultaneous cathodic evolution of hydrogen:

\[
2H^+ + 2e \rightarrow H_2
\]

This reaction increases the pH at the metal-solution interface to a value which promotes the reduction of hexavalent chromium to its trivalent state:

\[
Cr(VI) + 3e \rightarrow Cr(III)
\]

This rise in pH also encourages the precipitation of the metal hydroxide, followed by a basic chromium chromate:

\[
M^{2+} + 2OH^- \rightarrow M(OH)_2
\]

Precipitation:

\[
Cr(OH)_2 \cdot CrO_4
\]
The film then undergoes further consolidation and growth due to solution precipitation effects:

\[
\text{Film consolidation: } MO/M(OH)_2/CrOH\cdot CrO_4
\]

Most modern chromate conversion coating solutions contain additional additives including wetting agents which create a more uniform reaction, reduce "drag-out" and sludge formation, and prevent staining during the transfer to the first rinse.\(^{7,31,32}\)

2.2.3 Composition and Structure of Coatings

The exact composition of chromate coatings is still open to some debate. Clearly there can never be a precise general formula applicable to all coatings (i.e. differences in bath compositions, substrate metals etc) although the majority of authors tend to agree that the main constituents are tri- and hexavalent chromium compounds and chromates of the basis metal.\(^{7}\) The following formulae are quoted as examples of possible compounds occurring in chromate conversion coatings:

\[
\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3 \cdot x \text{H}_2\text{O}^{7,15,33}
\]

or

\[
\text{Cr(OH)}_3 \cdot \text{Cr(OH)}_3 \cdot \text{CrO}_4^{2,7}
\]

Biestek and Weber\(^7\) also note that Kalauch\(^{34}\) proposes the formula of the basic chromate as:

\[
\text{Cr(OH)}_3 \cdot \text{Cr}_2(\text{CrO}_4)_3
\]

The results of analysis of typical chromate coatings has been reported by various authors and a range of values for elements present is indicated below\(^{7,8,33}\):
Hexavalent chromium (Cr VI)  7 - 12%
Trivalent chromium (Cr III)  25 - 30%
Sulphur (as Sulphate, SO₄²⁻)  2 - 3.5%
Zinc* (as Zn²⁺)  2 - 2.5%
Sodium  0.2 - 0.5%
Water  15 - 20%

(* with zinc substrates)
(Balance oxygen)

Chromate films are generally non-crystalline, partly porous and gel-like, and, if applied by simple immersion, are subject to abrasion damage for 12-24 hours following formation. Dry heat is also injurious to coatings in that corrosion protection of the underlying substrate metal is drastically reduced because of transformations which greatly lessen the solubility of the hexavalent chromium. Film thicknesses range between 0.1 and 10 μm, the thinner films being iridescent or pale yellow-green, whilst the thickest films are dark brown.

2.2.4 Mechanisms of Protection

The actual mode of protection afforded by this type of conversion coating is still uncertain. Many authors cite two methods of protection. Firstly, the generally non-porous nature of the coating physically excludes any corrosive environment from the underlying metal. Secondly, the hexavalent chromium, being slightly soluble, can behave as an inhibitor at any discontinuities in the film. This role of hexavalent chromium can be further demonstrated when a pre-scratched, chromate-coated zinc surface is brought into contact with a corrosive medium. No corrosion occurs due to the release of the soluble Cr(VI) compounds and the subsequent inhibition of the uncovered area. However, this hypothesis of protection due to soluble components of the film does not fully explain why, when all such compounds are removed from a coating, the remaining insoluble part retains its protective properties. It has been suggested that the soluble constituents may only have limited influence on the general corrosion resistance of the coating.
Other theories as to the mode of protection include the possibility of the formation of a dipole coating being formed as a consequence of the adsorption of polar species from the chromating solution. With the resultant surface of the coating having a slightly positive charge the electrochemical potential of the metal is shifted towards more positive values.\textsuperscript{7} The idea of passivation of zinc and cadmium by chromating has, according to Biestek and Weber\textsuperscript{7}, been questioned by Elze.\textsuperscript{35,36} He suggests the stationary potentials of chromate coatings were very close to those of unchromated ones, adding that protection was afforded principally by the inhibition of the anodic and cathodic reactions.

2.2.5 Physical and Mechanical Properties\textsuperscript{7}

2.2.5.1 Porosity

Before drying is complete, chromate coatings exhibit a degree of porosity and hence in principle their surface characteristics, such as colouration, can be modified by the absorbance of dyestuffs etc. Thin chromate films, particularly those produced on coarse surfaces, are also to a certain extent porous. Thicker deposits, and those formed on smooth bright surfaces, are much less porous thereby promoting a higher degree of corrosion resistance.

2.2.5.2 Hardness

The surface hardness of a chromate coating depends essentially on its formation history. It has been shown that those coatings produced on cadmium have a higher hardness index when formed from high temperature process solutions. Also the condition of the underlying cadmium had some influence on this property, for example coatings produced on bright cadmium were harder than those formed on a dull substrate.

2.2.5.3 Abrasion resistance

Chromate coatings are particularly susceptible to damage by abrasion. This phenomenon is most apparent when the coatings are still wet, i.e. soon after treatment. The onset of drying improves the resistance, and
it is also claimed that considerable improvement can be achieved with careful choice of the treatment solution and other process parameters. It is also apparent that in the moist condition, thinner chromate coatings give a higher degree of abrasion resistance than do the thicker types.

2.2.5.4 Electrical properties

Chromate coatings have the inherent advantage of low electrical resistivity. This allows their widespread use in the electronics industry where electrical contact is required. The resistivity varies between coatings on different metal substrates. Coating thickness is also important with intensely coloured coatings having a higher resistance (approximately 50% greater than the unchromated metal surface).

2.2.5.5 Adhesion

Adhesion is generally good, the coating having been formed by a reaction at the metal-solution interface and consisting of compounds from both sources. The coatings also exhibit sufficient ductility to withstand pressing and forming operations although damage will occur due to abrasion, as noted earlier.

2.2.6 The Technology of Chromating

A typical cycle for the chromating of an electrodeposited coating is indicated below:

1. Electroplate  
2. Cold water rinse  
3. Cold water rinse  
4. Neutralise  
5. Cold water rinse  
6. Chromate  
7. Cold water rinse  
8. Cold water rinse  
9. Hot water rinse  
10. Dry

In the list it is assumed that the process is a continuous one with no time lag between electroplating and chromating. If large objects or castings are to be coated in this manner they must be degreased and
pickled to remove surface deposits before coating can begin. Pickling usually involves immersion in an acid solution. Efficient rinsing is deemed very important at all stages of the coating cycle as, for example, residues of chromating solution can impair the corrosion resistance of the final coating.\footnote{7}

The mode of application and the type of process solution depend upon the metal substrate to be treated. Generally, electrochemically deposited coatings are more rapidly applied, although simpler immersion coatings have the virtue of requiring less plant and consequently incur lower capital and operating costs. Activators are also added to the solutions, their application being to reduce treatment time, improve coating properties and modify the colour of the finished product.\footnote{7} Other process parameters such as temperature, hexavalent chromium concentration, pH etc also have a direct influence on coating properties and will be examined in more depth for the individual metals of tin and zinc (Sections 2.3 and 2.4).

The final stage in any coating system has to be the disposal of the process solution. Since hexavalent chromium solutions are very toxic certain steps have to be taken before discharge into public foul water courses. A full account of effluent treatment can be found in Section 2.6 on chromate toxicity.

2.2.7 Tests for Chromate Coatings

Several standards exist for the testing and specification of chromating, particularly on zinc and cadmium surfaces. Several are listed below with a summary of the type of tests:

   On zinc and cadmium, testing for the presence of colourless coatings, the presence and quantity of hexavalent chromium in such coatings, the total chromium content per unit area and the satisfactory adhesion of coloured coatings.
Chromate conversion coatings on electroplated zinc and cadmium coatings. This standard defines scope and methods of application, classification and service requirements.

Gravimetric method for determination of coating mass per unit area of conversion coatings on metallic materials. This covers chromate coatings on zinc and cadmium and on aluminium and its alloys.

Reference is also made to BS 5466:Part I 1977 (ISO 3768 - 1976) which considers the neutral salt spray test (NSS test) for metallic coatings.

2.3 CHROMATE CONVERSION COATINGS ON TIN AND TINPLATE

2.3.1 Introduction

The major use of tin is as a sacrificial coating in the production of tinplate food-packaging material. It is generally considered to be a moderately corrosion resistant metal in itself, although the variety of conditions it experiences in can production and subsequent use can cause dissolution corrosion, tarnishing and staining of an untreated surface. Discolouration of tinplate can be mainly attributed to elevated temperatures experienced during food processing or lacquering or as a result of prolonged storage. More unsightly staining can be caused by sulphur-containing foods producing tin and iron sulphide compounds on the metal surface. It is the object of a passivation treatment to prevent these phenomena by enhancing the stability of the tin surface coating and thereby improving corrosion resistance whilst at the same time maximising solderability. Gabe\textsuperscript{37} has summarised the reasons for the use of passivation treatments as:

a) to remove or reduce thermally formed oxides;
b) to form a new, protective oxide film;
c) to improve subsequent lacquering, printing and soldering of the tinplate;
d) to form a film stable to sulphide staining against protein (sulphur) containing foodstuffs.

2.3.2 Commercial Passivation Processes

Probably the best-known chromate passivation treatment for tin metal surfaces is the "Protecta-Tin Process". This unpatented solution composition was developed by the International Tin Research Institute in Great Britain. The process produces colourless, thin films, and has the important virtue of negligible tin dissolution, thereby allowing the use of very low tin coating weights to be used successfully on the steel substrates. The solution is based on sodium chromate and sodium hydroxide, the full composition being:

- sodium chromate: 3g/l
- sodium hydroxide: 10g/l
- wetting agent (e.g. Teepol): 2g/l
- pH: 11-12
- temperature: 90-95°C
- immersion time: 3-5 secs

The Protecta-Tin solution can be modified as reported by Fishlock:

- sodium dichromate: 2.8 g/l
- sodium hydroxide: 11 g/l
- wetting agent: 2 g/l
- temperature: 90-95°C
- immersion time: 3-5 secs

Neish and Donelson cite the problems associated with the discolouration and sulphide staining of tinplate and list chronologically, from 1931 to 1954, the patents and publications associated with treatments that provide protection against these phenomena. The number of chromate treatments is too numerous to list, but Gabe has classified commercial passivation processes for tinplate (see Table 1) and the treatments can be broadly divided into four classes.
1. alkali sodium carbonate solution based, cathodic current; 
2. acid phosphate-chromate solution, cathodic/anodic current; 
3. acid dichromate solution, cathodic/anodic current; 
4. chromic acid immersion type solution.

2.3.3 The Polarisation Characteristics of Tin in Hexavalent Chromium Solutions

The cathodic polarisation of tin in chromate and dichromate solutions has been reported. Bijimi and Gabe examined the cathodic characteristics of tin foil in 0.01-1.0M group (VIA) oxy-anion solutions. They found that 0.1M concentrations of group (VIA) oxy-anions at pH 7 and 40°C produced very similar cathodic polarisation curves. Wilcox and Gabe also examined tin foil in chromate solutions and noted inflections on the cathodic polarisation curves, indicating the possible reduction of a species from the processing solution on the tin surface. The existence of cathodic inflections due to Cr(VI) solutions (see also Section 2.4.3) has also been reported by other researchers. Tin in a dichromate solution of pH 1.5 promotes two steps (inflections) before a critical current density is reached. Tin, however, promotes three peaks in a solution of 0.085M Na2Cr2O7·2H2O of pH 5.2 and at 55°C (see Figure 2). Aubrun and Rocquet suggest peak I would correspond to the growth of a primary chromium oxide film (Cr6⁺ → Cr3⁺) following reduction of any surface tin oxides. Peak II was assumed to be the building up of a secondary chromium oxide film (Cr6⁺ → Cr3⁺) whilst peak III indicated a change in this secondary film and the onset of hydrogen evolution. These inflections have also been reported for mild steel in dilute chromic acid. The addition of sulphuric acid to the solution was also investigated and it was found that at a sufficient concentration the number of inflections was increased.

Although anodic treatments are specified for tin surfaces, they are generally far less numerous than their cathodic counterparts. Consequently the investigations into the anodic passivity of tin in chromate-based solutions are small in number. Bijimi and Gabe have, however, noted that solutions, in the pH range of 5-9 are most efficient
at concentrations greater than 0.01M and at a temperature of 20°C. Also, in a marked difference to its group (VIA) analogues of molybdate and tungstate, chromate regularly displays two passive regions at all pH levels studied (but most significantly at pH 7). At pHs 5 and 9 and 0.1M the two passive regions tended to merge into one and the authors commented that on balance the lower temperatures promoted better conditions of passivity i.e. lower passive currents and wider passive potentials.

2.3.4 The Structure and Composition of Chromate Coatings on Tin Surfaces

The film imparted by a cathodic dichromate (CDC) process appears to consist of chromium metal (Cr⁰), trivalent chromium (Cr(III)) presumably as Cr₂O₃ and traces of Cr(VI). Aubrun and Rocquet⁴³ have defined film growth during the CDC process as the sum of the following reactions:

1. the building up of a chromium oxide primary film;
2. the reduction of tin oxides and strengthening of the primary film;
3. the growth of a chromium secondary film;
4. alteration of the film at hydrogen evolution;
5. hydrogen evolution, deposition of metallic chromium and chromium oxide.

It is apparent that the chromium metal deposition is under markedly different conditions from those experienced in conventional chromium plating. This metallic deposition ceases once the tin metal surface is totally covered and becomes in all respects a chromium metal surface.⁴³

The presence of chromium metal as an integral constituent of the passivation film has been established by several researchers.⁴⁶-⁵¹ The use of XPS or ESCA techniques has highlighted that chromium metal is only present in CDC type films and not DCD (dichromate dipping -treatment 300).⁴⁶,⁴⁷ The XPS/ESCA technique has been further utilised by other investigators⁵²,⁵³, although Riviere⁵³ makes the cautionary note that the concentration of Cr³⁺ in films was dependent on ion beam energy, a rapid reduction of Cr(III) oxide occurring at 5 keV. Cathodically treated
tinplate has also been examined by transmission electron microscopy (ring
diffraction patterns). Analysis has indicated SnO₂ and SnO present and
possibly intermediate oxides, together with large single crystals of
β-Sn, Cr and Cr₂O₃.

The consequence of the deposition of metallic chromium is of more than
simple academic interest as it has been directly related to the sulphide
staining resistance of the tin surface. The amount of surface chromium
can be controlled by suitable adjustment of the process variables. It
can be increased by raising the temperature or lowering the pH of the
treatment solution. Increasing the coulomb level of the process also
raises the surface content, although at a constant coulomb level the
chromium falls with increasing current density. These observations were
suggested to be as a direct result of the Cr:O ratio in the film under
different treatment conditions. However, the technique of coulometric
reduction employed by Carter in this work can produce erroneous results
if surface chromium metal is present, a point noted by Gabe. Carter also pointed out that only 10% of the theoretical amount of
Cr(III) was deposited during treatment. This was explained in terms of
the remainder of the electricity being dissipated in hydrogen evolution.

The analysis of the films formed on tinplate after cathodic dichromate
treatment has been extensively reviewed by Azzerri and Splendorini. This is probably the most detailed critical assessment of CDC technology
for tinplate currently available.

Bijimi and Gabe have examined tin surfaces treated in more alkaline
(pH 9) solutions. By applying coulometrical and ESCA techniques they
have reported that the anodic films produced were around 200 Å thick with
tin present as Sn⁰, Sn(II) and Sn(IV), whilst chromium was present mainly
as Cr(III) with traces of Cr⁰ and Cr(VI). Cathodically formed films
tended to have Cr(III) present as the major constituent with much smaller
amounts of metallic chromium and Cr(VI). Tin existed in both the metallic
and oxidised states (a combination of Sn(II) and Sn(IV)). The coating was
also apparently zonal, having three distinct layers of differing composition.
2.4 CHROMATE CONVERSION COATINGS ON ZINC METAL SURFACES

2.4.1 Introduction

The inherent protection afforded by a zinc metal coating is dependent upon the maintenance of a sufficient thickness so that the underlying metal substrate can be protected, not only by physical exclusion but also by the sacrificial nature of the coating. Since zinc forms grey tarnish films in industrial atmospheres and can corrode rapidly in humid and marine conditions, forming a gross white corrosion product, a further protective coating in addition to the zinc is clearly highly desirable. A paint system would be effective, but the difficulty of obtaining suitable organic finishes for zinc is well known. Adhesion is the main problem, with etching or mechanical roughening techniques essential, although phosphated zinc surfaces do provide more adhesion for subsequent organic finishes. Chromate coatings have been established as a pretreatment for primer and subsequent enamel finishes, although their use is not as widespread as phosphating. However, where an inorganic system is required chromate is superior to phosphate, the latter having little intrinsic protective qualities, being regarded mainly as a pretreatment for painting.

2.4.2 Commercial Passivation Processes

Probably the best-known commercial treatment is the Cronak process based on dichromate:

\[ 182 \text{ g/l Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O} \]
\[ 6 \text{ ml/l H}_2\text{SO}_4 \]
\[ 5-10 \text{ secs immersion time} \]

Coatings produced by this process are golden - iridescent to green-yellow and yellow-brown. The sulphuric acid constituent of the treatment formulation is important as it effects the amount of zinc removed during film formation. 6 ml/l is normally considered as the optimum concentration, as the weight of film deposited is equal to the amount of
zinc dissolved. Higher concentrations create an imbalance, with greater zinc dissolution, whilst lower concentrations promote an increase in coating weight over zinc loss. The actual depth of zinc removed is low \(< 0.25 \mu m\)\textsuperscript{15} - an important factor when small articles such as nuts and bolts are being treated. However, this problem is not associated with zinc castings as dimensional tolerances are not so critical.

Many variations of the Cronak process have been developed. All solutions are fairly acidic, based on dichromate (or chromic acid) with one or more of the following: sulphuric acid, hydrochloric acid (or sodium chloride), nitric acid (or nitrate), phosphoric acid, formic acid and acetic acid.\textsuperscript{15} According to Biestek\textsuperscript{58} several of the variants are as good as the Cronak process, but none are superior.

Biestek and Weber\textsuperscript{7} suggest that chromating solutions for both zinc and cadmium can be classified according to pH as outlined by Ostrander.\textsuperscript{59} The groups being as follows:

**Group I** (pH 0.0 to 1.5): These solutions, which also encompass chemical polishing treatments, promote light, bright coatings resembling electroplated chromium. The coatings are formed by simple immersion and applications include household equipment and uses in the motor car, motorcycle and bicycle industry.

**Group II** (pH 1.0 to 3.5): These solutions promote coloured coatings which are also generally more corrosion resistant. They are widely utilised due to their cheap, simple method of application and have found uses as diverse as pre-treatments for paints and corrosion resistant coatings for zinc die-castings e.g. carburettors, oil pumps etc.

**Group III** (pH 2.5 - 6.0): These solutions also promote coatings with good inherent resistance to corrosion. However, they are applied electrolytically by an anodic current and are thus not as simple nor as cheap as their group I and II counterparts. They are most frequently used in the aviation industry (black coatings) and also for refrigeration equipment (light, transparent coatings).
2.4.3 Polarisation Characteristics of Zinc in Hexavalent Chromium Solutions

Significant polarisation studies have been carried out on the anodic treatment of zinc by Bijimi and Gabe.\textsuperscript{60} They found that passivation was most effective with sodium chromate between pH 9-10.5 at solution concentrations of 0.1 - 1.0M and at 20°C. pHs of <7 or >11 diminished the passivity to a large extent. Similar polarisation trials have been carried out for cathodically formed coatings.\textsuperscript{42} Inflections were noted, mainly in the initial sections, of some of the curves for zinc in 1.0M chromate solutions. The significance of this phenomenon was not altogether clear although very similar results have been reported during the rapid potentiodynamic polarisation of electrogalvanised steel sheet in 40 g/l CrO\textsubscript{3} solution.\textsuperscript{23} This fall in current has been attributed to essentially a reduction of hexavalent chromium (Cr\textsuperscript{6+}) to its trivalent (Cr\textsuperscript{3+}) or metallic (Cr\textsuperscript{0}) form.

2.4.4 The Structure and Composition of Chromate Coatings on Zinc

2.4.4.1 Mechanisms of Formation

The formation of a chromate coating is initiated by the action of the acid on zinc:\textsuperscript{8}

\[
\text{Zn} + 2\text{HCr}_2\text{O}_7^- + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + 2\text{HCr}_2\text{O}_7^- + \text{H}_2
\]

The hydrogen so formed reacts with the anions of the acid to form chromic hydroxide:\textsuperscript{8}

\[
\text{HCr}_2\text{O}_7^- + 3\text{H}_2 \rightarrow 2\text{Cr(OH)}_3 + \text{OH}^-
\]

The rise in pH leads to the formation of chromate ions:\textsuperscript{8}
The products of the secondary reaction can then form the coating consisting of chromic hydroxide and basic chromium chromate:

\[ \text{HCr}_2\text{O}_7^- + \text{H}_2\text{O} \rightarrow 2 \text{CrO}_4^{2-} + 3\text{H}^+ \]

\[ 2 \text{Cr(OH)}_3 + \text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr(OH)}_3 \cdot \text{CrOH} \cdot \text{CrO}_4 + 2\text{H}_2\text{O} \]

Williams notes that chemical analyses of the films formed on zinc are attributable to the following reactions:

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \]

It is thought that the reduced \( \text{Cr}^{3+} \) is precipitated on the surface of the zinc as a hydrated oxide. Little zinc dissolution occurs, although the reverse can be true on the addition of sufficient sulphate or chloride ions. It is suggested that the sulphate ions are incorporated into the chromate film as compounds with \( \text{Cr}^{3+} \).

2.4.4.2 Composition of Coatings

The chromate conversion coating on zinc, regardless of colour, can be considered to essentially consist of trivalent chromium compounds. Paatsch also suggests that the hexavalent chromate content of the film can be estimated to be less than 10%. However, this proposal has been partly challenged by Van de Leest, who, using precipitation titrations and electron energy dispersive analysis, suggests that yellow chromate coatings on zinc consist of a basic zinc chromate. A proposal of
formation according to a dissolution-precipitation regime has also been suggested:

Dissolution reaction:
\[
Zn \rightarrow Zn^{2+} + 2e \\
HCrO_4^- + 7H^+ + 3e \rightarrow Cr^{3+} + 4H_2O
\]

Precipitation reaction:
\[
5Zn^{2+} + HCrO_4^- + 8H_2O \rightarrow ZnCrO_4 \cdot 4Zn(OH)_2 + 9H^+
\]

Farr and Kulkarni\textsuperscript{67} have speculated that for coatings formed from chromate and dichromate solutions, zinc chromate (ZnCrO_4) is a major constituent. Cr_2O_3 was not found in films formed in chromate solutions, although dichromate solution at higher concentrations did promote its formation, along with an absence of ZnO. This suggests that dichromate solutions (at higher concentrations) form coatings by a different mechanism to their chromate solution counterparts.

2.5 CHROMATE CONVERSION TREATMENTS FOR OTHER METALS

2.5.1 Magnesium

Although pure magnesium metal is used to only a negligible extent in industry\textsuperscript{8}, when alloyed with other metals such as Al, Zn, Mn, Zr, Ti, Ce, Fe etc it finds widespread application in military equipment containers, automotive parts etc.\textsuperscript{68} In its pure metallic form magnesium will react with water or a neutral salt to form hydrogen gas and magnesium hydroxide, the latter reducing the initial rapid rate of corrosion. However, because magnesium is one of the strongly electronegative metals (standard electrode potential \( \sim -2.38V \)) it can corrode rapidly through galvanic action when coupled to a more noble metal.

In order to take full advantage of its good inherent physical properties, magnesium alloy products frequently receive a final layer of protection from a chromate conversion coating. It is vitally important that the surface of the magnesium alloy is free of oxides, grease and other impurities before treatment. The nature and type of chromate solution
obviously depends on the nature of the alloy constituents. However, it is suggested\textsuperscript{2} that dichromate solutions are most satisfactory:

\begin{align*}
75 \text{ g/l } & \text{Na}_2\text{Cr}_2\text{O}_7 \\
30 \text{ g/l } & \text{SeO}_2 \\
\text{Immersion time: around 1 min}
\end{align*}

This solution is most effective when used hot, however, when castings are to be treated, a cold solution (although inferior) is often used e.g:

\begin{align*}
25 \text{ ml/l } & \text{HNO}_3 \\
280 \text{ g/l } & \text{CrO}_3 \\
8 \text{ ml/l } & \text{HF}
\end{align*}

### 2.5.2 Aluminium

When surface finishing of aluminium articles is required, anodising is often considered as the most applicable method to produce a corrosion resistant finish. However, this process can be slow (often 30 minutes) and costly (consumption of electricity). These considerations have, in the recent past, led to the adoption of chromate-based conversion coating solutions for aluminium and its alloys.

Reference to the Pourbaix diagram\textsuperscript{69} for the Al-H\textsubscript{2}O system confirms that chromating should be possible in both acid and alkaline electrolytes (assuming metal dissolution is the first step in passivation). Typical treatment solutions can then be conveniently divided into two groups according to their pH.

Alkaline treatments are based on the original Bauer-Vogel process (consisting of a boiling solution of alkali carbonate and chromate).\textsuperscript{15} The most widely known process is probably the MBV (Modified Bauer-
Vogel\textsuperscript{70,71} treatment. This solution is based on Na\textsubscript{2}CrO\textsubscript{4} (1-3\% w/v) and Na\textsubscript{2}CO\textsubscript{3} (5\% w/v), the treatment temperature is high (90-95°C) and the time of immersion is 15-30 mins. A 1-2 μm thick film can be grown in 15-30 mins by adding sodium hydroxide, the treatment temperature being reduced (e.g. 65°C for 3-5 g/l or 35°C for 7 g/l)\textsuperscript{2} Some process solutions incorporate silicates or phosphates to reduce porosity and also to act as coating sealers. The films produced by alkaline treatment are light to dark grey in colour and consist mainly of aluminium oxide or hydroxide and probably some soluble chromate.

The acid treatments are usually based on chromates and chromic acid.\textsuperscript{8} Chromate-fluoride and chromate-phosphate are the main solutions, coatings from the former being thin and transparent (0.1 - 1.0 μm) whilst those from the latter are much thicker (1-5 μm) and often dark green in colour.\textsuperscript{2}

Chromates can also be utilised for the sealing of anodic films, the process increasing the inherent corrosion protection of the anodised metal surface. The most effective treatment is suggested as being 5-15 mins in a boiling chromate/dichromate at a pH of just less than 8.\textsuperscript{15} Other treatments are available\textsuperscript{15} and it should be noted that the chromate sealing process leaves a distinct yellow to brown colouration. This is probably due to a basic aluminium or alkali chromate and is adsorbed on to surface aluminium hydroxide.\textsuperscript{15}

2.5.3 Tin-Zinc Alloys

Since these investigations are primarily concerned with the passivation treatments for tin and zinc surfaces separately, it is also pertinent to examine the chromate-based solutions available for tin-zinc alloys. Cowieson and Scholefield\textsuperscript{72,73} examined the passivation of nominally 75\% Sn-25\% Zn alloys in solutions including chromic acid and dichromate. The cathodic/anodic, pH 4 dichromate process, in subsequent corrosion tests, proved superior to all other solutions tested. The chromic acid treatment (simple immersion pH 0.2-0.4) was the least effective, being in effect detrimental to the tin-zinc coating.
Biestek and Weber\textsuperscript{7} suggest two solutions for tin-zinc alloys:

1. $\text{CrO}_3$ 20 g/l
   30 secs at $80^\circ\text{C}$ to produce yellow or brown coatings, $50^\circ\text{C}$ produces colourless ones.
2. Sodium dichromate 10 g/l
   Sulphuric acid 0.0033%.

2.6 POTENTIAL HAZARDS OF HEXAVALENT CHROMIUM SOLUTIONS

2.6.1 Toxicity

It is generally believed that pure chromium metal (\text{Cr}^0) is biologically inert and there is no substantial evidence that the trivalent state of the metal (\text{Cr}(\text{III})) is toxic either. However, hexavalent (\text{Cr}^{\text{VI}}) chromates are extremely irritative, corrosive and, in some circumstances, toxic. The harmful effects are as a consequence of the powerful oxidising nature of these compounds.\textsuperscript{74}

2.6.2 Effluent Treatment

Due to the relatively low pH and high \text{Cr}^{\text{VI}} content, chromating solutions present a considerable problem in their safe disposal. Since hexavalent chromium has such a catastrophic effect on aquatic life, such as fish, the maximum permissible concentration should be below 1 mg/l.\textsuperscript{7} The main objectives of treatment are to neutralise the acidic nature of the solution and chemically reduce the hexavalent chromium to its less toxic trivalent form. This can be achieved by the addition of ferrous sulphate or sulphur dioxide (large plants) or on a smaller scale with sodium pyrosulphite.\textsuperscript{7}
CHAPTER 3
THE ROLE OF MOLYBDATES IN CORROSION PREVENTION

3.1 INTRODUCTION

Chromium, molybdenum and tungsten are the three transition metal analogues of group (VIA) of the periodic table and naturally have many similar properties and characteristics. In their oxy-anion form they are all used successfully as corrosion inhibitors and metal film forming agents: chromate is used most widely, but molybdate is gaining ground as a result of the inherent toxicity of hexavalent chromium solutions.

Molybdate and tungstate, however, differ considerably from chromate in their detailed reaction chemistry. Their ability to form isopoly and heteropoly compounds appears to be quite unique. So too is their ability to form the so called "blue" oxides which are mixed (V) and (VI) valency state compounds.

3.2 THE CHEMISTRY OF MOLYBDATES AND ASSOCIATED COMPOUNDS

3.2.1 Oxides

Molybdenum has several stoichiometric and non-stoichiometric oxides, the simple ones being MoO$_3$, Mo$_2$O$_5$ and MoO$_2$ (valency states VI, V and IV respectively). Their chromium analogues are CrO$_3$(VI), CrO$_2$(IV) and Cr$_2$O$_3$(III). MoO$_3$ is a white solid which does not form hydrates readily, but will, with its hydrates readily dissolve in solutions of excess bases. Mo$_2$O$_5$ is a violet solid which is soluble in warm acids. MoO$_2$ is a crystalline, violet or brown solid which, although insoluble in water, is dissolved by oxidising solutions. The existence of Mo$_2$O$_3$ is less well substantiated. Rollinson$^{75}$ states that Watt and Davies$^{76}$ prepared Mo$_2$O$_3$ by dehydrating Mo(OH)$_3$ or by the action of potassium on an ammonical solution of MoO$_3$. However, Pourbaix$^{69}$ notes that Guichard$^{77}$ has shown that the dehydration of Mo(OH)$_3$ by warming always results in MoO$_3$ being formed.
3.2.2 Molybdcic Acid

Molybdcic acid (H₂MoO₄) usually consists of fine white needles. It is made by moderately acidifying a molybdate solution, whereupon the hydrate H₂MoO₄·H₂O separates from the solution as yellow crystals and can be obtained as an anhydrous acid by gentle warming. Molybdcic acid is sparingly soluble and can be reduced to lower valency molybdenum compounds.

3.2.3 Molybdates

MoO₃ is strongly acidic and dissolves in aqueous sodium hydroxide to form sodium molybdate solution:

\[ \text{MoO}_3 + 2 \text{NaOH} \rightarrow 2 \text{Na}^+ + \text{MoO}_4^{2-} + \text{H}_2\text{O} \]

Molybdates (in common with tungstates) can be reduced (e.g. to the blue oxides as described later) but lack the strong oxidising properties of chromates. When molybdate solutions are acidified they condense to form polymolybdates.

3.2.4 Isopolymolybdates

When an alkaline solution, containing only MoO₄²⁻ and alkali metal or ammonium ions is acidified the molybdate ions polymerise and condense in stages to form a series of polymolybdates. The isopolymolybdate (VI) anions that have been isolated from both aqueous and non-aqueous solutions and have been structurally characterised are listed in Table 2.

Hexavalent molybdenum is generally found at pH > 6 as tetrahedral, colourless MoO₄²⁻. This is similar to chromium which exists as yellow CrO₄²⁻. Though both undergo acid hydrolysis and polymerisation, Cr(VI) remains tetrahedral with corner sharing in Cr₂O₇²⁻ and (CrO₃)ₓ while
Mo(VI) becomes octahedral in the process of forming polyacids and anions\textsuperscript{81}.

The actual process of condensation and the formation of the polymerisation products is complex. At the pH at which condensation begins\textsuperscript{78}:

\[ \text{MoO}_4^{2-} + \text{H}^+ \rightarrow \text{MoO}_3(\text{OH})^- \]

The co-ordination of water molecules then occurs whereby\textsuperscript{78}:

\[ \text{MoO}_3(\text{OH})^- + 2\text{H}_2\text{O} \rightarrow (\text{MoO}(\text{OH})_5)^- \]

The next step is the formation of an oxo-bridge:

\[ 2(\text{MoO}(\text{OH})_5)^- \rightarrow ((\text{HO})_4 \text{OMo-O-MoO(OH)}_4)^2- + \text{H}_2\text{O} \]

Further steps are complex and require a fall in the pH of the solution to about pH 6. The first main reaction in the polymerisation is the formation of the paramolybdate ion:

\[ 7 \text{MoO}_4^{2-} + 8 \text{H}^+ \rightarrow \text{Mo}_7\text{O}_{24}^{6-} + 4 \text{H}_2\text{O} \]

and at further lower acid pH

\[ \text{Mo}_7\text{O}_{24}^{6-} + 3\text{H}^+ + \text{HMOO}_4^- \rightarrow \text{Mo}_8\text{O}_{26}^{4-} + 2\text{H}_2\text{O} \]
The dimolybdates, such as Na$_2$0.2MoO$_3$.nH$_2$O which sometimes crystallise from pH 5-6 solutions, are probably mixtures of normal molybdates and paramolybdates. Anhydrous dimolybdates such as Na$_2$Mo$_2$O$_7$ do not contain simple Mo$_2$O$_7^{2-}$ ions but exist as an infinite chain anion of complicated structure. Similarly trimolybdates of general formula M$_2$I0.3MoO$_3$.nH$_2$O appear to contain acid paramolybdate or other ions containing seven or more Mo atoms, M$^+$ being a monovalent metal ion. Tetramolybdates or metamolybdates of general formula M$_2$I0.4 MoO$_3$.nH$_2$O are formed from concentrated solutions of alkali molybdates treated with 1.5 moles per mole of hydrochloric acid. Octamolybdates can be formed in a similar way from solutions containing 1.75 moles per mole of HCl. Tetra- and octamolybdates are derived from the ion [Mo$_8$O$_{26}$]$^{4-}$.

3.2.5 Heteropolydimolybdates

Heteropoly acids and their salts are formed when a molybdate solution containing another oxo-anion (e.g. P$_4$O$_7^{3-}$) or a metal ion is acidified. There are at least 35 known elements which can form these hetero-atoms. Most heteropoly compounds are very soluble in both water and in various oxygenated organic solvents. The heteropoly acids are decomposed by strong bases.

The heteropoly acids differ from the isopoly acids in that many are immune to depolymerisation in quite strongly acid solutions. In fact in many cases the heteropoly solutions themselves are strong acids. Table 3 indicates the principal types of heteropolydimolybdates. A more detailed review of the chemistry of heteropolydimolybdates can be found elsewhere.

3.2.6 Molybdenum Blue

Molybdenum blue is obtained by the mild reduction of acidified solutions of molybdates or of a suspension of MoO$_3$ in water by, for example, Sn(II), SO$_2$, N$_2$H$_4$, H$_2$S etc. This compound contains both oxide and hydroxide and has Mo in oxidation states of (VI) and (V). There are a whole series of genotypic compounds with olive green MoO(OH)$_2$ at one end of the series and MoO$_3$ at the other. Table 4 lists some of these blue
compounds which have been identified and more or less characterised as definite substances.

3.2.7 Electrolysis of Molybdates

Higashi et al. have reported that using a platinum cathode in an alkaline sodium molybdate bath has produced films which, after thermal analytical, X-ray diffraction, IR absorption spectra and trimethyl silation of the deposits, have been found to consist of amorphous $\text{MoO}_2\cdot n(\text{OH})_2$ where $n = 0-2$, and these can be dehydrated to $\text{MoO}_2$, $\text{Na}_2\text{Mo}_3\text{O}_{6.5}$ and a small amount of $\text{Na}_2\text{MoO}_4$, with elevated temperature.

Jacobson reports that by electrolysing a solution consisting of 60g of sodium molybdate in 350 cm$^3$ of water for 75 minutes, using a porous clay cylinder as a diaphragm, crystals of sodium paramolybdate or, after a longer duration, sodium trimolybdate are formed viz:

\[
i) \ 7 \text{ MoO}_3 + 5 \text{ Na}_2\text{MoO}_4 + 36 \text{ H}_2\text{O} \rightarrow (\text{Na}_2\text{O})_5\cdot(\text{MoO}_3)_{12}\cdot36 \text{ H}_2\text{O} \\
n) \ 2 \text{ MoO}_3 + \text{ Na}_2 \text{ MoO}_4 + 11 \text{ H}_2\text{O} \rightarrow \text{Na}_2\text{O}\cdot(\text{MoO}_3)_3 \text{ 11 H}_2\text{O}
\]

Ma and Offinger published a US patent in which they claimed that a deposit of $\text{Mo}_2\text{O}_3\cdot\text{H}_2\text{O}$ is produced on a metallic cathode from a solution containing 10-20% of an alkali molybdate maintained at pH 4-9, and by use of a current density of 0.5-2.5 A/cm$^2$ for 10-20 mins. This is part of a method for producing molybdenum plating (the $\text{Mo}_2\text{O}_3\cdot\text{H}_2\text{O}$ is then washed and heated to 700-1000°C with hydrogen, the oxide being reduced to molybdenum metal).

Mellor notes that, according to Chilesotti, when a solution of molybdic acid is electrolysed part of the hydrogen evolved at the cathode reduces the molybdic acid and the rest escapes as gas. Treadwell and Schaeppi suggest that electrolytic reduction of ammonium paramolybdate gives molybdenum blue oxide hydrate.
It is now well established that cathodic reduction cannot produce metallic molybdenum deposits in aqueous solution because the reduction potential is just too negative in relation to the hydrogen overpotential. It may be contrasted with chromium which can just be electrodeposited but the efficiency rarely exceeds 25%. However, in the presence of 'catalytic' metals such as nickel, cobalt or iron co-deposition becomes possible and alloys of Mo-Fe, Mo-Co or Mo-Ni are feasible. The same effect occurs with tungsten.

3.2.8 Toxicity of Molybdenum Compounds

Although molybdenum is classified as a heavy metal there have been no documented cases of deaths due to poisoning in man. The metal is required as a trace-element by plant life and is also found in adult humans at levels of about 20 mg and in urinary excretion at concentrations of about 10-20 µg/l.

Molybdates can similarly be classified as of relatively low toxicity. The main evidence results from an investigation of molybdates and chromates on daphnia and rainbow trout (see Table 5). Further information on the toxicity of molybdates can be found elsewhere.

3.3 MOLYBDATE AS AN INHIBITOR

3.3.1 Historical

Hexavalent chromium compounds such as chromate and dichromates have been utilised for many years as efficient corrosion inhibitors for a variety of metals. They are excellent film formers in that they oxidise the metal and in their accompanying reduction form intrinsically sound mixed metal-oxide films. Their main disadvantage is in the inherent toxic nature of the chromium (VI) oxidation state and the associated effluent disposal problems. The situation has grown worse with more stringent anti-pollution laws being enforced worldwide, but more particularly in the USA and W.Germany. This has led to a reappraisal of chromates and more particularly to a search for a less toxic alternative. A logical
alternative might therefore be the analogues of chromate from group (VIA) of the periodic table, i.e. molybdate and tungstate.

Early appraisals of the group's inhibitive properties were made by weight loss experiments in both aerated and deaerated solutions\textsuperscript{96-98}. Iron and steel were the main metals studied, although King et al\textsuperscript{97} also examined zinc and cadmium. Chromate, molybdate and tungstate were found to be effective inhibitors in aerated conditions although their mode of operation was quite different. Chromate was found to oxidise the ferrous ions and in so doing form a film which contained the precipitated products of oxidation and reduction. However, molybdate and tungstate were found to have little or no oxidising ability and were thought to possibly form an adsorbed film at the metal-solution interface\textsuperscript{96,99}. The ability of molybdates (and tungstates) to form blue complex hydrated oxides was noted by King et al\textsuperscript{97} and it was suggested that protection given in acid solutions (containing an oxidising agent) was partly due to the oxidation of the metal and partly to the adsorption of this colloidal blue complex. In deaerated conditions only chromate provided adequate inhibition as a result of its powerful oxidising nature. Molybdate and tungstate were found to form films in deaerated solutions but at a rate which was insufficient to prevent iron dissolution\textsuperscript{98}. Tungstates (and probably molybdates) could, however, be made to behave as effective oxidising agents towards iron by anodic discharge at a high current density.

Although these early investigations can be considered somewhat simplistic in their approach, they represent the first concerted investigation into group (VIA) inhibitive properties and their results have formed the basis for later work using more sophisticated experimental methods.

More recent work\textsuperscript{100-103} has on the whole approached the passivation achieved by molybdates from a more electrochemical stance. Although the work of Stern\textsuperscript{100} and Cartledge\textsuperscript{102} dealt with inhibitors in general and suggested their mechanisms of protection, other investigations\textsuperscript{101,103} have examined characteristic electrode potentials exhibited before the onset of decay of passivity\textsuperscript{101}, and have made various current-time and
potential-time measurements. These results agreed in general with the earlier classical work, thus suggesting that molybdates will only passivate iron effectively in the presence of oxygen. This situation can possibly be explained in terms of the insufficient cathodic depolarising power of molybdate\textsuperscript{101}. When conditions are preferable for passivation the film formed on iron was found to contain Fe(II), Fe(III) and Mo(VI)\textsuperscript{103}.

The ability of an inhibitor to reduce the tendency of a metal to undergo dissolution by pitting is clearly advantageous. In this respect molybdate is successful in that it improves the localised corrosion resistance in the pit by forming insoluble molybdate compounds. The inhibitive film has been reported to be FeMoO\textsubscript{4} due to the inherently lower pH and potential found inside pits when compared to the bulk solution\textsuperscript{104}. This theory has been partly challenged by Ogura and Ohama\textsuperscript{105} who have suggested that this compound is a polymolybdate rather than an iron molybdate. This assertion is supported, by the ability of Mo(VI) to form complexes at low pHs and thus the presence of a poly- rather than a simple molybdate could be expected.

It is evident that molybdate is an efficient inhibitor in aerated conditions. However, its oxidising ability is not unequivocal and its inability to confer protection in conditions where oxygen is absent is well-reported in early literature\textsuperscript{96-98} and more recently by Chew and Gabe\textsuperscript{106}.

\section*{3.3.2 Inhibition of Specific Metals by Molybdate}

By far the greatest inhibitive use for molybdate is for the protection of ferrous-based alloys; consequently the largest portion of data on their performance is for the inhibition of steels. The pioneering work of early investigators\textsuperscript{96-98} confirmed the ability of molybdate to render a ferrous surface passive in favourable conditions, so later work has been essentially an evaluation of its effectiveness for steels under specific conditions, such as a cooling water containing a certain amount of aggressive impurities.
In slightly alkaline conditions molybdate appears to be successful in conferring protection on low carbon steels, provided there is oxygen available\textsuperscript{94,95}. Its ability to passivate under aerated conditions has been confirmed and the nature of the protective film is generally considered to be an iron (III) molybdate\textsuperscript{94,107} (and possibly some additional iron (III) oxide)\textsuperscript{94,107}. The anodic polarisation characteristics of steel in aggressive, low-hardness waters containing molybdate has also been reported\textsuperscript{108}. In neutral and alkaline deaerated solutions passivity was exhibited with increasing molybdate concentration, it was also found that raising the temperature from 21\degree C to 60\degree C was detrimental. In acidic solutions molybdate was thought to be less effective. The nature of the passive films formed under alkaline and acidic conditions appears to be quite different. XPS and AES techniques have enabled up to 15 at \% Mo as MoO\textsubscript{4}\textsuperscript{2-} to be detected in alkaline solution films, whilst films formed from acidic solutions are generally thought to be based upon non-protective MoO\textsubscript{2}. The rapidity of the onset of protection afforded by molybdate has been questioned by Farr and Saremi\textsuperscript{109}, who have suggested that a "conditioning" time is required to establish passivity.

The effectiveness of an inhibitor may be judged on its ability not only to protect one metal but also others that might be encountered, for instance, in a multi-metal cooling system (e.g. automotive engines). In this respect several other metals have received consideration: for example, the efficiency of molybdate for aluminium in neutral or alkaline chloride solutions is improved with increasing concentration\textsuperscript{110}. If an etched aluminium surface is placed in such solutions molybdenum has been detected on the metal surface as both Mo(VI) and in the reduced state of Mo(IV)\textsuperscript{111}.

The recent interest in the anodic behaviour of titanium has led to the examination of its characteristics in molybdate solutions. Abdel Hady and Pagetti\textsuperscript{112} found that sodium molybdate was an effective corrosion inhibitor for titanium in 10 and 25N sulphuric acid at room temperature. Similar findings have been made by Glass\textsuperscript{24} who polarised titanium in deaerated, boiling 1N sulphuric acid. The passive film was thought to
form as a direct replacement of TiO₂ by a complex salt containing molybdenum.

3.3.3 Inhibitors for Commercial Uses

The main commercial use for molybdate-based inhibitors is in circulating cooling water systems. Their main advantage over chromates is in their inherently low toxicity and the accompanying ease of any effluent treatment that may be required. Due to their high toxicity the use of chromates is restricted under the USA Federal Water Protection Control Act. The use of molybdate-based formulations as alternatives to chromate appears to be quite widespread and in general they appear to be quite effective, especially when used in conjunction with other inhibitors such as HEDP, BZT, MBT etc. On its own, the effectiveness of molybdate is limited and has been found to be less efficient than silicate, polyphosphate and chromate.

Sodium molybdate has been investigated for its effectiveness in aiding rust resistance and corrosion protection when added to simulated and commercial metalworking fluids. The need for a replacement stems from increased concern over the potential toxicity of nitrite, a common anodic inhibitor and oxygen scavenger which is widely utilised in this field. It has been found that molybdate can reduce substantially the amount of nitrite required to provide protection. Encouraging results have also been found when adding molybdate to commercial amine, borate and carboxylate salt fluids.

Another common requirement for inhibitors is as additions to automotive engine coolants. Wiggle et al. investigated the effectiveness of coolant inhibitors for aluminium and found that when used alone molybdate was only effective in high concentrations. However, when mixed with phosphate excellent results are found.
3.3.4 Polarisation Characteristics

Potentiodynamic polarisation is a powerful tool in assessing not only the inhibitive properties of a solution towards a particular metal but also the feasibility of producing coated samples from said solution. The polarisation characteristics of group (VIA) oxy-anion solutions with different metals have been extensively examined\textsuperscript{19,20,40,42,45,60,117}. Iron was found to passivate to a degree in all three solutions at pH 6.5\textsuperscript{117}. The anodic passivation of tin\textsuperscript{45} was found to be most favourable in solutions of greater concentration than 10\textsuperscript{-2}M, and that over the pH range 5-9 molybdates were most effective at 40\degree-60\degree C. Zinc\textsuperscript{60} when treated anodically produced optimal coatings at pH 9 and concentrations $\geq$ 0.1M at 40\degree-60\degree C. Bijimi and Gabe assessed the optimum conditions in terms of a degree of passivity $D_p$ defined as

$$D_p = \frac{\Delta E_p}{i_p}$$

where $\Delta E_p$ is the potential range of passivity and $i_p$ is the passive current density.

Cathodic treatments of tin and zinc have also been assessed\textsuperscript{40,42}, molybdate being found to be capable of forming a passivating film on tin\textsuperscript{40}. However, the incidence of marked inflections on cathodic polarisation curves carried out in concentrated group (VIA) oxy-anion solutions has also been reported\textsuperscript{42} and in molybdate solutions has been attributed to a reduction of Mo(VI) to possibly the blue oxides (Mo(VI)/Mo(V)). Analysis using ESCA techniques of films produced before and after the inflections suggested that there was no significant change in the oxidation state of molybdenum. However, the films did exhibit a reduced state (i.e. on zinc, Mo(V), Mo(IV) and tin, Mo(V)) when compared to the hexavalent processing solution. The occurrence of cathodic inflections has been reported elsewhere\textsuperscript{24,25}; typically, on platinum Glass\textsuperscript{24} has suggested that the increase in current (before the tip of the inflection) was caused by a reduction of Mo(VI) to Mo(V). A diffusion-
limited region is then reached followed by a further increase in current due to hydrogen evolution. Wanklyn\textsuperscript{25} found similar effects with platinum and with type 316 and alloy 625 stainless steels. He considered films formed during cathodic polarisation to be MoO\textsubscript{2}, possibly in an hydrated form.

The occurrence of cathodic inflections has to be approached with a degree of caution. The presence of a surface, air-formed oxide can also produce an inflection or step on a cathodic polarisation curve and thus interpretation of curves can be made more difficult as noted by Subramanyan et al\textsuperscript{21}. However, the presence of an inflection due to the reduction of Cr(VI) to Cr(III) has been reported when polarising galvanised steel sheet in chromic acid at a rapid sweep rate\textsuperscript{23}, and other instances are found in relation to the production of tin free steel (a chromium-chromium oxide coated steel product formed cathodically from a dilute chromic acid solution).

### 3.3.5 Synergistic Effects with Molybdate

It is well-established that improvements can be made in the inhibition of metals, in specific solutions, by combining molybdates with other inhibitors such as phosphate\textsuperscript{118}, nitrite\textsuperscript{95}, citrate\textsuperscript{118}, HEDP\textsuperscript{109}, BZT\textsuperscript{109,119}, tolytriazole\textsuperscript{118} and zinc sulphate\textsuperscript{93}. Several investigators have also examined heteropoly compounds as possible corrosion inhibitors. It appears that sodium 12-molybdophosphate can be an effective inhibitor for both 430 type stainless steel\textsuperscript{120} and abraded mild steel\textsuperscript{121} and is also capable of protecting a wide range of non-ferrous metals and alloys. However, the mode of protection of sodium dodecamolybdophosphate must be considered with some care. Weissstuch and Schell\textsuperscript{122} observed that such heteropoly compounds are not normally produced in large commercial quantities and consequently there can be real differences between batches, a point also observed by Brasher and Rhoades-Brown\textsuperscript{121}. The protection afforded by sodium dodecamolybdophosphate was at first thought to be due to the heteropoly anion but was later shown to be as a result of the effects of sodium molybdate and sodium phosphate\textsuperscript{121,123}. Care must further be exercised since some heteropoly compounds can undergo
hydrolytic degradation in very dilute solutions and furthermore are not stable at pH >3.582.

3.3.6 Present-day Inhibitor Developments

Table 6 lists a number of the patented inhibitors using molybdate or other molybdenum compounds that have been disclosed since 1970. The main trend is to use molybdate not singly but as a constituent of an inhibitor formulation that contains other active compounds such as HEDP, nitrites etc. This trend confirms the view expressed in much of the literature that synergistic mixtures have clear advantages over simple molybdate formulations.

Heteropoly systems could also be promising for further development. The range of options is large (see Table 3) although for the protection mechanism to be due to the heteropoly anion the effect of the solution pH must be examined carefully.

3.4 MOLYBDATE FOR CONVERSION COATINGS

Molybdates have not been widely utilised as promoters of conversion coatings when compared to the present extensive use of chromates, dichromates etc. However, the application in coating formulations of molybdates has been known as long ago as the 1940s when an electrochemical process based on sodium molybdate, molybdic acid and nickel sulphate was patented for use in coating a variety of metals\(^{124}\). On zinc the nature of the coating produced is somewhat unclear, although a surface consisting of a complex molybdenum oxide, possibly sesquioxide may be produced\(^{125}\). Coatings tend to be semi-matt to glossy black in appearance but due to their intermediate oxidation state are prone to degradation in moist air, turning from black to brown and eventually to white. This process can be stemmed by lacquering. Inconsistency of coatings can be minimised by pre-electroplating the substrate with zinc. The main disadvantage with the overall process is the slow speed of formation of the coating. However, baths containing nickel and molybdate blackening materials do have the virtue of more rapid process times\(^{125}\).
By varying the process time a sample of zinc or zinc-nickel alloy immersed in a solution containing \((\text{NH}_4)_2 \text{MoO}_4\) can undergo a series of colour changes\(^{126}\). Coating thicknesses can be considered to be 0.1-0.25 \(\mu\text{m}\) for a 0.5-1.5 min immersion. Mild corrosion tests have indicated that molybdate-coated samples are superior to unpassivated ones and generally similar to chromated specimens.

Interest in molybdate coating systems has also been shown in Japan\(^{127}\). A solution based on molybdate adjusted to a low pH with, preferably, orthophosphoric acid has been applied to galvanised steel surfaces. Corrosion tests in brine prove the effectiveness of the system.

Recent interest in the commercial use of tin-zinc alloys, particularly in the protection of steel reinforcing bars in concrete and as an alternative to cadmium electrodeposits, has led to a reappraisal of the passivation treatments available for such alloys. A 75% Sn:25% Zn alloy has been examined in various passivating solutions based on chromic acid, dichromate, molybdate and tungstate\(^{72,73}\). In subsequent corrosion tests dichromate was the most effective ion but molybdate passivated alloy was found to be reasonable in a salt fog test and generally good in a cycled humidity test.

3.4.1 Molybdate Coatings on Solar Absorbers

Since the oil crisis of 1972-5 research on solar absorbing surfaces has increased tenfold. Many options exist but molybdenum features in two types of coating: black molybdenum produced by CVD techniques, possibly combined with layer anodised Al/Al\(_2\)O\(_3\), and black molybdate produced by solution reduction. Reduction of molybdate yields, of course, lower oxides not molybdenum metal and in appropriate circumstances give black films on aluminium\(^{128}\), zinc\(^{129}\) and nickel\(^{129}\). A detailed study has shown\(^{130}\) that cathodic reduction is preferable for aluminium substrates but a simple dip suffices for zinc or galvanised steel presumably because zinc dissolves first to provide the reducing electrons. The best product was produced using a solution of ammonium paramolybdate containing Ni\(^{2+}\) or
Pb$^{2+}$ ions at 50-80°C and 3 mA/cm$^2$ which is essentially an earlier formulation$^{131}$. The black film is essentially tetravalent molybdenum MoO$_2$ or MoO$_2$.2H$_2$O containing 10% Ni or Pb, a possible reduction reaction being

$$\text{Mo}_7\text{O}_{24}^{6-} + 24 \text{H}_2\text{O} + 14\text{e} \rightarrow 7 (\text{MoO}_2.2\text{H}_2\text{O}) + 20\text{OH}^-$$

The authors speculate that this film could also be a form of molybdenum blue, but as the molybdenum is in the four valency state this seems to be unlikely. Molybdenum blue is generally thought to be a mixture of oxides and hydroxides with the metal in the (V) and (VI) valency states. Hosseini et al.$^{130}$ also suggest that this blue oxide (molybdenum blue) is a mixture containing MoO(OH)$_2$ and MoO$_3$, although this again is an oversimplification in that these compounds form the limits of a series of "genotypic" compounds of which molybdenum blue forms part.$^{78}$

The black molybdate film is not regarded as a favoured solar absorber at present, largely because it is not stable for long periods towards water-based heat exchanger systems but in a suitable design could be more promising, e.g. glycol cooled systems.

Table 7 indicates recent publications of patented coated systems using molybdate as a constituent. The actual number of patents suggests that utilisation of molybdate is still small and there is scope for more research in the conversion coating field. A successful conversion coating system has been developed and patented for tin, based on tungstate$^{132,133}$ and if more stringent pollution laws are passed restricting the use of hexavalent chromium compounds, this may provide the incentive for further research into molybdates.
3.5 MOLYBDATE IN PIGMENT AND PAINT FORMULATIONS

The same restrictive laws that have brought pressure to bear on the use of chromates as inhibitors and promoters of conversion coatings have also forced paint manufacturers to seek alternatives to the more potentially toxic primer systems (e.g. chromate- and lead-based) that were once widespread on the market.

Zinc and calcium molybdate have found favour with several manufacturers. The toxicity of these compounds and the similar calcium-zinc molybdate appears to be low\textsuperscript{134,135}, although the degree of knowledge is not clear\textsuperscript{136}.

Experimental evaluations of calcium and zinc molybdate when formulated as rust inhibiting pigments in a given paint formulation are well-reported\textsuperscript{137-139}. Lapasin et al\textsuperscript{137} found one molybdate pigment considerably superior to others tested; however, in general the results of the tests have proved to be somewhat mixed. Most investigators found an ageing phenomenon causing embrittlement to films during elasticity tests. Results from tests showed excellent adhesion strengths\textsuperscript{138} although Lapasin et al\textsuperscript{137} concluded that zinc and calcium molybdates were inferior to chromic phosphate in this respect. Industrial atmosphere (IA) and salt fog tests again produced mixed results. Whilst the acid nature of the IA test has posed a question as to the ability of molybdates to provide adequate protection at low pHs, Lapasin et al\textsuperscript{137} suggest that the formation of less-protective polymolybdates reduces the corrosion resistance of the film. However, as mentioned earlier Ogura and Ohama\textsuperscript{105} postulate the formation of isopolymolybdates inside corrosion pits in iron and suggest that films formed by these stem the formation and growth of these features, therefore the production of isopolymolybdates may not necessarily result in a decrease in protective power, as the results of Marchese et al\textsuperscript{138} bear out. The salt fog experiments once again highlighted the problem of coatings becoming brittle during tests. While immersion tests in both fresh and sea water produced fair results, Marchese et al\textsuperscript{138} reported good rust inhibition in fresh water, but poor resistance to blistering. Cathodic tests carried out by Lapasin et al\textsuperscript{137}
exhibited the curious result in which once again one molybdate pigment performed far better than the other two tested.

The ability to incorporate molybdates with other inhibitor pigments has also been considered. Molybdated zinc oxide pigments (2ZnO:MoO₃) have been examined⁴⁰ and the phosphate-molybdate synergism is well reported¹³⁶-¹³⁸,¹⁴¹. Other formulations which are said to increase the effectiveness of the system include combining zinc molybdate with an organic nitroderivative¹³⁹ and also by mixing zinc molybdate with iron oxide¹⁴².

Although experimental tests have shown that the effectiveness of molybdate-based paint formulations is only moderate, they have been marketed as an effective rust inhibitor¹³⁴,¹³⁵. Molybdates are effective in the presence of sulphates and chlorides but their formulation costs are high¹⁴³, however their ability to perform adequately as flash rust inhibitors has been generally agreed¹⁴⁴.

3.5.1 Summary

The use of molybdates as inhibitive pigments in paint formulations appears to be increasing (see Table 3 for recent patent publications), their inherently low toxicity being a major advantage. However, the inconsistent results from reported trials does suggest that further work is required before a major replacement of chromate and lead-based paints can be contemplated (although Sherwin-Williams Chemicals market Molywhite 101 and 212 and Banke¹³⁴ cites several case histories of the effectiveness of molybdate based primers).

One avenue of further research could be in the formulation of synergistic mixtures containing molybdate and other inhibitors e.g. phosphate. These synergisms have proved under certain conditions to be more effective than molybdate alone. Furthermore, the parallel with solution inhibitors may be considered in that use of heteropoly)molybdates as pigments may be explored although at present there appears to be little published evidence that they have been considered.
3.6 MISCELLANEOUS USES FOR MOLYBDATE IN CORROSION PREVENTION

Molybdates have been used to seal conversion$^{145}$ and anodised$^{146}$ coatings on aluminium (see Table 9 for recent patented processes with regard to the finishing of aluminium). Molybdates have also been proposed as integral colouring components of anodised finishes$^{147}$. Ammonium paramolybdate has been found to give brown to black colours with an aqueous seal, and black through blue, green and brown with a non-aqueous seal$^{147}$. Sodium molybdate has also been used as an anion addition to AC anodised coloured finishes from sulphuric acid electrolytes$^{148}$.

Molybdate has been used as a chemical oxidant accelerator for phosphating solutions$^{32,149-151}$. A more recent application is in the passivation of zinc phosphate conversion coatings where molybdate is replacing chromate in response to the toxicity problem$^{90}$. None of these applications however, can yet be considered to be of major importance but does indicate the way in which options are being explored.
CHAPTER 4
OTHER POSSIBLE REPLACEMENT CONVERSION COATING PROCESSES

4.1 INTRODUCTION

Although in this investigation molybdate is considered as the prime replacement for chromate, it must be noted that there are several other potential alternatives, some of which are already in limited use.

Tungstate is a group (VIA) oxy-anion analogue of both chromate and molybdate and shares many features of the latter's unusual solution chemistry. It has found limited use as an inhibitor and, through the work of Van de Leest et al., has been applied as a coating treatment to tin surfaces. Trivalent chromium solutions are used in proprietary coating agents for zinc and have good protective abilities, but, unlike chromate solutions, do not suffer from intrinsically high toxicity. Phosphate coatings are widely used as a pre-paint treatment on ferrous metals, and, to a lesser degree, on zinc and its alloys. Their value as a "keying" pre-treatment is unquestioned, although their intrinsic corrosion resistance is clearly inferior to chromate.

An alternative to chromate solutions does not have to be based on the familiar system i.e. tungstate, trivalent chromium, molybdate etc. Metal Box Ltd have illustrated this by patenting a system, based on zirconium compounds, for the treatment of tinplate against sulphide staining.

It must be appreciated that tinplate itself is continually challenged by the so-called tin-free-steel (TFS) type products which usually consist of a Cr-CrOₓ based coating on the steel substrate. From this technology has evolved a product called "Zincrox" which in essence is a TFS type coating solution for electrogalvanised steel sheet. The process has received much acclaim in Italy, and treated electrogalvanised steel has been used for car-body panels by Ferrari.
4.2 TUNGSTATE TREATMENTS

Tungstate has not been widely utilised as a promoter of corrosion resistant conversion coatings. Although Markwell and Holt have examined cathode potentials in aqueous tungstate solutions, they were primarily concerned with the feasibility of tungsten metal deposition. McNeill and Gruss examined the anodic film growth of Al, Bi, Cd, Cu and Zn in 0.1N Na₂WO₄. Films formed were oxides of the substrate metal or mixed oxides including incorporated WO₃.

The polarisation characteristics (both anodic and cathodic) of tin and zinc in tungstate solutions have been examined as a part of an overall assessment of group (VIA) oxy-anion solutions. Tin was found to passivate most successfully in tungstate solutions of greater concentration than 0.01M at pH 7-9 and at a temperature of 60°C. Under cathodic polarisation, passivation was also noted. Zinc was found to undergo optimum passivation between pH 9 and 10.5 for concentrations of 0.1-1.0M, with 60°C being considered the most effective operating temperature. In alkaline processing solutions, tungsten was also found in the hexavalent form (Wo (VI)) in coatings on tin and zinc. However, it is probable that if cathodic coatings were formed from acidic solutions a reduced species may well be found on the surface of the substrate metal, as with molybdate treatments.

Tungstate has also been applied as an anion addition to anodising solutions for aluminium. With AC-anodised finishes it has little effect on the colouration of the treated article. However, when applied to alloys (e.g. KS 45), with a DC voltage, it forms medium tan/grey to black finishes.

Although tungstate conversion coatings have been applied to tin-zinc alloys with moderate success, it is the work of Van de Leest et al in forming a tungstate coating on tin that has shown the most promise. This was achieved by applying a periodic reverse current to a tinplate surface in a solution of 0.1M sodium tungstate, adjusted to pH 9 with a 10 g/l borax buffer. The corrosion resistance of the
coating was measured by monitoring potentials in acetate solution (pH 4.7) and also by extrapolating the cathodic Tafel slopes obtained from polarisation measurements.

Surface analysis of coatings formed on tinplate suggest that the following overall formula may be applied:

\[ x\text{SnO}_y\text{SnWO}_4_z\text{H}_2\text{O} \]

thus being considered predominantly a basic tin (II) salt. The coating is said to be protective, resisting aqueous corrosion and tarnishing.

Subsequent patents filed by Van de Leest, Krijl and Flaes\textsuperscript{133,152} have described the solution composition as:

- 10g Na\textsubscript{2}WO\textsubscript{4}.2H\textsubscript{2}O
- 10g Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}.10H\textsubscript{2}O
- 10g Na\textsubscript{2}SO\textsubscript{4} (pH = 9)
- \( T = 20\degree C \)

Periodic reverse current: 0.5A/dm\textsuperscript{2} at 0.5 c/s

However, they also mention that comparable results can be obtained with a solution based on phosphate:

- 40g Na\textsubscript{3}PO\textsubscript{4}
- H\textsubscript{3}PO\textsubscript{4} until pH = 9.5
- 20g Na\textsubscript{2}WO\textsubscript{4}.2H\textsubscript{2}O
- \( T = 20\degree C \)
4.3 TRIVALENT CHROMIUM TREATMENTS

The formation of a chromate conversion coating can be reduced, in essence, to three basic steps:

1. substrate metal dissolution;
2. precipitation of a metal-containing and film-forming compound;
3. film consolidation, recrystallization, dehydration etc.

Barnes et al\textsuperscript{29} have devised a trivalent (Cr(III)) based coating solution which possesses the inherent features of a regular hexavalent treatment i.e:

1. Oxidant, for Zn$^+$Zn$^{2+}$ + 2e: sodium nitrate;
2. Metal cation, which will precipitate as an insoluble hydroxide: 
   "Chrometan*", trivalent chromium;
3. Complexant, to increase the stability of Cr(III) over a larger range of pH: sodium hypophosphite.

Coatings formed from this type of solution appear to be equal to their hexavalent counterparts when corrosion tested. They also have the important virtue of a low level of toxicity and are thus free from the encumbrance of lengthy, costly and critical effluent treatments.

Trivalent chromium solutions appear to have been accepted by industry\textsuperscript{153} and have the potential to be applied successfully in aluminium finishing too.\textsuperscript{30} The scope for trivalent chromium solutions in the electroplating industry (e.g. "Envirochrome" or "Alecra"\textsuperscript{**}), as a direct replacement for chromic acid based treatments, has yet to be fully achieved, but also augers well for the future.

\* "Chrometan" is the trade name for a leather tanning salt of British Chrome and Chemicals Ltd
\** "Envirochrome" - trade name of W. Canning (Materials) Ltd
   "Alecra" - trade name of Albright and Wilson plc
4.4 PHOSPHATE-BASED TREATMENTS

4.4.1 Zinc Metal Surfaces
Zinc and its alloys can be successfully phosphated using solutions that are similar to those applicable for ferrous metals. Good results have been obtained by applying solutions at room temperature.\(^7\) Although efficient as pre-paint treatments, phosphate coatings do not possess the same level of inherent corrosion resistance as afforded by chromate treatments and are thus not widely used on their own as a purely protective film.

4.4.2 Tin Metal Surfaces
It is known that tin readily undergoes anodic passivation in phosphoric acid, the film being predominantly stannic oxide. The addition of nitrates increases the rate of passivation but promotes a film which is considerably more porous and does allow continued tin dissolution.\(^{158}\) Black anodised films have been produced on tinplate\(^{159}\) from phosphate-phosphoric acid based baths. The use of a reactive oil sealant gives the films good intrinsic corrosion resistance, water-repelling characteristics, lubricity, and the finish, because of its low contact impedance, is said to be particularly useful for articles providing electrical shielding.\(^{160}\)

In conclusion, although Britton\(^9\) suggests that phosphoric acid can promote a partially protective layer on tin, in essence phosphate treatments have never reached the degree of application achieved by chromate.

4.5 A ZIRCONIUM COMPOUND BASED CONVERSION COATING PROCESS FOR TINPLATE\(^{154}\)
This patented process proposes a conversion coating system, based on zirconium compounds, to protect tinplate from sulphide staining. It suggests the need for a non-toxic replacement for Cr(VI)-based passivating systems and states that zirconium compounds have been found
to confer, in conversion coating systems, a degree of corrosion protection to metal surfaces, particularly in phosphating processes.

The proposed solution is one containing zirconium as either:

- ammonium zirconium carbonate (AZC)
- or
- zirconium acetate

The solution can be further enhanced by the addition of an inorganic salt such as phosphate, silicate or borate. The corrosion test applied to investigate the effectiveness of this treatment was the sulphide stain test, in this case comprising of a 1 hr immersion in a pressure cooker at 121°C containing a dried pea/brine staining medium.

Several variations of the solution are mentioned, usually taking the form of a brief immersion treatment in:

- 0.2-2% w/w as ZrO₂, AZC solution

followed by drying at 20°C - 30°C.

The patent suggests a possible reason for the effectiveness of the coating as being the strong affinity of zirconium for oxygen, such that the AZC decomposes on the tinplate surface and the zirconium attaches to the tin oxides.

The solution seems very efficient at preventing or reducing sulphide staining. It is interesting to note that the patent claims the effectiveness of the treatment is nullified when the coated tinplate is not dried before staining. The author has used commercially passivated tinplate (from unused cans) as his material to be coated, and has argued that the influence of the conversion film is lost during the drawing and
forming operation. It seems unusual that all the investigations were not carried out using untreated tinplate. However, an example of unpassivated tinplate was tried and the film formed on it was effective. The inorganic salt additions seem to be mainly used for improving the resistance to iron sulphide formation and are claimed not to impair the corresponding tin sulphide stain resistance. The duration of the immersion period for coating the tinplate is unclear, the patent claiming a "brief immersion". It is probable that the period of time is immaterial and that the effectiveness and structure of the coating is more dependent on the drying time and conditions.

4.6 TIN-FREE-STEEL TYPE SOLUTIONS

4.6.1 Introduction

Although this research programme is concerned primarily with a replacement of chromating as a passivation process for tin and zinc, the following pages are a brief description of the so-called tin free steel (TFS) process, whereby a chromium metal-oxide film is deposited on steel. The reason for its inclusion is, as will be seen later, that the process has been successfully applied to galvanised steel and interest is now being shown in the application of TFS-type solutions for tinplate.

The search for an alternative to tinplate in the food-packaging industry was initiated by artificial shortages created by military conflict, or its imminent threat e.g. Second World War, Korean and Vietnam wars. The real progress in TFS-type solutions was made when a non-soldered joining method was available and the need for tin, with its excellent solderability, was negated.

4.6.2 Types of TFS Treatments

Smith162 sub-divided TFS products into categories according to their method of formation and the nature of the film produced.
The simplest film type is the oxide form, commercial examples of which include US steel 210 and "Hinac". The former is essentially a cathodic electrolyte process in which mild steel strip passes through a bath of the following composition: 163

\[ \text{2\% w/w } \text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O} \]

\[ \text{2\% v/v } \text{H}_3\text{PO}_4 \ (85\%) \]

\[ \text{1-4\% } \text{NaNO}_3 \text{ or } 0.2\% \text{ KMnO}_4 \]

\[ 120-130^\circ\text{F} \]

\[ 0.25 \text{ sec at } 90\text{A/ft}^2 \]

\[ 2 \text{ sec at } 15\text{A/ft}^2 \]

The coating produced is duplex in nature, the underlying film being a micro-crystalline phase containing phosphate. The adsorbed upper portion is amorphous and gel-like and contains both phosphate and chromate.

Coatings which are essentially chromium oxide have also been applied both electrolytically and non-electrolytically. 164 The cathodic electrolysis of steel sheet in a pure chromic acid solution produces a hydrated chromium oxide coating. The addition of various anions such as boric acid, trivalent chromium compounds, halogen ions and halogen oxyacids etc is considered to improve the quality of the coating thus formed. Non-electrolytic methods of producing similar coatings have long been applied to zinc and cadmium. However, steel passivates in a chromate-type bath and thus the reaction to form a chromium oxide film cannot progress. The addition of a reducing agent to the solution to overcome this problem has been reported. 165 The method requires coating the steel surface with the solution and heating it, thus forming the chromium oxide.
A further class of coatings is the one-step metal plus oxide group. Probably the most important example is the so-called "Hi-Top" product invented by Toyo Kohan of Japan\textsuperscript{166} and produced elsewhere under licence. A summary of the solution composition is illustrated below:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromic acid (CrO$_3$)</td>
<td>20-100 g/l</td>
</tr>
<tr>
<td>Aromatic sulphonic acids containing hydroxyl radical, or their water soluble salts</td>
<td>0.2-4.0 g/l</td>
</tr>
<tr>
<td>Treatment temperature</td>
<td>40$^\circ$-70$^\circ$C</td>
</tr>
<tr>
<td>Cathodic current density</td>
<td>$&gt;15$ A/dm$^2$</td>
</tr>
<tr>
<td>Treatment time</td>
<td>1-30 secs</td>
</tr>
</tbody>
</table>

In its original form the film was bluish in appearance, losing this sheen when coated with lacquer. The metallic chromium (Cr$^0$) content of the film was initially 30%, although later variations of the solution produced deposits with up to 95% Cr$^0$.

The third classification of film is the pure metal coating developed by Fuji Iron and Steel Co Ltd, Japan\textsuperscript{167} Designated the trade name of "Cansuper", this product is essentially a three-layer structure:

1. Metallic chromium 30-480 mg/m$^2$
2. Hydrated oxide 3-22 mg/m$^2$
3. Oil film 2-4 mg/m$^2$

The process can be regarded, in essence, as a typical chromium plating process (in which substantially all the chromium is deposited as the metal) followed by an electrochemical treatment which produces an amorphous non-metallic layer. It operates over a wide range of essentially high current densities and is operated in a high-speed, continuous plating mode. The final product is bright and lustrous and
is said to be ideal for can-making, although it has been little exploited.

The final category is the two-step metal + oxide coating. This classification is typified by National Steel's (USA) "Weirchrome" product. This could be confused with "Cansuper" in its mode of formation, i.e. chromium metal deposition followed by an electrochemical process to deposit a chromium oxide layer. However, the "Weirchrome" product does not contain as much metal since it is primarily required as packaging for beer and carbonated beverages, whereas Cansuper was to be a direct substitute for light coating tinplate. The two step process can be considered as the optimum processing method since both components of the duplex coating system can be controlled and varied independently.

4.6.3 "Zincrox"

A recent innovation\textsuperscript{23,155} has been the use of a TFS-type solution on galvanised (Zn) steel panels for the Italian automobile industry. The solution used is primarily a dilute chromium plating formula with CrO\textsubscript{3} at 40 g/l and minor additions of fluorides, fluoroborates and trivalent chromium cations (overall concentration < 5 g/l).

The "Zincrox" coating is deposited cathodically and consists of a chromium oxide film over a chromium metal layer deposited on the zinc electroplate. The overall depth of the complete coating (Cr-CrO\textsubscript{x}) is about 2000 Å and it is suggested that the chromium oxide seals the porosity of the chromium metal deposit and hence improves corrosion resistance.

4.6.4 Summary

Although a TFS-type treatment might achieve very good results on tinplate (there is a direct relationship between chromium metal of coatings and their sulphide stain resistance),\textsuperscript{54} the process would still suffer from the major drawback of the inherent toxicity of hexavalent chromium (e.g. CrO\textsubscript{3}) based solutions. It was with this particularly in
mind that molybdate and its derivatives were pursued as the major alternatives to chromate for forming conversion-type coatings on tinplate and zinc.
CHAPTER 5

EXPERIMENTAL PROCEDURE

5.1 INTRODUCTION

The main emphasis of the experimental work carried out was the collection and analysis of polarisation data for tin, tinplate, zinc and (to a lesser extent) blackplate in various possible conversion coating solutions. Both anodic and cathodic potentiodynamic polarisation curves were plotted and, using this data as an indication of film forming ability, coatings were produced on the substrates previously listed. Although electrochemical means of producing coatings are popular, simple immersion techniques will always require less plant and hence will be cheaper. Therefore, simple immersion type coatings were also produced from solutions primarily selected for the production of electrochemically formed coatings, in the hope that any advantageous film characteristics produced electrochemically might also be exhibited from a simple, cheaper immersion-type treatment.

The assessment of coatings produced was divided into two stages. Visual and electron microscopical techniques were employed initially to assess the aesthetics of the coatings and study their microstructure and composition. Secondly, corrosion tests were performed to study the integrity of coatings under aggressive and accelerated corrosion conditions. Twenty-four hour salt spray tests were employed for zinc test samples, whilst tin and tinplate specimens were subjected to thirty minute sulphide stain tests. Evaluation of the extent of degradation of coatings was made visually, although the amount of sulphide staining on selected tin and tinplate samples was also assessed by coulometric reduction.
5.2 POLARISATION STUDIES

Potentiodynamic polarisation was utilised as the main investigative approach. This method differs from potential-step polarisation in that an external voltage is applied to the potentiostat by means of a sweep unit incorporating a time-based motorised gearbox with differing ratios, and a set of potential sweep rates can thus be applied to a given electrochemical cell. This method is clearly less tedious to apply when compared to manual adjustment as with the potential-step method. Furthermore, it has been suggested that the former is more reproducible, although not necessarily more accurate.\(^{168}\)

5.2.1 Sweep Unit and Choice of Sweep Rate

A Rayleigh Instruments Model MP 120 sweep unit was used for these investigations. This model has been adapted to sweep through either a 1V or 3V range of overpotential. The unit had also the facility for sweeping at the following rates:

<table>
<thead>
<tr>
<th>Sweep Rates, mV/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1V Range 5, 10, 20, 50, 100, 200, 500, 1000</td>
</tr>
<tr>
<td>3V Range 15, 30, 60, 150, 300, 600, 1500, 3000</td>
</tr>
</tbody>
</table>

The choice of a sweep rate to be used experimentally is one that must cover two criteria. Firstly, it must be sufficiently slow to allow the system to be approaching equilibrium and hence allow salient curve features to be included rather than lost, as would be the case with a faster rate. Secondly the sweep rate must be rapid enough to allow a reasonable number of experiments to be completed in a given time. This is particularly important in an investigation where a large number of polarisation trials are to be completed.

Sweep rate and its effects on the shape of anodic active-passive polarisation curves has been reported previously.\(^{168,169}\) On titanium and 304 stainless steel increasing the sweep rate increases current densities of features such as \(i_{\text{pass}}\) and translates \(E_{\text{pp}}\) (the primary
passive potential) in a noble direction. However, there is a sizeable range of sweep rates where currents remain essentially similar.\textsuperscript{168} Neither of the two aforementioned publications\textsuperscript{168,169} state steadfast rules by which a sweep rate can be chosen, although Mansfield and Kendig\textsuperscript{170} do suggest a method by which rates can be derived for polarisation resistance studies by means of a complex electronic analogy.

The only satisfactory method of choosing a sweep rate is to compare a range of values experimentally. This was carried out in earlier work\textsuperscript{20} and a value of 60 mV/min was deemed satisfactory. Polarisation curves exhibited reasonable detail and the rate allowed a test and "turn-round" time of approximately 60-75 minutes. It was therefore decided that this rate should be applicable for the majority of tests carried out in these investigations. Later work examining possible molybdenum reduction reactions during cathodic polarisation employed a slower sweep rate of 30 mV/min, in order that no important curve features should be missed.

5.2.2 Potentiostat Type and Facilities

An H.B. Thompson and Associates Ministat Precision Potentiostat (model number 252) was used for the majority of the polarisation investigations. This particular model has an output of 26V and 2A and has the facilities for an external sweep unit, digital meters and chart recorder.

5.2.3 Chart Recorder

A Servoscribe RE 511-20 potentiometric chart recorder was employed for most experimental investigations. The unit has an input range selection of between 2 mV and 20V and a chart drive with speed options of 30, 120, 600 mm/hr and 30, 120, 600 mm/min.
5.2.4 Voltmeters and Ammeters

Thandar model TM 355 digital multimeters were used for potential and current monitoring. However, in later work an older Sinclair model DM 350 digital multimeter was employed for the measurement of rest potential, having the advantage of an ultra-high impedance facility on the 2000 mV range. The impedance under these conditions is greater than 1000 MΩ compared with 10 MΩ on other ranges of the DM 350 and all the ranges of the later Thandar model TM 355. The advantages of this high impedance facility are potentially more accurate rest potential readings and in theory a longer life for saturated calomel reference electrodes due to reduced current drain.

5.2.5 Water Bath

A Tecam Temperor water bath was used to enable experiments at elevated temperatures to be carried out. This unit has the facility for temperature variations of between 0°C and 100°C.

5.3 PROCESS CELL

The polarisation cell consisted of a 500 ml culture vessel with a separate lid (see Figure 3), which had five openings facilitating the insertion and removal of various electrodes, thermometer and gas bubbler. The lid of the vessel was sealed in the closed position with a gasket and clip.

5.3.1 Solutions

Anodic and cathodic polarisation curves were carried out in various group (VIA) oxy-anion solutions at various concentrations, temperatures and pH. Solutions containing molybdate and orthophosphoric acid, orthophosphoric acid alone, molybdate and sodium orthophosphate and molybdate and sodium nitrate were also tested.
### 5.3.2 Aeration and Deaeration

Polarisation curves were obtained from solutions that were still (i.e. no aeration or deaeration), aerated and deaerated. The introduction of air or nitrogen (white spot, oxygen-free grade) into the cell was made via a glass bubbler. Aeration was usually continuous throughout the test period, although in many instances, particularly in later experiments, it was found that it caused undue agitation resulting in current fluctuations. Therefore, in subsequent reduction work, where high clarity of curve features was required, deaeration was usually carried out before the test, for thirty minutes with a new solution and fifteen minutes for subsequent trials.

### 5.3.3 Reference Electrode

A saturated calomel electrode (SCE) was employed as the reference electrode in all potential measurements. It was positioned remotely (which lessens any detrimental effects from high temperatures experienced in the cell) using a salt (saturated potassium chloride) bridge connected to a probe, which could be positioned close to the working electrode.

### 5.3.4 Counter (Auxiliary) Electrodes

Twin platinum metal sheet counter electrodes were used for the polarisation trials. Platinum has the advantage of being relatively chemically inert and unlikely to be affected by the cell solution during inactive periods. Also during cathodic polarisation, when the platinum is acting as the anode, there will be little or no metallic dissolution which could affect the solution and hence the polarisation characteristics of the working electrode.
5.4 PREPARATION OF SPECIMENS

Tinplate and blackplate specimens were obtained in sheet form from the International Tin Research Institute. Zinc and tin were in the form of foil of thickness 0.38 mm and 0.10 mm respectively. All metal specimens were used in strip form in the polarisation cell, PTFE tape being used to delineate an area of 10 cm² (5 cm² each side, see Figure 4). The only exception was tinplate where, since only one side had been plated, an area of 5 cm² was blanked off with the tape. The edges and reverse side were painted with 'lacomit' to prevent any substrate steel coming into contact with the process solution.

5.4.1 Pickling and Cleaning Solutions
5.4.1.1 Zinc

Information on pre-treatments for zinc metal surfaces vary. Brasher and Rhoades-Brown¹² abraded the metal with Oakley's 1G emery paper. Bijimi and Gabe⁶⁰ pickled zinc in hot 15% hydrochloric acid for five minutes, followed by rinsing in boiling water and drying in hot air. Chew¹⁷¹ immersed zinc foil in 10% ammonium chloride for 30 secs, 5% chromic acid for 30 secs and 1% silver nitrate for 10 secs, a rinse in water followed each immersion. The sample was then abraded manually with fine emery paper before being rinsed with de-ionised water and acetone and finally dried. The author in earlier work²⁰ pickled zinc in two solutions suggested in the Metal Finishing Guidebook Directory.¹⁷² Both solutions were based on chromic acid, the second one in effect being a "de-smutting" solution. Ultimately it was decided to use a concentrated hydrochloric acid pickle (typically 66% vol/vol SG 1.16 HCl). Whilst chromic acid treatments produced visually clean surfaces, it was thought that the more aggressive hydrochloric acid would produce a severely attacked and hence reasonably oxide-free surface. This was deemed to be particularly important when the solutions used in cathodic polarisation trials were capable of undergoing reduction and hence exhibiting inflection points on the polarisation curves, a phenomenon which the reduction of an air-formed oxide layer could also cause. The standard pickling procedure for zinc was to immerse the metal until a
uniformly etched surface was obtained. This method has advantages over
immersing a specimen for a given period of time, since variability of
attack can occur with time due to depletion of the solution's acid
strength.

5.4.1.2 Tin and tinplate

A survey of tin pretreatments is listed in Table 10. It was thought
that a cathodic cleaning cycle in sodium carbonate was probably the
most effective. This type of pretreatment is widely used at the
Tinplate Laboratories of the International Tin Research Institute. Shah
and Davies\textsuperscript{173} suggest that according to Britton the cathodic cleaning
of tin in 1% sodium carbonate solution at room temperature gives a
reproducible surface. The author in earlier work\textsuperscript{20,42} used a cathodic
cleaning cycle consisting of ten minutes (five minutes per face) in
40 g/l sodium carbonate solution at 6 mA/cm\textsuperscript{2} at 65-77\textdegree{}C. This
treatment was modified somewhat to five minutes per face in 40 g/l
sodium carbonate solution at 10 mA/cm\textsuperscript{2} at room temperature. The cell
details were as follows:

\begin{itemize}
  \item Anode: Stainless steel
  \item Current: 10 mA/cm\textsuperscript{2}
  \item Time: 5 mins per face
  \item Temperature: Room temperature (~20\textdegree{}C)
\end{itemize}

The stainless steel anode was not left in the solution for undue
lengths of time because of possible contamination by constituents of
the metal (e.g. Ni, Cr).

5.4.1.3 Other metals tested

Blackplate specimens were pretreated in concentrated hydrochloric acid
(typically 50% vol/vol of SG 1.16 HCl). This solution quickly removed
any patches of surface corrosion. Platinum electrodes were pickled in
concentrated hydrochloric acid (66% vol/vol of SG 1.16 HCl). This
ensured the removal of any films formed during polarisation.
5.4.2 Measurement of Rest Potential

Rest potential values were recorded directly using a digital multimeter (Sinclair DM 350 multimeter on the high impedance range in later work, see Section 5.2.4). The choice of time interval before the rest potential can be recorded obviously depends on the electrode kinetics in a particular solution and at a given temperature. The onset of a near-equilibrium potential may take several minutes or several hours. It was therefore decided that a standard time interval of five minutes would be utilised.

5.5 EXPERIMENTAL PROCEDURE TO OBTAIN A POLARISATION CURVE

Once the experimental apparatus had been assembled (see photograph 1 and Figure 5, which is a circuit diagram) a polarisation curve measurement was made in the following steps:

1. With 'lacomit' and/or PTFE tape blank off the specimen until 10 cm² of the surface can be brought into contact with the solution (5 cm² for tinplate).
2. Deaerate or aerate the solution if required (see Section 5.3.2).
3. Pickle or clean the sample (see Section 5.4.1).
4. Place the specimen in the holder and introduce it into the cell.
5. Measure rest potential on digital multimeter.
6. Set rest potential on Ministat.
7. Set from STANDBY to RUN.
8. Set chart recorder running at required chart speed and range.
9. Activate sweep unit at convenient time (i.e. when chart recorder pen is on a division line of the chart paper).
10. When run is complete remove sample and wash in distilled water and dry.
5.6 PRODUCTION OF CORROSION TEST SPECIMENS

Test panels of passivated zinc were produced for salt spray tests. Similarly, coupons of treated tin foil and tinplate were assessed by sulphide stain testing. Coating was achieved both by immersion and electrochemical treatment (both anodic and cathodic). It must be noted that when using the Ministat Potentiostat for producing electrochemically treated coatings, each fresh pickled/cleaned panel entered the solution connected and with the potentiostat switched to RUN thus ensuring that no rest potential type films were formed.

5.7 ANALYSIS OF COATINGS
5.7.1 Optical and Electron Optical Analysis

Coatings produced were initially assessed visually. It should be remembered that in the case of a replacement conversion coating system for chromate/dichromate on tinplate an appealing colouration is preferable. Thus visual assessment of coatings was very important. Scanning electron microscopical (SEM) investigations were also carried out on various coatings to elucidate the microstructure.

The Electron Probe Microanalyser (EPMA) was employed to produce X-ray distribution maps and intensity plots of several tin foil and tinplate specimens which had been coated in a molybdate-orthophosphoric acid solution (MP solution).

Electron Spectroscopy for Chemical Analysis (ESCA) was used to investigate molybdenum oxidation states on selected cooled samples.

5.7.2 Corrosion Tests
5.7.2.1 Salt spray tests

Passivated zinc samples were assessed using a 24 hour salt spray test. The procedure and experimental apparatus followed that recommended in BS 3900. The salt solution was 3% (~30 g/l) sodium chloride. After 24 hours the specimens were assessed visually and an estimate of their
corroded area was made.

### 5.7.2.2 The sulphide stain test

This test was used to assess coatings produced on tin foil and tinplate. The sulphide stain test gives a fairly rapid assessment of the ability of a treated tinplate surface to resist unsightly staining from sulphur-containing foods (e.g. peas, onions, meats etc).

The actual staining medium has changed over the years. Many food products such as peas and ham, onions etc have been used and so too have polysulphide solutions, the latter however, led to inconsistent results. The most widely used medium at present is cysteine hydrochloride, \( \text{CH}_2(\text{SH})\text{CH(COOH)}\text{NH}_2\text{HCl} \), a sulphur-containing amino acid.

The apparatus used for these tests is shown in Figure 6. The reaction vessel consisted of a tall, 2 beaker with a stainless steel top which had a central hole drilled in it. A glass rod with a hooked end (achieved by heating in a bunsen flame) was used to support the samples in the solution. Each specimen was separated by a wide, one inch long, glass spacer. Specimen sizes were as follows: tin foil 5 cm x 5 cm, tinplate 5 cm x 2.5 cm.

A fresh 3g/l cysteine hydrochloride solution was prepared for each test, its pH was adjusted to 7 with 0.2M tri-sodium orthophosphate. The solution was then heated until boiling occurred. A spool of samples (six in all) was then placed in the solution and boiling was maintained, usually for thirty minutes. After testing, the spool was removed and the samples were washed, dried and examined, both visually and in some cases the sulphide staining was assessed quantitatively by coulometric reduction.

To improve the accuracy of the results achieved from the sulphide stain tests each passivation treatment was tested in duplicate. In addition each spool of specimens often contained unpassivated and commercially
(dichromate) passivated samples so that comparisons could be made.

5.7.3 Coulometric Reduction of Sulphide Stained Specimens

Although a visual assessment of a sulphide stained tin/tinplate surface is normally considered sufficient, for the purposes of these investigations a more quantitative measure was required for certain samples.

The use of coulometric analysis for sulphide stained surfaces is well-reported.9,10,174 For the purposes of this work the experimental apparatus and techniques were adapted from those suggested by Evans and Gabe.174 Initial investigations were involved with potentiodynamic reduction of varying thicknesses of sulphide stain on tin foil. Specimens were produced by staining cleaned tin foil sheets in boiling cysteine hydrochloride for varying times. Reduction (cathodic polarisation) curves were plotted for these stained samples in 0.5M Na₂CO₃ (which had been deaerated for thirty minutes), at a sweep rate of 60 mV/min and at room temperature.

Coulometric analysis of similarly stained samples and of those which had been pre-coated in various molybdate-based solutions was carried out. The following experimental parameters were applied:

Specimens: tin foil 5 cm²) cut from sulphide stained panels
           tinplate 1 cm²) stained panels
           (specimens tested in duplicate for accuracy)
Solution: 0.5 M Na₂CO₃ solution
Temperature: Room temperature (~ 20°C)
Applied current: 0.25 mA/cm²
Chart recorder speed: 120 mm/min
Chart recorder scale: 1V, backed off so that:
                     OV = -1100 mV (tin foil)
                     OV = -800 mV (tinplate)
A circuit diagram and a photograph of the apparatus are shown in Figure 7 and photograph 2. The specimen was placed in the solution, the chart recorder activated and then the constant current source switched on. The graph of \( t \) (time) vs \( E \) (potential) was then plotted automatically. An example of an idealised chart recorder output is shown in Figure 8, together with the necessary calculations to evaluate \( Q \), the quantity of electricity associated with the amount of sulphide present on the tin surface.

5.8 MISCELLANEOUS EXPERIMENTAL METHODS

5.8.1 Chemical Reagents

All chemicals used in these investigations were of SLR (standard laboratory reagent) grade or higher. With the exception of strong acids and alkalis, used for pickling and pH adjustment, sodium chromate was the only seriously toxic substance used. The harmful effects of chromates are mainly due to their powerful oxidising ability, therefore care was required when handling them i.e. immediate washing of any areas of skin which came into contact with them. Both molybdate and tungstate were considered to be much less toxic.

5.8.2 Weighings

All weight measurements of reagents were carried out on an Oertling model V10 balance, to the nearest thousandth of a gramme. When a higher degree of accuracy was required for weight gain versus time measurements a Stanton balance was utilised, providing measurements to the nearest ten-thousandth of a gramme.

5.8.3 Attainment of pH

Solution pH adjustments were achieved with concentrated additions of sodium hydroxide or sulphuric acid. The actual concentration was varied, for example when small adjustments were required the additions were diluted considerably. All pH measurements were made with a WPA model CD62 digital pH meter, the readings were measured to their nearest tenth of a pH unit (± 0.1 pH).
5.9 ACCURACY IN EXPERIMENTAL PROCEDURES

The reproducibility of a given polarisation curve depends to a large extent on the effectiveness of a pretreatment process to be capable of repeatedly producing metal specimen surfaces in a similar "clean" state. Other parameters such as solution composition, pH, temperature etc can be controlled more easily. Therefore, before the onset of extensive polarisation trials much thought was given to the question of pretreatment (see Section 5.4.1), and it is considered that the solutions and methods used are appropriate to the metals undergoing polarisation trials.

When such a large number of polarisation curves were plotted it was found to be impossible to repeat them all in entirety. However, a compromise was achieved whereby if interesting or unusual features did occur curves were repeated to examine if the phenomenon could be observed a second, third or maybe even fourth time.

When coated specimens were submitted for corrosion assessment they were always tested in duplicate, thus overcoming the chance of "rogue" specimens (i.e. poorly coated due to insufficient pre-treatment for instance) causing erroneous results. Similarly in coulometric reduction of sulphide stained tin/tinplate samples, duplicate specimens were tested i.e. one strip specimen from each duplicate stained sample.
CHAPTER 6
RESULTS

6.1 INTRODUCTION

The experimental results achieved during these investigations can be conveniently divided into five separate sections:

1. Molybdate immersion treatments for zinc (6.2)
2. Cathodic polarisation characteristics of zinc in group (VIA) oxy-anion solutions (6.3)
3. Molybdate-based conversion coating treatments for zinc (6.4)
4. Molybdate-based conversion coating treatments for tin and tinplate (6.5)
5. The cathodic electrochemistry of molybdate solutions (6.6)

The immersion solution treatment for zinc was carried out as an extension of the work by Yakimenko et al126. Immersion solutions have the distinct advantages of simplicity and low process costs over their applied current counterparts. However, in the case of chromate solutions (including chromic acid), this is often countered by a lower corrosion resistance of films so formed.

The second section of experimental investigations was a quantitative examination of the cathodic polarisation characteristics of zinc in three group (VIA) oxy-anion solutions (i.e. chromate, molybdate and tungstate). Each solution was examined at two concentrations i.e. 0.1M and 1.0 M, at four pHs: 5, 7, 9 and 11 and at three temperatures: 20°, 40° and 60°C. The effect of aeration as opposed to an otherwise still solution was also examined.

Sections three and four deal with the appraisal of different molybdate-based conversion coating treatments for zinc and tin. The general title of tin includes, to a large extent, tinplate (2.8 g/m² tin coating weight on mild steel prepared by the International Tin Research Institute, Uxbridge, Middlesex - see Appendix) and in view
of the inherent porosity of this product, also blackplate (mild steel sheet as used for can-making tinplate).

The final section of experimental work dealt with the unusual electrochemistry of molybdate solutions. The ability of molybdenum to undergo cathodic reduction was examined both potentiodynamically and galvanostatically. These investigations were augmented by an ESCA examination of selected coatings and preliminary SEM measurements of coating thicknesses.

6.2. MOLYBDATE IMMERSION TREATMENTS FOR ZINC
6.2.1 Weight Gain Versus Time Curves

Figures 9-11 illustrate the weight gain versus time characteristics for three pH5 solutions, of molybdate concentrations 5, 10 and 30 g/l. Each graph exhibits three curves, one each for the temperatures 20°C, 40°C and 60°C.

The majority of curves indicate a general rise in specimen weight with increasing immersion time. This relationship also applied to increasing treatment temperature when a rise from 20°C to 60°C resulted in up to a four-fold increase in coating weight. Raising the molybdate concentration also increased the coating weight, for example a rise in concentration from 5 to 30 g/l doubled the coating weight. However, the difference in weights between 10 and 30 g/l solutions was not found to be significant.

Reference to Figures 9-11 suggests that the initial portion of each curve exhibits a linear increase in coating weight with time. After a short period of immersion this increase slows and the curves flatten out. The effect of longer periods of immersion are exhibited in Figure 12 for a 5 g/l, pH 5 sodium molybdate solution at 20°C. After about three hours the coating weight begins to fall and after 24 hours (not shown in the figure) the weight change of the specimen becomes negative indicating a marked increase in zinc dissolution.
The addition of reducing agents, L-ascorbic acid and phenolsulphonic acid, were also examined (Figures 13 and 14). Figure 13 indicates that the addition of L-ascorbic acid promotes similar relationships to those experienced in its absence, i.e. increase in coating weight with immersion time and treatment temperature. However, although these trends were similar, the actual coating weights were increased with the addition of either of the aforementioned reducing agents to a 5 g/l pH 5 molybdate solution (Figure 14).

6.2.2 Potential vs Time Results

Potential-time measurements were initially undertaken for pH 5 solutions with sodium molybdate concentrations of 5, 10 and 30 g/l (Figures 15-17). All curves plotted indicated an initial fall in potential (i.e. an increase in the negative direction) for around three minutes, followed by a much flatter portion of curve which exhibited only a slowly diminishing potential. The 30 g/l curves did not illustrate such a flat plateau region, the fall in potential continuing more rapidly than in the case of the 5 and 10 g/l solutions.

The effect of temperature was not clearly distinguishable for the lower concentration solutions (5 and 10 g/l molybdate). Increasing the solution temperature from 20° to 60°C did not produce an appreciable change in potential. With the 30 g/l solution not only were potentials somewhat more negative than for the less concentrated solutions, but the changes brought about between curves of different temperature were much more marked.

The effect of adding reducing agents to a 5 g/l, pH 5 sodium molybdate solution was also investigated (Figure 18). Typically 1.65 g/l phenolsulphonic acid produced a shift in potentials in a more base (more negative) direction whilst 1 g/l of L-ascorbid acid produced a corresponding translation in the noble (less negative) direction and also produced an initial rise (in the first 30 seconds) although this is not shown in Figure 18 because of the large time interval.
6.2.3 Surface Appearance After Immersion

Tables 11-13 illustrate the surface appearance of zinc foil specimens immersed for differing periods of time in three pH 5 sodium molybdate solutions i.e. 5, 10 and 30 g/l at three treatment temperatures of 20°, 40° and 60°C. At a level of 5 g/l sodium molybdate, and at 20°C coatings varied from grey-blue to dark brown over a 30 minute period; increasing the process temperature brought about matt black coatings after 15 minutes at 60°C. Raising the molybdate concentration of the immersion solution increased the rapidity of the attainment of the matt black coating, e.g. at 40°C and 30 g/l sodium molybdate, formation was within one minute of immersion.

With the more concentrated solutions (10 and 30 g/l sodium molybdate) the occurrence of powdery deposits on the, presumably, thicker matt black coatings was also noted. These areas were generally moderate in size and were a distinct feature of the growth, in its later stages, of this type of coating. At 60°C for the 10 g/l, and at all temperatures for the 30 g/l sodium molybdate solution, the matt black coatings formed were of a very flaky consistency. This phenomenon was particularly noticeable at 40° and 60°C for the most concentrated solution (30 g/l sodium molybdate), a non-adherent coating being present at all immersion times except for 1 minute at 40°C.

6.2.4 3% Salt Spray Tests

Table 14 indicates the results of 3% salt spray tests for zinc samples coated from 5, 10 and 30 g/l sodium molybdate solutions at pH 5 and at 20°, 40° and 60°C. Tests were also carried out for samples immersed in a pH 5, 5 g/l sodium molybdate solution to which had been added 1.65 g/l; phenolsulphonic acid; the process solution being maintained at 20°C.

Results indicate that for the 5 g/l (sodium molybdate) solution, in general the 60°C specimens achieved the least degree of corrosion (white corrosion product). At 10 g/l the coatings produced at 40°
and 60°C achieved the greatest durability, with little significant corrosion visible after 48 hours. The 30 g/l specimens produced similar results, the higher temperature processing solutions evidently achieving more corrosion-resistant coatings.

Tests were also carried out on samples coated from a 20°C solution containing a reducing agent (phenolsulphonic acid). The results indicated the advantage, in corrosion performance, of an increased treatment time and also suggested better overall performance over 72 hours when compared to similar samples formed from a solution not containing such an agent.

6.3 THE CATHODIC POLARISATION CHARACTERISTICS OF ZINC IN GROUP (VIA) OXY-ANION SOLUTIONS

6.3.1 0.1M Still Solutions (Figures 19-30)

All curves plotted were of a typical cathodic shape, culminating in the approach to a limiting current.

6.3.1.1 Chromate (Figures 19-22)

There were marked inflections present on the curves in the initial 1V range of the polarisation curves. At pH 5 only one really distinct inflection was present, but at pH 7, 9 and 11 two were visible.

6.3.1.2 Molybdate (Figures 23-26)

The curves were similar to those produced from chromate solutions. However, inflections were not so marked and were, in general, an arrest rather than an actual fall in current.

6.3.1.3 Tungstate (Figures 27-30)

As with the molybdate curves these inflections, when present, were in general much shallower and less marked than those produced from chromate solutions. Curves produced from pH 5 and 7 solutions were
almost devoid of inflections.

6.3.2 1.0M Still Solutions (Figures 31-42)

Curves were similar in shape to their 0.1M counterparts, possessing typical cathodic features.

6.3.2.1 Chromate (Figures 31-34)

The pH 5 solution exhibited only one initial inflection, whereas those produced from pH 7, 9 and 11 produced two consecutive features.

6.3.2.2 Molybdate (Figures 35-38)

As with the 0.1M solutions inflections were generally less apparent than those from similar chromate solutions.

6.3.2.3 Tungstate (Figures 39-42)

Inflections were more apparent in these more concentrated solutions. Sizeable features were noted on curves plotted from pH 9 and 11 solutions, whereas pH 5 and 7 solutions produced only small initial inflections.

6.3.3 0.1M Aerated Solutions (Figures 43-54)

Curves were very similar in shape to their still (unaerated) counterparts.

6.3.3.1 Chromate (Figures 43-46)

Strong inflections were apparent in all but the pH 5 solution. Generally at pH 7, 9 and 11 two consecutive inflections were apparent. It was also noted in the initial sections of the curves that there were more current disturbances - manifesting themselves as an unsteady chart trace.
6.3.3.2 Molybdate (Figures 47-50)

Trends were generally similar to the unaerated curves in that inflections were shallow and less distinct than those from chromate solutions. The initial unsteady current characteristic was also noticeable.

6.3.3.3 Tungstate (Figures 51-54)

Curves produced from pH 5 and 7 solutions were of a normal cathodic form and exhibited no inflections or other unusual features. At pH 9 and 11 inflections, usually two per curve, were exhibited in the initial section of each. Current fluctuations during this period were also apparent.

6.3.4 1.0M Aerated Solutions (Figures 55-66)

Once again the general form of the curves was unchanged, being very similar to those produced from unaerated solutions.

6.3.4.1 Chromate (Figures 55-58)

The pH 5 solution exhibited only one inflection, whilst the pH 7, 9 ands 11 solutions had two. Some current fluctuations were present in the initial stages at pH 7 and 9.

6.3.4.2 Molybdate (Figures 59-62)

Inflections were once again less marked. Current fluctuations were only apparent at pH 7, 9 and 11.

6.3.4.3 Tungstate (Figures 63-66)

Current fluctuations were most noticeable in the more alkaline solutions (pH 9 and 11). Marked inflections were not generally apparent except for the pH 11 curves.
6.3.5 Rest Potentials

Rest potential values for each specimen tested are illustrated on each figure and in a separate table (Table 15) which allows easier comparison between different solutions and conditions.

The rest potential values exhibit the resultant combined action of zinc in water (as typified by the Pourbaix diagram for the Zn-H₂O system, Figure 67) and the protective or otherwise effect of the oxy-anion addition.

6.3.5.1 Chromate solutions

In essence these solutions produced the most noble (least negative) rest potentials. The more base values were obtained from the pH 5 solution and the most noble from the pH 7 solution. The effect of increasing the oxy-anion concentration from 0.1M to 1.0M did not bring about an appreciable change in rest potential values, nor did the application of aeration. The effect of increasing the solution temperature produced no clear trend in the response of the rest potentials.

6.3.5.2 Molybdate solutions

Molybdate solutions produced very similar values to their chromate counterparts, although at pH 7 more base values were apparent. The effect of aeration was only pronounced at pH 9 and 11 where a shift in the noble direction was generally exhibited. The effect of increasing the solution temperature was most clearly observed in the unaerated conditions when a general consistent shift in the noble direction was apparent.

6.3.5.3 Tungstate solutions

Of all the oxy-anions tungstate solutions produced the most base rest potential values for zinc samples with pH 5 and 7 solutions producing
the lowest values. The differences between aerated and unaerated solutions were only marked in the 0.1M, pH 11 tungstate solution. The effect of solution concentration was negligible, but increasing the process temperature appeared, in general, to produce a shift in the noble direction of the rest potential.

6.3.6 Surface Appearance after Polarisation

Table 16 summarises the nature of the zinc metal surfaces following cathodic polarisation.

6.3.6.1 Chromate

Surfaces in chromate solutions were, in general, a shade of brown or grey. The introduction of aeration did not bring about significant changes in final surface colouration.

6.3.6.2 Molybdate

Surfaces ranged in colour from brown to matt black with increasing solution temperature. It was noted that many of the latter coatings were of a powdery or very flaky consistency. The effect of aeration was not pronounced.

6.3.6.3 Tungstate

Tungstate solutions produced generally "dirty" colours. The overall range can be considered to be buff-gold to grey-gold. The effect of aeration was small, as was increasing the concentration (0.1M to 1.0M).

6.3.7 Hydrogen Evolution (HE) in Chromate Solutions

It was thought to be pertinent to examine the influence of hydrogen evolution on the inflections displayed on cathodic polarisation curves produced from several solutions. Since the chromate oxy-anion
derivatives produced the more significant examples of this phenomenon, a 0.1M pre-aerated solution was used as the basis of this examination at pH 5, 7, 9 and 11 and at 20°C. A slower sweep rate (30 mV/min) was employed and a directed lamp was used to illuminate the zinc cathode during polarisation. The observation of hydrogen evolution was further aided by the use of a magnifying glass. The results for the 0.1M sodium chromate solutions are as follows:

Results for 0.1M sodium chromate solutions

<table>
<thead>
<tr>
<th>pH</th>
<th>Approximate potential at which hydrogen bubbles begin to appear at the surface of the cathode/mV vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-1280</td>
</tr>
<tr>
<td>7</td>
<td>-1350</td>
</tr>
<tr>
<td>9</td>
<td>-1450</td>
</tr>
<tr>
<td>11</td>
<td>-1470</td>
</tr>
</tbody>
</table>

6.3.8 Processing Solution Characteristics

Chromate solutions were typically orange-red or yellow depending on their pH. The only other notable occurrence was the formation of large yellow crystals in a pH 5, 1.0M sodium chromate solution. The solution had been used for coating purposes and was a few months old.

With molybdate the immersion of a zinc sample into pH 5 solutions produced a dark blueing, accompanied by the formation of a dark iridescent (0.1M) or black (1.0M) immersion coating. The formation of this type of film occurred in both still and aerated conditions and was most adherent when deposited from a pH 9, 1.0M solution. The black-type coating appeared before significant hydrogen evolution was apparent.

After a test at 60°C, a pH 5, 1.0M solution remained light blue-black overnight. A fresh 0.1M solution when adjusted to pH 5 with
concentrated sulphuric acid was characterised by a slight green tinge. The attainment of pH 7 solutions was found to be difficult when using concentrated sulphuric acid additions, the need for further dilution of the acid being essential. On mild reduction tungstate solutions exhibited a similar blue colouration to molybdates. A 0.1M, pH 5 solution was turned blue by zinc as soon as the metal was placed in the solution. The colour was initially bright blue but faded after a period of time (after the polarisation tests when the specimen was removed). A 1.0M, pH 5 solution formed the blue colour with zinc instantaneously. When hydrogen evolution occurred the gas seemed to push the majority of the blue solution away from the cathode, leaving just an intimate layer next to the surface of the zinc. The film disappeared as the hydrogen evolution became stronger. Stirring the blue deposit at the bottom of the vessel turned the solution clear. More similar colouration formed during the 40°C test but did not disperse immediately on stirring, instead clearing with time. When the solution was adjusted to pH 7 it turned blue-black after the 40°C test but cleared overnight leaving a buff cloudiness. On leaving a pH 5, 1.0M solution to stand for a few days, colourless crystals formed. Subsequent experiments in such a solution revealed rest potential values that had increased by about 50% in a base direction.

6.3.9 24-hour Salt Spray Tests (Table 17)

24-hour tests were conducted using a continuous salt fog comprising of 3% (~30 g/l) sodium chloride as defined in BS 3900. Specimens were coated cathodically from the three 0.1M oxy-anion solutions at 20°C and at the potentials and treatment times indicated in Table 17. Specimens were removed after 24 hours and allowed to dry naturally overnight. The extent of surface corrosion was then estimated as the approximate percentage surface coverage by the white corrosion product.
6.3.10 SEM Examinations (Plates 3-5)

0.1M, pH 5 solutions were employed to produce films for SEM examination. (The precise process variables are noted next to each plate). The tungstate and chromate coatings were formed cathodically and the molybdate by simple immersion.

6.4 MOLYBDATE-BASED TREATMENTS FOR ZINC
6.4.1 Introduction

The investigation of treatments for zinc was purely of a preliminary nature, since it was considered that tin and tinplate surfaces were of more importance. The experiments stemmed from an appraisal of GB Patent 2,070,073127 (which is summarised in Section 7.4).

Initial work consisted of immersion tests for two solutions (each consisting of sodium molybdate and orthophosphoric acid) of differing pH. Weight gain measurements were carried out and both cathodic and anodic polarisation curves were plotted to examine the electrochemical characteristics of zinc in these types of solution. 24 hour salt spray tests were also undertaken on zinc samples coated in the most promising solutions. Polarisation work was also undertaken in simple orthophosphoric acid solutions.

6.4.2 Immersion Tests (Table 18)

Limited weight gain versus immersion time measurements were made. 43 g/l (as Mo) sodium molybdate, pH 6 and pH 3 (adjusted with 88% orthophosphoric acid) solutions were examined with zinc samples being immersed for periods of between 3 and 60 seconds. For the pH 6 solution, weight changes after processing generally showed a slight gain, whereas samples in the pH 3 solution exhibited a corresponding loss in weight.

The specimens mentioned earlier were washed in distilled water after being immersed in the solution and exhibited little surface
colouration (at best slight discolouration at the edges). Thus when a pH 1.5, molybdate-orthophosphoric acid solution (here on termed MP solution) was investigated, samples were dried on a paper tissue, before being dried in a hot air stream, thereby reproducing the conditions of the patent more closely. However, the colour of specimen surfaces was not enhanced to any great degree. For the pH 1.5 solution specimens immersed for 5 seconds exhibited a consistent weight loss averaging 1.26 mg for five samples.

6.4.3 Polarisation Trials (Figures 68-71)

Both cathodic and anodic trials were carried out for zinc samples in a standard 43 g/l (as Mo) sodium molybdate solution with different pH values of between 1.5 and 6, adjusted with 88% orthophosphoric acid (i.e. several different pH MP-type solutions). Tests were also carried out in solutions of a similar pH but consisting only of orthophosphoric acid. The MP cathodic curves were of a typical form, culminating in the approach to a limiting current at 100 mA/cm². Slight inflections were noted on the pH 5 and 6 curves at around -1200 mV vs SCE (pH 5) and -1700 to -1900 mV vs SCE (pH 5 and 6). The anodic MP curves did not exhibit "classical passivity" but reached a "limiting" current of between 10 and 100 mA/cm². Cathodic curves in the purely orthophosphoric acid solutions generally displayed much smaller currents. This was also generally true for the anodic curves which did not indicate any signs of passivation. The rest potentials were much more positive in the orthophosphoric acid solutions.

6.4.4 Salt Spray Tests (Table 19)

The corrosion resistance of various coating treatments on zinc formed from the standard MP solution (at pH 1.5) were tested by using a 24 hour, 3% salt spray test (Table 19). Generally, coated samples performed better than the 'as pickled' specimens. It seems that "blotting and drying" rather than rinsing does promote coatings of a higher corrosion resistance.
6.5 MOLYBDATE-BASED TREATMENTS FOR TIN AND TINPLATE

6.5.1 Simple Molybdate Treatment Solutions

It was found that a cathodic treatment of tinplate in a dilute acidic sodium molybdate solution would impart a strong, attractive iridescent coating, given sufficient treatment time. It was decided, therefore, to investigate whether this type of coating would endure the conditions necessary for its usage in tinplate can production.

6.5.1.1 Variations of Film Colouration

The following was adopted as the standard coating solution:

- 10 g/l sodium molybdate
- pH 3 (adjusted with concentrated H₂SO₄)
- T = 20°C
- Cathodic immersion at -800 mV vs SCE
- t = 2 mins

Table 20 illustrates the deviations from this “norm” and the resultant changes in the surface colour of tinplate so treated. The concentration of the molybdate solution was adjusted, similarly the solution pH and temperature were varied whilst maintaining the cathodic applied potential of -800 mV vs SCE and a process time of 2 minutes. In general it was found that pH had the greatest influence on surface colouration. A pH 5 solution produced slight colouring, whilst a pH 1 solution caused etching of the tinplate. Temperature increases produced a darkening of the coating, culminating in a brown colouration at 80°C. Reduction of the sodium molybdate concentration to 5 and 1 g/l still produced iridescent coatings although of a predominantly yellow-orange colouration. Colour Plate 1 shows a set of eight tinplate samples produced cathodically from the standard solution with varying immersion times. It can be noted that long immersion times (10 minutes upwards) produce black coatings which become flaky after 30 minutes immersion (c.f. also immersion treatments for zinc, Section 6.2.3). Colour Plate 2 is also included.
as an example of the capability of this standard solution to also form suitable coatings on zinc. Zinc does not produce coatings of iridescent-type colouration at the shorter immersion times, but does form a black colouration after approximately 10 minutes onwards.

6.5.1.2 Sulphide stain assessments

Table 21 indicates the results of the sulphide stain tests of the series of coatings formed on tinplate from simple molybdate solutions.

After 5 minutes of testing, only the samples processed in the 10 g/l, pH 1 and the 1 g/l, pH 3 solutions showed evidence of attack. After 15 minutes the 10 g/l, pH 5 was also exhibiting appreciable staining. After 30 minutes (and the end of the test) the 10 g/l, pH 3, 20°C and 40°C specimens had produced the most impressive results, with little surface discolouration. The 5 g/l, pH 3, 20°C specimens were also reasonably good. The 80°C, 10 g/l, pH 3 specimens had become a medium matt grey and were flaking at the edges. This flaking was also apparent, to a very small extent, on the 10 g/l, pH 3, 50°C specimens, and also on one of the 10 g/l, pH 3, 20°C specimens.

6.5.2 Molybdate-Orthophosphoric Acid Type (MP) Treatments for Tinfoil

6.5.2.1 Polarisation Curves (Figures 72-76)

The cathodic MP curves were of a typical cathodic form except for the appearance of inflections on each curve mainly at between -500 and -1000 mV vs SCE, although other very faint features were evident at much higher potentials. Under cathodic polarisation in a purely orthophosphoric acid solution, inflections were also apparent, mainly at around -550 to -900 mV vs SCE. At the higher pHs the cathodic currents were much diminished when compared to those in the MP solutions.
Anodic curves in the MP solutions did exhibit appreciable passivation, although at pH 5 the passive current was erratic but of a low value ($\sim 0.009 \text{ mA cm}^{-2}$). In the orthophosphoric acid solution classical passivation was only really apparent in the pH 1.5 solution. At pH 3 and 5 the sample appeared to passivate, before polarisation commenced. The anodic currents were very similar between the two types of solution.

6.5.2.2 Weight Gain vs Time Measurements

Some initial weight gain vs time measurements were made for tin foil specimens in the standard MP solution (43 g/l (as Mo) sodium molybdate, pH 1.5 with orthophosphoric acid). Six specimens were immersed, each for five seconds and they averaged zero weight gain/loss over the six samples. However, electrochemically formed specimens at differing cathodic potentials did exhibit a recurring increase in weight after immersion (see Table 22). Although the coating weights were low, they were considerably higher than naturally air formed oxide films.

6.5.2.3 Formation of Immersion Coatings

Immersion coatings were formed in solutions of differing pH, and temperature and of a molybdate concentration of 43 g/l (as Mo). The final colouring of the coatings on the tin foil specimens was noted (Table 23).

6.5.2.4 Duplicate Sulphide Stain Tests

Duplicate samples with immersion times of 5 secs, 30 secs, 1 min and 10 mins were prepared from an MP solution comprising of 43 g/l (as Mo) sodium molybdate, adjusted to pH 2.5 with 88% orthophosphoric acid and maintained at 60°C. Two identical batches of samples were thus formed, one batch being sulphide stain tested at Loughborough, whilst the other was tested in a similar manner at I.T.R.I. The results are summarised in Table 24.
6.5.2.5 EPMA Investigations

The following tin foil samples were examined with the EPMA:

Sample 1: MP-type coating: immersion in solution containing 43 g/l (as Mo) sodium molybdate, pH 1.5, 60°C, 1 minute immersion
Sample 2: As sample 1, but pH 2.5
Sample 3: As sample 1, but pH 3.5.

Sample 1 indicated some peaks but also had large areas of thinner coating. Sample 2 had quite a few high peaks, some of which were comparatively large. Sample 3, in comparison, had a smooth but thin coating. Typical EPMA traces are shown in Figures 77-79.

6.5.2.6 X-ray Distribution Photographs

X-ray distribution measurements were made for samples 1 and 2 (Section 6.5.2.5).

Sample 1: The tin X-ray pattern indicated an even distribution in the given area. The molybdate counts were also well distributed although tending to form clusters. However, the phosphorus pattern was more ordered, as well as forming a general pattern there was a tendency to follow grain boundaries and other surface features.

Sample 2: The X-ray "map" was taken from a thinner coating area. The tin map was well distributed and so too was the molybdenum, although there was a distinct tendency to form clustered areas with spaces in between showing no X-ray counts. Again the phosphorus map showed some order, with counts being greatest over surface features.

Plates 6-10 illustrate X-ray maps from sample 1, these were generally indicative of both specimens.
6.5.3 Molybdate-Orthophosphoric Acid (MP)-Type Treatments for Tinplate

6.5.3.1 Surface Appearance vs Time

Three solutions at different temperatures were examined for their effectiveness in producing an immersion coating on thin (2.8 g/m²) tinplate. The solutions were chosen from those which had showed promise from the work on tin foil. The results are summarised in Table 25.

6.5.3.2 Sulphide Stain Testing of Immersion Coated Samples

Fifteen minute sulphide stain tests were carried out on samples formed from the best of the immersion solutions. The results are summarised in Tables 26 and 27.

6.5.3.3 EPMA Investigations

The following tinplate samples were tested:

Sample 1: "As received" tinplate
Sample 2: Cathodically cleaned tinplate
Sample 3: MP coating: immersion in solution containing 43 g/l (as Mo) sodium molybdate, pH 2.5, at room temperature

Sample 2 exhibited reduced tin peaks compared with sample 1, as would be expected. Sample 3 indicated a generally smooth coating. A typical trace for sample 3 is shown in Figure 80.

6.5.3.4 X-ray Distribution Photographs

Sample 3 was investigated in this manner. The tin map was well distributed. The iron map showed less well populated areas over higher (raised) surface features as would be expected. The molybdenum map was fairly well distributed. The phosphorus map did show some tendency to follow a similar pattern to the iron map.
Plates 11-15 illustrate the results.

6.5.3.5 Polarisation Studies of Tinplate Samples in MP Solutions

Although extensive work has been carried out on the formulation of an immersion solution for tin foil and tinplate, the possibility of an electrochemical (i.e. anodic or cathodic) mode of formulation had to be explored for which 2.8 g/m² tinplate was used as the base metal on which the coatings were formed. Potentiodynamic polarisation was utilised as the basic investigative method to study the electrochemical characteristics of tinplate, both cathodic and anodic, in various MP-type solutions. Since the tinplate was of a low coating weight, extreme acid or alkaline solutions were not investigated as these could lead to unacceptable tin dissolution during testing.

Cathodic Polarisation

The following solution parameters were investigated:

i) Effect of molybdate concentration  (Figures 81 and 82)
ii) Effect of solution pH  (Figure 83)
iii) Effect of aeration/deaeration  (Figure 84)

The effect of increasing the molybdate concentration was generally to increase the cathodic current. The general shape of the polarisation curves remained the same. The curves exhibited two inflections when sodium molybdate was present in the solution, but only one when an orthophosphoric acid solution was tested. The first inflection was apparent at approximately -650 mV vs SCE whilst the second occurred at about -900 mV vs SCE. The second inflection became more pronounced at sodium molybdate concentrations of over 50 g/l.

Examining the effect of solution pH indicated the curves were generally of a typical cathodic shape. Most curves exhibited some indication of two inflections. The second inflection being most
The positions of the inflections were similar in terms of potential with reference to the SCE.

The effect of aeration/deaeration was marginal. The differences between an aerated, a deaerated, and a still solution, being very slight.

### Anodic Polarisation

Again the following solution parameters were investigated:

i) Effect of molybdate concentration (Figures 85-86)

ii) Effect of solution pH (Figure 87)

iii) Effect of aeration/deaeration (Figure 88)

Tinplate exhibited passivation characteristics in all solutions. The effect of increasing the molybdate concentration was to increase $i_{\text{crit}}$ but also in general to decrease $i_{\text{pass}}$. The attainment of $i_{\text{crit}}$ was, in many cases, accompanied by an unstable current. The $E_F$ area of the curve also, in many cases, exhibited the double "nose" associated with the anodic oxidation of tin in two stages$^{178}$ i.e:

$$\text{Sn}^0 + \text{Sn}^{2+} + 2e$$

$$\text{Sn}^{2+} + \text{Sn}^{4+} + 2e$$

The magnitude of the passive region in terms of potential ($\Delta E_p$) was similar for all molybdate concentrations.

The pH of the solution had a large influence on the shape of the anodic polarisation curve. A very low pH solution (e.g. pH 2.5) promoted high $i_{\text{crit}}$ values (≈1 mA cm$^{-2}$), low $i_{\text{pass}}$ values (≈0.08 mA cm$^{-2}$) and low $\Delta E_p$ values. Whereas a higher pH solution (i.e. pH 9.8) promoted much lower $i_{\text{crit}}$ values (0.05 mA cm$^{-2}$) but similar $i_{\text{pass}}$ values (≈0.07 mA cm$^{-2}$). $\Delta E_p$ values were somewhat larger for the alkaline solutions. The double oxidation of tin was
only really noticeable in the pH 2.5, 4 and 5 solutions.  
The effect of aeration/deaeration was to increase anodic currents, 
due possibly to an agitation effect. A still solution exhibited the 
lowest $i_{\text{pass}}$.  

6.5.3.6 A Further Investigation of the Anodic Characteristics of 
2.8 g/m² Tinplate in MP-type Solutions

Following initial investigative work into the polarisation 
characteristics of tinplate in various MP solutions, it was clear 
that passivation was widespread and that by adjusting the pH, 
appropriate values for $i_{\text{crit}}$ and $i_{\text{pass}}$ could be attained. It seemed 
from these initial results that large differences in molybdate 
concentration seemed to have little effect on $i_{\text{pass}}$. Therefore, 
concentrations between 5 and 20 g/l were studied (Figure 89) and also 
a batch of between 1 and 4 g/l (Figure 90). Both sets of curves 
exhibited broad passivation characteristics, although the very 
low molybdate concentration curve showed very little difference in 
$i_{\text{crit}} - i_{\text{pass}}$. 

Once a 10 g/l molybdate solution of pH 4 (with 88% H$_3$PO$_4$) (see also 
Figure 91) had been chosen (see Discussion, Section 7.7) the effect 
of varying the solution temperature was examined (Figure 92). 
Temperatures of 20° to 90°C were investigated and accompanying 
current-time curves were plotted (Figure 93) to investigate the 
rapidity of attainment of $i_{\text{pass}}$ at a predetermined potential in the 
passive region. The higher temperatures increased the passive 
current but, unusually, seemed to slow its attainment as indicated by 
the current-time curves.  

6.5.3.7 Passivation Studies on I.T.R.I. Blackplate

Anodic polarisation studies indicated broad passivation in both pH 5 
and 2.5 MP solutions (Figure 94). However, anodic polarisation in pH 
5 and 3 (Figure 95) orthophosphoric acid solutions indicated no 
"classical" passivation and attainment of very low anodic currents.
Cathodic polarisation in MP solutions (Figure 96) showed typical cathodic curves with no significant evidence of inflections. Purely orthophosphoric acid solutions (Figure 97) produced similar curves but at a much reduced cathodic current.

6.5.3.8 Further Sulphide Stain Tests

Further tests were carried out as follows on:

i) Samples formed anodically from an MP solution containing 10 g/l sodium molybdate, pH 4, 30°C. Anodic potential of +800 mV vs SCE (Table 28).

ii) Samples formed cathodically from an MP solution containing 10 g/l sodium molybdate, pH 4, 20°C. Cathodic potential of -2000 mV vs SCE (Table 29).

iii) Samples formed cathodically from an MP solution containing 10 g/l sodium molybdate, pH 3, 20°C. Cathodic potential of -2000 mV vs SCE (Table 30).

6.5.4 SEM Examinations of MP Coated Surfaces

Tin foil specimens were immersion coated in a 110 g/l (sodium molybdate) MP solution of pH 2.5 at 80°C for various periods of time. SEM analysis indicted a ridged formation over the tin grains as typified in plate 16.

Similarly, tinplate specimens were immersion coated in a 90 g/l (sodium molybdate) MP solution of pH 2.5 at 80°C for various lengths of time. There was no ridge structures as with the tin foil, but a more general coating, covering what appears to be a network of lines, these do not appear to be the grain boundaries of the tin substrate. An example is illustrated in plate 17.
6.5.5 Effect of Drying Methods on the Sulphide Stain Resistance of Tinplate Treated in an MP-type Solution

The effect of the method of specimen post-treatment was examined by comparing four drying methods for coatings in subsequent sulphide stain tests. The coating solution employed was:

\[
\begin{align*}
&10 \text{ g/l sodium molybdate}, \\
&\text{adjusted to pH 4 with 88\% } H_3PO_4 \\
&T=30^\circ C
\end{align*}
\]

The three methods of film formation were:

1. Immersion for 1 minute
2. Anodically at +800 mV vs SCE for 1 minute
3. Cathodically at -2000 mV vs SCE for 1 minute

The four methods of drying were:

1. Rinse in distilled water, blotted with paper tissue
2. No rinse, air dry in laboratory for 24 hours
3. No rinse, oven dry at 100^\circ C for 5 mins
4. No rinse, oven dry at 100^\circ C for 1 hour.

6.5.5.1 Immersion Coated Sample Results (Table 31)

All coated specimens were badly attacked in the stain test. The coatings conferred only marginally more protection than an untreated surface. Post-treatment drying seemed to improve the corrosion resistance by a small amount only.

6.5.5.2 Anodically Coated Sample Results (Table 32)

Anodically coated specimens offered very little extra corrosion resistance over uncoated ones. The 24-hour air dried specimen was attacked slightly less than the others.
6.5.5.3 Cathodically Coated Sample Results (Table 33)

Cathodically formed surfaces were in general heavily stained. However, the most encouraging results were obtained from the 1 hour oven-dried samples which displayed a post-staining surface of uniform, matt grey. Although heavily stained, these cathodically formed coatings were marginally more corrosion resistant than their anodic and immersion formed counterparts.

6.5.6 The Effect of Nitrate Additions on MP Solution Characteristics

6.5.6.1 Anodic Polarisation (Figure 98)

All curves exhibited a passive region, followed by a rapidly increasing current in the transpassive region. The values of $i_{\text{pass}}$ were low for the smaller additions of potassium nitrate (0.5 and 1.0 g/l). However, with increasing concentrations the value of $i_{\text{pass}}$ began to increase. Rest potentials were generally consistent at around -540 mV vs SCE.

After polarisation the tinplate surface had perhaps a slight gold sheen with a low concentration of nitrate, although with additions of 1.5 g/l and above staining was apparent with large areas of dark grey visible at 4.0 g/l KNO₃.

6.5.6.2 Cathodic Polarisation (Figure 99)

All curves were very close together (i.e. similar rest potentials and very close current densities on the polarisation curves). There was a single pronounced inflection at -850 mV vs SCE and no indication of any other such features.

Surfaces after polarisation had a loosely adherent matt gold coating. At larger KNO₃ additions the coating became coarser and was much darker (brown-black) in the region adjacent to the solution surface.
6.5.7 Alkaline Molybdate-Orthophosphate Solutions for Tinplate

6.5.7.1 Anodic Polarisation (Table 34, Figure 100)

The anodic polarisation curves exhibit an initial broad passive region and also a second, much smaller, region at higher overpotentials. \(i_{crit}\) rises uniformly with increasing orthophosphate additions, as in general does \(i_{pass}\). The second, smaller "passive" region is only apparent with the addition of orthophosphate, and is most prominent at a 1 g/l level, further increases reducing the prominence of this feature.

The rest potentials exhibited a decrease in value with increasing orthophosphate concentration (and consequently higher pH). Monitoring the rest potential over 5 minutes after the immersion of the tinplate indicated an increase in potential in the purely molybdate solution, and a decrease once orthophosphate additions were made.

Surface colouration was not vivid, with a change to matt buff and inconsistent colouration with increasing orthophosphate content.

6.5.7.2 Cathodic Polarisation (Table 35, Figures 101 and 102)

All curves were of a typical cathodic shape, culminating in an approach to a limiting current at higher overpotentials. Inflections were apparent in the initial sections of all curves, with one inflection at -950 mV vs SCE for the molybdate solution, and an additional feature at -1050 mV vs SCE with orthophosphate additions.

Rest potential values exhibited a similar trend as shown with the anodic trials (i.e. a fall in potential with increasing orthophosphate content).

Surface colouration was only strong in the absence of orthophosphate additions with a purely sodium molybdate solution producing a mainly
gold colour. Orthophosphate additions produced colourless coatings and eventual mottling with increasing concentration.

6.5.8 Sulphide Staining of Optimum Coating Systems

Table 36 lists the optimum coating systems applied to tinplate samples for the final sulphide stain tests. Table 37 indicates the performance of specimens after 5, 15 and 30 minutes of staining.

The simple molybdate solutions appear to promote coatings with an inherent resistance to sulphide staining, with the 10 g/l, pH 3, 20°C treatment producing the optimum. More concentrated molybdate process solutions produce coatings which are susceptible to flaking (at low pH) and are clearly unsuitable at higher pH (~9). Only the cathodically formed MP-nitrate coating indicated any significant resistance to staining. The molybdate-orthophosphate coatings were all heavily stained.

6.5.8.1 Initial Verification of the Coulometric Method for Reducing Sulphide Stains on Tin and Tinplate

Initial investigations were involved with potentiodynamic reduction of varying thicknesses of sulphide stain on tin foil. Specimens were produced by staining cleaned tin foil sheets in boiling cysteine hydrochloride as indicated below:

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Immersion time in staining solution / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cleaned, no staining</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
</tr>
</tbody>
</table>
Reduction (cathodic polarisation) curves were plotted for sections of stained samples, reduced in 0.5M Na₂CO₃ (which has been deaerated for 30 minutes), at a sweep rate of 60 mV/min and at room temperature. The resultant curves are illustrated in Figure 103. Oxide reduction peaks can be observed on each specimen at around -1050 mV vs SCE, whilst sulphide reduction peaks are evident on most samples at around -1400 mV vs SCE.

Full coulometric analysis of sections of the same stained samples was carried out utilising the experimental conditions outlined in 5.7.3 Table 38 outlines the charge in mC/cm² of the resulting reduced sulphide.

6.5.8.2 Coulometric Analysis of Selected Sulphide Stained Coatings (Table 39)

The least stained optimum coating systems were reduced galvanostatically in 0.5M sodium carbonate solution. An "as cathodically cleaned" and stained tinplate sample was also tested to act as a "control". The results confirmed the 10 g/l, pH 3, 20°C cathodic sodium molybdate system as clearly the most stain resistant. The 100 g/l, pH 3, 20°C cathodic molybdate and the MP-nitrate coatings also gave encouraging results.

6.6 THE CATHODIC ELECTROCHEMISTRY OF MOLYBDATE SOLUTIONS

6.6.1 Introduction

The aim of this series of experiments was to partly investigate further the work of Glass²⁴, who reported the occurrence of an inflection on the cathodic polarisation curve plotted from a platinum cathode in boiling 1N H₂SO₄ with an "Mo⁶⁺ content of 0.03M". It was also thought that with accompanying galvanostatic and ESCA techniques, a mechanism for, or cause of, the inflection(s) observed in many earlier polarisation curves of the present work could be made. Some preliminary measurements of film thicknesses were also attempted.
6.6.2 Cathodic Polarisation Trials

Cathodic polarisation curves were plotted from molybdate and non-molybdate solutions (essentially distilled water) at pH 1, 3, 5, 9 and 13. Solutions were examined in both the aerated and pre-deaerated conditions. Aeration in general caused an unsteady current response, manifesting itself in an erratic chart trace. Thus, in later experiments with more concentrated molybdate solutions (100 g/l) pre-deaerated conditions were applied.

6.6.2.1 Cathodic Polarisation of Platinum (Figures 104-108)

With the aerated solutions the two sets of curves (i.e. 10 g/l molybdate and non-molybdate) were remarkably similar. Unsteady currents were evident for several pHs at around 0.1 mA/cm² on both sets of curves. The addition of 10 g/l sodium molybdate reduced the rest potential at pH 1, 3 and 5 but raised it at pH 9 and 13. With the exception of the pH 1 curve, the addition of molybdate reduced the overpotential at which hydrogen was evolved. Coatings formed in the molybdate solution ranged from gold with pink-red at the edges at pH 5, becoming faint gold-grey at pH 3 and no visible coating at all at pH 1.

When pre-deaeration was employed the shapes of the curves were not drastically altered. The only sizeable irregularities were observed on the pH 9, 10 g/l sodium molybdate curve. There was no apparent sign of an unsteady current as with the continually aerated tests. Sodium molybdate appeared to lower the rest potential at pH 1, 3 and 5 and increase it at pH 9 and 11. Molybdate, as in the aerated tests, lowered the overpotential at which hydrogen was evolved (with the exception of the pH 13 curve). Coatings after polarisation were in general similar to their continually aerated counterparts. A pH 5 solution produced a lighter to medium gold colouration, whereas at pH 3 a darker iridescent coating appeared.
A 100 g/l pre-deaerated sodium molybdate solution promoted curves with marked inflections at pH 1, 3 and 5. Rest potentials were higher than in the pre-deaerated 10 g/l molybdate solution. Molybdenum blue was apparent during the polarisation of the platinum in the pH 1, 3 and 5 solutions. Coatings were only present after polarisation in the pH 3 and 5 solutions. At the latter pH the coating was dark gold but not adherent; at pH 3 a similar situation was apparent but the coating was purple-mauve and iridescent. At pH 1 the platinum cathode was coated with molybdenum blue, but this was easily washed off with water.

6.6.2.2 Cathodic Polarisation of Zinc (Figures 109-113)

The aerated solutions exhibited contrasting polarisation curve forms. There were no marked inflections, although in the molybdate solution at pH 5, 9 and 13 the point of hydrogen evolution was clearly increased; at pH 1 and 3 there was little difference between the two sets of curves. At pH 1, 3, 5 and 9 the molybdate decreased the rest potential, although at pH 13 the reverse was true. The agitation effects of aeration (i.e. unsteady current readings) were again evident. Coatings after polarisation in the molybdate solutions were most clear on the samples tested at pH 5 and 3 where adherent matt black films, with occasional brown streaks, were apparent. At pH 9 there was slight staining towards the top of the specimen.

When pre-deaeration was employed the two sets of curves were again somewhat different in shape. The distilled water solution did promote evidence of inflections on the cathodic polarisation curves. These were much less apparent in the 10 g/l molybdate solution, although there was some evidence of inflections at pH 9 and 13 just before hydrogen evolution commenced. Sodium molybdate increased the rest potential over the simple distilled water solutions. Agitation effects were not apparent with the continuously aerated solutions. Coatings formed from the molybdate solutions ranged from a slight staining at the solution meniscus at pH 9 and 13 to a matt black-brown coating with good adherence at pH 3 and 5. The pH 1 solution
produced an etched surface with brown staining along one edge.

The 100 g/l molybdate solution produced small inflections at pH 9 (very small) and 5. Currents were similar to the 10 g/l pre-deaerated solution and molybdenum blue was apparent in small amounts at pH 5 and more marked at pH 3 and 1. With the exception of the pH 1 solution all rest potential values were lower than those in the pre-deaerated 10 g/l solutions. Colouration of the zinc after polarisation was most apparent in pH 3 and 5 solutions with an adherent matt black coating (this in fact became flaky on drying). At pH 1 a molybdenum blue sludge was found on the cathode together with a dirty, inconsistent film. At pH 9 and 13 a dirty grey-fawn colouration was apparent.

6.6.2.3 Cathodic Polarisation of Tinplate (Figures 114-118)

Continually aerated molybdate solutions produced considerably different curves to their distilled water counterparts. Marked inflections were apparent on curves plotted from the former solutions at pH 5 and 3. These occurred at the end of the curves, just before hydrogen evolution. At pH 1, 3 and 5 molybdate had the effect of raising the rest potential of the tinplate. However, at pH 9 and 13 the reverse was true. Agitation effects were again apparent, particularly in the section of curve leading up to hydrogen evolution. Coatings produced during polarisation in the molybdate solution ranged from gold at pH 9 to generally black and flaky at pH 5 and 3 (with iridescence underneath) and etching at pH 1. Molybdenum blue formed readily at the lower pHs.

Pre-deaerated solutions produced curves which were generally similar. The 10 g/l molybdate solution increased cathodic currents and produced an inflection in a curve plotted from a pH 3 solution. The molybdate curves could be conveniently divided into two groups i.e. pH 9 and 13 and pH 1, 3 and 5, the latter showing evidence of a cathodic limiting current before the onset of hydrogen evolution. Molybdate, in all cases, raised the rest potential of the tinplate.
Coatings formed during polarisation ranged from faint gold and iridescent at pH 13 and 9, to a strong, attractive iridescence at pH 5, to flaky black on mottled iridescence at pH 3. Severe etching was noted at pH 1.

At a 100 g/l concentration, with pre-deaeration, the molybdate produced two inflections at pH 5 and 3 (at pH 3 there appeared to be two inflections close together). Cathodic currents were higher than at 10 g/l, pre-deaerated, and molybdenum blue was apparent at pH 3 and in large quantities at pH 1. Rest potentials, when compared to the 10 g/l pre-deaerated solutions, were higher at pH 1, 3 and 9 but lower at pH 5 and 13. Films formed during polarisation were poorly adherent gold-green iridescent at pH 13, brown-gold iridescent (flaky) at pH 9, to matt black and flaky at pH 5 and 3, with etching and a molybdenum blue sludge at pH 1.

6.6.3 Galvanostatic Trials (Table 40)

Platinum, zinc and tinplate were polarised galvanostatically in a 100 g/l sodium molybdate solution, which had been pre-deaerated, at 20°C and at pH 5 (Sn, Zn) or pH 3 (Pt). Various current densities were applied, but the only arrest points apparent were for zinc at 4.0 mA/cm² and at around -1300 mV vs SCE, and for tinplate at 10.0 mA/cm² around -1450 mV vs SCE. The appearance of these inflections was observed whilst hydrogen evolution was occurring. The zinc and tinplate surfaces were, at the time, covered in a flaking black coating. The platinum electrode never formed this thick coating.

6.6.4 ESCA Examinations of Molybdate Coatings on Zinc, Tinplate and Tinfoil

Table 41 indicates the specimens examined by ESCA and their pre-treatments. Samples of tinplate were examined which had been polarised up to, and also past, the inflection noted in cathodic polarisation curves from a pH 5, 100 g/l sodium molybdate solution.
A tinplate sample was also tested that had been cathodically processed in a 10 g/l, pH 3 sodium molybdate solution. Zinc samples were tested from an identical solution, and also tin foil specimens which had been immersion coated for various lengths of time in a 110 g/l, pH 3.5 MP solution.

A Vacuum Generators ESCA LAB 5 electron spectrometer was employed, with the experimental conditions as summarised in Table 42.

6.6.4.1 Experimental Results

The results of the analyses are given in Tables 43-47. Compositions were obtained using experimentally determined relative sensitivity factors derived from chemical standards. Absolute concentrations must be considered approximate (errors are typically about 10%), however a more accurate comparison may be made between similar samples.

Figures 119-125 show the Mo 3d doublet at the surface of each sample. Samples 2, 3, 6 and 7 contained molybdenum in only one state whilst the shape and broadness of these peaks on the remaining samples indicate a presence of more than one oxidation state of molybdenum.

In general binding energy increases with oxidation state. Possible assignments of the peaks are given in Table 47 as no reference for Mo (V) was available.

6.6.5 Preliminary Coating Thicknesses of Molybdate Films on Tinplate

Two samples were prepared for this examination:

Solution: 10 g/l sodium molybdate, pH 3, 20°C
Cathodic potential of -800 mV vs SCE for:
1. 2 minutes immersion
2. 30 minutes immersion
Scratches were made on these specimens in order to highlight, in side elevation, the different surface layers i.e. molybdate coating/tin/steel substrate. This method resulted in the "platelets" of molybdate being detached from the surface tinplate (see plate 18), although not always necessarily in the vicinity of the scratch. Once these "platelets" had lifted their thickness could be estimated. The 2 minute coating had a thickness of approximately 0.5 μm, whilst the 30 minute specimen was approximately 2.0 μm thick.
The discussion section of this thesis can be broadly divided into three separate sections. The first surveys the data relating to the experimental investigations, the second attempts to interrelate the findings (e.g. the cathodic inflection phenomenon in certain molybdate solutions and the subsequent ESCA investigations) and the third section briefly examines the future for molybdate-based conversion coating treatments, primarily for tin and zinc metal surfaces.

7.1 MOLYBDATE IMMERSION TREATMENTS FOR ZINC

This particular section of the investigation was essentially of an introductory nature surveying trends in a broad manner. Although all the experimental work was carried out accurately, the weight gain versus time curves were plotted from only single measurements, and as such should be viewed with a certain amount of caution, being regarded as an indication of trends rather than an exhaustive and detailed study. The potential-time curves, on the other hand, are average values of three separate trials, and can be considered highly representative. Similarly the salt spray samples were always tested in duplicate (as was the case with all such tests throughout the experimental investigations).

It can clearly be seen that a pH 5 molybdate solution can effectively form an immersion coating on a freshly pickled zinc foil surface. The weight gain of the coating appears to reach an equilibrium after approximately 30 mins; after three hours a decrease in coating weight begins which eventually results in an overall negative change, indicative of a high degree of zinc dissolution. The difference in weight gain between a 10 g/l and a 30 g/l sodium molybdate solution is small, which could prove advantageous as the cost of molybdate can be relatively high compared with other potential coating compounds. The
trends of the weight gain versus time curves agree to an extent with those of Yakimenko et al.,\textsuperscript{126} although the actual coating weights are much larger. (The fact that the results differ by 3 orders of magnitude does raise the possibility of an error or confusion of units in translation, e.g. g/m\textsuperscript{2} rather than mg/m\textsuperscript{2}, in Yakimenko's work).

The potential-time curves indicate a decrease in rest potential with time (except for approximately the first 30 seconds of the curve plotted from a solution containing 1 g/l ascorbic acid), with, in general, an equilibrium value being achieved after 10-30 minutes, depending on the solution and temperature conditions. The initial overall fall in potential is in disagreement with the findings of Yakimenko et al.,\textsuperscript{126} who found an initial rise before an approach to a near equilibrium potential. However, it must be remembered that their work was carried out with a slightly different composition of solution (i.e. (NH\textsubscript{4})\textsubscript{2} MoO\textsubscript{4} and NH\textsubscript{4}Cl).

The colouration of films formed at pH 5 seems to follow a well defined progression. Grey-blue coatings are formed with short immersion times, followed by darkening and the formation of a brown coating. Further immersion produced matt black coatings which became powdery and ultimately flaky in consistency. Again this disagrees to some extent with the findings of Yakimenko et al.,\textsuperscript{126} They reported a colour progression of blue, azure, yellow, orange, green, iridescent, brown and violet and after 15 minutes, black. Certainly there is agreement for the later stages of the progression (i.e. brown to black) but the initial colour stages were clearly not observed in this work with zinc. An answer may be found in the two surface preparations of the metal. Yakimenko et al\textsuperscript{126} had electrogalvanised steel, brightened in 1% HNO\textsubscript{3}, whereas for the immersion tests of these investigations, zinc foil, strongly pickled in HCl, was utilised. It may be conjectured that a brightened pre-immersion surface is required to obtain a full spectrum of coloured coatings. Clearly a rigorously pickled zinc foil surface would be microscopically "rough".
It may be pertinent to examine the action of white light on a smooth, and conversely roughened metal surface. A thin, transparent film on a smooth metal will often exhibit colours, similar to those from an oil film on water. This is due to interference of light reflected from the film and metal. Initially a certain portion of the light is reflected and the remainder transmitted, to re-emerge during several "internal" transmission/reflections as successive beams (see Figure 126) which will then recombine; certain wavelengths will interfere destructively and others constructively. Hence certain colours will be lost from the spectrum and others reinforced. Therefore, the film will give the appearance of integral colouration when in fact it is transparent.

If the metal surface is roughened (e.g. by pickling) light will be scattered in many directions. Also the film is unlikely to be parallel at the metal surface and its thickness will probably vary over short distances. Hence areas over which consistent interference effects can take place will be small, and adjacent areas are likely to display differences in the wavelengths at which constructive interference will take place. This leads to a "micro-mosaic" type of appearance or possibly just a grey looking surface (as seen with short immersion times for zinc foil).

This theory can be further reinforced by the fact that with flow melted (brightened) tinplate a similar range of colour changes, as reported by Yakimenko et al. on electroplated zinc was observed (see colour plate 1).

Salt spray tests illustrated that immersion formed molybdate coatings have a potential degree of corrosion resistance. The adherent black finishes seemed the most durable, although the boundary between adherent black and powdery/flaky black must be examined carefully. The addition of phenolsulphonic acid to the process solution appeared to increase the corrosion resistance and would warrant further investigation.
The addition of reducing agents to the immersion-type solutions has been reported to accelerate colouration, but with the disadvantage of a decrease in solution stability.\textsuperscript{126} The latter point is not explained satisfactorily, and in these investigations reducing agents generally had a beneficial effect, although it must be noted that phenolsulphonic acid did produce a decrease in electrode potentials when compared with a solution not containing it. The actual nature of phenolsulphonic acid is still open to argument. It is widely used as an inhibiting agent of the oxidation of stannous to stannic ions ($\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e$) in tin plating solutions. Its mode of operation could be to complex with soluble oxygen,\textsuperscript{179} although this is still open to doubt. Therefore when phenolsulphonic acid is described in the Results Section as a reducing agent this should be qualified in that it may be more accurately described as a complexing agent.

The commercial viability of a molybdate immersion type treatment is still uncertain. It has the important attributes of simplicity and low cost plant, and solutions can be dilute, typically around 10 g/l. However, a more concentrated solution may produce optimum coatings at a more rapid immersion time. Before this coating system can be seriously appraised, more extensive work is required, particularly with respect to pH and other possible addition agents.

7.2 CATHODIC POLARISATION CHARACTERISTICS OF ZINC IN GROUP (VIA) OXY-ANION SOLUTIONS

The cathodic polarisation curves plotted for zinc from 0.1M and 1.0M still and continuously aerated oxy-anion solutions are, in general, of a typical cathodic shape, culminating in the approach to a limiting current.

The general effect of continuous aeration was the appearance of current fluctuations, generally in the initial stages of the polarisation curves. The fluctuations represented in the figures are not to scale nor are they an accurate indication of the individual number of peaks during such disturbances. The overall shape, curve
features and current densities remained very similar. In essence continuous aeration during a test had little additional effects compared with a solution which had no ingress of air. The occasional current fluctuations exhibited on a few curves which had experienced aeration can probably be dismissed as purely an agitation phenomenon.

Raising solution oxy-anion concentrations from 0.1 to 1.0M had the primary effect of increasing cathodic currents, although the actual increase in most cases was very small. Generally, curve features were little changed, although in pH 5 tungstate solutions (both still and aerated), a 1.0M solution promoted clear inflections that were not present at a 0.1M concentration.

All three group (VIA) oxy-anion solutions showed remarkably similar responses at the different pHs tested. pH 5 curves exhibited high current densities for low overpotentials, and generally did not exhibit a large number of inflections. pH 7 solutions of molybdate and tungstate were, on the whole, very similar to their pH 5 counterparts. However, pH 7 chromate solutions exhibited smaller current values for given potentials and also the appearance of more marked inflection phenomena. For all pH 9 and 11 solutions currents at given potentials were generally smaller, and the overall appearance of inflections was more marked (although pH 9 molybdate solutions had fewer examples of this phenomenon).

Turning to the incidence of inflections on cathodic curves, Tables 48-50 list the approximate potentials at which these inflection or other allied phenomena occurred. The figures in brackets, followed by a question mark, refer to shallow inflections or periods of unsteady current ("zig-zagging" on polarisation curves).

In general the chromate solutions produced far more inflections than the corresponding molybdate and tungstate analogues. The majority from chromate solutions were also much more strongly defined than those from the other two types of solution. Broadly categorising the inflections is difficult because of the scatter of values from
individual solutions. However, there does appear to be some evidence of a trend whereby all oxy-anion analogues seem to produce inflection-type features at a range of values around -800 mV vs SCE and one also around -1400 mV vs SCE; although it must be reiterated these values should be regarded as very approximate.

Aeration did not produce appreciable differences in the potential values or numerical quantity of the inflection phenomenon.

Consideration of the observed rest potentials shows that chromate solutions produced the most noble values for zinc, these being closely followed by molybdate, with tungstate producing the most base values. The rest potential values were monitored over a period of five minutes, and in essence give a direct indication of each solution's protective (or otherwise) capabilities for zinc.

Chromates are clearly advantageous over most pH ranges tested, and this results in their popularity as inhibitors. Molybdates are also effective, whereas tungstate is clearly unsuitable, particularly at the lower pHs tested.

Surface colouration after cathodic polarisation was recorded (Table 16). Molybdate solutions produced the most striking coating colourations, with brown to black shades being prominent. Chromate and tungstate samples were generally less heavily coloured.

As a guide to corrosion resistance the 24 hour salt spray test was found to be useful. The results indicate that chromate coatings consistently produced the best performance. Tungstate coatings showed large variations between the duplicate samples tested for each processing condition. This suggests either the salt spray cabinet was producing uneven misting or that the specimens produced at a particular condition were truly variable. Molybdate coatings were clearly inferior to chromate, producing consistently high levels of surface zinc corrosion product.
The level of corrosion of the chromate coated samples must be regarded as artificially low since the 'as pickled' samples in the same batch produced consistently lower levels of corrosion than those 'as pickled' samples tested with the other batches. The overall inference being that the whole chromate batch was exposed to a less corrosive environment than the molybdate and tungstate batches.

As already stated, the molybdate samples, judging by the area of corrosion product, were most affected, although it must be noted that the matt black coating of the pH 5 samples was still partially visible.

The potentials assigned to the visual observation of the onset of hydrogen evolution can be superimposed on sketches of the 0.1M still, chromate polarisation curves as indicated below:

- pH5
  - The H.E. point appears just after the inflection

- pH7
  - The H.E. point falls just after the second inflection
Due to the difficulty in observing the actual commencement of hydrogen evolution, it is assumed that the actual onset occurred before these experimental potentials. This suggests the second inflection (usually "strong") on the chromate curve appears to coincide with H.E..

SEM investigations were carried out on chromate and tungstate coatings which were produced cathodically from 0.1M, pH 5 solutions. However, this type of processing produced a non-adherent coating from a 0.1M, pH 5 molybdate solution. Therefore to form a sound molybdate coating for examination a simple immersion technique was utilised. On examination the surface of the chromate specimen appeared to be made
up of platelets of parallel crystals. The molybdate coated surface was made up of five-sided platelets (some of which exhibited internal cracks) which could possibly be as a result of post-treatment drying which resulted in the cracking of the initially-formed film. The tungstate surface was very similar to that of the chromate, consisting of parallel crystals forming separate platelets.

7.3 MOLYBDATE-ORTHOPHOSPHORIC ACID-BASED TREATMENTS FOR ZINC

The investigation of the suitability of an MP-type solution for zinc was as a direct result of reference to GB patent 2,070,073.127 The plan was to assess this type of solution with zinc foil before applying it to tin and tinplate.

Initial investigation of the MP-type solutions, suggested originally in GB patent 2,070,073,127 indicated that they promoted little sign of a surface coating on zinc foil. However, weight gains were apparent on samples treated in a pH 6 solution suggesting that a coating was forming. Samples in a pH 3 solution exhibited a corresponding loss, presumably the tendency for zinc to undergo dissolution at this lower pH outweighing the formation of a protective coating on the metal surface. This theory was supported by the fact that samples immersed in an even lower pH solution experienced far greater weight losses.

Surface colouration was found to be poor, with the longest immersions producing, at best, a slight brown colouration at the edges of samples. It was first thought that the post-surface treatment of rinsing was reducing the potential colouring ability of the solution. The patent127 cites an example of a coating system in which a freshly immersed sample was removed from the treatment solution and any excess liquid was removed by "nip" rolls, followed by drying for 30 seconds at 130°C. So as to repeat this type of post-treatment more closely, coatings were blotted and air dried as opposed to rinsing. However, there was little evidence of any real, significant increase in colouring ability, although later corrosion experiments suggested increased coating integrity.
Polarisation measurements in both MP and orthophosphoric acid solutions provided some interesting results. Cathodic polarisation curves were generally of an orthodox nature, however, in solutions containing sodium molybdate there was some evidence of inflections or other inconsistencies in the curves. These were not apparent on curves plotted from specimens polarised in purely orthophosphoric acid solutions. This suggests that molybdates do cause irregularities on cathodic polarisation curves of zinc as suggested in earlier work, but the exact nature of these irregularities is not clear. It could well be due to changes during film formation or the reduction of an earlier formed film (perhaps before polarisation commences).

Anodic polarisation curves exhibited few signs of significant passivation. The addition of sodium molybdate increased the anodic current to such an extent that the sample in the pH 1.5 MP solution dissolved.

Rest potentials were generally consistent, allowing for the inherent differences caused by changes in the pH of the solution.

Comparing the 24-hour salt spray results, it appears that the actual post-treatment care of a coated sample is very important to its integrity. A post-treatment rinse appears to wash away or damage the film, whereas a drying and blotting action enhances the corrosion resistance of the coating. This suggests that the structure of the film is formed to a large extent during its post-treatment drying.

Although these superficial investigations for MP-type solutions for zinc have proved somewhat disappointing, it does appear that interest in the MP-type treatment is growing. The following section describes some of the more recent developments, beginning with a slightly more quantitative assessment of GB patent 2,070,073, filed by Kobe Steel.
7.4 AN ASSESSMENT OF RECENT DEVELOPMENTS IN MOLYBDATE-PHOSPHATE-BASED METAL TREATMENTS

MP-type conversion coatings have not been widely reported to date. The patent filed by Kobe Steel Ltd of Japan in 1980\textsuperscript{127} can be considered as representative of the small number of such patents that have been filed.

This patent describes an anticorrosive treatment for galvanised steel articles which is claimed to stem the formation of "white rust" in mildly corrosive atmospheres. The patent cites the inherent toxicity problems associated with "state of the art" chromate treatments and cites several solutions, which have recently received Japanese patent status,\textsuperscript{180-182} whose compositions include various molybdate compounds.

The Kobe Steel solution is based on an acidic treatment comprising of 10-100 g/l (calculated as molybdenum) of molybdic acid or molybdate and adjusted to pH 1-6 by the addition of an organic or inorganic acid. The solution is applied by immersion, spraying or roll coating. Figures 127 and 128 indicate the amounts of specific molybdates required to produce satisfactory corrosion resistant coatings. The acidification of the solution can be attained with the addition of any of the following inorganic and organic acids: orthophosphoric, nitric, sulphuric, hydrochloric, oxalic, acetic, citric, malonic, succinic, tartaric, and lactic. It is noted that orthophosphoric acid is superior owing to the formation of a stable solution of a heteropoly molybdate complex of phosphomolybdate, and the greater corrosion resistance of films so formed is due to the synergistic effects of a phosphate film formed on the zinc and a passive film formed in the acidic bath by molybdenum "in a similar manner to chromium".

The solution for forming these coatings must be in the pH range of 1 to 6 if the molybdate concentration is desired to be in the range (10-200 g/l as Mo). Films formed in solutions of a higher pH are of an unsatisfactory anticorrosive nature. At pHs less than 1 there is difficulty in actually forming a coating with molybdate concentrations
of between 10 and 200 g/l (as Mo). Process temperatures are usually maintained at 20°C thus negating the problem of high vapourisation rates of the acid at increased temperatures. A treatment time of 2-3 secs immersion is considered the optimum. The effects of change in molybdate concentration and solution pH on the corrosion resistance rating is indicated in Tables 51 and 52. An optimum solution based on sodium molybdate can be considered to be 43 g/l (as Mo) at pH 1.5 (adjusted with orthophosphoric acid).

Several other patents have been filed using a molybdate-orthophosphoric acid type solution. C Allen of Teleflex Inc\textsuperscript{183} has proposed a solution for "protective adhesive coatings" which is based on orthophosphoric acid (H\textsubscript{3}PO\textsubscript{4}) but also containing one metal chromate, bichromate or molybdate, and at least one compound from the group: MgO, Mg(OH)\textsubscript{2}, Mg\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}, MgHPO\textsubscript{4}, Al(OH)\textsubscript{3}, AlPO\textsubscript{4}, Zn(OH)\textsubscript{2}, Zn\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}. A solution suggested is as follows:

1 part H\textsubscript{3}PO\textsubscript{4} (85%)
3-6 parts H\textsubscript{2}O
8-20/100 ml acid solution of dichromates, chromates etc
2-10g/100 ml aqueous acid solution of constituent from list including MgO, Mg(OH)\textsubscript{2} etc.

Consolidated Mining and Smelting Co (Canada) Ltd have filed another patent based on the phosphate ion\textsuperscript{184} The formulation is for anodising zinc and zinc alloys and consists of an aqueous solution of:

\[
0.5 - 0.8M \text{PO}_4^{3-}/l \\
0.3 - 0.5M \text{CrO}_4^{2-}/l
\]

and sodium or potassium cations.

It must be noted that the chromate can be partially replaced by molybdate, tungstate or vanadate.
Operating temperature: 60 - 95°C

Current density: 10.7 - 107 A/dm²

until sparks appear between the electrodes and thereafter:

Current density: 2.3 - 23.2 A/dm² at 35-110V

Technilith Inc, USA have also formulated a possible molybdate/phosphoric acid type solution for forming a coating on aluminium. A cleaned aluminium sheet or foil is treated with a solution containing sodium or ammonium molybdate with H₃PO₄, HNO₃, H₃AsO₃ or HasO₂, NaHSO₄, NaH₂PO₄ or AlCl₃. A reducing agent is then applied (thiosulphate or FeSO₄).

T Yamada of the Mitsubishi Motor Corporation of Japan has patented a process for forming a conversion coating on zinc and zinc based alloys. The solution is sodium molybdate based, but does contain a small amount of orthophosphoric acid i.e:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium molybdate</td>
<td>15 - 50 g/l</td>
</tr>
<tr>
<td>K₂Cr₂O₇</td>
<td>0.1 - 0.5 g/l</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>0 - 25 ml/l</td>
</tr>
<tr>
<td>CH₃COOH (acetic acid)</td>
<td>0 - 20 ml/l</td>
</tr>
</tbody>
</table>

For example a die cast zinc article was treated in the following solution:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium molybdate</td>
<td>30 g/l</td>
</tr>
<tr>
<td>K₂Cr₂O₇</td>
<td>0.2 g/l</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>15 ml/l</td>
</tr>
<tr>
<td>T = 65°C</td>
<td></td>
</tr>
<tr>
<td>pH = 4.5</td>
<td></td>
</tr>
<tr>
<td>Immersion time = 30 mins</td>
<td></td>
</tr>
</tbody>
</table>

Articles thus coated exhibited corrosion in a brine spray in 16-96 hrs. It is interesting to note that although Britton states that
phosphate coatings on tin impart questionable corrosion resistance to the metal surface, two Japanese companies have patented surface treatments for tinplate based on orthophosphoric acid/orthophosphates.

The Nippon Paint Co Ltd have formulated a chemical conversion treatment for tinplated cans.\(^{187}\) The aqueous solution contains:

- $H_3PO_4$ and/or phosphates: 0.5 - 10 g/l (based on $P_4O_{10}$)
- Phytic acid and/or phytates: 0.2 - 2 g/l

A typical solution:

\[
H_3PO_4
\]

50% Phytic acid

pH 3.0, $T = 50^\circ C$

forms a highly corrosion resistant product.

The Toyo Kohan Co Ltd of Tokyo have also formulated a solution to treat tinplated steel.\(^{188}\) It contains orthophosphoric acid, orthophosphates, polyphosphoric acid, polyphosphate, metaphosphoric acid, a metaphosphate or phosphorus pentachloride or their combinations. The film is formed by anodising at 0.02-10 $C/dm^2$. The film imparted is said to improve yellowing resistance, scratch resistance and soldering.

### 7.5 SIMPLE MOLYBDATE TREATMENTS FOR TINPLATE

Simple molybdate type treatments (i.e. a dilute sodium molybdate solution, adjusted to an acidic pH with concentrated sulphuric acid) exhibited good resistance to sulphide stain tests. A 10 g/l, pH 3 solution, used to impart coatings cathodically on tinplate, was deemed the optimum. pH changes to 1 and 5 produced inferior coatings as did
reducing the sodium molybdate concentration to below the 10 g/l level. The main drawback with this type of coating was the susceptibility to flaking which was highlighted by coatings formed from high temperature solutions and, to a much lesser extent, from the optimum solution. The flaking on a coating from the latter solution was more evident 24 hours after sulphide staining, and was more apparent at the edges where the coating was probably thicker (edge effect - due to a higher charge).

7.6 MP-TYPE COATINGS ON TIN FOIL

It is interesting to note that inflections were observed on cathodic polarisation curves carried out in both MP-type solutions and orthophosphoric acid, this being the complete reverse to zinc. At the higher pHs tested sodium molybdate had the effect of increasing the cathodic current, but at pH 1.5 its effect seemed to be negligible.

Anodic curves carried out suggested that at the higher pHs tested sodium molybdate does induce passivation, although at pH 1.5 in a purely orthophosphoric acid solution, tin foil did exhibit a high degree of passivation, but at higher pHs anodic currents were very low suggesting instantaneous passivation.

Rest potentials, even taking differences in solution pH into account, were not as consistent as with the zinc. This could suggest that the cathodic cleaning of tin foil in a sodium carbonate solution does not create as reproducible a surface as does pickling zinc in concentrated hydrochloric acid.

Once the method of post-treating the samples (i.e. blotting with a paper tissue to remove excess solution and then leaving to air dry) had been adopted it was found that colourful, adherent coatings could be formed on tinfoil surfaces. Immersion coatings were tested extensively by varying the solution characteristics of pH and temperature. Generally a 1 to 10 minute immersion formed the best coloured coatings. Clearly a much shorter immersion time would be
preferable particularly for an industrial application. However, it may be possible to speed up the formation of the coating with the imposition of a cathodic potential, although this was not fully tested for tin foil.

Duplicate immersion coated samples tested in a sulphide staining environment at both ITRI and at Loughborough showed close correlation. This exercise was undertaken to verify the suitability of the sulphide stain testing technique that was to be used on later tinplate samples. The tests indicated that the 30 sec and 1 min immersion coated samples endured the tests quite satisfactorily.

7.7 MP-TYPE COATINGS ON TINPLATE

Initial investigations of MP coatings on 2.8 g/m² tinplate consisted of testing the most promising solutions from the tinfoil work. Immersion coatings so formed were similar to those on tinfoil at fairly rapid immersion times (typically less than 1 minute). However, for immersions of ten minutes and longer more iridescent coatings were formed. This perhaps suggests that longer immersion times may promote excessive tin removal and that the iridescent coatings are indicative of a mainly iron surface being present. It could also be possible that the mainly gold coatings are much thinner than their iridescent counterparts and that the formation of the latter type of film is just a stage in the thickening process of the MP coating.

Sulphide stain tests indicated that the longer immersion coated specimens endured the test far better than the rapidly formed coatings. Again the immersion times were far too slow for industrial use.

An SEM and EPMA investigation of MP coated tinplate was only of a preliminary nature. However there does appear to be some considerable difference in the morphology of coatings on tinplate when compared with those on tinfoil. At a pH of 2.5 the coatings on tinfoil are irregular in height with several pronounced high spots, whereas from
the same solution on tinplate a much smoother coating is formed. X-ray distribution maps taken from the EPMA have shown that on tin foil samples phosphorus signals tend to emanate from surface irregularities, whilst molybdenum, on the whole, tends to be pretty well dispersed. On tinplate there seems to be less tendency for the phosphorus signals to be grouped around surface features, although there are areas where the density of phosphorus signals are slightly higher.

Examination of the early polarisation trials indicated that the concentration of sodium molybdate had little effect on the passivation characteristics during anodic polarisation. Effects on cathodic currents were a general increase with increasing molybdate concentration.

The main influence on the passivation characteristics of tinplate was the pH of the solution. In essence a very low pH solution resulted in a high value for $i_{\text{crit}}$ and consequently, a high tin dissolution rate for anodically formed coatings from this type of solution. Higher pH solutions exhibited little difference between $i_{\text{crit}}$ and $i_{\text{pass}}$ which is unacceptable because a degree of tin dissolution must take place before an intrinsically sound anodic conversion coating can be formed. Aeration and deaeration had little effect on passivation, their main contribution was the promotion of solution agitation which led to an unacceptably high value of $i_{\text{pass}}$.

One of the inherent disadvantages of molybdates is their relatively high purchase cost when compared to potential rivals such as chromates. It was this problem which led to the appraisal of much lower molybdate concentration solutions for use in the formation of anodic coatings. It had been shown that varying the molybdate concentration between 30 and 90 g/l had little effect on the passivation characteristics of the solution. Solutions with a molybdate concentration as low as say 3 g/l did promote reasonable passivation, however it was decided that 10 g/l gave better defined passivation and there was sufficient molybdate present to eliminate
the need for constant replenishment.

The effect of solution temperature was also investigated. Anodic polarisation data indicated that a temperature of about 30°C was the optimum. This was because the 30°C specimen exhibited the lowest passive current, presumably indicating a more protective film. However, if when the application of a suitable potential from the middle of this passive region results in a long passage of time before \( i_{\text{pass}} \) is attained, the temperature is clearly unsuitable for commercial usage (time, cost etc). Thus it may be more profitable to use a higher temperature with an inherent shorter time to \( i_{\text{pass}} \). It therefore follows that the nature of the film forming process must be reduced i.e. is it chemically or thermally activated? Current-time (I vs t) trials proved that a specimen at 30°C does in fact attain its passive current more rapidly than at the other temperatures tested.

The preceding work allowed the formulation of an anodic MP solution for tinplate i.e.

\[
\begin{align*}
10 \text{ g/l sodium molybdate} \\
to \text{pH 4 with 88% orthophosphoric acid} \\
T &= 30^\circ\text{C} \\
\text{No agitation}
\end{align*}
\]

Sulphide stain tests on coated tinplate specimens formed from this solution have proved disappointing. The protection conferred by the coatings was considerably less than that of a commercially formed dichromate coating on tinplate (CDC) that was also tested. Cathodically formed coatings from this solution were also heavily attacked, although the degree of staining may be considered to be slightly less. A slightly more resilient surface was obtained by lowering the pH to 3 and again forming the coatings cathodically.

Relating to blackplate, if an MP-type solution is to be of practical use it must be able to coat the bottom of pores on the tinplate surface. The actual nature of the base of these features can be
considered to be either an inclusion, iron-tin alloy (FeSn₂) or mild steel substrate (blackplate). Anodic polarisation in MP solutions indicated good passivation characteristics. This in essence should promote an inherently sound coating, as the pores on a tinplate surface could promote localised galvanic action depending on the nature of the internal environment of the tin can or container.

The pH of solutions was adjusted using orthophosphoric acid (H₃PO₄). However, since sodium molybdate is alkaline in nature (a 90 g/l solution has a pH of 9.8) an increase in molybdate concentration at a given pH will result in an increase in the H₃PO₄ content of the solution, even though the acidity of the solution is required to remain the same. This means the changing of the parameter of molybdate concentration could not be made without altering the orthophosphoric acid content of the solution.

7.8 EFFECT OF DRYING METHODS ON THE SULPHIDE STAIN RESISTANCE OF TINPLATE TREATED IN AN MP-TYPE SOLUTION

The type of post treatment (i.e. rinsing or blotting) was discussed for zinc in Section 7.3. However, a more rigorous analysis was made for MP-type coating systems on tinplate. Generally there was no marked difference, in a subsequent sulphide stain test, between rinsed and variously dried specimens, although oven or air dried examples were often slightly superior to rinsed samples.

Most conversion coating processes do require a final rinse treatment to remove excess coating solution from the surface of the substrate. Phosphate coatings require thorough rinsing, basically to remove salts which could cause blisters under the surface of subsequent paint coatings. The regime employed is usually two-stage, the first in cold running water and the second in hot water, to aid subsequent drying. Often the final rinse can have inhibitive compounds added (e.g. chromic acid) to improve the corrosion resistance of the final product. Chromate coatings are said to benefit from up to three rinsing processes, usually in cold water, although the final rinse can
be up to 40°C. Prolonged rinsing should be avoided due to the possible leaching out of protective constituents.7

"No-rinse" type systems have been reported and are mainly chromate-based. There is some argument as to whether these treatments can be classed as true conversion coatings or merely a dried film which has partially reacted with the substrate. However, their technology has advanced and chromate free systems have been reported, although as yet only on a small scale.6

The rinse versus dry choice for MP-type coatings does not seem to have been resolved. The advantage of post-treatment drying may only be small for MP coated samples, but as yet it is untested for simple molybdate or other type coatings. Blotting (and in effect air drying) instead of rinsing does improve the corrosion resistance of MP-type coatings on zinc (see Section 7.3) and clearly more research into post-treatment is required. It must also be remembered that chromate treatment solutions (Cr(VI)-based) are toxic and thus, in many cases, a post-rinse is required to reduce the inherent toxicity of a treated surface. Therefore, a no-rinse system will be of limited use to such treatments. However, molybdate solutions are relatively non-toxic and hence any unreacted treatment solution, left behind after drying, would not pose such a health threat.

7.9 THE EFFECT OF NITRATE ADDITIONS TO MP-TYPE SOLUTIONS

Although the MP coatings examined had proved useful, in some cases, in conferring a moderate degree of corrosion resistance to both zinc and tin-based surfaces, their performances have fallen well below those exhibited by films from Cr(VI)-based solutions (see results of sulphide stain tests on commercially passivated tinplate, Tables 28-30). This led to a reappraisal of the MP system and an examination of an additional oxidising agent.
7.9.1 The Philosophy of Utilising Nitrate Additions in MP-type Solutions

The mode of formation of sound chromate coatings has been analysed in essence as oxidation of the metal surface, reduction of chromium species, followed by precipitation of chromium compounds and followed by consolidation of the film.

Barnes et al\textsuperscript{29} have formulated a trivalent chromium solution which possessed the inherent features of a chromate solution, utilising sodium nitrate as an oxidant (see also Section 4.3). The effects of nitrate on the passivation of tin are thus examined in the following sections.

7.9.2 The Effect of the Nitrate Ion on the Passivation of Tin Surfaces

The effect of the nitrate ion on the passivity of tin is not clear from previous work. Schon\textsuperscript{190} showed that tin becomes passive in nitric acid when in contact with platinum. However, Rothmund\textsuperscript{191} and Steinherz\textsuperscript{192} suggested that tin could not be made passive in nitric acid (along with iodic, perchloric and acetic acids). Knowlton\textsuperscript{192} indicated that the film formed during the passivation of tin in nitric acid is an oxide rather than stannic nitrate.

Wakkad et al\textsuperscript{194} investigated the passivation of tin in 0.1N nitric acid galvanostatically with a current of 400 μA/electrode. They found that when a tin electrode was dipped in the nitric acid solution, it became passive by chemical means. However, when the electrode was polarised cathodically, the constant potential registered was found to coincide with the Sn-Sn(OH)\textsubscript{2} potential at the corresponding pH value. Yet when the polarising current was reversed anodically, the potential of the electrode did not immediately jump to the oxygen evolution value, instead forming a well defined step indicating oxide formation.
Ragheb and Kamel investigated the passivation of tin in orthophosphoric acids and the effects of low concentrations of nitrates. They plotted current-time (I vs t) and potential-time curves (E vs t) and concluded that in a current-time measurement for tin in 2N H₃PO₄ only 2.6% of the surface was free for a passivation film to form, the rest being covered by an oxide film that had either not been removed during polishing, or that had reformed before testing. The areas free for passivation were calculated using the method suggested by Muller which states if mechanical passivation takes place the log io (current)/log t_p (time of passivation) plots would be straight lines and

\[ t_p = B \left( \frac{i_0}{F_0 - F} \right)^{-n} \]

B = constant representing the time of passivation in seconds for current density of 1A/cm² when the surface area is completely free

n = slope of log i_0/log t_p curve

F₀ = total surface area of the electrode

F = covered area

Hence (F₀-F) = free surface area on which the passivating layer is likely to be formed. (This may be equal to, greater than or smaller than that of the pre-immersion surface film according to the type of interaction between the electrode and the electrolyte).

The effect of temperature on the time of passivation of tin in 2N H₃PO₄ was also examined. Temperatures of between 20°C and 60°C had little effect on t_p. However, temperatures greater than 60°C exhibited dissolution at much greater rates.

The effect of small additions of nitrate ions as HNO₃ and potassium nitrate to the 2N H₃PO₄ is to increase t_p to a maximum and then to decrease values to a stage where they are lower than those obtained
for orthophosphoric acid alone. The values of \((F_o-F)\) (the free surface on which passivation can take place) are also increased. Thus it is concluded that the nitrate ion has the effect of activating the tin surface.

Ragheb and Kamel\(^{158}\) suggest that this activation of the tin is possibly due to undermining of the film, leading to the formation of soluble stannous nitrate and an increase in film porosity. They add that although the attainment of passivation is more rapid in a relatively high nitrate containing solution, the films formed are non-inhibitive. Under these conditions tin dissolution continues through the pores which causes etching to be visible when the white layer formed on the surface is scraped away. This layer could be either metastannic acid or basic stannic phosphate.

### 7.9.3 The Role of MP Solutions with Nitrates

It is clear from the work of Wakkad et al\(^{194}\) and Ragheb and Kamel\(^ {158}\) that nitrates can passivate tin either chemically or electrochemically. However, the inherent porosity of these films does promote significant tin dissolution.

If, however, the nitrate additions were made to an MP-type solution it was thought that the pores might be "plugged" by absorbed molybdate. The overall films could be produced chemically by immersion or electrochemically by the application of an anodic current.

It has been reported\(^ {104}\) that molybdate is effective in reducing the pitting of iron in chloride solutions through the formation of \(\text{FeMoO}_4\) at the pit wall, thus contributing to the repassivation of the pit and displacing chloride ions. If a similar tin-molybdate compound were to form in the pores of the orthophosphoric acid/nitrate formed film, the integrity and corrosion resistance of such a treatment could be greatly increased.
7.9.4 Experimental Findings

Anodic polarisation produced broad passive regions with a low but rising passive current with increasing nitrate additions. Cathodic polarisation curves indicated few distinguishable features with increasing nitrate additions. An inflection was present at low overpotentials and this feature was very prominent, particularly when compared to zinc surfaces cathodically polarised in simple molybdate solutions. The subsequent sulphide stain analyses are discussed in Section 7.11.

7.10 THE APPLICATION OF ALKALINE MOLYBDATE-ORTHOPHOSPHATE SOLUTIONS FOR COATING TINPLATE

The application of the alkaline molybdate-orthophosphate solutions allowed the examination of $\text{PO}_4^{3-}$-type additions at alkaline pHs as opposed to the more acid MP-type solutions.

Anodic polarisation curves exhibited broad passive characteristics with a second 'passive'-type region at higher overpotentials. Cathodic polarisation curves exhibited clear inflections at low overpotentials, becoming larger in terms of current and frequency (two instead if one) with increasing orthophosphate content (and consequently higher pH).

It could be said that the differences exhibited in both sets of polarisation curves were due to a rising pH phenomenon rather than a higher orthophosphate content. However, it must be noted that the pH increase for orthophosphate additions of between 1 g/l and 10 g/l was only pH 12.99 to pH 13.96 (see also Tables 34 and 35).

7.11 FINAL SULPHIDE STAIN ASSESSMENTS FOR COATED TINPLATE

The sulphide stain analysis of the optimum coating systems for tinplate clearly indicated that a 10 g/l, pH 3 simple molybdate solution provided, by far, the greatest staining resistance. The molybdate-orthophosphate and MP with nitrate-based solutions produced
coatings that had, in the case of the former, little or no protective qualities, and, in the case of the latter could only confer a small degree of protection.

As mentioned previously (Section 7.5) the only drawback with the simple molybdate treatments is the flaking of the heavier coatings (typified by cathodically produced coatings from the 100 g/l, pH 3, sodium molybdate solution). This phenomenon was more strikingly apparent a few days after sulphide staining had taken place.

The coulometric reduction method utilised as a final assessment was first employed on stained, uncoated tin foil to examine its suitability. Initial potentiodynamic cathodic polarisation curves (Figure 103) indicated a progressive increase in the amount of sulphide on the tin foil surfaces (larger arrests at -1400 mV vs SCE) with respect to the exposure time in the staining medium. This suggested the staining was progressive, and subsequent coulometric analysis (Table 38) confirmed this with stained surface charges of 2.52 to 57.28 mC/cm² (1 to 30 minutes staining). The inflections displayed on the coulometric curves were quite clear and calculation was therefore reasonably easy, although hydrogen evolution was apparent before the reduction end point. Therefore, in subsequent calculations the reduction charge from areas of the curve in which HE had occurred were divided by two (see Figure 8). This process was carried out for all calculations of coulometric charge for sulphide stained tin foil.

Once the system had proved acceptable for stained tin foil, it was utilised for a final assessment of optimum coatings formed on 2.8 g/m² tinplate, following a 30 minute sulphide stain test.

In direct contrast to the stained, uncoated tin foil this pre-coated tinplate produced inflections that were less precise, and calculation of end points became quite difficult. Also the surfaces, following coulometric reduction, were not clean and showed evidence of unreduced staining. With such a thin tin coating (2.8 g/m²) it may be construed
that a sizeable proportion of the sulphide may be iron sulphide (bottom of pores) and that this solution (0.5M Na₂CO₃) may be incapable of reducing it satisfactorily. Certainly the sulphide start point was at a less negative potential than suggested by ITRI₁⁰, a problem which does cause some concern.

The results from the final overall test are shown in Table 39. The average coulometric charge for each specimen tallies very well with visual assessments. ITRI₁⁰ suggest a sample with a value over 5 (mC/cm²) usually has a visible stain, and one over 10, a severe stain. If this is so, it would have been expected that the 10 g/l pH 3, 20°C molybdate specimen would have produced a lower figure. Although it must be noted that determination of endpoints was difficult and results can only be considered as an indication rather than a true value.

7.12 THE CATHODIC ELECTROCHEMISTRY OF MOLYBDATE SOLUTIONS

Extensive cathodic polarisation trials were undertaken for platinum, tinplate and zinc on both molybdate and non-molybdate solutions at pH 1, 3, 5, 9 and 13, at 20°C and under aerated and pre-deaerated conditions. The non-molybdate curves were plotted so as to isolate the solution effects of the molybdate from the cathodic electrochemistry of the substrate metals. Platinum was tested as its highly noble characteristics would preclude excessive chemical or electrochemical reaction with the test solutions - particularly the growth of oxides/hydroxides in the period between pickling and the measurement of rest potential.

Cathodic polarisation produced some interesting results. Platinum only produced substantial inflections when the molybdate concentration was high i.e. 100 g/l and the pH was ≤ 5. Zinc produced somewhat confusing results. Inflections were produced from non-molybdate solutions, presumably as a result of zinc oxide/hydroxide reduction. Tinplate exhibited more marked inflections than zinc. With the largest examples of the phenomenon being produced in the concentrated
molybdate solution (100 g/l).

Later galvanostatic studies in the 100 g/l molybdate solutions did produce arrest points for zinc at \(-1300 \text{ mV vs SCE}\) and for tinplate at \(-1450 \text{ mV vs SCE}\). Both these inflections were produced during HE.

### 7.12.1 Estimation of the Thicknesses of Molybdate Coatings on Tinplate

The method for estimating the coating depth was simplistic in approach, but nevertheless effective. It does, however assume that the platelets of coating lift "cleanly" from the tinplate substrate. The depths of 0.5 μm for a 2 minute coating and 2 μm for a 30 minute treatment are comparable with chromate conversion coatings, where thicknesses of 0.01-1.5 μm have been reported.\(^7\)

### 7.12.2 ESCA Analysis of Selected Molybdate-Based Coatings

Specimen numbers 1 and 2 (Table 41) showed no signs of a reduction of surface molybdenum after the appearance of the late inflection on the cathodic polarisation curve for tinplate in a pre-deaerated 100 g/l sodium molybdate solution of pH 5, and at 20°C. The ESCA results for specimen 3, the optimum simple molybdate coating system for tinplate, revealed an Mo(V) oxidation state for molybdenum present in the surface. Light brown and black molybdate coatings on zinc foil specimens 4 and 5), from the 10 g/l, pH 3, 20°C cathodic sodium molybdate produced a surface containing molybdenum as Mo(V) and Mo(VI) (as MoO₃). MP-type coatings on tin foil (specimens 6 and 7) produced molybdenum in the hexavalent state (as MoO₃).

### 7.13 THE CATHODIC REDUCTION PROCESSES OF MOLYBDATE FILMS

#### 7.13.1 Analysis of Cathodic Inflections Using ESCA

When tinplate was cathodically polarised in a 100 g/l, pre-deaerated sodium molybdate solution of pH 5 and at 20°C (see Figure 118) a marked inflection was exhibited, at high experimental overpotentials,
on the resulting reduction curve. An attempt to analyse the surface both before and after the phenomenon was made by polarising one tinplate sample up to the beginning of the inflection, followed by a separate one to a potential past the phenomenon, and then examining their surface compositions with ESCA (see Tables 43 and 47). The surface "before" illustrated Mo(IV) (as MoO₂) and some Mo(V). The "after" sample exhibited only Mo(V). This evidence can then be combined with visual observations made during cathodic polarisation which revealed an iridescent coating forming initially, which then turned black as it thickened and which eventually flaked off (before the inflection). After the inflection, the metal surface below the black coating revealed a fresh, iridescent coating. The black coating could be MoO₂ with vestiges of Mo(V) remaining from the earlier iridescent coating. When this flakes off, revealing a fresh metal surface, a new iridescent Mo(V) coating grows. An annotated, idealised cathodic polarisation curve for tinplate in an acidic molybdate solution, indicating film growth can be drawn (see Figure 129). The cause of the flaking of the matt black film is not clear. It is apparent that HE occurs near the flaking potential and it may be construed that the actual physical disturbance created by the HE could destroy the integrity of the coating. However, it may also be true that the natural thickening mechanism of the coating causes an imbalance which leads to the flaking phenomenon.

It is very probable that the iridescent film formed cathodically on tinplate in an acidic molybdate solution is predominantly Mo(V) as revealed by ESCA sample 3. The actual form of the Mo(V) was not clear as no reference was available for binding energy comparisons due to the rarity of pentavalent Mo compounds. Pourbaix notes that in solution, pentavalent molybdenum is known only in the form of complexes. The hydroxide MoO(OH)₃ or Mo₂O₃·3H₂O, molybdenyl hydrate being obtained as a dark brown precipitate by treating a solution of ammonium molybdenum oxychloride ([NH₄]₂(MoOCl₅)) with NH₃. However, it is apparent that Mo₂O₅·3H₂O is easily oxidised by air and decomposes into compounds of Mo(III) and Mo(IV).
7.13.2 ESCA Analysis of Molybdate Films by Other Investigators
(See also Section 3.3.4).

The overall inferences from the separate investigations reported in
Section 3.3.4 and those carried out by the author is that when treated
(cathodically) from an alkaline molybdate solution, a metal surface
will have molybdenum present as Mo(VI) whereas a coating formed from
an acidic solution can be predominantly Mo(VI), (V) or (IV) or a
mixture.

7.14 FINAL OBSERVATIONS ON THE CATHODIC INFLECTION PHENOMENON
EXHIBITED BY GROUP (VIA) OXY-ANION SOLUTIONS

The analysis of the cathodic inflection phenomenon is not easy. The
inflections apparent in chromate solutions may be attributed to
successive reduction steps (i.e. \( \text{Cr}^{6+} \rightarrow \text{Cr}^{3+} \), \( \text{Cr}^{6+} \rightarrow \text{Cr}^{0} \)) as reported
by several authors.\(^{21,23,43}\) Certainly in the cathodic polarisation
work for zinc (Section 7.2) chromate solutions did produce the
strongest examples of the inflection phenomenon. Molybdates and
tungstates produced less severe examples and this may be due to their
weaker oxidising nature.\(^{96}\)

Over the range of pHs and concentrations tested for zinc there were
broadly two potential ranges at which inflections occurred i.e. -800
to -1000 mV vs SCE and -1400 mV vs SCE. The initial inflection was
usually at low overpotentials and could possibly be attributed to
oxide reduction. Although pickling and pre-cleaning was thorough, the
possibility of oxides/hydroxides forming on test metals during the
duration of rest potential measurement (5 mins) cannot be precluded.
The other possibility is that this initial inflection is an indication
of the reduction of a molybdenum species. Latimer\(^{196}\) suggests
molybdic acid can be reduced to molybdenum blue at 1M H\(^+\) in the
following manner:
This defines a "partial" reduction process of $\text{Mo}^{6+} \rightarrow \text{Mo}^{6+/5+}$ (molybdenum blue). This reaction could be attributed to the initial inflection in molybdate solutions. However, inflections were apparent in alkaline solutions where the formation of molybdenum blue would be precluded. Earlier investigations of these "initial" type inflections also produced little evidence of a reduction process defined by an inflection on the cathodic polarisation curve.

The second inflection, occurring at around -1400 mV vs SCE could possibly be associated with a physical film process (as with tinplate in molybdate, see Section 7.13) rather than a reduction process.

7.15 OTHER REPORTED (NON-CHROMATE) CATHODIC INFLECTION PHENOMENON

The phenomenon of cathodic inflections exhibited in molybdate solutions by various metals has been reported. For tin and zinc solutions were of 1.0M concentration and the inflections were attributed to a possible electrochemical reduction process. ESCA analysis revealed reduced molybdenum species of Mo(V) and Mo(IV) for films produced from acidic solutions, although it appeared no direct reduction process was responsible for the inflection. Glass reported inflections displayed on cathodic scans for a platinum electrode in boiling, deaerated, 1N H$_2$SO$_4$ containing "0.003 and 0.03M Mo$_6^{4+}$". An Mo$_6^{4+} \rightarrow$ Mo$_5^{4+}$ process is suggested for the initial portion of the curve. The inflection(s) area is described as a diffusion limited region just prior to HE.
Wanklyn reported unusual cathodic polarisation characteristics for platinum, stainless steel (316-type) and alloy 625 in sodium chloride/0.03M Mo(VI) solutions. He reported a colour change sequence during polarisation, culminating in a black colouration at -600 mV vs SCE. Steps were reported in the cathodic polarisation curve, associated with film formation. The films were said to exist as MoO₂, possibly hydrated. At lower pHs Wanklyn found "different" films forming of poor adherence and changing directly from blue to black on thickening during polarisation.

This type of inflection phenomenon has also been reported for acidic tungstate solutions. The inflection was described as cathodic passivation. It was suggested that H⁺ ions discharge on the cathode before WO₄²⁻ reduction. Evolved hydrogen then reduces the WO₄²⁻ ions.

7.16 THE FUTURE FOR MOLYBDATE-BASED CONVERSION COATING TREATMENTS

Before discussing the relative performance of the various molybdate-based coating systems examined, it is relevant to discuss the industrial processes in which they would be applied.

Zinc metal surfaces suitable for coating treatments would include die-castings, hot-dipped coatings and electrogalvanised surfaces. Die-castings would be eminently suitable to receive molybdate coatings. Process times are not rapid for such articles and a molybdate immersion type treatment could be envisaged. Hot-dipped zinc coatings would presumably require a faster process time, and it is unclear whether molybdate films could be imparted with sufficient rapidity. The pH of the treatment solution becomes vitally important with longer process times. This is particularly relevant to electroplated zinc surfaces where a long immersion in a low pH molybdate solution could lead to unacceptable zinc dissolution and a reduction in the protective qualities of the metallic coating. Electrochemically applied molybdate coatings have the potential advantage of a more rapid application rate but, as yet, findings have indicated they cannot be formed as rapidly as conventional chromate techniques.
Tin coated articles, such as cooking utensils, could also benefit from molybdate-based conversion coatings. Again, rapid process times are not critical although the inherent solderability of tin metal surfaces must be maintained, and it is not clear at present whether a molybdate-based surface would maintain such a property.

It is envisaged that a major application for molybdate conversion coatings would be for protection of tinplate surfaces often in conjunction with a final lacquer coating. Unfortunately, simple immersion-type processes are out of the question due to their inherent slow formation time. Electrochemically applied coatings show more promise, but as stated before, at present do not possess the rapid process times of their chromate analogues, a feature which is essential for the fast processing of tinplate. The stain resistance of cathodically processed coatings from simple molybdate solutions has proved to be good, although the lacquerability of such coatings, a vital stage in tinplate production, has yet to be examined.

The experimental investigations have presented few clear answers to molybdate's future as a promoter of conversion coatings. What has been established is that there is promise for molybdate solutions, whether alone or as a synergistic mixture, to be used commercially on a wider scale than at present.

The experimental findings for zinc when first viewed are somewhat disappointing. It has been found that molybdate coatings are, to a degree, inferior to their chromate counterparts in a 24-hour salt spray corrosion test. However, there is a moderate degree of corrosion protection, and for uses in relatively mild atmospheres, such as the interiors of buildings etc, there is scope for their use. The effect of additions to the molybdate solution was not widely explored. MP-type solutions produced only moderate corrosion resistance, but the additions of nitrate or phosphate was not studied. These potentially synergistic mixtures may convey more protection than a predominantly molybdate solution.
The results for tin and tinplate are more encouraging. MP-type solutions promote attractive, mainly gold coatings, which are efficient at resisting sulphide staining on tin foil. On tinplate they are less successful, conferring only moderate protection. MP-nitrate-type systems promoted a similar level of protection, whilst the alkaline molybdate-orthophosphate coatings were clearly inferior. It was the simple, relatively dilute molybdate solutions which produced the most promising results; a cathodically applied 10 g/l, pH 3, 20°C solution being considered an optimum. The sulphide stain resistance of this type of coating was far in advance of any other molybdate-based system, and could be easily classed in the same category, on these experimental findings, as a conventional CDC-type coating. The only drawback in the author's opinion is the tendency of the coating to flake, in its thickest areas, at the edges. It would seem that careful control of the coating thickness must be maintained, as the inferior results from higher temperature and more concentrated solutions have proved.

In conclusion it would seem that molybdate coatings, formed from simple relatively dilute solutions, warrant further investigation and trials. The process seems to produce inherently sound coatings from only a narrow band of coating solution compositions and process parameters. This is not a good situation for a potential industrial process, yet this disadvantage can be partly offset by increasingly stringent anti-pollution laws making the effluent control of Cr(VI) based systems highly expensive. The molybdate coating of tinplate has still to prove its compatibility with can-making lacquers, but its good performance in staining tests and its low level of toxicity augurs well for the future.

Molybdate coatings for zinc as already noted, have not produced such promising results as have those for tinplate. It may be that the coating system for zinc should be a synergistic one and recent patents filed, summarised in Section 7.4, suggest this could be the case.
CONCLUSIONS

The following conclusions can be drawn from the experimental investigations:

**Molybdate Immersion Treatments for Zinc**

1. A 5 g/l, 10 g/l and 30 g/l, pH 5 sodium molybdate solution will impart satisfactory coatings by a simple immersion technique.

2. Coatings range from grey-blue to black depending on treatment time, solution temperature, pH and molybdate concentration.

3. The adherent matt black coatings exhibit the highest degree of corrosion resistance.

4. Weight gain vs time experiments indicate a levelling off in the increase in coating weight after a short period of time (typically 20-30 mins).

5. Potential vs time curves indicate a general decrease in potential, with a levelling off of values (after about 5-30 mins, depending on the solution and process conditions).

**Cathodic Polarisation Characteristics of Zinc in Group (VIA) Oxy-anion Solutions**

1. The occurrence of inflections on the cathodic polarisation curves in all three oxy-anion solutions was noted.

2. The phenomenon was most pronounced in chromate solutions and least pronounced in tungstate formulations.
3. The effect of aeration was generally to cause current fluctuations as a result of an agitation effect.

4. 24 hour salt spray corrosion tests indicated that chromate coatings afforded the optimum corrosion protection.

5. A visual assessment of the point of HE in a 0.1M chromate solution suggested the phenomenon occurred after the second inflection (pH 7, 9 and 11) or after the first and only inflection (pH 5).

6. SEM examinations of coated zinc foil revealed a "microcracked" coating for molybdate and a surface of platelets made up of parallel crystals for chromate and tungstate.

Molybdate-Orthophosphoric Acid (MP)-Based Treatments for Zinc

1. The MP-type coating solution generally formed faint or colourless coatings on zinc foil.

2. MP conversion coatings impart additional corrosion resistance to a zinc metal surface.

3. Pre-treatment blotting on tissue and air drying, as opposed to normal rinsing, promotes coatings with a higher corrosion resistance.

Simple Molybdate Treatments for Tinplate

1. A cathodic treatment at -800 mV vs SCE in a solution containing 10 g/l sodium molybdate at pH 3 and 20°C gave the most encouraging results in sulphide stain tests.

2. Typical molybdate coating thicknesses were 0.5 μm after 2 mins treatment and 2.0 μm after 30 mins.
**Molybdate-Orthophosphoric Acid (MP)-Based Treatments for Tin Foil**

1. Attractive gold coloured coatings were formed on tin foil by simple immersion. The optimum solution was considered to be 43 g/l (as Mo) sodium molybdate at pH 2.5 (adjusted with 88% H₃PO₄).

2. Satisfactory sulphide stain performances were achieved by these coatings, although formation times were very slow.

3. EPMA investigations indicated MP-type coatings are irregular in thickness with several high points. X-ray distribution maps indicate that phosphorus signals tend to emanate in large numbers from surface irregularities e.g. grain boundaries.

**Molybdate-Orthophosphoric Acid (MP)-Based Treatments for Tinplate**

1. MP-type solutions produced gold or iridescent coatings on tinplate after simple immersion.

2. EPMA work suggested coatings on tinplate were much smoother than on tin foil, although there was still a tendency for phosphorus rich areas around surface irregularities.

3. Coatings produced from a 10 g/l sodium molybdate, pH 4, 30°C MP solution, tested in a sulphide staining environment, indicated that cathodically formed coatings, although stained, produced the best results.

4. Blackplate exhibited good passivation in MP solutions.

5. Different post-treatment drying regimes produced no significant changes in sulphide stain performance.

6. MP-nitrate solutions do not appear to exhibit a clear advantage over a simple MP formulation.
7. Alkaline molybdate-orthophosphate systems are clearly ineffective.

The Cathodic Electrochemistry of Molybdate Solutions

1. Platinum, tinplate and zinc exhibited significant inflections on cathodic polarisation curves produced from molybdate solutions.

2. In subsequent galvanostatic trials only tinplate and zinc produced arrest points.

3. ESCA analysis of molybdate films on tin, tinplate and zinc indicated molybdenum in the (VI), (V) and (IV) valency states.

4. Analysis of cathodic polarisation data and ESCA results indicate the inflection phenomenon for tinplate in certain simple molybdate solutions can be explained in terms of a physical degradation of the surface coating as opposed to a specific reduction process.

Suggestions for Further Work

These investigations have suggested there is scope for the use of molybdates as conversion coating agents for zinc, tin and tinplate. However, the main problem associated with their application is the long process times, which at present negate their potential use for tinplate. Thus any further work should include attempts to reduce these process times. Experimental investigations should include particular attention to parameters such as temperature, pH, addition agents and perhaps agitation of the process solution. Other aspects of further work suggested are:

1. An investigation into the lacquerability of molybdate coated tinplate.

2. Possible addition agents to the successful simple molybdate formulation to improve the range of and temperature over which it is effective.
3. Investigation into other synergistic formulations with molybdate for tin, tinplate and zinc.

4. Further investigations into simple molybdate immersion solutions for zinc in an attempt to optimise this inexpensive technique.

5. An extensive appraisal of tungstate-based treatments bearing in mind the reported success made by Van de Leest et al.¹³²,¹³³,¹⁵²
REFERENCES


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5. US 1,887,967 and US 1,888,189 (from ref. 6).


34. G. Kalauch. Information uber Probleme des Klimaschutzes 1965, 4, 91 (from ref. 7).


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125. L.J. Durney. Met. Prog. 1962, 82(1), 73.


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203. US Pat. 3,313,714.

APPENDIX

PRODUCTION OF EXPERIMENTAL TINPLATE

All the 2.8 g/m² tinplate used in these trials was provided by the International Tin Research Institute (ITRI), Uxbridge, Middlesex. The tinplate was produced on a rig which is a laboratory simulation of the actual industrial manufacturing process. A diagram of the ITRI equipment is shown in Figure 130. To simulate the high relative motion between the steel surface and the solution in the industrial process, the laboratory simulation employs a rotating cylinder on to which the sheet steel blank is wrapped and then rotated in the various solutions. Each solution is housed in a cylindrical vessel and five of these vessels make up the normal stages of a tinplate line i.e. degrease, rinse, pickle, rinse, plate (currently the Ferrostan electrolyte). The sheet steel/cylinder assembly is rotated in each solution in turn for a given length of time (see Table 53 for process solution and variables). Temperatures are maintained inside the cylindrical vessel (where required) by means of thermostatically controlled immersion heaters. Process currents are passed either anodically or cathodically depending on the stage of the process.

The resultant tinplate is in the matt state and this can be further processed by means of a flow-brightening. This apparatus consists of a flowmelter in which the tinplate specimen is clamped between two gold plated contacts and an electrical current passed which heats the steel and is sufficient to melt the tin coating. The sample is then quenched in a water bath producing tinplate of the traditional bright finish.\textsuperscript{197}
<table>
<thead>
<tr>
<th>Coating Film Character</th>
<th>Chromium (μg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin Oxide (mC cm⁻₂)</td>
<td>2-12</td>
</tr>
<tr>
<td>Current Requirements (C m⁻²)</td>
<td>4-5 (cath)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20-50</td>
</tr>
<tr>
<td>pH</td>
<td>9-10</td>
</tr>
<tr>
<td>Electrolyte Class</td>
<td>Na₂CO₃ 10 - 30 g⁻¹</td>
</tr>
<tr>
<td></td>
<td>NaH₂PO₄</td>
</tr>
</tbody>
</table>

TABLE 1: CLASSES OF COMMERCIAL PASSIVATION TREATMENTS FOR TEMPLATES
(After Gabez)
<table>
<thead>
<tr>
<th>Acidity, Z*</th>
<th>Formula</th>
<th>Acidity, Z*</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>MoO$_4^{2-}$</td>
<td>1.33</td>
<td>([Mo$<em>{3.10}^{2-}$])$</em>\infty$</td>
</tr>
<tr>
<td>1.00</td>
<td>[Mo$_{2.07}^{2-}$]</td>
<td>1.40</td>
<td>[Mo$_{5.17}H]^3-$</td>
</tr>
<tr>
<td>1.00</td>
<td>([Mo$<em>{2.07}^{2-}$])$</em>\infty$</td>
<td>1.50</td>
<td>$\alpha$-[Mo$_{8.06}^{6-}$]</td>
</tr>
<tr>
<td>1.14</td>
<td>[Mo$_{7.04}^{6-}$]</td>
<td>1.50</td>
<td>$\beta$-[Mo$_{6.04}^{4-}$]</td>
</tr>
<tr>
<td>1.20</td>
<td>[Mo$_{10.03}^{8-}$]</td>
<td>1.67</td>
<td>[Mo$_{6.09}^{2-}$]</td>
</tr>
<tr>
<td>1.25</td>
<td>[Mo$_{8.06}(OH)_2^{6-}$]</td>
<td>1.78</td>
<td>[Mo$<em>{36.12}(H_2O)</em>{16}^{8-}$]</td>
</tr>
<tr>
<td>1.25</td>
<td>([Mo$<em>{8.07}^{6-}$])$</em>\infty$</td>
<td>1.80</td>
<td>([Mo$_{5.16}H(H_2O)]^{-}\infty$</td>
</tr>
</tbody>
</table>

*NB: Z refers to inflections in a potentiometric titration

**TABLE 2: ISOPOLYMOYDATE ANIONS ISOLATED FROM SOLUTION**

(After Thor Pope$^{80}$)
<table>
<thead>
<tr>
<th>Ratio of hetero atoms to Mo atoms</th>
<th>Principal hetero atoms occurring</th>
<th>Anion formulas</th>
</tr>
</thead>
</table>
| 1:12                             | Series A: P(V), As(V), Si(IV), Ge(IV), Sn(IV)?, Ti(IV), Zr(IV)  
                                     Series B: Ce(IV), Th(IV), Sn(IV)? | [X_{n+}Mo_{12}^{0}0_{40}]^{(8-n)-}  
                                     [X_{n+}Mo_{12}^{0}4_{2}]^{(12-n)-}  
                                     [X_{n+}Mo_{11}^{0}3_{9}]^{(12-n)-}  
                                     (possibly dimeric) |
| 1:11                             | P(V), As(V), Ge(IV)             |                |
| 1.10:                            | P(V), As(V), Pt(IV)             | [X_{n+}Mo_{10}^{0}x_{x}]^{(2x-60-n)-}  
                                     (possibly dimeric) |
| 1:9                              | Mn(IV), Ni(IV)                  | [X_{n+}Mo_{9}^{0}3_{2}]^{(10-n)-} |
| 1:6                              | Te(IV), I(VII), Co(III), Al(III), Cr(III)  
                                     Fe(III), Rh(III) | [X_{n+}Mo_{6}^{0}2_{4}]^{(12-n)-} |
| 2:18                             | P(V), As(V)                     | [X_{2}^{n+}Mo_{18}^{0}6_{2}]^{(16-2n)-} |
| 2:17                             | P(V), As(V)                     | [X_{2}^{n+}Mo_{17}^{0}x_{x}]^{(2x-102-2n)-} |
| 1m:6m                            | Ni(II), Co(II), Mn(II), Cu(II), Se(IV),  
                                     P(III), As(III), P(V) | [X_{n+}Mo_{6}^{0}x_{x}m]^{(2x-36-n)-} |

**TABLE 3: PRINCIPAL TYPES OF HETEROPOLYMOLYBDATES**  
(After Cotton and Wilkinson\textsuperscript{78})
<table>
<thead>
<tr>
<th>Mean oxidation number of Mo</th>
<th>Crystalline</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.76</td>
<td>MoO$_{2.88}$·H$_2$O</td>
<td>MoO$_{2.88}$·xH$_2$O</td>
</tr>
<tr>
<td>5.66</td>
<td></td>
<td>H[Mo$<em>{3}O</em>{9}$]</td>
</tr>
<tr>
<td>5.50</td>
<td>MoO$<em>{2.5}$(OH)$</em>{0.5}$</td>
<td>MoO$_{2.75}$·xH$_2$O</td>
</tr>
<tr>
<td>5.20</td>
<td>MoO$_{2.60}$·xH$_2$O</td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>MoO$_{2.0}$(OH)</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4: "BLUE" OXIDES OF MOLYBDENUM**
(After Cotton and Wilkinson$^{78}$)
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Species</th>
<th>T&lt;sub&gt;L&lt;/sub&gt; - 50* test duration, h</th>
<th>Toxicity ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdate</td>
<td>Rainbow trout</td>
<td>96</td>
<td>7,340</td>
</tr>
<tr>
<td>Chromate</td>
<td>Rainbow trout</td>
<td>96</td>
<td>285</td>
</tr>
<tr>
<td>Molybdate</td>
<td>Daphnia</td>
<td>48</td>
<td>3,220</td>
</tr>
<tr>
<td>Chromate</td>
<td>Daphnia</td>
<td>48</td>
<td>3</td>
</tr>
</tbody>
</table>

* The T<sub>L</sub>-50 results indicate the concentration at which the designated exposure interval produces a mortality rate of 50% in the test population

**TABLE 5: COMPARATIVE ACUTE TOXICITY OF SODIUM MOLYBDATE AND SODIUM DICHROMATE**
(After Robitaille and Bilek<sup>93</sup>)
KEY TO TABLES 6-9 INCLUSIVE

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
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<tr>
<td>GO</td>
<td>Ger. Offen.</td>
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<tr>
<td>JK</td>
<td>Japan Kokai</td>
</tr>
<tr>
<td>JKTK</td>
<td>Japan Kokai Tokkyo Koho</td>
</tr>
<tr>
<td>BUKPA</td>
<td>British UK Patent Application</td>
</tr>
<tr>
<td>B</td>
<td>Brit.</td>
</tr>
<tr>
<td>J</td>
<td>Japan</td>
</tr>
<tr>
<td>EPA</td>
<td>European Patent Application</td>
</tr>
<tr>
<td>AUTHOR(S)</td>
<td>COMPANY</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Fujita</td>
<td>Kiresuto Gityutsu K.K.</td>
</tr>
<tr>
<td>Nishio, Bird</td>
<td>Wright Chem. Corp.</td>
</tr>
<tr>
<td>Saito, Oka,</td>
<td>Nippon Steel Corp</td>
</tr>
<tr>
<td>Katayama, Kamata</td>
<td>Katayama Kagaku Kogyo Kenkyusho Co Ltd</td>
</tr>
<tr>
<td>Kanata, Kanada</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Kanata, Kamata</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Ohta, Sugano</td>
<td>Nitta Chemical Ind Co Ltd</td>
</tr>
<tr>
<td>Sekimoto,</td>
<td>Nippon Steel Corp</td>
</tr>
<tr>
<td>Takayama, Endo</td>
<td>Niishin Steel Co Ltd</td>
</tr>
<tr>
<td>Takayasu, Sato</td>
<td>-</td>
</tr>
<tr>
<td>Kawasaki, Kanada</td>
<td>Katayama Kagaku Kogyo Kenkyusho Co Ltd</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Takayasu, Sato</td>
<td>-</td>
</tr>
<tr>
<td>Ikeuchi, Kino</td>
<td>Nitta Kako K.K.</td>
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<tr>
<td>Okubo, Miki,</td>
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<tr>
<td>Lipinski</td>
<td>Mogul Corp.</td>
</tr>
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<td>Takasaki, Hirano,</td>
<td>Kurita Water Industries Ltd; Chiyoda Kagaku Kenkyusho</td>
</tr>
<tr>
<td>Maeda</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Amax Inc</td>
</tr>
<tr>
<td>Ita, Tanno,</td>
<td>Hitachi Ltd</td>
</tr>
<tr>
<td>Yamaguchi</td>
<td></td>
</tr>
<tr>
<td>Freudlinger,</td>
<td>Signl Elektrographit GmbH</td>
</tr>
<tr>
<td>Hirschvogel</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Inventor(s)</td>
<td>Institution</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Harris, Zalucha, Seasmith, Hornaman</td>
<td>-</td>
</tr>
<tr>
<td>Kawasaki, Asano, Kanada, Katayama</td>
<td>Katayama Kagaku Kogyo Kenkyusho Co Ltd</td>
</tr>
<tr>
<td>Noda, Nakai, Sasaki, Kanna</td>
<td>Yushiro Chemical Industry Co Ltd</td>
</tr>
<tr>
<td>Suzuki</td>
<td>Quatic Chemicals Ltd</td>
</tr>
<tr>
<td>-</td>
<td>Katayama Kagaku Kogyo Kenkyusho Co Ltd</td>
</tr>
<tr>
<td>Senior, Corke</td>
<td>Raychem Ltd</td>
</tr>
<tr>
<td>Gray, Waller</td>
<td>Metallgesellschaft A-G</td>
</tr>
<tr>
<td>Lipinski</td>
<td>Mogul Corp</td>
</tr>
<tr>
<td>Freudlinger, Hirschvogel</td>
<td>Sigri Elektographit GmbH</td>
</tr>
<tr>
<td>Pelikan, Horejs, Smrz, Vosta</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>Suntitomo Metal Inds Ltd</td>
</tr>
<tr>
<td>Vukasovich, Robbattile</td>
<td>Amex Inc</td>
</tr>
<tr>
<td>-</td>
<td>Katayama Chemical Works Co Ltd</td>
</tr>
<tr>
<td>Suzuki</td>
<td>-</td>
</tr>
<tr>
<td>Suzuki</td>
<td>-</td>
</tr>
<tr>
<td>Foroulis, Feather, Sky, Hays, Chung</td>
<td>Exxon Research and Eng. Co.</td>
</tr>
<tr>
<td>-</td>
<td>Kurita Water Industries Ltd</td>
</tr>
<tr>
<td>Company</td>
<td>Application</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Kurita Water Industries Ltd</td>
<td>Mild steel in tap water</td>
</tr>
<tr>
<td>Sanyo Chemical Inds</td>
<td><strong>Similar to JKTK JP 58,171,576</strong></td>
</tr>
<tr>
<td>Showa Denko K.K.</td>
<td>SS-41 steel sheets tested in boiling mixture</td>
</tr>
<tr>
<td>Otsuka Chemical Co Ltd</td>
<td>Aluminium alloy engines</td>
</tr>
<tr>
<td>Matsushita Electrical Ind Co Ltd</td>
<td>Inhibitor for stainless steel case in Li-MnO₂ battery</td>
</tr>
<tr>
<td>Sanyo Electric Co Ltd, Tokyo Sanyo Electric Co Ltd</td>
<td>Absorption refrigerator, prevents dissolution of Fe and Cu</td>
</tr>
<tr>
<td>Katsayama Chemical Works Ltd</td>
<td>Soft water boilers</td>
</tr>
<tr>
<td>Katayama, Asano, Marugame, Kanada, Kawasaki</td>
<td>Mild steel sheet tested</td>
</tr>
<tr>
<td>Engelhardt, Ventura</td>
<td>Corrosion preventing antifreeze solution</td>
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**TABLE 6:** PATENTED DEVELOPMENTS OF MOLYBDATE CONTAINING INHIBITORS
<table>
<thead>
<tr>
<th>AUTHOR(S)</th>
<th>COMPANY</th>
<th>NOTES</th>
<th>MOLYBDATE CONSTITUENT</th>
<th>PATENT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burden</td>
<td>Metallgesellschaft A-G</td>
<td>Phosphatizing of steel, Zn or Al</td>
<td>Preferable use of NH₄⁺ molybdate as accelerator</td>
<td>GO 1,900,527</td>
</tr>
<tr>
<td>Iwamiya, Sotoyama, Haekita, Matsumoto</td>
<td>Nippon Steel Co Ltd</td>
<td>Plating solution for stainless steel</td>
<td>(NH₄)₂MoO₄, 13-50 g/l, pH 8.5-9.5</td>
<td>J. 73 27,181</td>
</tr>
<tr>
<td>Ohishi, Sakamoto, Inada</td>
<td>Dipsolu Co Ltd</td>
<td>Black dyeing agent for iron for improved corrosion resistance</td>
<td>(NH₄)₂MoO₄ e.g. solution could include 25 g/l at room temperature</td>
<td>J. 73 24,138</td>
</tr>
<tr>
<td>Hoshino, Hameda</td>
<td>-</td>
<td>Anodically oxidised corrosion resistant black coating on Fe, Cu and Cu alloys</td>
<td>Na₂MoO₄·2H₂O 2-10 g/l, 50°C</td>
<td>JK 74 31,549</td>
</tr>
<tr>
<td>Okada, Hosoi, Yamamoto, Ito</td>
<td>Nippon Steel Corp.</td>
<td>Increase corrosion resistance of Mo free stainless steel by passivating or overpassivating in solution of Mo²⁺</td>
<td>Mo³⁺ solution e.g. anodisation in 5% H₂SO₄ solution containing 0.2 g/l H₂MoO₄</td>
<td>J. 74 13,703</td>
</tr>
<tr>
<td>Matsumoto, Ohishi, Sakamoto, Dipsolu Co Ltd</td>
<td>Dai Nippon Toryo Co Ltd</td>
<td>Corrosion resistant coating for steel</td>
<td>Possible use of (phospho) molybdates</td>
<td>GO 2,518,275</td>
</tr>
<tr>
<td>Uchida</td>
<td>Uemura Kogyo Co Ltd</td>
<td>Colouring for copper and its alloys</td>
<td>Possible use of molybdate acid, e.g. copper in 35°C solution containing sodium orthomolybdate</td>
<td>JK 76,144,346</td>
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<tr>
<td>Kronstein</td>
<td>Int. Lead Zinc Research Org. Inc.</td>
<td>Phosphatisation solution</td>
<td>Contains MoO₃</td>
<td>US 4,233,088</td>
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<tr>
<td>-</td>
<td>Kobe Steel Ltd</td>
<td>Rustproofing of galvanised steel</td>
<td>Includes molybdate acid/molybdate e.g. 132 g/l K₂MoO₄, pH2</td>
<td>JKT 82,05,875</td>
</tr>
<tr>
<td>-</td>
<td>Mitsubishi Motors Corp</td>
<td>Black film on substrate e.g. Al</td>
<td>Possible use of molybdate</td>
<td>JKT JP 82,70,287</td>
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<tr>
<td>-</td>
<td>UOP Inc</td>
<td>Corrosion preventing compositions</td>
<td>Salts of molybdenum, e.g. Cu, steel coupons treated in solution including 10 ppm aqueous solution of sodium molybdate</td>
<td>JKT JP 82,41,381</td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>Treating metal surfaces to improve corrosion resistance</td>
<td>Chromate based but requires oxidising agent, list includes molybdenum compounds</td>
<td>BUKPA GB 2,097,024</td>
</tr>
</tbody>
</table>

TABLE 7: MISCELLANEOUS COATING APPLICATIONS FOR MOLYBDATE
<table>
<thead>
<tr>
<th>AUTHOR(S)</th>
<th>COMPANY</th>
<th>PAINT DETAILS</th>
<th>MOLYBDATE CONSTITUENT</th>
<th>PATENT NUMBER</th>
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</thead>
<tbody>
<tr>
<td>Kronstein</td>
<td>Oakite Prods Inc</td>
<td>Adherent conversion coating containing poly(acrylic acid) latex</td>
<td>Zinc molybdate, molybdates and/or MoO₃</td>
<td>US 3,528,860</td>
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<tr>
<td>Kirkpatrick, Nilles</td>
<td>Sherwin-Williams Co</td>
<td>Corrosion resistant paints</td>
<td>x ZnOₐMo₃</td>
<td>US 3,677,783</td>
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<tr>
<td>Moore, Robitaille</td>
<td>American Metal Climax Inc</td>
<td>Anticorrosive pigments for steel</td>
<td>Calcium or zinc molybdate</td>
<td>GO 2,200,654</td>
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<tr>
<td>Sera, Kasari</td>
<td>Kansai Paint Co Ltd</td>
<td>Non-toxic, flowable, electrophoretic compounds</td>
<td>Alkaline earth molybdate</td>
<td>GO 2,416,789</td>
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<tr>
<td>Nikaidom Shirai, Iihashi, Umemoto</td>
<td>Kansai Paint Co Ltd, Fuji Sash Industries Ltd</td>
<td>On bccomite (Al) electrocoating formulated with resin solution</td>
<td>Contains salt of molybdic acid</td>
<td>GO 2,426,281</td>
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<tr>
<td>Shibasaki, Tsuchiya, Michikawa</td>
<td>Kikuchi Pigment Mfg Co Ltd</td>
<td>Anticorrosive pigments</td>
<td>Complexes (K₂Oₓ.xMoO₃.yMoO₃; ZP₂O₅.nH₂O)</td>
<td>JK 75,119,833</td>
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<tr>
<td>Yamagishi, Murao, Tsutsumi</td>
<td>Nippon Kokan K.K.</td>
<td>For steel sheets, epoxy resin acrylate maleate or phosphate solutions</td>
<td>Ammonium molybdate</td>
<td>GO 2,526,980</td>
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<tr>
<td>Kirkpatrick, Nilles</td>
<td>Sherwin-Williams Co.</td>
<td>Corrosion resistant pigments</td>
<td>Zinc molybdate</td>
<td>Can 974,734</td>
</tr>
<tr>
<td>Ito, Komatsu</td>
<td>Dai Nippon Toryo Co Ltd</td>
<td>For steel</td>
<td>Possible alkaline metal or ammonium salt of molybdic acid</td>
<td>JK 76 73,533</td>
</tr>
<tr>
<td>Ito, Komatsu</td>
<td>Dai Nippon Toryo Co Ltd</td>
<td>Similar to JK 76 73,533</td>
<td></td>
<td>JK 76 73,534</td>
</tr>
<tr>
<td>Vukasovich, Sullivan</td>
<td>Amax Inc</td>
<td>Acrylic co-polymer, non-toxic pigments</td>
<td>Calcium molybdate</td>
<td>US 4,017,315</td>
</tr>
<tr>
<td>Ito, Kogure</td>
<td>Kansai Paint Co Ltd</td>
<td>Inorganic coating composition</td>
<td>Alkaline metal or ammonium salts of molybdenum</td>
<td>JK 77 38,544</td>
</tr>
<tr>
<td>Fukagawa</td>
<td>Chugoku Marine Paints Ltd</td>
<td>Polyester resin</td>
<td>Molybdenum acid compounds</td>
<td>JK 77 65,527</td>
</tr>
<tr>
<td>Matsuda, Urushibara, Saito</td>
<td>Kansai Paint Co Ltd</td>
<td>Aqueous dispersion</td>
<td>Possible molybdate</td>
<td>JK 77 90,435</td>
</tr>
<tr>
<td>Ito, Kogure</td>
<td>Kansai Paint Co Ltd</td>
<td>Water-thinned anticorrosive coating materials</td>
<td>Possible molybdate</td>
<td>JK 77 89,136</td>
</tr>
<tr>
<td>Mita, Maruyama, Mika</td>
<td>Sankin Speciality Paint Co Ltd</td>
<td>Anti-corrosive primer</td>
<td>Possible zinc molybdate</td>
<td>JK 77 86,425</td>
</tr>
<tr>
<td>Takase, Tsuji, Fukuda, Miyamoto</td>
<td>Dainippon Toryo Co Ltd</td>
<td>Corrosion preventing primer material</td>
<td>Possible molybdate</td>
<td>GO 2,716,588</td>
</tr>
<tr>
<td>Nishimoto, Murakami</td>
<td>Chugoku Marine Paints Ltd</td>
<td>Zinc-containing shop primers for steel</td>
<td>Molybdenum compounds</td>
<td>JK 77,111,933</td>
</tr>
<tr>
<td>Matsuda, Nurihara, Nonoshita</td>
<td>Kansai Paint Co Ltd</td>
<td>Water-thinned anticorrosion primers</td>
<td>Possible molybdate</td>
<td>JK 77,130,444</td>
</tr>
<tr>
<td>Name</td>
<td>Company/Institution</td>
<td>Application</td>
<td>Molybdate Type</td>
<td>Patent Number</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>---------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Blachowicz, Kokietek, Kodura, Stencil</td>
<td>-</td>
<td>Pre-paint wash</td>
<td>Ammonium molybdate</td>
<td>Pol 96,547</td>
</tr>
<tr>
<td>Takase, Tsuji, Fukuda, Hiyamori</td>
<td>Dainippon Toryo Co Ltd</td>
<td>Anticorrosion coating composition</td>
<td>Molybdates</td>
<td>JK 78 63,440</td>
</tr>
<tr>
<td>Sole, Vallyy</td>
<td>Colores Hispania SA</td>
<td>Anti-corrosive zinc molybdate based pigments</td>
<td>MoO$_3$·nZnO</td>
<td>Spain 485,461</td>
</tr>
<tr>
<td>Yamamoto, Okai, Oda</td>
<td>Nippon Paint Co Ltd</td>
<td>Protection of steel against hydrogen embrittlement. Natural or synthetic resin</td>
<td>Possible MoO$_3$</td>
<td>GO 3,438,506</td>
</tr>
</tbody>
</table>
| -                           | Toshiba Corp.                 | Coatings for self-cleaning oven frames                                       | 30% MoO$_2$                     | JKTG          

|               |                              |                                                                              |                                 |               |

**Table 8: Applications of Molybdate in Paint and Pigment Formulations**
<table>
<thead>
<tr>
<th>AUTHOR(S)</th>
<th>COMPANY</th>
<th>NOTES</th>
<th>MOLYBDATE CONSTITUENT</th>
<th>PATENT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dorsey</td>
<td>-</td>
<td>Anodising solution</td>
<td>Ammonium paramolybdate e.g. 17.6 g/l</td>
<td>GO 2,062,507</td>
</tr>
<tr>
<td>Fassell</td>
<td>Philco-Ford Corp.</td>
<td>Duplex sealing process for anodised aluminium</td>
<td>Possible use of molybdate</td>
<td>US 3,852,124</td>
</tr>
<tr>
<td>Pitton</td>
<td>Swiss Aluminium Ltd</td>
<td>Black, corrosion resistant conversion coating</td>
<td>(NH₄)₆Mo₇O₂₄ e.g. 5% in a processing solution</td>
<td>GO 2,419,819</td>
</tr>
<tr>
<td>Nikaido, Shrai, Ishi, and Unemoto</td>
<td>Kansai Paint Co Ltd</td>
<td>Anodic treatment of Al and Al alloys</td>
<td>Possible use of molybdate e.g. 10 parts of calcium molybdate to 90 parts water</td>
<td>JK 75,79,443</td>
</tr>
<tr>
<td>Tanaka and Iriya</td>
<td>Nikkei Aluminium Co Ltd</td>
<td>Beige colouring of aluminium and its alloys by electrolys</td>
<td>e.g. (NH₄)₆Mo₇O₂₄ at 8 g/l and AC voltage after conventional anodising</td>
<td>JK 75,109,835</td>
</tr>
<tr>
<td>Reinhold</td>
<td>Amchem Products Inc</td>
<td>Conversion coating for aluminium and its alloys</td>
<td>Can include for example, 0.475 g/l molybdic acid (84% MoO₃)</td>
<td>US 4,146,410</td>
</tr>
<tr>
<td>Saruwata, Ishika, Maeszima, and Kyota</td>
<td>Fujikura Cable Works</td>
<td>Cathodic treatment for anodised aluminium or its alloys</td>
<td>Colouring solution can include for example 10g ammonium molybdate, pH 4</td>
<td>JKTK 80 06,448</td>
</tr>
<tr>
<td>Reinhold</td>
<td>Amchem Products Inc</td>
<td>Chromium conversion coating for aluminium surfaces</td>
<td>Includes 56% MoO₃ (as Mo) at 0.02-3 g/l</td>
<td>GO 2,854,355</td>
</tr>
<tr>
<td>Reinhold</td>
<td>Amchem Products Ltd</td>
<td>Conversion coating of aluminium</td>
<td>For example solution can include 9.5 g/l molybdic acid, pH 1.5</td>
<td>BUKPA 2,036,807</td>
</tr>
<tr>
<td>Chatterjee</td>
<td>British Aluminium Co Ltd</td>
<td>Brightening of aluminium and italloy surfaces</td>
<td>1-6 g/l per 100 ml of molybdic acid</td>
<td>B. 1,582,134</td>
</tr>
<tr>
<td>-</td>
<td>Dipsol K.K.</td>
<td>Anodisation with colouring of aluminium and its alloys</td>
<td>Can include molybdates</td>
<td>JKTK JP 59 16,994</td>
</tr>
</tbody>
</table>

**TABLE 9: APPLICATIONS OF MOLYBDATE IN THE COATING OF ALUMINIUM**
<table>
<thead>
<tr>
<th>Authors</th>
<th>Type of Tin Electrode</th>
<th>Pretreatment Method</th>
<th>Thesis Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.M. Brasher and J.E. Rhoades-Brown</td>
<td>Foil</td>
<td>Degreased in A.R. benzene, stored in dessicator for at least one day, then abraded with wet pumice and linen</td>
<td>121</td>
</tr>
<tr>
<td>A. Ragheb and L.A. Kamel</td>
<td>Rods</td>
<td>Polished with different grades of emery paper</td>
<td>158</td>
</tr>
<tr>
<td>S.C. Britton and J.C. Sherlock</td>
<td>Tin metal, tinplate (both electrodeposited and hot dipped)</td>
<td>Cathodically cleaned in 1% sodium carbonate solution at room temperature</td>
<td>55</td>
</tr>
<tr>
<td>J.C. Sherlock and S.C. Britton</td>
<td>Tin electrodes, 99.99% pure</td>
<td>Lightly etched in acid, rinsed and dried. Then cathodically cleaned in 1% sodium carbonate solution, rinsed in distilled water and dried</td>
<td>198</td>
</tr>
<tr>
<td>M. Pugh, L.M. Warner and D.R. Gabe</td>
<td>Anal-R tin electrodes</td>
<td>Polished on successive grades of emery paper, followed by fast-cutting alumina</td>
<td>178</td>
</tr>
<tr>
<td>N.A. Darwish and S. Fateen</td>
<td>Spec pure tin electrodes</td>
<td>Polished with 0.00 and 0.000 emery paper, degreased with acetone, and then washed in bidistilled water</td>
<td>199</td>
</tr>
<tr>
<td>B.N. Stirrup and N.A. Hampson</td>
<td>Annealed tin, 99.999% pure</td>
<td>Polished on roughened glass</td>
<td>200</td>
</tr>
<tr>
<td>S.N. Shah and D. Eurof Davies</td>
<td>99.9999% pure tin</td>
<td>Degreased in A.R. benzene in a Soxhlet apparatus. Cathodic cleaned in open beaker of 0.1N sodium carbonate solution with Pt gauze anode C.d 5 mA/cm², each face turned towards anode for 7 mins</td>
<td>173</td>
</tr>
<tr>
<td>S.N. Shah and D. Eurof Davies</td>
<td>Tin foil, 99.9999% pure</td>
<td>Vapour degreased with AR benzene in a Soxhlet apparatus</td>
<td>201</td>
</tr>
<tr>
<td>D.R. Gabe and P. Sripatr</td>
<td>High purity tin rods cut into discs</td>
<td>Polished in emery paper, finished with n-Al₂O₃</td>
<td>202</td>
</tr>
<tr>
<td>D. Bijimi and D.R. Gabe</td>
<td>0.1 mm thick tin foil</td>
<td>Cathodically cleaned in 13 g/l sodium carbonate solution at 40°C, for 30 secs at 25 mA/cm², rinsed, dried</td>
<td>40</td>
</tr>
<tr>
<td>D. Bijimi and D.R. Gabe</td>
<td>0.1 mm thick tin foil</td>
<td>Pickled in 5% nitric acid for 2 mins, rinsed in deionised water, dried in acetone and hot air. The oxide film formed was deemed to be thin and thought to form a reproducible surface</td>
<td>45</td>
</tr>
<tr>
<td>G.D. Wilcox and D.R. Gabe</td>
<td>0.1 mm thick tin foil</td>
<td>Cathodically cleaned in 40 g/l sodium carbonate solution at 65-77°C and 6 mA/cm² for 5 mins on each face</td>
<td>43,203</td>
</tr>
<tr>
<td>K.K. Chew</td>
<td>Tin rod, rolled into sheet (0.048 cm thick)</td>
<td>Immersed in 15% tri-sodium phosphate at boiling for ten mins. Rinsed with water, abraded manually with fine emery, rinsed with deionised water, acetone</td>
<td>171</td>
</tr>
<tr>
<td>S. Wolynec</td>
<td>Tin discs</td>
<td>Abraded 150 sec with α-alumina, 30 sec with γ-alumina, washed under running water, then acetone</td>
<td>176,204</td>
</tr>
<tr>
<td>Immersion Time /mins</td>
<td>Surface Appearance at Given Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20°C</td>
<td>40°C</td>
<td>60°C</td>
</tr>
<tr>
<td>1</td>
<td>Grey-blue, matt</td>
<td>Mottled grey and olive</td>
<td>Grey and brown</td>
</tr>
<tr>
<td>2</td>
<td>Grey-blue, matt</td>
<td>Mottled grey and olive</td>
<td>Grey and darker brown</td>
</tr>
<tr>
<td>3</td>
<td>As before but gold-brown at edge</td>
<td>Mottled grey and olive</td>
<td>Mid to dark brown</td>
</tr>
<tr>
<td>4</td>
<td>As before but darker sides</td>
<td>Grey, gold and brown</td>
<td>Dark brown</td>
</tr>
<tr>
<td>5</td>
<td>As before but darker sides</td>
<td>Grey, gold and brown</td>
<td>Dark brown</td>
</tr>
<tr>
<td>10</td>
<td>Gold-brown</td>
<td>Mid-brown and iridescent</td>
<td>Dark brown</td>
</tr>
<tr>
<td>15</td>
<td>Brown-iridescent</td>
<td>Mid to dark brown</td>
<td>Matt black</td>
</tr>
<tr>
<td>20</td>
<td>Brown-iridescent</td>
<td>Dark brown</td>
<td>Matt black</td>
</tr>
<tr>
<td>25</td>
<td>Dark brown, matt</td>
<td>Dark brown</td>
<td>Matt black</td>
</tr>
<tr>
<td>30</td>
<td>Dark brown, iridescent</td>
<td>Dark brown</td>
<td>Matt black</td>
</tr>
</tbody>
</table>

**TABLE 11: SURFACE APPEARANCE OF ZINC SAMPLES WITH IMMERSION TIME IN 5 g/l SODIUM MOLYBDATE SOLUTION, pH5**
<table>
<thead>
<tr>
<th>Immersion Time /mins</th>
<th>Surface Appearance at Given Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>1</td>
<td>Light brown, iridescent</td>
</tr>
<tr>
<td>2</td>
<td>Olive brown, iridescent</td>
</tr>
<tr>
<td>3</td>
<td>Olive brown, iridescent</td>
</tr>
<tr>
<td>4</td>
<td>Mid-brown, iridescent</td>
</tr>
<tr>
<td>5</td>
<td>Mid-brown, iridescent</td>
</tr>
<tr>
<td>10</td>
<td>Dark brown</td>
</tr>
<tr>
<td>15</td>
<td>Very dark brown</td>
</tr>
<tr>
<td>20</td>
<td>Matt black</td>
</tr>
<tr>
<td>25</td>
<td>Matt black</td>
</tr>
<tr>
<td>30</td>
<td>Matt black</td>
</tr>
</tbody>
</table>

x Some powdery areas
• Flaking of coating

TABLE 12: SURFACE APPEARANCE OF ZINC SAMPLES WITH IMMERSION TIME IN 10 g/l SODIUM MOLYBDATE SOLUTION, pH5
<table>
<thead>
<tr>
<th>Immersion Time /mins</th>
<th>Surface Appearance at Given Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>1</td>
<td>Mid-brown</td>
</tr>
<tr>
<td>2</td>
<td>Mid-brown</td>
</tr>
<tr>
<td>3</td>
<td>Mid-brown</td>
</tr>
<tr>
<td>4</td>
<td>Mid-brown</td>
</tr>
<tr>
<td>5</td>
<td>Mid-brown</td>
</tr>
<tr>
<td>10</td>
<td>Darker coating</td>
</tr>
<tr>
<td>15</td>
<td>Darker coating</td>
</tr>
<tr>
<td>20</td>
<td>Darker coating</td>
</tr>
<tr>
<td>25</td>
<td>Darker coating</td>
</tr>
<tr>
<td>30</td>
<td>Darker coating</td>
</tr>
</tbody>
</table>

- Flaking of coating

**TABLE 13**: SURFACE APPEARANCE OF ZINC SAMPLES WITH IMMERSION TIME IN 30 g/1 SODIUM MOLYBDATE SOLUTION, pH5
<table>
<thead>
<tr>
<th>Treatment Solution, Concentration &amp; pH</th>
<th>Solution Temperature and Immersion Time</th>
<th>Surface Appearance After Set Period of Test</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>5 g/l, pH5</strong></td>
<td>20°C, 5 mins</td>
<td>Around 50% of film still intact. Little white corrosion</td>
</tr>
<tr>
<td></td>
<td>40°C, 5 mins</td>
<td>20-40% of film intact</td>
</tr>
<tr>
<td></td>
<td>60°C, 5 mins</td>
<td>80-95% of film intact</td>
</tr>
<tr>
<td><strong>10 g/l, pH5</strong></td>
<td>20°C, 30 mins</td>
<td>Very small amount of white corrosion product</td>
</tr>
<tr>
<td></td>
<td>40°C, 30 mins</td>
<td>More attacked than 40°C and 60°C specimens</td>
</tr>
<tr>
<td></td>
<td>60°C, 4 mins</td>
<td>Least affected of 10 g/l, pH 5 specimens</td>
</tr>
<tr>
<td><strong>30 g/l, pH5</strong></td>
<td>20°C, 5 mins</td>
<td>Little or no surface change</td>
</tr>
<tr>
<td></td>
<td>40°C, 5 mins</td>
<td>As for 24 hrs</td>
</tr>
<tr>
<td></td>
<td>60°C, 5 mins</td>
<td>As for 24 hrs</td>
</tr>
<tr>
<td><strong>5 g/l, pH5 + 1.65 g/l Phenolsulphonic acid</strong></td>
<td>20°C, 1 min</td>
<td>Around 40% of white corrosion product</td>
</tr>
<tr>
<td></td>
<td>20°C, 10 mins</td>
<td>General attack around 60-70% covered with corrosion</td>
</tr>
<tr>
<td></td>
<td>20°C, 30 mins</td>
<td>Still best of group</td>
</tr>
</tbody>
</table>

**TABLE 14:** 3% SALT SPRAY CORROSION TESTS FOR IMMERSION COATED ZINC SPECIMENS FROM 5, 10 AND 30 g/l, pH5 SOLUTIONS AT 20°, 40° AND 60°C
<table>
<thead>
<tr>
<th>Oxy-Anion Solution</th>
<th>pH</th>
<th>Rest Potential/mV vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>Chromate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>-935</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>-577</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>-590</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>-651</td>
</tr>
<tr>
<td>Molybdate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>-883</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>-702</td>
</tr>
<tr>
<td>Tungstate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>-1068</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>-1118</td>
</tr>
</tbody>
</table>

**TABLE 15:** REST POTENTIAL VALUES FOR ZINC SPECIMENS PRIOR TO CATHODIC POLARISATION IN GROUP (VIA) OXY-ANION SOLUTIONS
<table>
<thead>
<tr>
<th>Oxy-anion Solution</th>
<th>pH</th>
<th>0.1M</th>
<th>1.0M</th>
<th>0.1M Aerated</th>
<th>1.0M Aerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromate</td>
<td>5</td>
<td>Dark brown to gold sheen</td>
<td>Silver buff to khaki gold</td>
<td>Buff sheen, 40°C dark brown</td>
<td>Light buff to olive brown</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Buff brown-grey to grey stain</td>
<td>Virtually colourless to dark brown-gold</td>
<td>Mustard sheen - darkening</td>
<td>Buff grey to light mustard</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Dark grey to brown-gold sheen</td>
<td>Grey to buff sheen</td>
<td>Faint buff-brown sheen</td>
<td>Light green-buff</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>Buff brown to grey</td>
<td>Buff sheen, darkening</td>
<td>Dark grey to buff sheen</td>
<td>Light green-buff</td>
</tr>
<tr>
<td>Molybdate</td>
<td>5</td>
<td>Dark brown-iridescent to matt black, very flaky</td>
<td>Dark brown-mustard, to matt black, very flaky</td>
<td>Grey-brown to matt black, very flaky</td>
<td>Matt black, flaky</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Iridescent to mustard and iridescent to matt black, powdery</td>
<td>Smooth matt black to powdery matt black on gold</td>
<td>Patchy grey-blue to matt mid-brown to matt black and powdery</td>
<td>Dark iridescent to black, less flaky</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Dirty iridescent to mustard-iridescent to matt black, powdery</td>
<td>Brown iridescent to dark brown-black to flaky black</td>
<td>Patchy grey-blue/brown to dark mid-brown to very dark brown-black and powdery</td>
<td>Dark iridescent to black, less flaky</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>Iridescent to mustard-iridescent to bright iridescent to dark brown-black, powdery</td>
<td>Mid-brown to powdery matt black</td>
<td>Blue-grey iridescent to gold iridescent to powdery dark brown-black iridescent</td>
<td>Dark brown-iridescent</td>
</tr>
<tr>
<td>Tungstate</td>
<td>5</td>
<td>Buff silver to buff gold and grey staining to buff and black staining</td>
<td>Buff gold tinge and a little dark staining</td>
<td>Iridescent sheen to buff gold to golden brown and black</td>
<td>Matt buff</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Buff gold to grey iridescent to buff gold</td>
<td>Grey to dirty buff</td>
<td>Gold sheen, darkening</td>
<td>Matt blue-grey to gold iridescent</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Dark iridescent buff gold and black staining to light blue-brown and dark brown/black staining to buff gold and black staining</td>
<td>Cleaner buff-silver</td>
<td>Buff-brown stained to brown sheen, black stained to gold stained</td>
<td>Matt gold to blue-grey iridescent</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>Buff gold and black staining to buff gold and iridescent staining</td>
<td>Dirty buff-grey</td>
<td>Grey-gold sheen to increasing gold sheen</td>
<td>Grey-gold buff to dark grey-gold</td>
</tr>
</tbody>
</table>

**TABLE 16: ZINC SURFACE APPEARANCE AFTER CATHODIC POLARISATION. VARIATIONS WITH INCREASING SOLUTION TEMPERATURE**
<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Processing Potential /mV vs SCE</th>
<th>Treatment Time/mins</th>
<th>Approximate Percentage Coverage by Corrosion Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O.1M Oxy-anion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Solution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Chromate</strong></td>
<td>5</td>
<td>-1500</td>
<td>5</td>
<td>20-40</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5-15</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5-20</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>&quot;</td>
<td>&quot;</td>
<td>10-15</td>
</tr>
<tr>
<td><strong>'As pickled'</strong></td>
<td></td>
<td></td>
<td></td>
<td>20-40</td>
</tr>
<tr>
<td><strong>Molybdate</strong></td>
<td>5</td>
<td>-1500</td>
<td>1</td>
<td>50-80</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>&quot;</td>
<td>5</td>
<td>60-75</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>50-75</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>&quot;</td>
<td>&quot;</td>
<td>40-65</td>
</tr>
<tr>
<td><strong>'As pickled'</strong></td>
<td></td>
<td></td>
<td></td>
<td>50-80</td>
</tr>
<tr>
<td><strong>Tungstate</strong></td>
<td>5</td>
<td>-1500</td>
<td>5</td>
<td>5-70</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5-70</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>10-65</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>&quot;</td>
<td>&quot;</td>
<td>10-50</td>
</tr>
<tr>
<td><strong>'As pickled'</strong></td>
<td></td>
<td></td>
<td></td>
<td>60-80</td>
</tr>
</tbody>
</table>

**TABLE 17:** 24-HOUR SALT SPRAY CORROSION TEST RESULTS FOR ZINC METAL SPECIMENS COATED CATHODICALLY IN O.1M OXY-ANION SOLUTIONS
<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Immersion Time /secs</th>
<th>Average Weight Change /mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3</td>
<td>+ 0.2</td>
</tr>
<tr>
<td>&quot;</td>
<td>10</td>
<td>- 0.15</td>
</tr>
<tr>
<td>&quot;</td>
<td>30</td>
<td>+ 0.2</td>
</tr>
<tr>
<td>&quot;</td>
<td>60</td>
<td>+ 0.1</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>- 0.3</td>
</tr>
<tr>
<td>&quot;</td>
<td>10</td>
<td>- 0.4</td>
</tr>
<tr>
<td>&quot;</td>
<td>30</td>
<td>- 0.65</td>
</tr>
<tr>
<td>&quot;</td>
<td>60</td>
<td>- 0.15</td>
</tr>
</tbody>
</table>

**TABLE 18:** WEIGHT CHANGE VERSUS TIME RESULTS FOR ZINC FOIL SPECIMENS IN A 43 g/l (AS Mo) MP-TYPE SOLUTION AT 20°C. AVERAGE OF DUPLICATE TESTS.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Process Type</th>
<th>Potential/mV vs SCE</th>
<th>Immersion time/secs</th>
<th>Fraction of Surface Covered by White Corrosion/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>'As pickled'</td>
<td>-</td>
<td>-</td>
<td>70-90</td>
</tr>
<tr>
<td>Zinc</td>
<td>Immersion</td>
<td>-</td>
<td>3</td>
<td>50-80</td>
</tr>
<tr>
<td>Zinc</td>
<td>&quot;</td>
<td>-</td>
<td>30</td>
<td>60-70</td>
</tr>
<tr>
<td>Zinc</td>
<td>&quot;</td>
<td>-</td>
<td>60</td>
<td>40-50</td>
</tr>
<tr>
<td>Zinc</td>
<td>Electrochemical</td>
<td>-1200</td>
<td>300</td>
<td>50-80</td>
</tr>
<tr>
<td>Zinc</td>
<td>&quot;</td>
<td>-1500</td>
<td>&quot;</td>
<td>50-80</td>
</tr>
<tr>
<td>Zinc</td>
<td>&quot;</td>
<td>-2000</td>
<td>&quot;</td>
<td>50-80</td>
</tr>
<tr>
<td>Zinc</td>
<td>&quot;</td>
<td>-3000</td>
<td>&quot;</td>
<td>50-70</td>
</tr>
<tr>
<td></td>
<td>The following samples were blotted but not rinsed after processing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>'As pickled'</td>
<td>-</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>Zinc</td>
<td>Immersion</td>
<td>-</td>
<td>5</td>
<td>30-50</td>
</tr>
<tr>
<td>Zinc</td>
<td>&quot;</td>
<td>-</td>
<td>10</td>
<td>20-30</td>
</tr>
<tr>
<td>Zinc</td>
<td>&quot;</td>
<td>-</td>
<td>30</td>
<td>40-50</td>
</tr>
</tbody>
</table>

NB: All samples have been duplicate tested

TABLE 19: ASSESSMENT OF 24 HOUR SALTSpray TESTS ON MP-COATED ZINC SPECIMENS
<table>
<thead>
<tr>
<th>Solution and Treatment Conditions, Cathodic Potential -800 mV vs SCE for 2 mins</th>
<th>Surface Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 g/l molybdate, pH 5, 20°C</td>
<td>Grey, slight gold-iridescence</td>
</tr>
<tr>
<td>10 g/l molybdate, pH 3, 20°C</td>
<td>Strong iridescence-red, yellow, green, blue, purple</td>
</tr>
<tr>
<td>10 g/l molybdate, pH 1, 20°C</td>
<td>No visible coating, etched</td>
</tr>
<tr>
<td>10 g/l molybdate, pH 3, 50°C</td>
<td>Very strong iridescence-green, rose, maroon</td>
</tr>
<tr>
<td>10 g/l molybdate, pH 3, 80°C</td>
<td>Matt light-mid brown</td>
</tr>
<tr>
<td>5 g/l molybdate, pH 3, 20°C</td>
<td>Red at edges, yellow-gold</td>
</tr>
<tr>
<td>1 g/l molybdate, pH 3, 20°C</td>
<td>Deep orange-gold</td>
</tr>
</tbody>
</table>

**TABLE 20: APPEARANCE OF COATINGS PRODUCED ON TINPLATE FROM SIMPLE MOLYBDATE SOLUTIONS**
<table>
<thead>
<tr>
<th>Solution and Treatment Parameters</th>
<th>Surface After Sulphide Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After 5 mins</td>
</tr>
<tr>
<td>10 g/l molybdate, pH 5, 20°C</td>
<td>Slight mottling over all of the surface</td>
</tr>
<tr>
<td>10 g/l molybdate, pH 3, 20°C</td>
<td>No change</td>
</tr>
<tr>
<td>10 g/l molybdate, pH 1, 20°C</td>
<td>Stained</td>
</tr>
<tr>
<td>10 α/l molybdate, pH 3, 50°C</td>
<td>Little attack</td>
</tr>
<tr>
<td>10 α/l molybdate, pH 3, 80°C</td>
<td>Little attack</td>
</tr>
<tr>
<td>5 α/l molybdate, pH 3, 20°C</td>
<td>Little attack</td>
</tr>
<tr>
<td>1 α/l molybdate, pH 3, 20°C</td>
<td>Etched</td>
</tr>
</tbody>
</table>

**Table 21:** Sulphide Staining results of coatings on tinplate produced from simple molybdate solutions
<table>
<thead>
<tr>
<th>Tin Foil Coating Potential /mV vs SCE</th>
<th>Weight gain/mg (Average of two separate trials)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1000</td>
<td>+ 0.25</td>
</tr>
<tr>
<td>-1500</td>
<td>+ 0.3</td>
</tr>
<tr>
<td>-2000</td>
<td>+ 0.6</td>
</tr>
<tr>
<td>-2500</td>
<td>+ 0.5</td>
</tr>
<tr>
<td>-3000</td>
<td>+ 0.35</td>
</tr>
<tr>
<td>-3500</td>
<td>+ 0.35</td>
</tr>
<tr>
<td>Immersion only</td>
<td>+ 0.35</td>
</tr>
</tbody>
</table>

**TABLE 22:** WEIGHT GAIN MEASUREMENTS FOR TIN FOIL SPECIMENS IMMERSED FOR 5 MINUTES AT VARYING CATHODIC POTENTIALS IN A 43 g/l (AS Mo) SODIUM MOLYBDATE, pH 1.5 AERATED, MP SOLUTION
<table>
<thead>
<tr>
<th>pH of Solution</th>
<th>5s RT 40</th>
<th>5s 60</th>
<th>30s 40</th>
<th>30s 60</th>
<th>1m RT 40</th>
<th>1m 60</th>
<th>10m RT 40</th>
<th>10m 60</th>
<th>30m RT 40</th>
<th>30m 60</th>
<th>60m RT 40</th>
<th>60m 60</th>
<th>Time /°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3.5</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2/3</td>
<td>3/4</td>
<td>2</td>
<td>5</td>
<td>4/5</td>
<td>2</td>
<td>5</td>
<td>+</td>
</tr>
<tr>
<td>pH 2.5</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>+</td>
<td>4/5</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>pH 1.5</td>
<td>2</td>
<td>1</td>
<td>1/2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1/2</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>3</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

**KEY**

0   No coating apparent  
1   Brown patches  
2   Faint gold/iridescent coating  
3   Light gold coating  
4   Medium gold coating  
5   Good, strong gold coating  
+  Gold with grey patches  
*  Etched

**TABLE 23:** Coatings formed on tin foil from an MP-type solution containing 43 g/l (as Mo) sodium molybdate and adjusted to the pHs indicated with 88% orthophosphoric acid.
<table>
<thead>
<tr>
<th>Specimen Immersion Time/secs</th>
<th>Surface Colouration Prior to Testing</th>
<th>Surface Colouration after sulphide stain test at Loughborough test time: 30 mins</th>
<th>Surface Colouration after sulphide stain test at ITRI test time: 15 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Cathodic clean only</td>
<td>Etched, stained light grey</td>
<td>Etched, dark grey</td>
</tr>
<tr>
<td>5</td>
<td>Light gold surface</td>
<td>No etching, little or no staining, good gold colour remaining</td>
<td>20-30% stained. Gold colour still apparent in remaining areas</td>
</tr>
<tr>
<td>30</td>
<td>Good gold surface</td>
<td>&quot;</td>
<td>Less than 10% staining. Good colour retention</td>
</tr>
<tr>
<td>60</td>
<td>Deep gold surface</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>600</td>
<td>Grey-gold surface, gold is patchy</td>
<td>Stained pink-blue</td>
<td>Uniformly stained pink-blue</td>
</tr>
</tbody>
</table>

**TABLE 24:** RESULTS OF DUPLICATE SULPHIDE STAIN TESTS CARRIED OUT ON MP-COATED TIN FOIL SPECIMENS AT ITRI AND LOUGHBOROUGH.

**PROCESS SOLUTION:** 43 g/l (as Mo) SODIUM MOLYBDATE, pH 2.5 (with 88% H₃PO₄) 60°C
<table>
<thead>
<tr>
<th>Processing Solution</th>
<th>Immersion Time</th>
<th>Comments on Surface Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 g/l sodium molybdate pH 2.5, 60°C</td>
<td>5 secs</td>
<td>Incomplete gold sheen</td>
</tr>
<tr>
<td></td>
<td>30 secs</td>
<td>Patchy gold and grey sheen</td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>Darker gold but patchy, little coating at edge</td>
</tr>
<tr>
<td></td>
<td>10 mins</td>
<td>Iridescent, red/blue-green</td>
</tr>
<tr>
<td></td>
<td>30 mins</td>
<td>Iridescent, mainly green</td>
</tr>
<tr>
<td></td>
<td>60 mins</td>
<td>Iridescent, red-grey/blue-green</td>
</tr>
<tr>
<td>90 g/l sodium molybdate pH 3.5, 60°C</td>
<td>5 secs</td>
<td>Gold tinge</td>
</tr>
<tr>
<td></td>
<td>30 secs</td>
<td>Darker gold tinge</td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>Darker than 30 secs sample</td>
</tr>
<tr>
<td></td>
<td>10 mins</td>
<td>As 1 min</td>
</tr>
<tr>
<td></td>
<td>30 mins</td>
<td>Good gold coating</td>
</tr>
<tr>
<td></td>
<td>60 mins</td>
<td>Except for base, strong gold-red iridescence</td>
</tr>
<tr>
<td>90 g/l sodium molybdate pH 2.5, 60°C</td>
<td>5 secs</td>
<td>Slight gold sheen</td>
</tr>
<tr>
<td></td>
<td>30 secs</td>
<td>Darker gold, but incomplete coverage</td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>Gold-green sheen</td>
</tr>
<tr>
<td></td>
<td>10 mins</td>
<td>Mottled gold-iridescence</td>
</tr>
<tr>
<td></td>
<td>30 mins</td>
<td>Green plus a little iridescence</td>
</tr>
<tr>
<td></td>
<td>60 mins</td>
<td>Dark gold to green tinge</td>
</tr>
<tr>
<td>90 g/l sodium molybdate pH 2.5, 80°C</td>
<td>5 secs</td>
<td>Mottled gold-brown iridescence</td>
</tr>
<tr>
<td></td>
<td>30 secs</td>
<td>Very light grey-gold. More gold at base</td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>Green-gold iridescence</td>
</tr>
<tr>
<td></td>
<td>10 mins</td>
<td>Darker gold-red-gold iridescence</td>
</tr>
<tr>
<td></td>
<td>30 mins</td>
<td>As 30 mins, but more green</td>
</tr>
<tr>
<td></td>
<td>60 mins</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 25: MP COATINGS FROM SELECTED SOLUTIONS ON 2.8 g/m² TINPLATE
<table>
<thead>
<tr>
<th>Specimen Immersion Time</th>
<th>Surface Before Staining</th>
<th>Surface After Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 secs</td>
<td>Faint mottled gold sheen</td>
<td>Very little difference to untreated tinplate. Widespread staining and etching</td>
</tr>
<tr>
<td>15 secs</td>
<td>As 5 secs</td>
<td>No evidence of any film remaining</td>
</tr>
<tr>
<td>30 secs</td>
<td>Gold tinge</td>
<td>Samples attacked less severely. Some coating still intact</td>
</tr>
<tr>
<td>1 min</td>
<td>Darker gold tinge</td>
<td>Least attacked. Surfaces were light grey with darker grey staining around edges. Pink-blue sheen evident. Some coating intact.</td>
</tr>
<tr>
<td>3 mins</td>
<td>Darker still gold tinge</td>
<td></td>
</tr>
<tr>
<td>5 mins</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 26:** SPECIMENS FORMED BY IMMERION IN AN MP SOLUTION CONTAINING 90 g/1 SODIUM MOLYBDATE, pH 3.5 AT 60°C. TESTED FOR 15 MINS IN A SULPHIDE STAIN TEST

<table>
<thead>
<tr>
<th>Specimen Immersion Time</th>
<th>Surface Before Staining</th>
<th>Surface After Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 secs</td>
<td>Good light gold sheen</td>
<td>Very light grey, slightly etched</td>
</tr>
<tr>
<td>15 secs</td>
<td>As above but a darker</td>
<td>Similar to above</td>
</tr>
<tr>
<td>30 secs</td>
<td>Gold, patchy in colour when held up to the light</td>
<td>Some coating intact, particularly on 1 min sample. Etching on all samples. Light grey in colour</td>
</tr>
<tr>
<td>1 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 mins</td>
<td>Good coating, but mottled when held up to the light</td>
<td>Coating colour reduced. Mottled bluish sheen. Little etching</td>
</tr>
<tr>
<td>5 mins</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 27:** SPECIMENS FORMED BY IMMERION IN AN MP SOLUTION CONTAINING 90 g/1 SODIUM MOLYBDATE, pH 2.5 AT 60°C. TESTED FOR 15 MINS IN A SULPHIDE STAIN TEST
<table>
<thead>
<tr>
<th>Sample and Treatment</th>
<th>Pre-Test Surface Finish</th>
<th>After 5 mins Sulphide Staining</th>
<th>15 mins Staining</th>
<th>30 mins Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 secs</td>
<td>Colourless</td>
<td>Stained and etched</td>
<td>Heavily stained</td>
<td>Heavily stained and badly discoloured</td>
</tr>
<tr>
<td>30 secs</td>
<td>Colourless</td>
<td>Stained and etched</td>
<td>Heavily stained</td>
<td>Heavily stained and badly discoloured</td>
</tr>
<tr>
<td>1 min</td>
<td>Colourless</td>
<td>Stained and etched</td>
<td>Heavily stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>5 mins</td>
<td>Colourless</td>
<td>Stained and etched</td>
<td>Heavily stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>10 mins</td>
<td>Colourless</td>
<td>Stained and etched</td>
<td>Heavily stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>30 mins</td>
<td>Colourless</td>
<td>Stained and etched</td>
<td>Heavily stained</td>
<td>Heavily attacked except for a corner of one sample</td>
</tr>
<tr>
<td>Commercially passivated</td>
<td>Colourless</td>
<td>Very little attack</td>
<td>A few patches of attack</td>
<td>Patchy attack</td>
</tr>
<tr>
<td>Cathodically cleaned only</td>
<td>Colourless</td>
<td>Stained and etched</td>
<td>Heavily attacked</td>
<td>Heavily attacked</td>
</tr>
</tbody>
</table>

TABLE 28: SULPHIDE STAIN DATA FOR TINPLATE SPECIMENS ANODICALLY COATED IN THE FOLLOWING MP SOLUTION:

- 10 g/l sodium molybdate
- pH 4 (with 88% orthophosphoric acid)
- 30°C
- + 800 mV vs SCE
- Varying treatment times
<table>
<thead>
<tr>
<th>Sample and Treatment</th>
<th>Pre-Test Surface Finish</th>
<th>After 5 mins Sulphide Staining</th>
<th>15 mins Staining</th>
<th>30 mins Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 secs</td>
<td>Little or no colouration</td>
<td>Etched, slightly less than cathodically cleaned</td>
<td>Etched and stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>30 secs</td>
<td>Slightly patchy gold-brown</td>
<td>Etched, less than 5 secs</td>
<td>Etched and stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>1 min</td>
<td>Stronger patchy gold-brown</td>
<td>Some etching + discolouration</td>
<td>Etched and stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>5 mins</td>
<td>Mottled surface</td>
<td>Discolouration</td>
<td>Stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>10 mins</td>
<td>Mottled surface iridescent sheen</td>
<td>Etched</td>
<td>Etched and stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>30 mins</td>
<td>As above but darker Colourless</td>
<td>Etched</td>
<td>Etched and stained</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>Commercially passivated</td>
<td>Colourless</td>
<td>Slight attack</td>
<td>Patchy attack</td>
<td>Medium attack</td>
</tr>
<tr>
<td>Cathodically cleaned only</td>
<td>Colourless</td>
<td>Etched</td>
<td>Etched and stained</td>
<td>Heavily stained</td>
</tr>
</tbody>
</table>

**TABLE 29: SULPHIDE STAIN DATA FOR TINPLATE SPECIMENS CATHODICALLY COATED IN THE FOLLOWING MP SOLUTION**

- 10 g/l sodium molybdate
- pH 4 (with 88% orthophosphoric acid)
- 20°C
- -2000 mV vs SCE
- Varying treatment times
<table>
<thead>
<tr>
<th>Sample and Treatment</th>
<th>Pre-Test Surface Finish</th>
<th>After 5 mins Sulphide Staining</th>
<th>15 mins Staining</th>
<th>30 mins Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 secs</td>
<td>Generally colourless</td>
<td>Etched</td>
<td>General etching</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>30 secs</td>
<td>Slight gold-brown tinge</td>
<td>Etched</td>
<td>General etching</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>1 min</td>
<td>Mottled gold-brown surface</td>
<td>Etched</td>
<td>Heavily etched</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>5 mins</td>
<td>Heavily mottled</td>
<td>Etched</td>
<td>Heavily etched</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>10 mins</td>
<td>Heavily mottled</td>
<td>Some etching and some coating intact</td>
<td>Heavily etched, very few patches of gold</td>
<td>Heavily etched, a little gold left</td>
</tr>
<tr>
<td>30 mins</td>
<td>Heavily mottled</td>
<td>Some etching and some coating intact</td>
<td>Heavy etched but some areas still gold</td>
<td>Etched and stained, some gold left</td>
</tr>
<tr>
<td>Commercially passivated</td>
<td>Colourless</td>
<td>A few patches of staining</td>
<td>Patchy attack</td>
<td>Patchy attack + slight etching</td>
</tr>
<tr>
<td>Cathodically cleaned only</td>
<td>Colourless</td>
<td>Etched</td>
<td>Heavily etched</td>
<td>Heavily stained</td>
</tr>
</tbody>
</table>

**TABLE 30: SULPHIDE STAIN DATA FOR TINPLATE SPECIMENS CATHODICALLY COATED IN THE FOLLOWING MP SOLUTION**

- 10 g/l sodium molybdate
- pH 4 (with 88% orthophosphoric acid)
- 20°C
- -2000 mV vs SCE
- Varying treatment times
<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-Test Surface Colouration</th>
<th>Surface Colouration After Given Staining Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>After 5 mins</td>
</tr>
<tr>
<td>As cathodically cleaned</td>
<td>None</td>
<td>Badly etched</td>
</tr>
<tr>
<td>Distilled water rinse and blotted</td>
<td>Slight gold-brown iridescence</td>
<td>Badly etched</td>
</tr>
<tr>
<td>5 mins in oven at 100°C</td>
<td>Slight gold-brown iridescence</td>
<td>Badly etched</td>
</tr>
<tr>
<td>24 hour air dry</td>
<td>Slight gold-brown iridescence</td>
<td>Heavy etching</td>
</tr>
<tr>
<td>1 hour in oven at 100°C</td>
<td>Slight gold-brown iridescence</td>
<td>Heavy etching</td>
</tr>
</tbody>
</table>

**TABLE 31: EFFECT OF DRYING METHODS ON THE SULPHIDE STAIN RESISTANCE OF TINPLATE TREATED IN 10 g/l SODIUM MOLYBDATE, ADJUSTED TO pH 4 WITH 88% H₃PO₄ AT 30°C. IMMERSION FORMED FILMS, 1 min**
<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-Test Surface Colouration</th>
<th>Surface Colouration After Given Staining Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>After 5 mins</td>
</tr>
<tr>
<td>As cathodically cleaned</td>
<td>None</td>
<td>Etched and stained</td>
</tr>
<tr>
<td>Distilled water rinse and blotted</td>
<td>Little or no visible coating</td>
<td>Etched and stained</td>
</tr>
<tr>
<td>5 mins in oven at 100°C</td>
<td>Very pale blue iridescence</td>
<td>Etched and stained</td>
</tr>
<tr>
<td>24 hour air dry</td>
<td>Very pale blue iridescence</td>
<td>Etched but probably least severely</td>
</tr>
<tr>
<td>1 hour in oven at 100°C</td>
<td>Very pale blue iridescence</td>
<td>Etched</td>
</tr>
</tbody>
</table>

**Table 32:** Effect of drying methods on the sulphide stain resistance of tinplate treated in 10 g/l sodium molybdate, adjusted to pH 5 with 88% H₃PO₄ at 30°C. Anodically formed coatings, +800 mV vs SCE for 1 minute.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-Test Surface Colouration</th>
<th>Surface Colouration After Given Staining Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After 5 mins</td>
<td>After 15 mins</td>
</tr>
<tr>
<td>As cathodically cleaned</td>
<td>None</td>
<td>Etched and stained</td>
</tr>
<tr>
<td>Distilled water rinse and blotted</td>
<td>Mottled iridescence</td>
<td>Etched, but not as badly as cathodically cleaned only specimens</td>
</tr>
<tr>
<td>5 mins in oven</td>
<td>Light gold sheen</td>
<td>Etched, but not as badly as cathodically cleaned only specimens</td>
</tr>
<tr>
<td>24 hour air dry</td>
<td>Mottled gold-iridescence</td>
<td>Etched, one quite badly</td>
</tr>
<tr>
<td>1 hour in oven at 100°C</td>
<td>As 24 hour air dry, perhaps a little darker</td>
<td>Stained but not heavily etched, still a little iridescence visible</td>
</tr>
</tbody>
</table>

Table 33: Effect of drying methods on the sulphide stain resistance of tinplate treated in 10 g/l sodium molybdate, adjusted to pH 4 with 88% H₃PO₄ at 30°C. Cathodically formed coatings, -2000 mV vs SCE for 1 minute.
<table>
<thead>
<tr>
<th>Solution: 10 g/l Sodium Molybdate + following additions</th>
<th>pH Before Polarisation Test</th>
<th>Surface Colouration After Polarisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>No addition</td>
<td>8.96</td>
<td>Colourless</td>
</tr>
<tr>
<td>1 g/l Na₃PO₄</td>
<td>12.99</td>
<td>Colourless, slightly more matt</td>
</tr>
<tr>
<td>2 g/l Na₃PO₄</td>
<td>13.22</td>
<td>Slightly buff</td>
</tr>
<tr>
<td>4 g/l Na₃PO₄</td>
<td>13.52</td>
<td>Slightly buff overall, but with some darker patches</td>
</tr>
<tr>
<td>6 g/l Na₃PO₄</td>
<td>13.66</td>
<td>As 4 g/l but slightly more darker patches</td>
</tr>
<tr>
<td>8 g/l Na₃PO₄</td>
<td>13.78</td>
<td>Patchy colouration, possible etching</td>
</tr>
<tr>
<td>10 g/l Na₃PO₄</td>
<td>13.96</td>
<td>Similar to 8 g/l</td>
</tr>
</tbody>
</table>

**Table 34:** Surface Colouration after Anodic Polarisation of Tinplate in a 10 g/l Sodium Molybdate Solution after Various Additions of Tri-Sodium Orthophosphate
<table>
<thead>
<tr>
<th>Solution: 10 g/l Sodium Molybdate + Following Addition:</th>
<th>No addition</th>
<th>1 g/l Na₃PO₄</th>
<th>2 g/l Na₃PO₄</th>
<th>4 g/l Na₃PO₄</th>
<th>6 g/l Na₃PO₄</th>
<th>8 g/l Na₃PO₄</th>
<th>10 g/l Na₃PO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Colouration After Polarisation</td>
<td>Strong gold colouration with slight streaks of dark red</td>
<td>Colourless</td>
<td>Colourless</td>
<td>Colourless</td>
<td>Becoming matt and mottled</td>
<td>Slightly mottled</td>
<td>Mottled</td>
</tr>
</tbody>
</table>

**TABLE 35:** SURFACE COLOURATION AFTER CATHODIC POLARISATION OF TINPLATE IN 10 g/l SODIUM MOLYBDATE SOLUTION AFTER VARIOUS ADDITIONS OF TRI-SODIUM ORTHOPHOSPHATE
<table>
<thead>
<tr>
<th>Treatment No.</th>
<th>Solution</th>
<th>pH</th>
<th>Type of Treatment</th>
<th>Surface Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 g/l sodium molybdate</td>
<td>9</td>
<td>Cathodic: -900 mV vs SCE, 2 mins</td>
<td>Colourless</td>
</tr>
<tr>
<td>2</td>
<td>10 g/l sodium molybdate</td>
<td>9</td>
<td>Immersion: 2 mins</td>
<td>Colourless</td>
</tr>
<tr>
<td>3</td>
<td>10 g/l sodium molybdate</td>
<td>3</td>
<td>Cathodic: -800 mV vs SCE, 2 mins</td>
<td>Strong iridescence</td>
</tr>
<tr>
<td>4</td>
<td>10 g/l sodium molybdate</td>
<td>3</td>
<td>Immersion: 2 mins</td>
<td>Weak gold-iridescence</td>
</tr>
<tr>
<td>5</td>
<td>100 g/l sodium molybdate</td>
<td>9</td>
<td>Cathodic: -1100 mV vs SCE, 2 mins</td>
<td>Gold tinge</td>
</tr>
<tr>
<td>6</td>
<td>100 g/l sodium molybdate</td>
<td>9</td>
<td>Immersion: 2 mins</td>
<td>Colourless</td>
</tr>
<tr>
<td>7</td>
<td>100 g/l sodium molybdate</td>
<td>3</td>
<td>Cathodic: -800 mV vs SCE, 2 mins</td>
<td>Very dark green-red iridescence</td>
</tr>
<tr>
<td>8</td>
<td>100 g/l sodium molybdate</td>
<td>3</td>
<td>Immersion: 2 mins</td>
<td>Strong yellow-gold with iridescence at edges</td>
</tr>
<tr>
<td>9</td>
<td>10 g/l sodium molybdate, 0.5 g/l KN0₃, to pH4 with 88% H₃PO₄</td>
<td>4</td>
<td>Cathodic: -2000 mV vs SCE, 2 mins</td>
<td>Gold mottling on blue iridescence</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>4</td>
<td>Immersion: 2 mins</td>
<td>Possible slight gold sheen</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>4</td>
<td>Anodic: +800 mV vs SCE, 2 mins</td>
<td>Colourless</td>
</tr>
<tr>
<td>12</td>
<td>10 g/l sodium molybdate, 1 g/l tri-sodium orthophosphate</td>
<td>13.2</td>
<td>Cathodic: -2000 mV vs SCE, 2 mins</td>
<td>Colourless</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>13.2</td>
<td>Immersion: 2 mins</td>
<td>Colourless</td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>13.2</td>
<td>Anodic: +1000 mV vs SCE, 2 mins</td>
<td>Colourless</td>
</tr>
</tbody>
</table>

**Table 36:** Appearance of coatings produced on tinplate for final sulphide stain tests.
<table>
<thead>
<tr>
<th>Treatment Number</th>
<th>Surface after Sulphide Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After 5 mins</td>
</tr>
<tr>
<td>1</td>
<td>Stained</td>
</tr>
<tr>
<td>2</td>
<td>Stained</td>
</tr>
<tr>
<td>3</td>
<td>No change</td>
</tr>
<tr>
<td>4</td>
<td>Some staining</td>
</tr>
<tr>
<td>5</td>
<td>Mottled staining</td>
</tr>
<tr>
<td>6</td>
<td>Heavily stained</td>
</tr>
<tr>
<td>7</td>
<td>No change</td>
</tr>
<tr>
<td>8</td>
<td>Slight patchy staining</td>
</tr>
<tr>
<td>9</td>
<td>Some staining</td>
</tr>
<tr>
<td>10</td>
<td>Stained</td>
</tr>
<tr>
<td>11</td>
<td>Stained</td>
</tr>
<tr>
<td>12</td>
<td>Stained</td>
</tr>
<tr>
<td>13</td>
<td>Stained</td>
</tr>
<tr>
<td>14</td>
<td>Stained</td>
</tr>
</tbody>
</table>

TABLE 37: SURFACE APPEARANCE OF OPTIMUM COATING SYSTEMS FOR TINPLATE AFTER SULPHIDE STAINING. (To be used in conjunction with Table 36)
<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Duration of Staining /mins</th>
<th>Sulphide Coulometric Charge, mC/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2.52</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>11.44</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>20.78</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>39.48</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>57.28</td>
</tr>
</tbody>
</table>

**TABLE 38: COULOMETRIC CHARGE OF SULPHIDE PRESENT ON SULPHIDE STAINED UNCOATED TIN FOIL**
<table>
<thead>
<tr>
<th>Treatment Number</th>
<th>Optimum Solution Composition</th>
<th>Average Sulphide Coulometric Charge, mC/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 g/l sodium molybdate, pH 9, cathodic</td>
<td>22.81</td>
</tr>
<tr>
<td>3</td>
<td>10 g/l sodium molybdate, pH 3, cathodic</td>
<td>9.69</td>
</tr>
<tr>
<td>5</td>
<td>100 g/l sodium molybdate, pH 9, cathodic</td>
<td>18.75</td>
</tr>
<tr>
<td>7</td>
<td>100 g/l sodium molybdate, pH 3, cathodic</td>
<td>13.75</td>
</tr>
<tr>
<td>9</td>
<td>10 g/l sodium molybdate, 0.5 g/l KNO₃ to pH 4 with 88% H₃PO₄, cathodic</td>
<td>14.06</td>
</tr>
<tr>
<td>12</td>
<td>10 g/l sodium molybdate, 1 g/l tri-sodium orthophosphate, cathodic</td>
<td>18.75</td>
</tr>
</tbody>
</table>

TABLE 39: AVERAGE COULOMETRIC CHARGE OF SULPHIDE STAIN PRESENT ON TINPLATE SPECIMENS, COATED IN THE OPTIMUM SOLUTIONS, AND CORROSION TESTED IN BOILING 3 g/l CYSTEINE HYDROCHLORIDE (TO BE USED IN CONJUNCTION WITH TABLE 37)
<table>
<thead>
<tr>
<th>Cathode Metal</th>
<th>Current Density mA/cm²</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.0</td>
<td>Arrest point at ~ -1300 mV vs SCE</td>
</tr>
<tr>
<td>Tinplate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>&quot;</td>
<td>10.0</td>
<td>Arrest point at ~ -1450 mV vs SCE</td>
</tr>
</tbody>
</table>

TABLE 40: GALVANOSTATIC TRIALS FOR PLATINUM, ZINC AND TINPLATE IN 100 g/l SODIUM MOLYBDATE PRE-DEAERATED, 20°C, pH 5 (Sn, Zn), pH 3 (Pt)
<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Metal Substrate</th>
<th>Treatment Solution and Process Variables</th>
<th>Film Colouration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tinplate</td>
<td>100 g/l sodium molybdate, pH 5, 20°C, pre-deaerated. Potentiodynamically polarised up to inflection</td>
<td>Flaky black</td>
</tr>
<tr>
<td>2</td>
<td>Tinplate</td>
<td>100 g/l sodium molybdate, pH 5, 20°C, pre-deaerated. Potentiodynamically polarised to after inflection</td>
<td>Flaky black on iridescent</td>
</tr>
<tr>
<td>3</td>
<td>Tinplate</td>
<td>10 g/l sodium molybdate, pH 3, 20°C, pre-deaerated 2 mins at -800 mV vs SCE</td>
<td>Iridescent</td>
</tr>
<tr>
<td>4</td>
<td>Zinc</td>
<td>10 g/l sodium molybdate, pH 3, 20°C, pre-deaerated 2 mins at -1050 mV vs SCE</td>
<td>Light brown</td>
</tr>
<tr>
<td>5</td>
<td>Zinc</td>
<td>10 g/l sodium molybdate, pH 3, 20°C, pre-deaerated, 2 mins at -1050 mV vs SCE</td>
<td>Black</td>
</tr>
<tr>
<td>6</td>
<td>Tin Foil</td>
<td>110 g/l sodium molybdate, to pH 3.5 with 88% orthophosphoric acid, 20 mins immersion</td>
<td>Gold</td>
</tr>
<tr>
<td>7</td>
<td>Tin Foil</td>
<td>110 g/l sodium molybdate, to pH 3.5 with 88% orthophosphoric acid, 60 mins immersion</td>
<td>Grey</td>
</tr>
</tbody>
</table>

**TABLE 41: COATING TREATMENTS FOR TINPLATE, ZINC AND TIN FOIL SPECIMENS EXAMINED BY ESCA**
<table>
<thead>
<tr>
<th>Instrument:</th>
<th>VG ESCALAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background pressure:</td>
<td>$10^{-8}$ mbar</td>
</tr>
<tr>
<td>XPS Analysis Parameters:</td>
<td></td>
</tr>
<tr>
<td>X-ray energy</td>
<td>Al Kα</td>
</tr>
<tr>
<td>Anode voltage</td>
<td>15 kV</td>
</tr>
<tr>
<td>Anode current</td>
<td>20 mA</td>
</tr>
<tr>
<td>Analysis area</td>
<td>0.4 cm²</td>
</tr>
<tr>
<td>Emission angle</td>
<td>Normal</td>
</tr>
<tr>
<td>Pass energy</td>
<td>100, 20 eV</td>
</tr>
<tr>
<td>Count rate</td>
<td>$10^4$ cps⁺</td>
</tr>
<tr>
<td>Ion Beam Parameters:</td>
<td></td>
</tr>
<tr>
<td>Ion species</td>
<td>Ar⁺</td>
</tr>
<tr>
<td>Ion energy</td>
<td>5 keV</td>
</tr>
<tr>
<td>Ion current</td>
<td>20 μA</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>$10^{-5}$ mbar</td>
</tr>
</tbody>
</table>

TABLE 42: EXPERIMENTAL CONDITIONS FOR ESCA INVESTIGATIONS
<table>
<thead>
<tr>
<th>Etch Time (min)</th>
<th>Mo</th>
<th>Sn</th>
<th>C</th>
<th>O</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.0</td>
<td>10.3</td>
<td>19.7</td>
<td>52.9</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>27.1</td>
<td>17.1</td>
<td>9.0</td>
<td>46.7</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>29.0</td>
<td>17.8</td>
<td>12.5</td>
<td>40.7</td>
<td>1</td>
</tr>
<tr>
<td>15</td>
<td>29.5</td>
<td>18.9</td>
<td>10.7</td>
<td>40.9</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>14.4</td>
<td>1.7</td>
<td>36.6</td>
<td>47.3</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>29.6</td>
<td>4.1</td>
<td>9.5</td>
<td>56.8</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>32.7</td>
<td>4.1</td>
<td>10.4</td>
<td>52.8</td>
<td>2</td>
</tr>
</tbody>
</table>

**TABLE 43: ATOMIC COMPOSITION OF ESCA SAMPLES 1 AND 2**
(see also Table 41)

<table>
<thead>
<tr>
<th>Composition (Atom %)</th>
<th>Mo</th>
<th>C</th>
<th>O</th>
<th>Sn</th>
<th>Cl</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.1</td>
<td>42.5</td>
<td>41.5</td>
<td>2.9</td>
<td>0.9</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 44: ATOMIC COMPOSITION OF ESCA SAMPLE 3**
(see also Table 41)
### TABLE 45: ATOMIC COMPOSITION OF ESCA SAMPLES 4 AND 5
(see also Table 41)

<table>
<thead>
<tr>
<th>Composition (Atom %)</th>
<th>C</th>
<th>Mo</th>
<th>Zn</th>
<th>O</th>
<th>Cl</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.1</td>
<td>9.9</td>
<td>13.7</td>
<td>39.3</td>
<td>0.0</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>18.3</td>
<td>6.0</td>
<td>35.5</td>
<td>37.8</td>
<td>2.4</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

### TABLE 46: ATOMIC COMPOSITION OF ESCA SAMPLES 6 AND 7
(see also Table 41)

<table>
<thead>
<tr>
<th>Composition (Atom %)</th>
<th>C</th>
<th>O</th>
<th>Mo</th>
<th>Sn</th>
<th>P</th>
<th>Ca</th>
<th>Na</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.5</td>
<td>33.3</td>
<td>6.0</td>
<td>3.5</td>
<td>9.2</td>
<td>0.8</td>
<td>1.8</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>40.6</td>
<td>38.0</td>
<td>6.1</td>
<td>1.8</td>
<td>9.6</td>
<td>1.1</td>
<td>2.8</td>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>
### TABLE 47: BINDING ENERGIES FOR ESCA SAMPLES 1-7

(See also Table 41)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding Energies/eV</th>
<th>Possible Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>230.0 and 231.1</td>
<td>Mo^{IV}, MoO_{2} and Mo^{V}</td>
</tr>
<tr>
<td>2</td>
<td>231.0</td>
<td>Mo^{V}</td>
</tr>
<tr>
<td>3</td>
<td>231.5</td>
<td>Mo^{V}</td>
</tr>
<tr>
<td>4</td>
<td>230.6 and 231.8</td>
<td>Mo^{V} and Mo^{VI}, MoO_{3}</td>
</tr>
<tr>
<td>5</td>
<td>230.6 and 231.8</td>
<td>Mo^{V} and Mo^{VI}, MoO_{3}</td>
</tr>
<tr>
<td>6</td>
<td>231.9</td>
<td>Mo^{VI}, MoO_{3}</td>
</tr>
<tr>
<td>7</td>
<td>232.1</td>
<td>Mo^{VI}, MoO_{3}</td>
</tr>
</tbody>
</table>

* Measured against C 1s at 284.6 eV
<table>
<thead>
<tr>
<th>Solution Conditions</th>
<th>pH</th>
<th>Approximate Potential at which Inflection(s) Occurred, mV vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>0.1M Still</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-1010, (-1540?)</td>
<td>-1010, (-1580?)</td>
</tr>
<tr>
<td>7</td>
<td>-680, -1120 (-1420?)</td>
<td>-750, -1130 (-1420?)</td>
</tr>
<tr>
<td>9</td>
<td>-810, -1430</td>
<td>-840, -1440</td>
</tr>
<tr>
<td>11</td>
<td>-750, -1430</td>
<td>-720, -1380</td>
</tr>
<tr>
<td>1.0M Still</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-970, (-1640?)</td>
<td>-1010, -1110 (-1750?)</td>
</tr>
<tr>
<td>7</td>
<td>(-710)?, -1090</td>
<td>(-630)?, -1030</td>
</tr>
<tr>
<td>9</td>
<td>-750, -1360</td>
<td>-740, -1320</td>
</tr>
<tr>
<td>11</td>
<td>(-1140)?, -1410</td>
<td>(-1020)?, -1360</td>
</tr>
<tr>
<td>0.1M Aerated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-1000</td>
<td>-1050</td>
</tr>
<tr>
<td>7</td>
<td>(-660)?, -1140</td>
<td>-920, -1120 (-1560?)</td>
</tr>
<tr>
<td>9</td>
<td>-910, -1360 (-1890?)</td>
<td>(-850)?, (-1030)?, -1300, (-2050?)</td>
</tr>
<tr>
<td>11</td>
<td>-850, -1410</td>
<td>-900, -1380</td>
</tr>
<tr>
<td>1.0M Aerated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-980</td>
<td>(-1020)?</td>
</tr>
<tr>
<td>7</td>
<td>-740, -1140</td>
<td>(-610)?, -1130</td>
</tr>
<tr>
<td>9</td>
<td>(-780)?, -1320</td>
<td>(-880)?, -1280</td>
</tr>
<tr>
<td>11</td>
<td>-860, -1350</td>
<td>(-850)?, -1360</td>
</tr>
</tbody>
</table>

**TABLE 48: POTENTIALS AT WHICH INFLECTIONS OCCURRED IN CHROMATE SOLUTIONS**
<table>
<thead>
<tr>
<th>Solution Conditions</th>
<th>pH</th>
<th>Approximate Potential at which Inflection(s) Occurred, mV vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>20°C</strong></td>
</tr>
<tr>
<td><strong>0.1M Still</strong></td>
<td>5</td>
<td>(-1180)?</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>-</td>
</tr>
<tr>
<td><strong>1.0M Still</strong></td>
<td>5</td>
<td>(-1090)?</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-830</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>(-1180)?, (-1480)?</td>
</tr>
<tr>
<td><strong>0.1M Aerated</strong></td>
<td>5</td>
<td>(-1220)?</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>(-900)?</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>(-700)?</td>
</tr>
<tr>
<td><strong>1.0M Aerated</strong></td>
<td>5</td>
<td>(-1040)?</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>(-1040)?, (-1430)?</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>(-980)?, (-1460)?</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>(-740)?</td>
</tr>
</tbody>
</table>

**TABLE 49: POTENTIALS AT WHICH INFLECTIONS OCCURRED IN MOLYBDATE SOLUTIONS**
<table>
<thead>
<tr>
<th>Solution Conditions</th>
<th>pH</th>
<th>Approximate Potential at which Inflection(s) Occurred, mV vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>0.1M Still</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>(-1180)?, (-1380)?</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>-1350</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>-1370</td>
</tr>
<tr>
<td>1.0M Still</td>
<td>5</td>
<td>-1170</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>(-1140)?</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>(-1120)?, -1360</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>(-1240)?, -1390</td>
</tr>
<tr>
<td>0.1M Aerated</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>(-820)?, -1370</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>(-790)?, -1410</td>
</tr>
<tr>
<td>1.0M Aerated</td>
<td>5</td>
<td>(-1130)?</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>(-1150)?, (-1640)?</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>(-780)?</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>(-790)?, -1390</td>
</tr>
</tbody>
</table>

**TABLE 50: POTENTIALS AT WHICH INFLECTIONS OCCURRED IN TUNGSTATE SOLUTIONS**
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Concentration of molybdenum (g/l)</th>
<th>pH Adjustment</th>
<th>pH</th>
<th>Rating of anti-corrosive resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic solution of sodium molybdate</td>
<td>53</td>
<td>Phosphoric acid</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>&quot;</td>
<td>53</td>
<td>&quot;</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>&quot;</td>
<td>53</td>
<td>1.5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Invention</td>
<td>43</td>
<td>&quot;</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>&quot;</td>
<td>43</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>43</td>
<td>1.5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>21</td>
<td>&quot;</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>&quot;</td>
<td>21</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>21</td>
<td>1.5</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Alkaline solution of sodium molybdate</td>
<td>53</td>
<td>Sodium hydroxide</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Comparative Example</td>
<td>Neutral solution of sodium molybdate</td>
<td>53</td>
<td>-</td>
<td>7</td>
</tr>
</tbody>
</table>

**TABLE 51:** ASSESSMENT OF DIFFERENT SODIUM MOLYBDATE BASED TREATMENTS FOR GALVANISED ZINC SURFACES

<table>
<thead>
<tr>
<th>White Rust Formation</th>
<th>Corrosion Resistance Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 1%</td>
<td>5</td>
</tr>
<tr>
<td>2 - 5%</td>
<td>4</td>
</tr>
<tr>
<td>6 - 10%</td>
<td>3</td>
</tr>
<tr>
<td>11 - 50%</td>
<td>2</td>
</tr>
<tr>
<td>51 - 100%</td>
<td>1</td>
</tr>
</tbody>
</table>

**TABLE 52:** CORROSION RATINGS FOR TABLE 51
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Solution Composition</th>
<th>Temperature/°C</th>
<th>Current/A</th>
<th>Time/secs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degrease</td>
<td>300g Gramosol 26 (mainly NaOH)</td>
<td>85-90</td>
<td>40-60</td>
<td>1 anodic</td>
</tr>
<tr>
<td>Hot rinse</td>
<td>-</td>
<td>70-90</td>
<td>-</td>
<td>1 cathodic</td>
</tr>
<tr>
<td>Electrolytic Pickle</td>
<td>125g H₂SO₄ (2.5-3% w/v)</td>
<td>25</td>
<td>15</td>
<td>2 anodic</td>
</tr>
<tr>
<td>Cold rinse</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4 cathodic</td>
</tr>
<tr>
<td>Plating</td>
<td>270g Stannous sulphate 400 ml Phenolsulphonic acid 30g Diphane V</td>
<td>50-55</td>
<td>50</td>
<td>3.2</td>
</tr>
<tr>
<td>Cold rinse</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Sample size: 32.5 cm x 10.3 cm  
Area plated: 31.5 cm x 10.3 cm + (10.7 cm x 2)i esample + clamps  
Flowmeter: ~2000A through sample  
phase angle = 70°  
time = 3 secs  
quenched in water at 60°C  

TABLE 53: TIN PLATING PROCESS VARIABLES AS OPERATED BY ITRI
FIGURE 1: Layers existing on the steel substrate in commercial tinplate. Typical thicknesses produced/µm.

(After ITIR).
FIGURE 2: Cathodic polarisation curve plotted potentiokinetically with pure tin in an aqueous solution of Na₂Cr₂O₇·2H₂O, 0.085M; pH 5.2; temperature 55°C, sweep rate 6V/hr. (Curve shape remains unchanged in the range of: Na₂Cr₂O₇·2H₂O, 0.02-0.25M; temperature 25°C-70°C; sweep rate). 166-60V/hr.

(After Aubrun and Rocquet⁴³)
R.E. - Reference electrode
W.E. - Working electrode
G.B. - Gas bubbler

There were two Pt auxiliary electrodes in front of and behind the W.E. (not shown in figure)

FIGURE 3: Five-necked flask used for polarisation cell

FIGURE 4: Specimen holder
FIGURE 5: Circuit diagram for polarisation apparatus
FIGURE 6: Reaction vessel for sulphide staining

Glass rod
Tall beaker
Coated tinplate specimen
Glass spacer
3 g/l cysteine hydrochloride adjusted to pH7
Heat
Key:  
CCS - Constant current source  
REIC - Reference electrode impedance convertor  
CR - Chart recorder  
V - Voltmeter  
R - Reference electrode  
C - Cathode  
A - Anode

FIGURE 7: Coulometric analysis apparatus, circuit diagram
\[ t = \frac{a + b}{2} \quad \text{NB: HE occurs in area b, hence the time component is divided by 2 (see Section 7.11) (applicable to tin foil only)} \]

\[ Q = It \quad \text{where} \quad I = 0.250 \, \text{mAcm}^{-2} \]

FIGURE 8: Idealised coulometric trace for sulphide stained tin foil and method of computation of sulphide charge
FIGURE 9: Weight gain versus time for zinc foil in 5 g/l sodium molybdate, pH5 at 20°C, 40°C and 60°C.

FIGURE 10: Weight gain versus time for zinc foil in 10 g/l sodium molybdate, pH5 at 20°C, 40°C and 60°C.
FIGURE 11: Weight gain versus time for zinc foil in 30 g/l sodium molybdate, pH5 at 20°C, 40°C and 60°C.

FIGURE 12: Weight gain versus time for zinc foil in 5 g/l sodium molybdate, pH5 at 20°C for 4 hours.
FIGURE 13: Weight gain versus time for zinc foil in 5 g/l sodium molybdate, pH 5 with the addition of 1 g/l L-ascorbic acid at 20°C, 40°C and 60°C.

FIGURE 14: Weight gain versus time for zinc foil in 5 g/l sodium molybdate, pH 5, 20°C. Effect of reducing agents.

No additions
1 g/l L-ascorbic acid
1.7 g/l phenolsulfonic acid
FIGURE 15: Potential versus time curves for zinc foil in 5 g/l sodium molybdate, pH 5 at 20°C, 40°C and 60°C.

FIGURE 16: Potential versus time curves for zinc foil in 10 g/l sodium molybdate, pH 5 at 20°C, 40°C and 60°C.
FIGURE 17: Potential versus time curves for zinc foil in 30 g/l sodium molybdate, pH5 at 20°C, 40°C and 60°C.

FIGURE 18: Potential versus time curves for zinc foil in 5 g/l sodium molybdate, pH5, 20°C. Effect of reducing agents.
Rest potential/mV vs SCE
20°C - -577
40°C - -591
60°C - -549

FIGURE 20: Cathodic polarisation of zinc in 0.1M, still sodium chromate solution, pH7, 20°C, 40°C and 60°C
FIGURE 21: Cathodic polarisation of zinc in 0.1M, still sodium chromate solution, pH9, 20°, 40° and 60°C

Rest potential/mV vs SCE
20°C  -590
40°C  -570
60°C  -579
FIGURE 22: Cathodic polarisation of zinc in 0.1M, still sodium chromate solution, pH11, 20°, 40° and 60°C
Rest potential/mV vs SCE

20°C - -703
40°C - -684
60°C - -628

FIGURE 24: Cathodic polarisation of zinc in 0.1M, still sodium molybdate solution, pH7, 20°C, 40°C and 60°C
FIGURE 25: Cathodic polarisation of zinc in 0.1M, still sodium molybdate solution, pH9, 20°C, 40°C and 60°C
FIGURE 26: Cathodic polarisation of zinc in 0.1M, still sodium molybdate solution, pH1, 20, 40, and 60°C.
FIGURE 28: Cathodic polarisation of zinc in 0.1M, still sodium tungstate solution, pH7, 20°, 40° and 60°
FIGURE 29: Cathodic polarisation of zinc in 0.1M, still sodium tungstate solution, pH9, 20°C, 40°C and 60°C.

Rest potential/mV vs SCE
20°C = -933
40°C = -900
60°C = -871

Current Density/mA cm⁻²
0.1
0.01
0.001

Overpotential/V
FIGURE 30: Cathodic polarisation of zinc in 0.1M, still sodium tungstate solution, pH11, 20°C, 40°C and 60°C.
FIGURE 31: Cathodic polarisation of zinc in 1.0M, still sodium chromate solution, pH 5, 20°, 40° and 60°C
FIGURE 32: Cathodic polarisation of zinc in 1.0M, still sodium chromate solution, pH7, 20°, 40° and 60°C.
FIGURE 33: Cathodic polarisation of zinc in 1.0M, still sodium chromate solution, pH9, 20°C, 40°C and 60°C
FIGURE 34: Cathodic polarisation of zinc in 1.0M, still sodium chromate solution, pH11, 20°, 40° and 60°.
Rest potential/mV vs SCE

20°C  -  -948
40°C  -  -944
60°C  -  -830

FIGURE 35: Cathodic polarisation of zinc in 1.0M, still sodium molybdate solution, pH5, 20°C, 40°C and 60°C
Rest potential/mV vs SCE

20°C - -686
40°C - -654
60°C - -628

FIGURE 36: Cathodic polarisation of zinc in 1.0M, still sodium molybdate solution, pH7, 20°C, 40°C and 60°C
Rest potential/mV vs SCE

20°C - -732
40°C - -604
60°C - -554

FIGURE 37: Cathodic polarisation of zinc in 1.0M, still sodium molybdate solution, pH9, 20°C, 40°C, and 60°C
Rest potential/mV vs SCE

20°C - -703
40°C - -524
60°C - -410

FIGURE 38: Cathodic polarisation of zinc in 1.0M, still sodium molybdate solution, pH11, 20°C, 40°C and 60°C
FIGURE 39: Cathodic polarisation of zinc in 1.0M, still sodium tungstate solution, pH5, 200, 400 and 600°C
Rest potential/mV vs SCE

20°C - -650
40°C - -613
60°C - -627

FIGURE 41: Cathodic polarisation of zinc in 1.0M, still sodium tungstate solution, pH9, 20°, 40° and 60°C
FIGURE 42: Cathodic polarisation of zinc in 1.0M, still sodium tungstate solution, pH11, 20°C, 40°C and 60°C
FIGURE 43: Cathodic polarisation of zinc in 0.1M, aerated sodium chromate solution, pH5, 20°C, 40°C and 60°C
Rest potential/mV vs SCE

- 20°C - -556
- 40°C - -559
- 60°C - -485

FIGURE 44: Cathodic polarisation of zinc in 0.1M, aerated sodium chromate solution, pH7, 20°C, 40°C and 60°C
FIGURE 45: Cathodic polarisation of zinc in 0.1M, aerated sodium chromate solution, pH9, 20°C, 40°C and 60°C.
Figure 46: Cathodic polarisation of zinc in 0.1M aerated sodium chromate solution, pH1, 20°, 40° and 60°C.

Rest potential/mV vs SCE

- 20°C: -607
- 40°C: -584
- 60°C: -634

Current Density/mA cm⁻²

Overpotential/V
FIGURE 47: Cathodic polarisation of zinc in 0.1M, aerated sodium molybdate solution, pH5, 20°C, 40°C and 60°C
Rest potential/mV vs SCE

20°C - -766
40°C - -843
60°C - -713

FIGURE 48: Cathodic polarisation of zinc in 0.1M, aerated sodium molybdate solution, pH7, 20°C, 40°C and 60°C
FIGURE 49: Cathodic polarisation of zinc in 0.1M, aerated sodium molybdate solution, pH9, 20°, 40° and 60°C
Rest potential/mV vs SCE

- 20°C  -  -592
- 40°C - -604
- 60°C - -523

FIGURE 50: Cathodic polarisation of zinc in 0.1M, aerated sodium molybdate solution, pH11, 20°C, 40°C and 60°C
FIGURE 51: Cathodic polarisation of zinc in 0.1M, aerated sodium tungstate solution, pH5, 20°C, 400 and 60°C
FIGURE 52: Cathodic polarisation of zinc in 0.1M, aerated sodium tungstate solution, pH7, 20°, 40° and 60°C
FIGURE 53: Cathodic polarisation of zinc in 0.1M, aerated sodium tungstate solution, pH9, 20°, 40° and 60°C
FIGURE 54: Cathodic polarisation of zinc in 0.1M, aerated sodium tungstate solution, pH11, 20°C, 40°C and 60°C
FIGURE 55: Cathodic polarisation of zinc in 1.0M, aerated sodium chromate solution, pH5, 20°, 40° and 60°C.
FIGURE 56: Cathodic polarisation of zinc in 1.0M, aerated sodium chromate solution, pH7, 20°C, 40°C and 60°C
FIGURE 57: Cathodic polarisation of zinc in 1.0 M, aerated sodium chromate solution, pH 9, 20°C, 40°C and 60°C.
FIGURE 58: Cathodic polarisation of zinc in 1.0M, aerated sodium chromate solution, pH11, 20°, 40° and 60°
Rest potential/mV vs SCE

20°C  -  -939
40°C  -  -962
60°C  -  -936

FIGURE 59: Cathodic polarisation of zinc in 1.0M, aerated sodium molybdate solution, pH5, 20°, 40° and 60°C
FIGURE 60: Cathodic polarisation of zinc in 1.0M, aerated sodium molybdate solution, pH7, 20°C, 40°C and 60°C.
FIGURE 61: Cathodic polarisation of zinc in 1.0M aerated sodium molybdate solution, pH9, 20°C, 40°C and 60°C.
FIGURE 62: Cathodic polarisation of zinc in 1.0M, aerated sodium molybdate solution, pH11, 20°C, 40°C and 60°C.
FIGURE 65: Cathodic polarisation of zinc in 1.0M, aerated sodium tungstate solution, pH9, 20°, 40° and 60°C
FIGURE 66: Cathodic polarisation of zinc in 1.0M, aerated sodium tungstate solution, pH1, 20°C, 40°C and 60°C.
FIGURE 67: Potential-pH equilibrium diagram for the system zinc-water, at 25°C. Established by considering $\epsilon$-Zn(OH)$_2$.

(After Pourbaix $^6$)
FIGURE 68: Cathodic polarisation of zinc in an aerated MP solution containing 43 g/l (as Mo) sodium molybdate, at 20°C and pH 1.5, 3, 5 and 6.
FIGURE 70: Cathodic polarisation of zinc in aerated orthophosphoric acid, at 20°C and pH 1.5, 3 and 5
FIGURE 7.1: Oxidative polarization of zinc in aerated orthophosphoric acid, at 20°C, and pH 1.5, 3, and 5.
FIGURE 72: Cathodic polarisation of tin foil in an aerated MP solution containing 43 g/l (as Mo) sodium molybdate, at 20°C and pH 1.5, 3 and 5.
FIGURE 73: Cathodic polarisation of tin foil in aerated orthophosphoric acid, at 20°C and pH 1.5, 3 and 5
FIGURE 74: Anodic polarisation of tin foil in an aerated MP solution containing 43 g/l (as Mo) sodium molybdate, at 20°C and pH 1.5 and 3
FIGURE 75: Anodic polarisation of tin foil in an aerated MP solution containing 43 g/l (as Mo) sodium molybdate, at 20°C and pH 5.
FIGURE 76: Anodic polarisation of tin foil in aerated orthophosphoric acid at 20°C and pH 1.5, 3 and 5
FIGURE 77: Typical EPMA traces illustrating X-ray intensity against distance traversed across the sample, for a tin foil sample coated in an MP solution containing 43 g/l (as Mo) sodium molybdate, pH 1.5, 60°C, 1 min immersion.
FIGURE 78: Typical EPMA traces illustrating X-ray intensity against distance traversed across the sample, for a tin foil sample coated in an MP solution containing 43 g/l (as Mo) sodium molybdate, pH 2.5, 60°C, 1 min immersion.
FIGURE 79: Typical EPMA traces illustrating X-ray intensity against distance traversed across the sample, for a tin foil sample coated in an MP solution containing 43 g/l (as Mo) sodium molybdate, pH 3.5, 60°C, 1 min immersion
FIGURE 80: Typical EPMA traces illustrating X-ray intensity against distance traversed across the sample, for a tinplate sample coated in an MP solution containing 43 g/l (as Mo) sodium molybdate, pH 2.5, 20°C, 1 min immersion
FIGURE 81: Cathodic polarisation of tinplate in MP solutions at pH2.5 & 20°C. Effect of molybdate concentration, g/l
FIGURE 82: Cathodic polarisation of tinplate in MP solutions at pH 2.5 and 20°C. Effect of molybdate concentration, g/l
Rest potential/mV vs SCE
pH 2.5 - 575
pH 5 - 576
pH 7 - 565
pH 9.8* - 579

* (No orthophosphoric acid)

FIGURE 83: Cathodic polarisation of tinplate in an MP solution containing 90 g/l sodium molybdate at 20°C. Effect of solution pH.
FIGURE 84: Cathodic polarisation of tinplate in an MP solution containing 90 g/l sodium molybdate, pH 2.5, 20°C. Effect of aeration/deaeration
FIGURE 85: Anodic polarisation of tinplate in MP solutions at pH 2.5 and 20°C. Effect of molybdate concentration, g/l
FIGURE 87: Anodic polarisation of tinplate in an MP solution containing 90 g/l sodium molybdate at 20°C. Effect of solution pH.
FIGURE 88: Anodic polarisation of tinplate in an MP solution containing 90 g/l sodium molybdate, pH 2.5 and 20°C. Effect of aeration/deaeration.
FIGURE 89: Anodic polarisation of tinplate in MP solutions at pH 5 and 20°C. Effect of molybdate concentration, g/l
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FIGURE 92: Anodic polarisation of tinplate in an MP solution containing 10 g/l sodium molybdate, at pH 4 and temperatures of 30°, 50°, 70° and 90°C.
FIGURE 93: Current-time curves for tinplate in an MP solution containing 10 g/l sodium molybdate at pH4 and at +800 mV vs SCE and temperatures of 20°C, 30°C, 50°C and 70°C.
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FIGURE 95: Anodic polarisation of blackplate in orthophosphoric acid solutions at 20°C and at pH 2.5 and 5
FIGURE 96: Cathodic polarisation of blackplate in an HP solution containing 10 g/l sodium molybdate, at 20°C and at pH 2.5 and 5.

Rest potential/mV vs SCE
- pH 2.5 - 603
- pH 5 - 670

Current density/mA cm⁻²
- 10
- 1
- 0.1
- 0.01

Overpotential/V
FIGURE 97: Cathodic polarisation of blackplate in orthophosphoric acid solutions at 20°C, and at pH 3 and 5.

Rest potential/mV vs SCE
pH 3 = 663
pH 5 = 372

Current density/mA cm⁻²

Overpotential/V
Anodic polarisation of tinplate in an MP solution containing 10 g/l sodium molybdate, pH, 20°C.

Effect of nitrate additions.

FIGURE 98: Anodic polarisation of tinplate in an MP solution containing 10 g/l sodium molybdate, pH, 20°C.
FIGURE 99: Cathodic polarisation of tinplate in an MP solution containing 10 g/l sodium molybdate, pH4, 20°C. Effect of nitrate additions.
FIGURE 100: Anodic polarisation of tinplate in a molybdate-orthophosphate solution containing 10 g/l sodium molybdate, 20°C. Effect of orthophosphate additions.
FIGURE 101: Cathodic polarisation of tinplate in a molybdate-orthophosphate solution containing 10g/l sodium molybdate, 20°C. Effect of orthophosphate additions.
FIGURE 102: Cathodic polarisation of tinplate in a molybdate-orthophosphate solution containing 10 g/l sodium molybdate, 20°C. Effect of orthophosphate additions.
FIGURE 103: Cathodic polarisation of sulphide stained tin foil in 0.5M Na₂CO₃. Effect of staining time
FIGURE 104: Cathodic polarisation of platinum in continually aerated, distilled water at $20^\circ\text{C}$. Effect of pH.
FIGURE 105: Cathodic polarisation of platinum in continually aerated, 10 g/l sodium molybdate solution at 20°C. Effect of pH.
FIGURE 106: Cathodic polarisation of platinum in pre-deaerated distilled water at 20°C. Effect of pH.
FIGURE 107: Cathodic polarisation of platinum in pre-deaerated, 10 g/l sodium molybdate solution at 20°C. Effect of pH.
FIGURE 108: Cathodic polarisation of platinum in pre-deaerated, 100 g/l sodium molybdate solution at 20°C. Effect of pH
FIGURE 109: Cathodic polarisation of zinc in continually aerated distilled water at 20°C. Effect of pH.
FIGURE 110: Cathodic polarisation of zinc in continually aerated, 10 g/l sodium molybdate solution at 20°C. Effect of pH
FIGURE 111: Cathodic polarisation of zinc in pre-deaerated distilled water at 20°C. Effect of pH
FIGURE 112: Cathodic polarisation of zinc in pre-deaerated, 10 g/l sodium molybdate solution at 20°C. Effect of pH.
FIGURE 113: Cathodic polarisation of zinc in pre-deaerated, 100 g/l sodium molybdate solution at 20°C. Effect of pH.
FIGURE 114: Cathodic polarisation of tin plate in continually aerated distilled water at 20°C. Effect of pH.
FIGURE 115: Cathodic polarisation of tinplate in continually aerated, 10 g/l sodium molybdate solution at 20°C. Effect of pH.
FIGURE 116: Cathodic polarisation of tinplate in pre-deaerated distilled water at 20°C. Effect of pH.
FIGURE 117: Cathodic polarisation of tinplate in pre-deaerated, 10 g/l sodium molybdate solution at 20°C. Effect of pH.
FIGURE 118: Cathodic polarisation of tinplate in pre-deaerated, 100 g/l sodium molybdate solution at 20°C. Effect of pH.
FIGURES 119-125: Mo 3d peaks for ESCA samples 1-7. (For coating compositions see Table 41)
FIGURE 126: Interference in thin transparent films
FIGURE 127: Concentration of molybdenum required to produce satisfactory coatings at different pHs, using potassium molybdate. (After Kobe Steel Ltd [127])

FIGURE 128: Concentration of molybdenum required to produce satisfactory coatings at different pHs, using sodium molybdate. (After Kobe Steel Ltd [127])
FIGURE 129: Annotated cathodic polarisation curve for tinplate in 100 g/l sodium molybdate solution, pH 3-5
FIGURE 130: Laboratory scale rig used for the production of tinplate at ITRI
PLATE 1: Experimental apparatus for obtaining anodic and cathodic polarisation curves

PLATE 2: Experimental apparatus for obtaining coulometric reduction curves
PLATE 3: Chromate conversion coating on zinc.
Treatment solution: 0.1M sodium chromate, pH5, 40°C.
Applied cathodic potential: -1500 mV vs SCE
Treatment time: 10 mins
Magnification x600

PLATE 4: Molybdate conversion coating on zinc.
Treatment solution: 0.1M sodium molybdate, pH5, 40°C.
Immersion treatment for 10 mins
Magnification x575

PLATE 5: Tungstate conversion coating on zinc.
Treatment solution: 0.1M sodium tungstate, pH5, 40°C.
Applied cathodic potential: -1500 mV vs SCE
Treatment time: 10 mins
Magnification x575
PLATES 6-10  X-ray distribution maps for MP coated tin foil.
Treatment solution: 43 g/l (as Mo) sodium molybdate,
pH 1.5 (with 88% H₃PO₄), 60°C.
Immersion treatment for 1 minute

PLATE 6: Micrograph
Magnification x1000

PLATE 7: Tin X-ray distribution 1x

PLATE 8: Phosphorus X-ray distribution 8x
PLATE 9: Molybdenum X-ray distribution 8x

PLATE 10: Background X-ray distribution 8x
PLATES 11-15: X-ray distribution maps for MP coated tinplate
Treatment solution: 43 g/l (as Mo) sodium molybdate, pH 2.5 (with 88% H₃PO₄), Immersion treatment for 1 min

PLATE 11: Micrograph
Magnification x1000

PLATE 12: Tin X-ray distribution 4x

PLATE 13: Phosphorus X-ray distribution 8x
PLATE 14: Molybdenum X-ray distribution 8x

PLATE 15: Iron X-ray distribution 4x
PLATE 16: MP-type coating on tin foil
Treatment solution: 43 g/l (as Mo) sodium molybdate, pH 2.5
(with 88% H₃PO₄), 80°C
Immersion treatment for 30 minutes
Magnification x1000

PLATE 17: MP-type coating on tinplate
Treatment solution: 90 g/l sodium molybdate, pH 2.5 (with
88% H₃PO₄), 80°C
Immersion treatment for 10 minutes
Magnification x1000

PLATE 18: Coating thickness measurements. Dislodged grain of molyb-
date coating on tinplate
Treatment solution: 10 g/l sodium molybdate, pH 3, 20°C.
Applied cathodic potential: -800 mV vs SCE
Treatment time 30 minutes
Magnification x5300
COLOUR PLATE 1: Effect of treatment time on cathodically formed molybdate conversion coatings on tinplate.
Treatment solution: 10 g/l sodium molybdate, pH3, 20°C. Applied cathodic potential: -800 mV vs SCE

1 No treatment
2 30 secs treatment
3 1 min treatment
4 2 mins treatment
5 4 mins treatment
6 6 mins treatment
7 10 mins treatment
8 20 mins treatment
9 30 mins treatment

COLOUR PLATE 2: Effect of treatment time on cathodically formed molybdate conversion coatings on zinc.
Treatment solution: 10 g/l sodium molybdate, pH3, 20°C. Applied cathodic potential: -1050 mV vs SCE

1 No treatment
2 30 secs treatment
3 1 min treatment
4 2 mins treatment
5 4 mins treatment
6 6 mins treatment
7 10 mins treatment
8 20 mins treatment
9 30 mins treatment