ADDITION AGENT BEHAVIOUR IN

ACID TIN PLATING

by

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SUMMARY

Dihydroxy diphenyl sulphone (DDS) and sulphonated diphenylol propane (DPP), the addition agents used commercially in the high speed tin plating of steel strip were separated into their constituent compounds. To identify the active constituents tin was electrodeposited from a series of solutions containing the separate compounds and the structure of the deposits examined.

The solid addition agent DDS was separated into two main constituents; by means of infra-red and nuclear magnetic resonance spectroscopy it was shown that the two compounds separated were structural isomers. Using mass spectroscopy the separation of the 22' and 44' isomers of dihydroxy diphenyl sulphone was confirmed since the compounds had the same molecular weight and fragmentation pattern. Commercial DDS was shown to contain about 8 - 10% of the 22' isomer.

The liquid addition agent DPP could not be separated into its constituent chemical compounds but the mixture was separated into acid and non-acid components and also into water soluble and ether soluble components. Each of the components separated was used separately as an addition agent in the electrodeposition of tin and topography of the tin deposited examined by scanning electron microscopy.

It was found that some constituents had no beneficial properties on the tin deposited and their presence merely diluted the effectiveness of the active constituents. The two isomers of DDS had different but complementary effects on the structure of tin deposited. The 22' isomer increased the density of nucleation sites initially formed but when used alone dendritic growth commenced after about 30 seconds plating time. The 44' isomer when used alone was totally unsatisfactory, giving very poor covering and crystals which very soon showed dendritic growth. However, when the two isomers were used together it would appear that the high nucleation rate produced by the 22' isomer results in a large number of small crystals which in the presence of the 44' isomer did not develop dendritic growth until at least 60 seconds plating time.

The two isomers appeared to act synergistically. By altering the ratio of 22' to 44' isomer present, the structure of the tin deposited could be improved.

Using the components of DPP separately as addition agents it was possible to identify two active constituents. The water soluble compounds which improved the structure of the tin deposited were only active when present as acids. As salts they were inactive.

It was thought possible that both of the active components separated contained the same functional group and that the difference in solubility may have been due to a difference in molecular weight.

It was found impractical to separate the compounds or their degradation products from the electrolyte used. However the effect of the break down products formed on the tin deposited was investigated satisfactorily. By analysis it was shown that over a ten hour plating period the concentration of tin and phenol sulphonic acid varied only marginally and could easily be held constant. By plating from the electrolyte continuously for up to eight hours the break down of the addition agents could be charted. Test pieces were plated in the normal way at hourly intervals throughout this period.

The break down products from DPP were not detrimental to the tin deposited over periods of time up to five hours. The tin deposited from solution containing DDS as addition agent, however, showed a change in structure after a short plating period.

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1.0. INTRODUCTION

1.1. Use of addition agents in the commercial electrodeposition of tin

Electrodeposition of tin from an electrolyte containing no organic additives results in a coarse crystalline deposit. The presence of addition agents in the electrolyte results in the deposition of smooth electroplate which can be shown to consist of fine grained compact crystal structure. Consequently the selection of suitable additives for use in the commercial deposition of tin for the production of tin strip is one of major importance.

Early work shows the use of colloids as addition agents in tin plating baths but these have been replaced by simpler compounds often of the detergent type.

The compounds supplied as addition agents by the manufacturers are usually made on the large scale by conversion of a cheap easily obtainable raw material into the compound active in the electrolyte. Frequently both the raw materials and the solvents used initially contain some impurities, and side reactions during the addition agent manufacture also result in impurities being present in the commercially available addition agent. Generally it is not economically feasible to separate the active compounds from the mixture. Consequently at times the identity of the active compound is not certain. The present American legislation dictates that the presence of any organic material occluded in the electrodeposited tin must be non-toxic at the concentration involved. It is therefore desirable to establish the nature of the active components in the addition agent and to determine their degree of incorporation.

Two addition agents are at present in use by manufacturers of tin strip in this country and each is known to be a mixture of compounds. This research sets out to separate the addition agents into their component parts, to identify the structure of the active compounds and to establish the amount of these compounds incorporated in the tin.

2.1. GENERAL

Since tin is an amphoteric metal, it can be deposited electrolytically from both acid and alkaline solutions. The throwing power of the alkaline bath is better than that of the acid bath but it must be operated above room temperature. Also, since the tin is present in the stannic state (Sn IV) in the alkaline bath, the current required to deposit a given thickness is twice that required by the acid bath containing tin as (Sn II). Also the cathode efficiency in the alkaline bath is approximately 75 per cent whereas in the acid bath it is close to 100 per cent. Both these factors contribute to the widespread use of the acid bath for tin plating in tin strip production where throwing is only of secondary importance.

Any of the soluble stannous salts can be used as the electrolyte, but stannous sulphate finds the widest use since it is the cheapest salt (1). However, tin can be deposited from a fluorborate bath (2) and halide bath (3).

Many metals can be electrodeposited from solutions containing the metal ion, dissolved as a soluble salt, and an acid or alkali to increase the conductivity of the solution. The metal deposited is adherent and relatively smooth, e.g. nickel and copper, However, if tin is deposited from a bath containing stannous

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sulphate dissolved in sulphuric acid the deposit contains large discontinuous crystals, and is not adherent to the base metal. Further the electrolyte is unstable and basic tin salts precipitate out causing the solutions to become cloudy. Hothersall and Bradshaw (4) discovered that deposition of tin from baths containing three different types of addition agents produced a smooth compact coating suitable for corrosion protection.

- A sulphonated aromatic compound to retard the oxidation of stannous salts.
- A colloid (e.g. gelatin) to improve the structure of the tin deposited causing fine-grained, smooth, compact coatings to be formed.
- A hydroxy-aromatic compound to aid the deposition of smooth matte tin and to reduce porosity in the electrodeposit.

Hothersall and Bradshaw's work formed the basis of further work done on the electrodeposition of tin from acid solutions. The solution now widely used for the commercial production of tin plate is a modification of this original solution. The cresol sulphonic acid used in the original work to retard oxidation of the stannous salts frequently contained oily impurities some of which were insoluble in the electrolyte. For this reason and on economic grounds the cresol sulphonic acid has been replaced by phenol sulphonic acid. An investigation into the mechanism of inhibition of Sn (II) oxidation by phenol sulphonic acid (5) suggests that the acid either forms a complex with the Sn (II) ion or reduces the solubility of the oxygen in the electrolyte.

The aromatic hydroxy compound and the colloid have been replaced by a variety of compounds most of which are sulphur containing compounds. The sulphur is frequently present as a sulphonic acid group providing a hydrophilic group so improving the wetting characteristics of the solution. In the process patented by the United States Steel Corporation as the Ferrostan process (6) dihydroxydiphenyl sulphone (DDS) replaces the colloid and aromatic hydroxy compounds which usually have restricted solubility. However, more recently this solid sulphone has been replaced by a liquid; sulphonated diphenylol propane. (DPP). In the Ferrostan bath the anode efficiency is close to 100 per cent whereas the cathode efficiency is about 95 per cent; there is a consequent build up in the concentration of tin present in the electrolyte. This can be overcome by using modified anodes to restrict the dissolution of tin in the solution. The anode material must be very high purity tin and in particular the presence of lead and antimony must be avoided as these have a detrimental effect on the tin deposited (7).

The electrolyte can be operated satisfactorily at room temperature. However, if DDS is used as the addition agent, it is more usual to operate the vat at about 50° C., since this organic compound is not easily soluble in the cold solution. Higher temperatures simply accelerate the oxidation of the stannous ion.

The Ferrostan solution is generally cloudy. This is due in part to anode slime which can be eliminated by anode bagging. Other causes are the oxidation products of the stannous ion and the products formed by the decomposition of the addition agent. Agitation of the bath causes these particles to become entrapped in the electrodeposit and produces unsatisfactory coatings. In practice the steel strip passes through the solution at such high speeds that entrapment of solid particles is avoided and anode

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bagging has been found unnecessary in practice (8).

In still baths the current density is limited to 1 amp/dm², but in agitated solutions the current density can be increased to approximately 10 amps/dm².

The majority of tin strip produced is used in the packaging of food-stuffs and for this purpose the tin deposited must provide a corrosion resistant coating. The ATC method of measuring the corrosion resistance of tin plated steel strip (9) is a galvanic test known as the alloy tin couple test. In this test the tin is dissolved from the tin plated strip and the intermediate tin - iron alloy surface is made one electrode in a cell containing grapefruit juice with 10 ppm of soluble stannous tin as the electrolyte and pure tin as the other electrode. The cell is operated at 26° C. The current density after 20 hours is measured in microamperes/cm² and the figure referred to as the ATC value. Low ATC values indicate good corrosion resistance properties and a value of 0.07 has arbitrarily been selected as the acceptable value.

It has been shown that the ATC value of tinned strip can be improved significantly by flow melting the electroplated tin so increasing the thickness of the iron-tin alloy layer.

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This process also improves the appearance of the tin plate changing the matte, as deposited tin, to a bright smooth coating.(10)

2.2. ORIGIN OF THE INVESTIGATION

The Ferrostan process originated in 1936 by the United States Steel Corporation is based on the Schlotter Patent (11). The addition agents involved were sulphonated cresol products and glue. These addition agents were changed to DDS in 1962 (12). DDS is a solid compound and is soluble with difficulty in solution at about 80° C. The electrolyte is generally brought to this temperature, the DDS added and the solution allowed to cool to the operating temperature of 50° C. Some difficulties have been encountered with this addition agent since, if any precipitates out of solution it tends to block up filters etc. The compound is generally added to the vat by removing a small volume of electrolyte from the vat, dissolving the addition agent in this and then returning the whole to the vat.

Both of these difficulties have been overcome by the use of a liquid addition agent DPP. This can be added to the vat as a drip feed, continuously replacing the addition agent lost by drag out or breakdown. It is a liquid highly soluble in the electrolyte and so no precipitation occurs. The only disadvantage of this additive is its detergent action on the plant, dissolving oil from rollers and bearings, which can then have a detrimental effect on the electrod posited tin.

About 1930 the American government introduced legislation controlling the use of chemicals used in the packaging of food stuffs in industry. Chemicals used prior to this date were considered satisfactory but any newly introduced compounds had to be shown to be non-toxic in the quantities in which they were incorporated in the deposited metal. Consequently DPP, if used in the deposition of tin plate for the American market, would have to be shown to be non-toxic.

The commercially available samples of DPP are not pure compounds but a mixture of compounds which results from the large scale sulphonation of diphenylol propane. The mixture probably contains sulphonated and acylated products as well as free acetic and sulphuric acid since the sulphonation is carried out in a mixture of sulphuric acid - acetic anhydride. Other compounds may be formed during the sulphonation, be present as impurities in the raw materials, or be formed as break-down products during electrolysis.

At this point it became clear that if the compound or compounds responsible for the improvement in the structure of the electrodeposited tin could be separated from the mixture, detection of these compounds and hence quantitative analysis in the electrodeposit would be simplified. By determining the amount of the active compound initially present and the concentration in the electrolyte after depositing a known volume of tin the amount incorporated could be determined.

The recommended concentration of DPP in the bath is 5cc/litre. Since large quantities of tin can be deposited from 1 litre of solution without noticeable difficulty, the quantities of addition agent incorporated into the electrodeposit are likely to be very small and consequently very accurate methods of analysis are necessitated. The possibility of labelling the appropriate compound with a radioactive isotope has been used previously for analysis of this kind and the method was investigated (13) (14). Thus the problems were:

- To identify the components in DPP responsible for the improvement of the structure of the electrodeposited tin.
- 2. Since it had been reported that dihydroxy diphenyl sulphone, although fairly pure, became less active when further purified it was decided to separate and identify the impurity present which appeared to be responsible for improved properties of the electrodeposited tin (15).
- 3. To investigate methods of separating the addition agents from the electrolyte during use, and to determine quantitatively the amount used during plating. To detect the presence of any break-down products and to identify them if possible.
- 4. To determine the effect of break-down products on the structure of the tin deposited and to determine whether they also acted as active addition agents.

5. To compare the tin deposited from electrolytes containing each of the addition agents and to recommend the most effective compound for use in the electrodeposition of tin.

3.0. EXPERIMENTAL PROCEDURE

3.1. Composition of addition agents

The two addition agents used in the investigation are:-

- 1. dihydroxy diphenyl sulphone (DDS)
- dihydroxy diphenyl propane (Sulphonated)
 (DPP)

The addition agents supplied commercially are not pure but mixtures of compounds resulting from the preparation of the compounds. It is, therefore, important to examine the possible methods of preparation of these compounds and so determine the impurities which result from side reactions, solvents used or impurities in the raw materials.

Possible methods of manufacturing these compounds:

1. DDS

If benzene is treated with concentrated sulphuric acid a variety of compounds are formed dependent on conditions of concentration and temperature. The major product will be benzene sulphonic acid.

 $+H_2SO_4 \rightarrow OSO_3H + H_2O_1$

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Some diphenyl sulphone is formed and since it is a solid compound relatively insoluble in water it can be separated from the sulphonic acid by filtration (16).

 $) + H_2SO_4 \rightarrow O + 2H_2O + 2H_2O + 2H_2O$

However, the yield of diphenyl sulphone by this method is small and it is not considered to be a suitable preparative method.

2. If benzene is sulphonated using SO_3 (in the vapour phase) in place of H_2SO_4 a higher proportion of the sulphone results. At temperatures between 150 - 200° C. the yield is 50 per cent of the sulphone (17).

Other compounds are also reported to result from this preparation including o and p benzene disulphonic acid and mono and disulphonated diphenyl sulphone (18). A possible reaction sequence is





However, another possible side reaction



Hence the use of SO₃ with benzene appears to result in a large number of compounds formed by side reactions and is not considered a reliable method of preparing DDS (19). 3. The sulphone group is reported to be meta directing and consequently in order to produce 22' dihydroxy diphenyl sulphone or the 44' isomer the hydroxyl groups must be present on the benzene ring before formation of the sulphone (20). Migrdichian (21) reports that a Friedel Craft reaction between aromatic sulphonyl chloride and an aromatic hydrocarbon in the presence of aluminium chloride gives good yields of the sulphones. He further reports this method to be especially successful for the preparation of hydroxy phenyl sulphones (22).

OAICI2+HCI OH + AICI3 -

50,CI-> +HCI + AICIA

4. A method especially useful for the preparation of substituted aryl sulphones has been reported by McClement and Smiles.(23) An aromatic sulphur chloride can be reacted with a substituted phenol. The resulting diaryl sulphide can be oxidised with hydrogen peroxide converting the sulphide to sulphone. It is reported that the hydroxy group is not attacked by the oxidation procees



Either of these methods (3 and 4) would provide a suitable preparative method for the sulphone on the large scale. Although Method 4 is more likely to result in a large number of partially oxidised sulphur compounds.

Since the sulphone is a solid, not very soluble in water, it can be purified by recrystallisation from water and the resulting compound should contain only the two structural isomers 22' dihydroxy diphenyl sulphone and the 44' compound. 2. DPP

The commerical grade DPP is a liquid and is known to be a mixture of several compounds. The possible impurities are sulphuric acid, acetic acid, monochlorobenzene and phenol. However, since the sulphonation of the dihydroxy diphenyl propane is carried out in a mixture of sulphuric acid and acetic anhydride monosulphonated and acylated compounds are also possible.

- Possible preparative methods for DPP are as follows:-
 - 1. Migrauhin states that 1, 2, 3 trichloro propane will react with benzene to give diphenyl propane with some dibenzyl methane(24) as an impurity the diphenyl propane would then have to be converted to the dihydroxy compound and finally sulphonated.
 - Phenols can be reacted with ketones or aldehydes to yield diaryl alkanes (25).
 (a) from phenol and ketone.

If phenol is reacted with acetone dihydroxy diphenyl propane results.



The dihydroxy diphenyl propane so produced would then require sulphonating.(26)

2. (b) from phenol and an aldehyde (27).

If phenol is reacted with an aliphatic aldehyde a reaction occurs known as the Baeyer reaction.

While this reaction can be used to prepare 44' dihydroxy diphenyl ethane it cannot be used to produce symmetrical dihydroxy diphenyl alkanes.

It is, therefore, suggested that the most likely method of manufacture of DPP is from the reaction between a phenol and a ketone as shown in 2 (a), and subsequent sulphonation of the compound.

The position of the OH groups cannot be guaranteed since they may be present in the 22', 44' or 24' positions.

3.2. GENERAL METHODS OF SEPARATING MIXTURES OF SOLID ORGANIC COMPOUNDS

If a sample of a solid gives a constant sharp melting point without visible signs of decomposition it is considered to be a pure compound. If the solid is found to have an indefinite melting point it may be due either to the presence of impurities or to the decomposition of the compound at temperatures approaching the melting point. The second of these possibilities can be easily checked by rapidly heating the sample to a temperature a few degress centigrade below its suspected melting point and heating through the melting point range before the compound has time to decompose.

If the compound is impure a method of separating the impurity must be found and this will be based on the differences in physical properties between the compound and the impurity.

1. Differential reaction rates.

If the compound and the impurity have different functional groups present then there will be a difference in the rates of reaction in the formation of derivatives. Hence a derivative of either the compound or the impurity is prepared such that it can easily be separated from the unreactive material and the original compound easily regenerated from the derivative.

(a) Purification using activated charcoal (28)

If the substance required in a pure state contains a very small proportion of an impurity it can sometimes be removed by the action of activated charcoal. This preferentially adsorbs compounds depending on the functional groups present. Generally functional groups which increase solubility decrease the absorbability since the compounds are less likely to leave the solution. The removal of impurities from organic compounds using activated charcoal is widespread.

(b) Chromatography

Although chromatography is used widely as a means of identifying the components in a mixture of compounds by comparing the chromatograms of the unknown with those of known standards, it is not often used as a method of separating large quantities of material.

Chromatography is based on the differential retention rates of compounds on to an adsorbent surface. The various possible phases of the adsorbent surface and the compounds being adsorbed result in a variety of chromatographic methods. In thin layer chromatography (29) the absorbent is a thin solid layer often of silica or alumina and the substance, dissolved in a suitable solvent, is placed on the adsorbent surface and then eluted with pure solvent. This method can be particularly useful for separating and identifying small quantities of material especially those which have radioactively labelled atoms present since the adsorbent can be cut up and each bit separately scanned with a Gieiger Muller counter.

Paper chromatography is often used to separate mixtures of natural products and depends on the relative ease of adsorption of the compounds on to a paper column from an eluting solvent.

Gas chromatography (30) is used to separate mixtures of liquids. I^t depends on the variation in adsorption of the compounds in the liquid mixture at high temperatures between a liquid phase, usually a hydrocarbon oil on a kieselguhr surface, and an inert gas.

(c) Differential Solubility

If a solid mixture contains some compounds soluble in a certain solvent then these solvent soluble compounds can be separated by a Soxhlet extraction. This apparatus allows the solid material to be continuously brought into contact with pure hot solvent into which the soluble compounds pass. The solution is then siphoned off into a lower flask, the solid often separating from the solvent as the concentration increases and the solvent being vaporised and re-used in the extraction process.

This process of separation is useful when the mixture is a solid from which the required compounds can be easily removed by dissolving in a hot solvent. If several or all of the compounds present are soluble in the solvent little or no separation will occur. Soxhlet extractions are usually used on compounds like rubber and other natural products to determine the components which would be lost if the product was used in an atmosphere of the solvent under investigation. The method has been successfully applied to extraction of impurities from natural products.

c. 2. Fractional crystallisation (31)

This method has been found particularly useful in the separation of mixtures of isomers, especially optically active isomers.

The process involves a method similar to that used in fractional distillation before the advent of fractionating columns. The solid mixture A is brought into contact with enough solvent to dissolve about half the weight of A used. The undissolved solid is called the head fraction B_1 and the solid which passes into the solvent is called the tail fraction B_2 . See diagram.

 B_1 is recrystallised in the same way from a fresh sample of solvent to give C_2 the soluble portion and C_1 the insoluble portion.



 B_2 is concentrated, some pure solid separating out C_2 , and some remaining in solution. This is combined with C_3 above. The process is repeated until the head fraction shows some constant physical property e.g. melting point, optical rotation, etc. The tail fraction eventually becomes too small to handle and is withdrawn. Eventually most of the original solid is present either in the head or tail fraction.

3.3. GENERAL METHODS OF SEPARATING MIXTURES OF LIQUID ORGANIC COMPOUNDS

If a liquid compound has a constant narrow boiling point range and leaves no residue on distillation, it is deemed to be pure.

If the liquid decolourises during distillation, shows several separate boiling point ranges or leaves a residue after distillation it is considered impure. Mixtures of liquids can be separated in the following ways.

1. Differential reaction rates.

 Differential adsorption.
 For 1 and 2 the notes under preparation of solid mixtures apply also to liquid mixtures.

3. Differential volatility.

(a) If all the impurities are insoluble in the pure liquid the liquid can be separated by simple distillation.

- 3. (b) If the impurities are soluble in the pure liquid, are themselves liquids and have no reaction with the pure liquid even at its boiling point, then the pure liquid can be separated by fractional distillation.
 - (c) If the pure liquid appears to decompose at the boiling point or has a very high boiling point distillation under reduced pressure is recommended.
 - (d) If the impurity is water soluble and the pure liquid complete insoluble in water then the impurity can be removed by steam distillation.
 All methods involving the separation by distillation are satisfactory only if there is no reaction between the pure liquid and the impurities at the temperature of distillation.

4. Differential solubility (32)

If a solvent can be found in which one component of the mixture is soluble and the rest is insoluble this component can be removed from the rest by repeated extraction with a small volume of solvent. This process is generally carried out in a separating funnel on small quantities of material and can be made to give a moderately good separation after repeated extraction. A more effective method is similar to fractional crystallisation discussed under separation of solid mixtures. In this case the first extraction yields a solvent layer A and a layer of the impure mixture B.

Solvent layer A is reserved.

Impure mixture B is again extracted with pure solvent.

The solvent with any dissolved compound is retained and the undissolved mixture is again extracted.

This multicontact separation can be made much more effective and semi automatic by using the Craig countercurrent extraction apparatus (33) in which the impure liquid is continuously extracted with fresh solvent and these portions of solvent containing soluble impurities are combined and further extracted.

3.4. GENERAL METHODS OF IDENTIFICATION OF ORGANIC COMPOUNDS

Once a mixture has been separated into its component compounds, these compounds can be identified fairly readily. The identification follows four main stages. Identification of the elements present in the compound (34).

This can easily be achieved by the normal wet methods if a quantitative determination is required the method used depends on the amount of substance available. If a sample weight over 0.1 g is available semi-micro methods are suitable. If the sample weight is less than this micro methods have to be used.

 Identification of the functional groups present (35).

Many simple functional groups can be identified by spot tests. However, many of the lesser known functional groups and compounds containing more than one functional group can be identified using one of the numerous sophisticated instrumental methods now available (36).

(a) Infra Red, Ultra violet and visible spectrometry.

Absorption spectra in the ultra violet and visible regions indicate the type of bonds probable in the structure of the molecule.

(b) Raman Spectra.

This indicates the polarisability of the molecule.

- (c) Nuclear magnetic resonance spectra gives information about the environment of each hydrogen atom in the organic molecule.
- (d) Mass spectrometry.

When organic molecules are bombarded with free electrons the molecule fragments. From the spectra produced the molecular weight of the parent molecule can be established and from the molecular weight of the fragments produced the bonding and structure of the original molecule can be suggested.

(e) Gas chromatography.

By comparing the adsorption rate of the known compound with a series of standards identification of the unknown compound can be achieved. See under separation of solid mixtures.

(f) Optical rotary dispersion.

Many compounds in solution rotate the plane of polarised light. The degree of rotation will depend on the concentration of the solution, the frequency of the polarised light and the size of cell used. Again an unknown substance can be compared with known standards to aid its identification.
(g) Polarography

If an electrolytic solution contains an organic compound it will be subject to reduction in the cathode area and oxidation in the anode area. The molecule will become polarised in the solution and will travel towards one of the electrodes. It will be discharged at the dropping mercury cathode potential. and will develop a characteristic half wave which can be identified from standard data. The method is not yet widely used for the detection of organic compounds but is used to determine the concentration of organic compounds present in electrolytic solutions. 3. Confirmation of structure of compounds.

By comparison of one or more physical properties of the unknown compound with those of a known sample of the compound. Usually melting points are together with molecular weights and presence of the same elements are sufficient to identify a solid compound. A liquid compound is identified when its boiling point is in agreement with a known standard having the same molecular weight and empirical formula.

3.5. Methods investigated in the separation and purification of the components of DDS

The addition agent material as supplied is a solid and has a melting point which is not sharp but in the region of $220-230^{\circ}$ C. It had been reported that if the addition agent was further purified the structure of the tin plate

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produced from the bath was unsatisfactory (15). Hence it seemed probable that the impurities present were active as addition agents in the electrolyte and should be investigated further.

A suitable method of separating the addition agent into its component parts and identifying these compounds was now sought.

From the probable method of preparation of the addition agent it seemed possible that a large number of sulphur containing compounds could be present in small quantities, e.g. the (38) sulphide, disulphide and sulphoxide. It was thought improbable that these compounds were present in anything but trace quantities and consequently removal of these impurities by recrystallisation from water was carried out. The melting point of the compound which separated out was sharper and was in the region 238-240° C. When the recrystallisation was repeated using animal charcoal to adsorp the possible impurities the melting point of the recrystallised material was increased to 242° C. and was now sharp suggesting that the material produced in this way was relatively pure. In an attempt to recover the impurity from the charcoal it was washed with copious amounts of water and the solution concentrated. Crystals separated out at different stages during the concentration process and their melting point ranged from 180° C. to 242° C.

Since it seemed possible to separate the components of the mixture by recrystallisation this process was repeated in an attempt to increase the amount of impurity separated so that identification tests could be carried out. This time a system of fractional recrystallisation was used to increase the yield of product. The addition agent was satisfactorily separated into two major components:- one having a melting point 242° C and designated DDS 1 and a second having a melting point in the region 168 - 170° C and designated DDS 2.

A mass spectrograph of the two compounds showed them to have the same molecular weight (250) and to have the same fragmentation patterns. From a consideration of the molecular weight, confirmation that both components were dihydoxy diphenylsulphone resulted since the molecular weight of this compound is 250. Also since both compounds have the same molecular weight it seemed likely that they are in fact structural isomers.

The 44 dihydroxy diphenyl sulphone is known to have a melting point of 242° C and consequently from a consideration of the melting points the 22' isomer must be the compound designated DDS 2 and having a melting point between 168 and 170° c. (64).

Both IR and NMR spectra showed the two compounds to have a similar structure and it was concluded that the method of fractional recrystallisation from water had resulted in the separation of the isomers.

From this preliminary investigation it became clear that methods of separation of the two compounds would have to be based on physical properties i.e. differential solubility since the separation by difference in functional groups and hence reaction rates was not acceptable.

The fractional recrystallisation from water had been a long and tedious process resulting in a very small yield and high losses. The method seemed completely unsuitable as a preparative method.

It was found possible to fractionally recrystallise the isomers from ether at room temperature. While every precaution was taken to prevent loss of the 22' isomer some transferance losses were inevitable. Starting with 15 g of the as received DDS and 750 mls of dried and deoxidised ether 1.3 g of the 22' isomer (mpt 168 - 170° C) was recovered. However a third compound also separated from the 22' isomer having a melting point in the region 145 - 150° C. About 0.07 g separated from the 15 g of as received DDS and it was insufficient to carry out further tests to identify its structure or for assessment as an addition agent in the Ferrostan tinplating bath.

3.6 METHODS INVESTIGATED FOR THE SEPARATION AND PURIFICATION OF THE COMPONENTS OF DPP

From the outset it was known that DPP was a mixture of several compounds. The diphenylol propane is sulphonated in a mixture of sulphuric acid and acetic anhydride and the following compounds could be present as impurities:

- a. diphenylol propane
- b. sulphonated diphenylol propane
- c. acylated diphenyl propane
- d. sulphonated and acylated diphenyl propane
- e. acetic acid by hydrolysis
- f. sulphuric acid

A sample of diphenylol propane proved to be completely insoluble in water and since the addition agent is a liquid of which all the components are highly soluble in water, it was not thought to be present in the DPP.

A 25 ml sample of the DPP was treated with PbCO₃ until the lead carbonate was just in excess. The precipitate was filtered off, treated with dilute sulphuric acid to convert the slight excess of lead carbonate to lead sulphate and this was then weighed. The results showed that the original DPP solution contained about 30 g/l free sulphuric acid.

An attempt at separation by fractional distillation resulted in the removal of about 30% of the sample at 100° C. This sample was acid to litmus and was probably water containing traces of acetic acid and sulphuric acid. At temperatures in excess of 100° C the mixture frothed and white fumes were given off which were insoluble in water. The mixture then darkened and yielded a charred mass probably due to a reaction between the free sulphuric acid and the other compounds present. 34

A method of separating compounds b, c, and d, as a mixture was then sought. Wet methods of preparing derivatives, separating and regenerating were investigated.

To separate the required compounds from the free sulphuric acid was the first problem as then it might have been possible to separate the compounds from the mixture by distillation perhaps under reduced pressure.

The free sulphuric acid was removed from the addition agent by treatment with lead carbonate and the resulting lead sulphate filtered off. Unfortunately even after dilution lead sulphate remained suspended in the liquid addition agent and all attempts to separate compounds from the sulphuric acid free liquid were unsuccessful.

Another and more successful method of separation was found to be liquid - liquid extraction using ether as solvent.

A 100 ml sample of DPP was mixed thoroughly with 350 mls ether. Further separations were as follows:-



Smells strongly of phenol. (3a) (3b)

Consequently the addition agent has been separated into four components.

- Component (2) a deep red brown liquid containing the components insoluble in ether. Thought to contain most of the acidic and any other strongly ionic species present.
- Component (2a) This resulted when a sample of component (2) was completely neutralised with concentrated sodium hydroxide solution to establish whether any advantages can be gained by reducing the acidity of the addition agent.
- Component (3a) This would seem to be a water soluble phenol which is also readily soluble in ether, since it was not removed from the ether layer by washing.
- Component (3b) This component contains compounds which after distillation are insoluble in water. Consequently no tests could be made on this component as it was not soluble in the electrolyte.
- Compound (4) This component must contain compounds more readily soluble in ether than water but removed by washing the ether layer. In fact this component and component (2)

are later shown to be similar in effectiveness as addition agents and may well be liquids containing the same compounds in differing concentrations.

3.7. METHODS INVESTIGATED FOR THE SEPARATION AND IDENTIFICATION OF ADDITION AGENTS AND BREAK-DOWN PRODUCTS FROM THE ELECTROLYTE USED COMMERCIALLY

One of the original aims of the project was to identify the active compounds in the addition agents together with any active compounds formed during the break-down of the addition agents and to determine the concentration of these compounds in the electrolyte. Further, the concentration of these compounds entrapped in the deposited tin was to be determined if possible.

Ideally this work would have been carried out using commercial Ferrostan solution as the electrolyte. Unfortunately the electrolyte used commercially contains traces of addition agents other than those specified in this work together with metallic impurities, the most important of which are iron and silicon.

Since the quantitative separation of the addition agents from the electrolyte required very accurate techniques the presence of large quantities of interfering ions would create extra problems and it was decided to discount the uses of the commercially available solution. A simpler solution, used in the laboratory testing of addition agents in Hull cell tests was utilised instead of the commercially available solutions. This solution contained

64 g/l stannous sulphate

160 ml/l 33% phenol sulphonic acid and either 5 ml/l DPP

or 6 g/l DDS

The solution is used at 50° C $\pm 2^{\circ}$ C with a 99.75% tin anode.

Separation and identification of addition agents and break-down products from this solution were investigated.

Methods of separation depend on the type of functional groups present in the compound. Since both the addition agents used dissolved in phenol sulphonic acid, methods of separating them from (a) stannous sulphate, (b) phenol sulphonic acid, were investigated.

Wet methods based on the separation of the Sn^{2+} ion as the insoluble hydroxide were used. Barium hydroxide was added to the electrolyte until all the Sn^{2+} ion had precipitated as Sn(OH)_4 and together with the BaSO_4 precipitated out, were filtered off. This left the addition agent and any break-down products formed in solution together with the barium salt of phenol sulphonic acid. Solutions containing DDS as addition agent were then passed through a strongly acid ion exchange column to convert the barium salt of phenol sulphonic acid back to the acid. This solution is then passed through a weakly basic ion exchange column which removes the acid from solutions and the solution leaving the base of the column should contain only the DDS originally added and any break-down products formed.

Since the addition agent in solution during electrolysis is in a reducing environment the most likely type of product to be formed are sulphoxides sulphides and thic alcohols. Other compounds could be formed by the fragmentation of the molecule during electrolysis to give free radicles which would then combine with other ions or molecules in solution to give new products. The separation, identification and quantitative analysis of these compounds could probably be accomplished by a chromatographic technique.

When the electrolyte contained DPP as addition agent the separation was further complicated because both the addition agent and the phenol sulphonic acid contain the sulphonic acid group. The separation of $S n^{2+}$ ion was the same as that used for solutions containing DDS. The resulting solution contained the barium salt of phenol sulphonic acid and DPP together with the several impurities present in the DPP solutions. The barium salts can be converted

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back to the original sulphonic acids by passing/through a strongly acid ion exchange column but further separation proved impossible.

The results of this particular aspect of the work were disappointing. When the solution containing DDS as addition agent was passed through the weakly basic ion exchange column very little solid compound was collected.

800 mls of a solution containing 4.5 g/l was passed through a weakly basic ion exchange column and diluted with a further litre of water. The solution issuing from the base of the column was collected in 100 ml portions and the weight and melting point of any solids separating out on concentration was determined.

The total weight of solid collected was 0.60 g (i.e. approximately 17%). The twelfth 100 ml portion contained only 0.007 g of solid material and later aliquots contained negligible amounts of solid. The melting points of the solids collected varied from 216° to 232° C.

As already described due to the similarity of the sulphonated DPP and the phenol sulphonic acid these compounds could not be separated.

A new approach to the problem of determining the effect of the constituent compounds in the addition agents and of the break down products on the structure of the tin deposited was sought. It was decided to

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carry out electroplating tests using the constituents of each addition agent separately and to determine which of the constituents were active in improving the structure of the tin deposited. In order to determine the effect of any break down products formed tests were carried out using the same sample of electrolyte over a long period of time with no replenishment of addition agents after initial make-up. It was hoped that in this way any break down products formed would build up in the solution and any effects related to this build up would be noticeable from a study of the structure of the tin plate deposited. Initial tests showed that the concentration of tin and phenol sulphonic acid in the electrolyte remained constant over a period of about ten hours continuous plating at 6.2 A/dm². Hence any variation in the structure of tin deposited must be due to the change in concentration of the addition agent and break down products formed.

4.0 EFFECT OF ORGANIC COMPOUNDS ON STRUCTURE OF ELECTRO-DEPOSITED METALS

4.1. Use of addition agents in the electrodeposition of tin Some metals, e.g. Copper, can be electro-deposited satisfactorily from solutions containing only the metal salt and an acid to increase the conductivity of the solution. If tin or lead are deposited from such a solution a coarse, crystalline deposit results which is non-adherent.

The use of organic compounds to improve the structure of electro-deposited metals began empirically Schlotter, 1930 (39) and the investigation of the mechanism involved has only recently been carried out.

Edwards (40) has shown in his extensive investigation that the structure of the deposited metal is modified by adsorption of the organic compounds on to the surface of the cathode. Foreign substances in the electrolyte may be ionic metal salts which result from impurities left in the metal salt on preparation of the technical grade usually used in the electroplating industry. Oxides and hydroxides of the metal salt are also often present in the electrolyte formed by aerial oxidiation. This type of impurity moves through the solution by electric transport. Organic compounds used in the electrolyte to improve the structure of the deposited metal and the break down products of these compounds are not necessarily affected by the electric field. These compounds move through the solution due to diffusion and convection. Consequently high temperature and agitation of the electrolyte increase the concentration of these molecules at the cathode surface. Edwards (41) has shown that these organic compounds are in dynamic equilibrium being continuously adsorbed and desorbed from the cathode surface. There appears to be three major categories of organic addition agents:-

- Compounds which react irreversible with the cathode.
- Compounds in which the whole molecule is reversibly adsorbed.
- Compounds which may themselves be adsorbed but which have break-down products which are not adsorbed.

The adsorption of types 2 and 3 is reversible and a dynamic equilibrium is set up. The adsorption is not strongly influenced by electrode potential and the molecules are adsorbed at definite sites and do not diffuse over the surface of the cathode, since the adsorption energy of all sites can be shown to be the same.

The adsorption and desorption process occurs much faster than the renewal of the cathode surface but the organic molecules do not escape incorporation due to the high speed of the equilibrium. Molecules of different structural formulae are adsorbed with equal ease by any given site although the density of adsorption is not absolutely constant. For example the rate of adsorption of saccharin is temperature dependent.

4.2. Experimental procedure in the electrodeposition of tin

Since one of the major aims of the project was to establish which components of the addition agents were responsible for the improvement in the structure of electrodeposited tin from the Ferrostan solution, a method of comparing the structure of tin deposited under different conditions was sought.

It was found that the Scanning Electron Microscope gave an excellent photographic record of the surface topography of the deposited tin and from a comparison of the resulting photographs much useful information was gained.

Initially the intention was to follow commercial practice as closely as possible and consequently tin plate quality steel strip was used as the substrate. Several tests were carried out in a Hull cell to determine optimum electroplating conditions. Unfortunately, it was not possible to gain reproducible results by this method due to the variability of the steel surface resulting even after electropolishing.(42) This problem has been investigated by Leeds & Clarke in their study of porosity in gold electrodeposits.(43) They showed that zoning occurred within the thickness of the substrate metal surface and deposition was influenced by the amount of metal removed from the surface and by the method used to remove the metal, i.e. etching, polishing or electropolishing. However, two important points were settled after initial Hull cell tests and were later incorporated into other test procedures. These were 1) that the

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electrolyte gave similar results for both bagged and unbagged anodes, and 2) that the concentration of tin and phenol sulphonic acid did not vary widely after long periods of plating, i.e. up to 10 hours plating time. These two factors are discussed on pp. 48. and Appendix I.

Since the steel substrate did not give reproducible results it was replaced by copper which could easily be electropolished to give a good substrate for comparative work.

Oxygen free high conductivity copper sheet of approximately 0.5 cms thickness and 50% cold reduced was reduced further by cold rolling to give a total reduction of 95%. The copper sheet was then annealed for 6 hours at 600° C in a muffle to give a cube texture. From these sheets panels were cut and these were descaled in 50 : 50 sulphuric acid and washed and dried. The descaled samples were polished mechanically to 600 grade emery paper, and at this stage the copper was approximately 0.015 thick. From this panels were cut and stopped off with Lacomit* leaving an area of 2.5 x 2.5 cm for electroplating tests. These test pieces were then electropolished in a 900 g/l orthophosphoric acid solution. A potential of 1.8 volts was applied across the electrodes for 1 minute and this caused the particles left on the surface from the mechanical polishing process to be loosened. The test piece was removed from the polishing solution and washed with a jet of water to remove any residue.

* Stop-off lacquer supplied by W.Canning & Co. Ltd.

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The electropolishing process was then continued for a further 15 minutes and finally the test piece was washed w ith deionised water and used immediately in the plating tests. (Fig.1).

A standard electrolyte was used as the basis of each test and addition agents added as required. The electrolyte contained 64 g/l stannous sulphate and 160 mls/litre 33% phenol sulphonic acid.

(66% phenol sulphonic acid was recommended for the Ferrostan bath but this was not available for these tests).

The electrolyte was freshly made immediately prior to use to eliminate any chance of oxidation of the electrolyte.

The anode used was of 99.75% purity tin. Initial Hull cell tests showed no differences in structure of tin deposited with the anode bagged or not bagged. When the anode was not bagged any tin particles from the surface of the anode fell to the bottom of the cell during electroplating and did not appear to interfere with the electrodeposition.

It was considered that difficulties would arise from contamination if the anode were bagged, due to the difficulty of completely removing all traces of addition agent from the bag between separate tests. This would be particularly difficult when investigating the two isomers present in DDS and it was thought wiser to leave the anode unbagged especially since the length of time taken for each test was generally short. Therefore the anode was simply washed carefully between tests, any loose material being completely removed before re-use.

The plating bath was maintained at a temperature of 50 \pm 2[°] C and the current was variable from 0.3A to 3A with an accuracy of 0.05A. The current was supplied from a 24 volt battery.

Timing was one of the greatest problems, especially during very short term tests which lasted between 1 and 10 seconds. In these cases the cell was set up ready for the test with the cathode in position. The current and timer were started together and the test piece removed at the end of the test before the current was switched off. In this way the whole cell had time to come to equilibrium before the test commenced.

The electrolyte contained 64 g/l stannous sulphate in 160 g/l 33% phenol sulphonic acid with additions and conditions as shown.

Bath	Addition agent	Current Density
1	No addition agent	6.2 A/dm ²
2	5 ml/l DPP as supplied	6.2 A/dm ²
3	6 g/l DDS as supplied	6.2 A/dm ²
4	6 g/l DDS 44' isomer	6.2 A/dm ²
5	6 g/l DDS 22' isomer	6.2 A/dm ²
6	6 g/l DDS partially purified	6.2 A/dm ²
7	5 ml/l DPP Component 2	6.2 A/dm ²
8	5 ml/l DPP Component 2a	6.2 A/dm ²
9	5 ml/l DPP Component 3a	6.2 A/dm ²
10	5 ml/l DPP Component 4	6.2 A/dm ²
11	5 ml/l DPP as supplied	12.5 A/dm ²
12	5 ml/l DPP as supplied	18.7 A/dm ²
13	6 g/l DDS as supplied	12.5 A/dm ²
14	6 g/l DDS as supplied	18.7 A/dm ²
15	Long term DPP test	6.2 A/dm ²
16	Long term DDS test	6.2 A/dm ²

The detection of organic compounds occluded in the electrodeposit and the identification of these fragments together with an estimate of the rate of depletion of the addition agent in the bath formed an important part of the original problem. It was hoped to be able to label the addition agents with radioactive isotopes to assist in the detection, quantitative analysis, and recognition of a possible path of decomposition of the addition agent. Similar work has been carried out by Edwards (44) in determining the role of thiourea in the deposition of bright tin. Edwards labelled both the sulphur and the carbon atom in thiourea. He showed that the concentration of labelled sulphur was much higher in the deposit than the concentration of labelled carbon. At the time this was thought to show conclusively that the thiourea molecule must break down before occlusion in the electrodeposit. Now, however, some doubt has been thrown on to the exact interpretation of these results since it is recognised that thiourea is not a stable organic compound under the conditions of the electrolysis, and some decomposition may have occurred before electrolysis.

More recent work by Rogers and Taylor (45) who used a rotating disc electrode to study the kinetics of coumarin consumption in the electrodeposition of nickel over a fairly wide pH range. These workers have identified two breakdown products and found a relationship between the path of decomposition and the acidity of the solution.

It had been hoped to carry out similar work on DDS by labelling the carbon and sulphur atoms in the C - S bond and with DPP by labelling the central carbon atom. However, this work has not yet been investigated.

4.3. Theory of nucleation and growth

During electrodeposition metal ions move, under the influence of an electric field, from the bulk of the electrolyte to the surface of the cathode. Here they are neutralised by electrons to become atoms, which are incorporated in the crystal structure of the cathode.

The metal ions are not generally present in the electrolyte as simple ions. More usually the metal ions are surrounded by a hydration sheath of water molecules. This is also affected by the electric field due to the high dipole moment of the water molecule. Alternatively the metal can be present in the electrolyte as part of a larger complex ion which may itself be hydrated.

The metal ion is transported from the bulk of the electrolyte to the cathode surface by one of three mechanisms. (46)

- (1) Effect of electric field
- (2) Diffusion
- (3) Convection

Convection may be due either to the concentration gradients within the electrolyte close to the cathode i.e. natural convection or due to agitation of the solution or heating the solution, i.e. forced convection.

Cathode	Helmhdtz Double Layer	Diffusion Layer	Bulk of Electro- lyte

Metal

As the metal ion moves from the bulk of the electrolyte to the surface of the cathode it first passes through the diffusion layer. This layer varies widely in thickness depending on cathode configuration and electrolyte composition but is most strongly affected by the type of convection in the solution. In solutions in which there is forced convection the diffusion layer can be in the region of 10 μm thick w hereas in solutions which are at room temperature and unstirred the diffusion layer may be up to 500 μm . The metal ion moves through the diffuse layer at a velocity dependant on the concentration gradient. The field strength of the diffuse layer is insufficient to liberate the metal ion from its hydration sheath, although the sheath may be displaced and form a cloud behind the metal ion which acts as a brake and reduces the velocity of the metal ion through the diffuse layer.

As the metal ion enters the Helmholtz double layer the field strength increases and the water molecules are lost from the hydration sheath and become part of the double layer.

The dehydrated metal ion moves through the double layer to the surface of the cathode where it is neutralised by the acceptance of one or more electrons. The neutral atom then diffuses across the surface of the cathode to a growth site.(47)

Earlier work suggested that the incoming metal ion moved through the double layer until it was opposite to the nearest active or growth site.(48) It then diffused through the solution to the growth site where it accepted electrons and was immediately incorporated as a metal atom in the growth of the cathode surface. This theory is not now tenable as the high field strength within the double layer would be sufficient to hold the metal ion at whatever point in the outer zone it entered the double layer. Also movement of the metal ion across the double layer would be inhibited by the presence of other metal ions of the same charge in this area. (49)

The deposited metal ion having become a metal atom moves across the surface of the cathode and is incorporated into the growing lattice at active or growth sites. These occur at discontinuities in

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the crystal lattice, which frequently results from dislocations in the substrate surface.

Active or growth sikes have been summarised by Conway & Bockris (30) as follows:-

Planar	co-ordination	number	3.
Edge	п	n	5.
Kink	п	п	6.
Vacancies	п	н	9.

From this it can be seen that the most stable position for the incoming atom to fill is either a kink or a vacancy.

4.3.1. Growth of Crystal Structure

The study of the mechanism of electro-crystallisation is made difficult due to the presence of the many ions and molecules present in the electrolyte. The metal forming the crystal may be present in the electrolyte either in a hydrated form or as a complex ion.

These difficulties do not occur when crystallisation from the gas phase is studied. Kossel (51) showed that least energy is required when the incoming metal atom can be built into the existing crystal lattice. An atom present in the interior of a metal lattice is held in place by symmetrical electrostatic forces. An atom on the surface of a crystal lattice has unused electrostatic forces and these can be used to attract incoming atoms. These forces are strongest at edges and corners of the lattice where the current density is highest or at the centre of crystal planes. The position of new growth is determined by the minimum crystallisation energy. (52)

Although the growth of the crystal lattice from the gas phase is simpler than electro-crystallisation the same basic mechanism exists and much useful information can be obtained from gas phase crystallisation.

When electro-crystallisation is considered the growth form depends on the local current density at the surface of the cathode and the concentration of metal ions in the electrolyte immediately adjacent to the cathode surface. In electrolytes with high concentration of hydrated metal ions the depletion of the cathodic diffusion layer with respect to the metalion is slight and the concentration polarisation is low. The formation of nucleation sites is easy and results in a good compact coating. At higher current densities however the diffusion layer becomes more quickly depleted in metal ion and the nucleation rate is reduced resulting in large single crystal growth.

The effect of the current density on the type of crystallisation occurring has been investigated by Faust for copper, nickel and silver. (53) They have shown that the type of crystal structure formed depends on current density applied, growth on a particular crystal face commencing at a threshold value of current density.

Wranglen also investigated the relationship (54) between the type of crystal structure formed and the current density used. For solutions containing no inhibitors he showed that metals of low over-voltage grow laterally due to growth layers about 1 μ thick. At low current densities growth layers start at the interior of crystal faces whilst at higher current densities growth layers start at edges and corners. For tin below 0.05 A/cm² one dimensional needles are formed whereas for current densities in excess of 0.05A/cm²

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two dimensional dendrites occur.

It must also be borne in mind that electro-(55) crystallisation cannot occur in free space as can crystallisation from gas phase. The cathode acts as a substrate and the crystal lattice of the cathode material must affect the growth of the metal being deposited. If a metal is deposited on a single crystal, single crystal growth occurs. On a normal polycrystalline surface, however, the cathode lattice influences the structure of the metal lattice formed. After some time the depositing metal will form its own crystal lattice irrespective of the lattice of the substrate.

In the work recorded here it should be borne in mind that commercially tin is deposited on to a steel substrate whereas this investigation involved the deposition of tin on copper.

The organic compounds dissolved in the electrolyte are preferentially adsorbed at high energy growth sites and so control crystal growth. Consequently, since these high energy sites are in use the metal atoms are adsorbed at less active sites on the cathode. Since this type of site is more numerous there is an increase in the rate of nucleation and a finer grained deposit results. The process of organic compound adsorption is continuous and consequently throughout crystal growth on the cathode the most active sites are inhibited, and growth occurs at less active sites. A very small concentration of any given active component is normally sufficient to cause fine grained deposits. In fact too much additive frequently results in brittle non-adherent deposits.

4.3.2. SULPHUR CONTAINING COMPOUNDS AS ADDITION AGENTS

Many compounds added to the electrolyte are termed brighteners and result in bright highly reflective coatings of metals being formed. The same metals when deposited without brighteners yield matte or dull coatings. It is thought that brightness is due to the formation of very small crystallites (i.e. high degree of nucleation) or to perfect orientation. (56). Obviously bright coatings can only be achieved on substrates which have no surface protrusions. Hence brightener is a term referred to organic compounds which increase nucleation and help maintain a growth of fine grain compact crystals. Many addition agents, including brighteners, involve organic components containing sulphur atoms.

If a metal is to be deposited from a solution containing an addition agent more energy will be required as the most active sites will not be available for deposition as they will already have molecules adsorbed on to them. Consequently the deposition of bright deposits usually takes place with higher polarisation than for matte or dull deposits.

Roth & Leidheiser have shown that the cathode (57) potential/current density curves are always more negative when bright deposits are formed. Raub et al have shown that for bright nickel deposits the capacity of the double layer is decreased by the use of additives in the solution. Additives not containing sulphur caused a 20% reduction in capacity whilst sulphur containing additives caused the double layer capacity to fall by up to 50%.

The considerable decrease in the capacity of the double layer indicates the growth of a strongly adsorbed film on the cathode. Meibuhr suggests that the reduction in double layer capacity is due to a compact adsorbed layer on the cathode causing the discharge of the metal ion to be retarded. (59) He suggests micelle formation on the cathode surface since his results show that there is a critical concentration of addition agent equivalent to a saturation of the active sites.

All this points to a growing belief that organic compounds containing sulphur atoms alter the surface of the cathode by preferential adsorption at active sites. This results in a modification of the dectrical properties of the double layer through which the tin ion must pass to be discharged at the cathode and be incorporated in the crystal growth.

It has been shown that the effect of organic compound as an addition agent is to increase polarisation and its ability to do this depends on the size of the molecule, its acidity and the number of electron pairs available in the molecule.

According to Fischer, (60) tin has a low inhibitor sensitivity and consequently requires a very efficient additive to be deposited as a fine grained bright deposit.

5.0. RESULTS

5.1. Comparison between tin deposited from a bath containing no addition agent and baths containing commerically available addition agents

As discussed under 4.2 the presence of an addition agent in a tin plating bath is essential for the formation of a smooth, coherent deposit. If the bath does not contain an addition agent coarse crystalline deposits result and the deposit is non-coherent.

Figures 2 and 3 show tin deposited from an electrolyte containing no addition agent. The deposit consists of clusters of individual crystals. The substrate is not fully covered even after 30 seconds plating time. The deposits from both baths containing commercially available addition agents show many more sites of nucleation after only 1 second plating time. (Figures 4 and 6). When the current has passed for 30 seconds both baths show complete coverage of the substrate. (Figures 5 and 7).

5.2. Comparison of the effectiveness of each of the commercially available addition agents

The deposit from the bath containing DDS as addition agent shows a marked change in structure between that deposited initially (Figure 6) and the deposit formed after plating for 60 seconds. (Figure 16). Initially the deposit formed is of small smooth crystals with a definite preference for deposition on certain favoured crystal faces in the substrate. (Fig.6). The deposit does not appear to fully cover the substrate until after 20 seconds plating time (Figs. 12 and 14). The deposit although initially of small smooth crystals shows signs of individual crystal growth after 30 seconds plating time and at 60 seconds plating time shows a coarse crystalline structure which is not acceptable in the deposition of tin for corrosion protection.

The deposit from the bath containing DPP as addition agent is much more uniform over the period of time for which the tests were carried out. Initially (Fig. 9) the deposit showed some signs of deposition on preferred crystal faces in the copper substrate and some orientation of the crystals deposited which is not noticable in tin deposited from baths containing DDS as addition agent.

However after only 10 seconds the deposit fully covers the substrate with small smooth coherent crystals the size of which are not greatly affected by the length of time of deposition. Indeed the structure of the deposited tin formed after 10 seconds plating is similar in appearance to that produced after 60 seconds plating time.

Both baths give deposits of tin which are a great improvement on the deposit from a bath containing no addition agent. From this comparison between the effectiveness of the commercially available addition agents the DPP addition agent quite obviously gives a much more smooth, compact, coherent coating and under the conditions of the test is preferable to the deposit from the bath containing commercially available DDS.

5.3. Comparison of the effectiveness of each of the components of DPP as addition agents

Section 3.5 showed that on the separation of DPP into its various components the following fractions resulted.

a) Component 2a.

A deep red brown liquid containing the majority of the ether insoluble components of DPP and consequently strongly acidic. The most likely compounds present in this fraction are acetic acid and sulphuric acid and sulphonated compounds.

b) Component 2b.

This component was prepared by neutralising a portion of component 2 and converting all acids present (i.e. acetic, sulphuric and sulphonic) to their sodium salts.

c) Component 3a.

This component results from ether soluble fraction originally but boils at 100° C and smells strongly of phenol and probably contains compounds having a phenolic group. d) Component 3b.

This was also a deep red brown viscous liquid similar to the fraction designated 2. However this component is insoluble in water probably containing compounds similar to those contained in Component 2 but of higher molecular weight. Due to its insolubility in the electrolyte it was not possible to use this component as an addition agent.

e) Component 4.

This component was once again a deep red brown liquid but it was water soluble. This component probably contained compounds similar to those contained in Component 2.

The effectiveness of each of these components when used as an addition agent, is compared below.

Component 2.a.

This component, when used as an addition agent, gave a tin deposit which after short periods of plating produced a satisfactory coating. The crystals are compact and smooth although they show signs of the lath structure. The deposit after only 5 seconds completely covers the substrate (fig. 18) After 10 seconds plating, however, there is growth on individual crystals giving a much coarser structure. (fig. 19) After 30 seconds plating time the deposit is of sharp edged individual crystals and although the coating is dense and compact, it is not satisfactory, as a corrosion protective surface. (Fig.20) Note all photographs at magnification 11.5 - 14.5 K.
Component 2b.

From the photographs Fig. 21 and 22, it is quite obvious that when component 2a is converted to the sodium salts of the acids present all additive effects are negated. The deposit formed in this bath is similar to that formed in a bath having no addition agent.

Component 3a.

This component produced deposits which initially showed a high rate of nucleation and the formation of small smooth crystals. (Fig.23) However, after only 10 seconds plating time the addition agent effectiveness had been reduced and the deposit was similar to that from baths containing no addition agent. (Fig.24)

Component 4.

From the photographs (Fig.25) it can be seen that this component must contain the most effective addition agents from the DPP solution. Fig.25-28 are at magnifications between 2.3 and 2.4k and show the finest grained deposit so far produced.

In figure 25 the very small crystals seem to show signs of the lath structure. A very compact coherent deposit is produced at a deposition time of 1 second. This feature of very small smooth edged crystals continues up to and including deposition time of 30 seconds. Fig. 29 which is at a magnification of 13 K is an enlargement of figure 28 and shows the coherent smooth edged crystals formed after 30 second plating time.

In a comparison of the deposit from this bath with that from the bath containing the commercially available DPP it can be seen that the covering power of the bath containing component 4 is much greater in the early stages of deposition than the bath containing the commercially available DPP. The deposit is much denser and the crystals formed are smaller. (Compare figure 4 and figure 25). After 30 seconds plating time the deposit from the bath containing component 4 has a smoother surface appearance. These features are due to the concentration of the addition agent in the electrolyte. In the bath containing the commercially available additive the active component is present together with non-active components. In the bath containing component 4 the majority of the active ingredient from 100 ml sample of DPP has been concentrated into 50 mls of water which was concentrated down to 5 mls all of which was added to the 1 litre of electrolyte made up for the test. The electrolyte containing component 4 is consequently 20 times more concentrated in the active ingredient.

5.4. Comparison of the effectiveness of each of the components of DDS as addition agents

Four different solutions were used as electrolytes in this comparison. The as-received DDS (designated DDSO) was shown to consist of the 44' isomer (melting point 242° C) designated DDS1, the 22' isomer (melting point 168° C) designated DDS2 and possibly other isomers designated DDS3.

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It had been reported that while the commercially available DDSO was satisfactory as an addition agent in the tin plating bath, if the addition agent was purified exhaustively by recrystallisation the efficiency of the addition agent was reduced.⁽¹⁵⁾ This suggested that some impurity present in the commercially available DDSO is active in the tin plating bath and on removal from DDSO renders the addition agent less effective. From the work discussed under 3.5 it is clear that the impurity so described would be the 22' isomer.

The bath (4) containing the mixture was included in this comparison to determine whether the two isomers of DDS had a synergistic effect and whether this effect was impaired at low concentrations. The DDS 3 had a melting point in the region 240° C. Since the pure 44' isomer has a melting point 242° C and since 15 gms of DDSO yielded about 1 gm of the 22' isomer showing the as received addition agent contains about 6 - 7% DDS2, it is suggested that bath 4 contained less than 2% DDS2.

Taking each bath separately:-

The bath containing commercially available DDSO has already been assessed (5.2) and shows a good covering of tin after short periods of plating, fig. 6 and 10 although there are definitely signs that there is preferred deposition on certain crystal faces in the copper substrate. The copper substrate does not appear to be completely covered until plating has continued for 30 seconds and at 60 seconds the crystals formed are becoming sharper and coarser. DDS1

The bath containing the 44' isomer gave unsatisfactory tin deposits and confirmed the opinion that the purified 44' isomer is unsatisfactory as an addition agent used alone. The deposit after 1 second is sparse and of individual coarse crystals. After 10 seconds plating time the deposit shows definite dendritic growth and is totally unsuitable for a corrosion protection coating (Fig. 34 and 35).

DDS2

The 22' isomer definitely shows good addition agent properties for short periods of time. After 1 second (Fig.38) an exceptionally high number of nucleation sites can be seen, a feature not always noticeable using other addition agents. The crystals deposited are smooth and small and for periods up to 30 seconds plating time a satisfactory deposit is formed. However for plating times in excess of 30 seconds the 22' isomer is not satisfactory as dendritic growths are noticeable. (Fig.41). In fact the 22' isomer gives a tin structure which is less satisfactory than that produced over 30 seconds by the commercially available mixture of isomers.

Bath 4

The deposit from this bath clearly shows that a synergistic effect does occur for periods of plating in excess of 30 seconds. The deposit as shown in figs. 44 and 45 are similar to those given by the commercially available DDSO (compare figs. 14 and 16). However the degree of nucleation after short plating periods

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is definitely less than that for DDSO (compare figs 6 & 34) and the initially deposited crystals are coarser and less coherent than those from the DDSO bath.

In summary it would seem that both isomers must be present in the DDS addition agent to promote a satisfactory tin deposit from the Ferrostan electrolyte. The 22' isomer appears to promote nucleation at a large number of sites in the very first stages of electrodeposition (compare figs 6 & 38). However, since neither addition agent is effective alone after periods of plating in excess of 30 seconds (figs 37 & 41) a suitable mixture of the two isomers is recommended.

The mixture used in these tests, Bath 4, containing less than 2% of the 2,2' isomer gave coarse grained crystals and poor covering power after short periods of time. The DDSO as-received mixture gives a good deposit up to 60 seconds plating time but the initial nucleation rate is low. Hence it is suggested that if the concentration of the 2,2' isomer in the mixture be increased the effectiveness of this addition agent would be improved.

5.5. Comparison of the commercially available addition agents at current densities of up to 18/3 A/dm²

Both commercially available addition agents were used at current densities of 12.4 A/dm² and 18.6 A/dm² to determine whether these addition agents were effective at high current densities in still baths.

Figures 46, 48, 50 and 52 show the deposit after 1 second plating time.

Both DPP and DDS gave deposits which were acceptable since they show a coherent smooth crystal coating at 12.4 A/dm^2 (figs. 46 & 50), but both were unsuitable at 18.6 A/dm^2 since in figs. 48 & 52 there are signs of the formation of dendrites. The lower photograph on each page show the time of onset of definite dendritic growth. Both DPP and DDS show some dendritic growth after 3 seconds at 18.6 A/dm^2 . (Figures 49-53) However at 12.4 A/dm^2 DPP does not show dendritic growth until 30 seconds plating time (fig.47) whereas DDS shows the formation of dendrites at 10 seconds. (Fig. 51)

5.6. Comparison of the effects of allowing the concentration of the addition agents to be reduced while the concentration of any break down products formed increased

Considering the series of results obtained using DPP as addition agent, each of the test pieces has been electroplated for 30 seconds at 6.2 A/dm² and consequently any variation in the surface topography must be due to the effect of the change in concentration of addition agent or to the increase in concentration of break down products formed by decomposition of the addition agent. The concentration of the addition agent can be reduced by losses due to drag out or by losses due to decomposition. From the series of photographs (figs 54 - 69) it can be seen that the effectiveness of DPP as an addition agent varies very little over the 7 hour period of the test. The deposit is coherent, smooth and lacks surface features indicative of a good compact surface coating. Thedeposit formed during the first 3 hours of the test shows a smaller grained deposit than that formed at later stages. After 7 hours of testing the deposit is tending to show a coarser structure which would not be acceptable as those deposits initially formed. 👘 From this series of tests it would seem that DPP is satisfactory as an addition agent under the conditions of this test for at least five hours.

When the same test was repeated using DDS as addition agent the results were not so satisfactory.

Figs. 62 - 69 show the results of this test. Initially a good coherent fine grained deposit is formed but after 1 hour of use the electrolyte produced a new type of surface structure. This lath-like deposit had been deposited in earlier tests from two components of the DPP addition agent (ref. fig. 25) but had not previously been noticed using DDS as addition agent.

After 2 hours testing the deposit again showed the lath structure but superimposed on this there is individual crystal formation. (Fig. 64)

The deposit formed after 2 hours continuous use would be unsuitable as a corrosion resistant layer and test pieces produced after the bath had been in use for longer periods of time were totally unsuitable since coarse crystalline deposits were formed and after 5 hours a high incidence of dendritic growth occurred. This addition agent could only be recommended as satisfactory under the conditions of this test for periods of not more than 1 hour.

6. 0. DISCUSSION OF RESULTS

6.1. Separation and purification of components of DDS

Commercially available DDS was separated by fractional recrystallisation from water and shown to contain at least two compounds of widely different melting point.

The information obtained from the infra red spectra of the two compounds separated from the mixture suggested that these compounds had slight structural differences but had the same functional groups present. From the mass spectra it was possible to show that the two compounds had the same molecular weight and that they fragmented in the same way, so suggesting that the two components present were structural isomers of the same compound.

A sample of pure 44' dihydroxy diphenyl sulphone was made available and the melting point obtained was 242° C. This compared well with one compound separated from the mixture and previously designated DDSl which had a melting point in the range 241 - 242° C. The compound designated DDS2 which had been separated from DDSl and shown to have a melting point 168 - 170° C is probably the 22' isomer.

From the work carried out on the fractional recrystallisation of these two isomers from water it would seem that the as-received sample of DDS contained about 6-7% DDS2. It has been stated that DDS1 can be made to give a melting point in the region of $248 - 250^{\circ}$ C by purifying a 5% solution from activated charcoal. However repeated efforts to raise the melting point both of the as supplied pure 4^{*i*}/_{*i*} isomer and of the sample separated from the as received DDS0 were unsuccessful.

When the DDSO was separated to give samples of DDS1 and DDS2 for use in the electrolyte the fractional crystallisation was carried out from ether as solvent to speed up the separation. During this work a very small quantity (less than 0.07 gm) of a third compound was separated. The melting point of this compound was of the order of 150° C but decomposition occurred near the melting point and it was not possible to determine the melting point with any degree of accuracy. So little of this compound was separated that no identification tests could be carried out.

6.2. Separation of DPP into its various components

This addition agent, which is available commercially, is known to be a mixture of several compounds and to contain some free sulphuric acid. Consequently separation by fractional distillation or any other method requiring heating is precluded since further reactions between the compounds present and the free sulphuric acid would alter the composition of the mixture.

Methods of removing the free sulphuric acid, for example as lead sulphate or barium sulphate, were not successful since the resulting mixture was so viscous that the precipitated sulphates were not easily separated by filtration. Dilution to reduce the viscosity resulted in final evaporation methods to concentrate the products and reactions between the various components of the mixture could have taken place at this stage.

The method of diferential solubility in a non polar solvent succeeded in dividing the material into water soluble compounds and ether soluble compounds. The water soluble compounds would be the sulphonated diphenylol propane, sulphuric acid, acetic acid and any other molecules which have become sulphonated. The ether soluble compounds would be any molecules which have been acylated but not sulphonated and high molecular weight phenols.

6.3. Effectiveness of the components of DDS as addition agents in electrodeposition of tin

From the Stereoscan photographs it can be seen that both isomers present in commercially available DDS are necessary to the electrodeposition of a satisfactory tin plate.

From a comparison of Figs 34 and 38 it would seem that the 22' isomer increases the initial number of nucleation sites, but used on its own it does not have a satisfactory long term effect.

The electrolyte made up using an addition agent with some of the $2^{2'}$ isomer removed showed an improved long term effect (Fig. 4^5) but the number of nucleation sites initially formed is unsatisfactory. From the work carried out it would seem that if the concentration of the $2^{2'}$ isomer in the mixture could be increased the uses of DDS as an addition agent could be extended. It is not possible to increase the concentration of the addition agent in the bath since it is already used as a saturated solution. Consequently it is suggested that if further work (using DDS) is considered important it should be used in solutions having the current concentration (6g/1) but containing a higher proportion of the $2^{2'}$ isomer.

However, from the Stereoscan photographs it can be seen that DDS is not such an effective addition agent as DPP especially over larger plating periods. Since the

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compound is a solid and only dissolves in the electrolyte with difficulty it has been virtually replaced by the liquid DPP addition agent.

6.4. Effectiveness of the constituents of DPP as addition agents in the electrodeposition of tin

As previously described the DPP addition agent was separated into water soluble and ether soluble components. From the Stereoscan photographs it can be seen that the ether soluble components are not effective as addition agents (Figs. 18 & 24) whereas the water soluble components are efficient as addition agents. However when the acid groups present in the water soluble components have been neutralised (Component 2a) the resulting solution is not effective in improving the structure of the tin deposited. Hence the effective components must contain acidic groups and conversely there are no molecules acting as beneficial addition agents in DPP which are non polar. The ether s oluble components (3a, 3b, and 4), definitely contained compounds from the DPP mixture and

as these were shown to have no effect on the structure of tin deposited they must act as diluents in the addition agent.

From a consideration of the structure of various possible compounds present in DPP it would seem that the active constituent is sulphonated diphenylol propane together with other molecules of similar structure.

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The water soluble components of the DPP addition produce a deposited tin layer which is of smaller grain size and more compact than that produced by the components of DDS under the same conditions. (Figs. 25, 34 and 38).

6.5. Effectiveness of using the Scanning Electron Microscope to identify active constituents in the addition agents.

The scanning electron microscope is finding increasing use in the study of the surface topography of deposited metals. (61, 62) The photographic record of the growth of the deposited metal is simple to produce and the detail obtainable is clear even at magnifications in the region of 15K - 20 K.

The work here reported is based on the ability of two addition agents to improve the structure of deposited tin. The ease with which the components of, for example, DPP could be labelled active or inactive made the identification of active components quick and simple.

From the photographic record produced it can be seen that different components of the addition agents appear to have different functions. DDS 1 can easily be seen to increase the initial rate of nucleation although its long term effects are not good. Component 4 of DDP can be seen to have good long term effect as well, the deposit after 30 seconds being of approximately the same crystal size and shape as that initially deposited.

Addition agents which were more effective on certain crystal faces in the substrate were also readily discernible. (Fig. Hence by distinguishing the good properties of these addition agents recommendations for the tailor-making addition agent could be made.

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6.6. Use of DDS and DPP at current densities higher than that recommended

Since the crystal structure of the metal deposited is known to be related to the current density used, tests were carried out to determine whether these additions could be used at current densities higher than that recommended.

The work was carried out in still baths and is hence not applicable to the industrial production of tin plate where the steel strip moves at speeds up to 250 ft/min through the solution.

It was shown that the change from an acceptable fine grained compact deposit of tin to a coarse non-adherent deposit occurred very quickly. The photographs (fig. 46, 48, 50, 52) show that in fact neither DDS or DPP could be recommended for use at current densities higher than 6.2 A/dm² under the conditions of the test.

From the results however, (fig. 46) it would seem that if tests on the use of the addition agents at higher current densities were carried out in the future DPP may show itself more suitable in agitated than DDS.

6.7. Effect of reducing the concentration of the addition agent and allowing any break-down products formed to increase in concentration.

This series of tests shows conclusively the advantages of DPP as an addition agent. The structure of the tin deposited is of a consistently high quality over the first 5 hours of the test. The grain size is small and the coating compact. In comparison DDS is shown to be satisfactory for only short periods of time.

Although break down products may have been formed from the DPP addition agent their effect if any is not noticeable. Hence we can assume that if any are formed they have a similar effect on the electrodeposit to the main constituents of the DPP solution.

With DDS however it appears that the compounds present do break down since after 1 hour a new type of crystal structure is shown. (Fig. 63). This structure had not been given previously from DDS solutions. After 3 hours plating time the effect is no longer noticeable and hence it would appear that the original compounds present in DDS break down to give a new compound responsible for this lath-like crystal structure, and that the effect of this compound is lost after 3 hours plating. Since subsequent deposits are of poor quality it would seem that the active dihydromy diphenyl sulphone has been removed from solution in this way. Two addition agents are currently used in the electrodeposition of tin for the tin plate industry. The subject of this investigation was to compare the effectiveness of these addition agents using the scanning electron microscope to study the surface structure of the deposited tin.

Since both commercially available addition agents were known to be not pure compounds but mixtures of compounds, an attempt was made to identify the active component of each addition agent and to separate it from the inactive components. It was hoped that some correlation might be discovered between the structure of the organic compound active in the electrolyte and its effect on the structure of tin deposited.

Since a large proportion of the tin plate manufactured in this country is used in the packaging of foodstuffs and since American legislation controls the toxicity of addition agents used in depositing metals used in the foodstuffs industry it was hoped to be able to determine to concentration of any organic compounds occluded in the deposited metal.

During the investigation information concerning the uses of these addition agents at current densities in excess of that recommended was also gained and is here presented. In the comparison of the two commercially available addition agents for use in the Ferrostan bath it has been shown that DPP is definitely more effective than DDS. From the photographic record presented DPP is shown to give a finer grained more compact electrodeposit and is active over a longer period of time than is DDS.

When the addition agents were separated into their components it was shown that the most effective component in DPP is a water soluble compound containing strongly acid and/or phenol groups. If it is necessary to improve the effectiveness of DPP this could be achieved either by removing some of the inactive components at present acting as diluents or by separating the active component labelled (DPP4a in this work) as shown and using alone in greater concentration than is currently the case. Further work would be necessary to determine the maximum concentration at which this component can be used effectively.

The second addition agent investigated, namely DDS, was found to be a mixture of isomers. When these isomers were separated and used individually as addition agents it was found that the structure of tin deposited was coarser grained than that produced by the as received addition agent. It was found that the 44' isomer was

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responsible for improving the long term effect of the addition agent but that the 22' isomer was responsible for a high initial nucleation rate. It would seem therefore that both isomers are necessary to produce a fine grained compact deposit over a long period and that the isomers have a synergistic effect. Further work could well investigate the optimum ratio of these isomers and determine the point at which the effectiveness of each becomes negligible.

It had been hoped that the break down products formed in the bath from the addition agents might be separated, identified and their effectiveness as addition agents in the bath estimated. Following Edwards' work it was then hoped that it might be possible to prepare samples of the compounds formed during break down containing radioactively labelled key atoms so that the identification and quantitative estimation of the compounds occluded in the deposited metal could be determined. Unfortunately it was found impossible to separate these compounds from the electrolyte. However a different approach yielded some interesting results. By analysis it was found that over periods of up to 10 hours continuous plating the concentration of the tin and phenol sulphonic acid in the electrolyte remained virtually constant. Hence the effect of break down products from the addition agents

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could be studied using the scanning electron microscope to investigate the surface of the deposited metal.

Using DPP as addition agent no change in the type of structure deposited could be discerned over periods up to 5 hours. After this the deposit appeared to be similar to deposits from baths containing insufficient addition agent. This indicated that the DPP addition agent was either breaking down over a period of time to give new compounds which do not affect the structure of tin deposited or that the concentration of DPP in the electrolyte was reduced with time by incorporation in the deposited tin.

Using DDS as addition agent, however, a new type of structure was discovered on the test piece plated after 1 hour of plating time. This lath like structure had not been found at any other point in the investigation although it has been recorded in work on gold electrodeposits. This lath type structure continued to be deposited until the 3 hour test piece was plated when the effect was no longer noticeable. It seems likely that the DDSO addition agent has here broken down to give new organic compounds which cause this type of structure to be produced. Since test pieces after longer periods of time with this addition agent were unsatisfactory it would seem that the addition agent is being removed from the electrolyte in this way. Future work might well include an investigation to determine the relationship between the structure of the organic compounds in solution and their effect on the deposited metal. A comparison between possible break down products from this sulphone and the break down products possible in the electrodeposition of gold would make a good starting point.

During the work reported tests were carried out on current densities higher than those recommended. It was evident that neither addition agent gave satisfactory results at current densities above 6.2 A/dm^2 .

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APPENDIX I.

Analysis of the acid tin electrolyte. (63)

The electrolyte was analysed over a period of ten hours plating time to check the variation in tin content and free acid content.

The Sn²⁺ ion was estimated volumetrically against a standardised iodine solution. The free acid was estimated against standardised sodium hydroxide solution. The analysis was carried out on 10 ml samples at hourly intervals.

Time	Concentration of tin in g/l	Free acid concentration as mls N/10 NaOH
Initially	27.3	19
1	25.3	22
2	25.9	23
3	26.2	22
4	26.7	22
5	27.1	24
6	25.4	20
7	26.1	22
8	26.7	23
9	27.8	24
10	28.4	24

The solution was filtered after 5 hours plating time to remove anode sludge and hydrated tin oxide suspended in the solution. In this way it was possible to hold both the tin and free acid concentration almost constant.



Fig.1. Copper Substrate

Not plated

Mag. 100 K



Fig.	2.	No addition agent	Time	1	sec.
		Current density 6.2 A/dm ²	Mag.	2.	.2 K



Fig.3.

No addition agent Current density 6.2 A/dm² Time 30 sec Mag 2.8 K



Fig. 4.		Addition agent DPP		Time	1	se	С		
		Current	density	6.2	A/dm ²	Mag.	2.	4	K



Fig. 5. Addition Agent DPP Current density 6.2 A/dm2

Time 30 sec Mag. 2.4 K



Fig.	6.	Addition agent DDS	Time 1 sec
		Current density 6.2 A/dm ²	Mag. 2.4 K



Fig. 7. Addition agent DDS Current density 6.2 A/dm²

Time 30 sec Mag. 2.6 K



Fig.	8.	Addition agent DDS	Time	5 s	sec
		Current density 6.2 A/dm2	Mag.	2.4	1 K



Fig. 9. Addition agent DPP Current density 6.2 A/dm² Time 5 sec Mag. 11.5 K



Fig.	10.	Addition agent DDS	Time 10 sec
		Current density 6.2 A/dm ²	Mag. 2.4 K



Fig. 11. Addition agent DPP Current density 6.2 A/dm²

Time 10 sec Mag. 2.2 K



Fig. 12.	Addition agent DDSO	Time 20 sec
	Current density 6.2 A/dm ²	Mag. 2.6 K



Fig. 13.Addition agent DPPTime 20 secCurrent density 6.2 A/dmMag. 2.5 K



Fig. 14. Addition agent DDSO Current density 6.2 A/dm² Time 30 sec. Mag. 2.6 K



Fig. 15.Addition agent DPPTime 30 secCurrent density 6.2 A/dm2Mag. 2.4 K


Fig. 16.	Addition agent DDSO	Time 60 sec.
	Current density 6.2 A/dm2	Mag. 2.6 K



Fig. 17. Addition agent DPP Current density 6.2 A/dm²

Time 60 sec Mag. 2.6 K



Fig.18.	Addition agent DPP2a	Time	5 sec
	Current density 6.2 A/dm ²	Mag.	12 K



Fig. 19.		Addition agent DPP2a	Time	10	se	C
		Current density 6.2 A/dm ²	Mag.	11.	.5	K



Fig. 20. Addition agent DPP2a Time 30 sec Current density 6.2 A/dm² Mag. 14.5 K.



Fig.	21.	Addition agent DPP 2b.	Time 5 sec
		Current density 6.2 A/dm ²	Mag. 1.8 K



Fig. 22. Addition agent DPP2b. Current density 6.2 A/dm²

Time 30 sec Mag. 1.9 K



Fig. 23.	Addition agent DPP3a	Time 1 sec
	Current density 6.2 A/dm ²	Mag. 2.2 K



Fig. 24. Addition agent DPP3a Current density 6.2 A/dm²

Time 10 sec Mag. 2.4 K



Fig.	25.	Addition agent DPP4a.	Time 1 sec
		Current density 6.2 A/dm ²	Mag. 2.4 K



Fig. 26. Addition agent DPP4a. Time 5 sec Current density 6.2 A/dm² Mag. 2.4 K



Fig. 27.	Addition agent DPP4a.	Time 10 sec
	Current density 6.2 A/dm ²	Mag. 2.3 K



Fig. 28. Addition agent DPP4a Current density 6.2 A/dm²

Time 30 sec Mag. 2.3 K



Fig.	29.	Addition agent DPP4a.	Time 30 s	sec
		Current density 6.2 A/dm ²	Mag. 13 1	ĸ



Fig.30.	Addition agent DDSO.	Time 1 sec.
	Current density 6.2 A/dm ²	Mag. 2.4 K



Fig.31. Addition agent DDSO. Current density 6.2 A/dm²

Time 10 sec. Mag. 2.4 K



Fig. 32. Addition agent DDSO. Time 30 sec. Current density 6.2 A/dm². Mag. 2.6 K



Fig. 33. Addition agent DDSO. Current density 6.2 A/dm²

Time 60 sec. Mag. 2.6 K



Fig. 34. Addition agent 44' DDS. pure Time 1 sec. Current density 6.2 A/dm² Mag. 6.5 K



Fig.35. Addition agent 44' DDS pure Time 10 sec. Current density 6.2 A/dm² Mag. 2.8 K



Fig. 36. Addition agent 44' DDS Pure Time 30 sec. Current density 6.2 A/dm² Mag. 2.6 K



Fig. 37. Addition agent 44' DDS Pure Time 60 sec. Current density 6.2 A/dm² Mag. 3.1 K



Fig. 38.	Addition agent 22' DDS	Time 1 sec
	Current density 6.2 A/dm ²	Mag. 2.8 K



Fig. 39. Addition agent 22' DDS Time 10 sec Current density 6.2 A/dm² Mag. 2.7 K



Fig. 40.	Addition agent 22' DDS	Time 30 sec
	Current density 6.2 A/dm ²	Mag. 2.9 K



Fig. 41. Addition agent 22' DDS Current density 6.2 A/dm²

Time 60 sec. Mag. 2.0 K.



Fig. 42 Addition agent impure 44' DDS Time 1 sec Current density 6.2 A/dm² Mag. 2.7 K



Fig.43 Addition agent impure 44' DDS Time 10 sec Current density 6.2 A/dm² Mag 2.7 K



Fig.	44.	Addition	agent	impure	44'	DDS	Time	30	sec
		Current d	lensity	6.2 A	$/dm^2$		Mag.	2.6	K



Fig.45. Addition agent impure 44' DDS Time 60 sec Current density 6.2 A/dm² Mag. 2.7 K



Fig.	46.	Addition agent DPP	Time 1 sec
		Current density 12.4 A/dm2	Mag. 2.6 K



Fig. 47. Addition agent DPP Current density 12.4 A/dm² Mag. 2.0 K

Time 30 sec



Fig.	48.	Addition	n agent I	OPP		Time	1 s	ec	2
		Current	density	18.6	A/dm ²	Mag.	10.	2	ĸ



Fig.	49.	Addition	agent DPP	Time 5 sec
		C urrent	density 18.6 A/dm ²	Mag. 2.0 K



Fig.	50.	Addition agent DDS	Time	1	sec
		Current density 12.4 A/dm ²	Mag.	2	K



Fig. 51. Addition agent DDS Current density 12.4 A/dm² Time 10 sec Mag. 2 K



Fig.	52.	Addition agent DDS	Time 1 sec
		Current density 18.6 A/dm ²	Mag. 2 K



Fig. 53. Addition agent DDS Current density 18.6 A/dm²

Time 5 sec Mag. 2 K



Fig. 54. Addition agent DDSO Addition agent DDSO Time 30 sec Current density 6.2 A/dm² Mag. 2.6 K

Time 30 sec



Fig. 55. Addition agent DPP Current density 6.2 A/dm²

Time 1 hour Mag 1.7 K



Fig. 56.	Addition agent DPP	Time 2 hours
	Current density 6.2 A/dm2	Mag. 1.7 K



Fig.	57	Addition	agent	DPP	
		Current	density	6.2	A/dm ²

Time 3 hours Mag. 1.8 K



Fig. 58. Addition agent DPP Time 4 hours Current density 6.2 A/dm² Mag. 1.8 K



Fig. 59. Addition agent DPP Current density 6.2 A/dm²

Time 5 hours Mag. 1.6 K



Eig.	60.	Addition agent	DPP	Time	6 hrs
		Current density	6.2 A/dm	2 Mag.	1.8 K



Fig.	61.	Addition agent DPP	Time	7	hrs	5
		Current density 6.2 A/dm2	Mag.	1.	.8 K	5



Addition agent DDS Starting co Current density 6.2 A/dm² Mag. 1.6 K Fig. 62. Addition agent DDS

Starting condition



Fig. 63. Addition agent DDS Current density 6.2 A/dm²

Time 1 hour Mag. 2.2 K



Fig.	ig. 64. Addition agent DDS		Time 2 hours
		Current density 6.2 A/dm2	Mag. 2.4 K



Fig. 65. Addition agent DDS Current density 6.2 A/dm²

Time 3 hours Mag. 2.0 K



Fig. 66.	Addition agent DDS	Time 4 hours		
	Current density 6.2 A/dm2	Mag. 2.8 K		



Fig. 67. Addition agent DDS Current density 6.2 A/dm²

Time 5 hours Mag. 2.6 K



Fig.	68.	Addition agent DDS				
		Current	density	6.2	A/dm ²	

Time 6 hours Mag. 6.3 K



Fig. 69. Addition agent DDS

Current density 6.2 A/dm²

Time 7 hours Mag. 1.1 K