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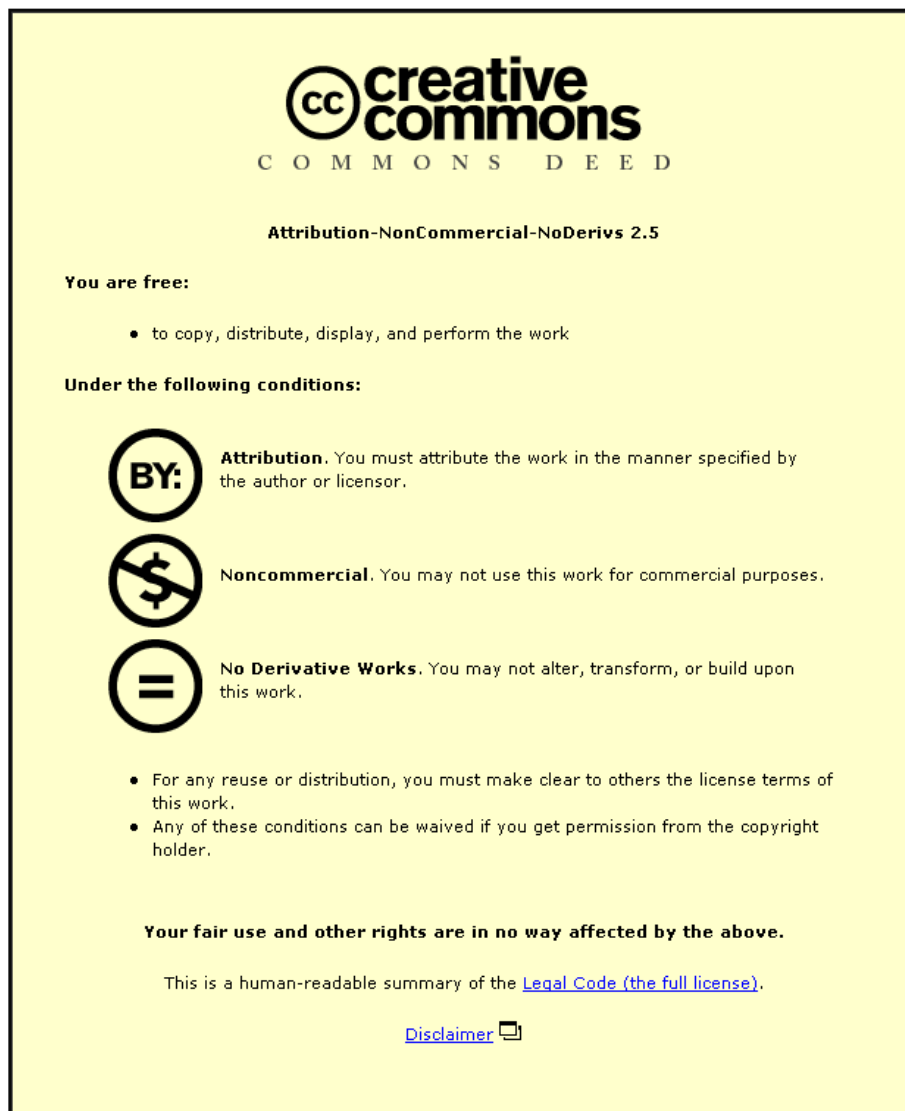
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THE ELECTRODEPOSITION OF TIN AND LEAD-TIN BASED ALLOYS

by

M.A.F. SAMEL, BSc (Aleppo), MSc (Loughborough)

This thesis is submitted in partial fulfilment of the  
requirements for the degree of  
Doctor of Philosophy  
of the  
Loughborough University of Technology

December 1984

Supervisor  
Dr D.R. Gabe  
Department of Materials Engineering and Design

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*DEDICATION*

*In memory of my father and mother.*

*To my wife Basima and children.*

## SYNOPSIS

A summary of the conditions for alloy electrodeposition follows a brief introduction which includes the history and the scope of the tin and lead-tin alloy coating industry. The roles of the different variables in the electrodeposition of alloys have been briefly described. A detailed review of the different types of solutions which have been used in tin and lead-tin based alloy electroplating introduces the main industrial applications of such alloys.

A detailed study, including the investigation of many methods of preparing a tin sulphamate solution for tin-plating, has been carried out. The optimum conditions for such a solution have been defined following detailed experiments concerning the effect of the different parameters (polarization, current density, additives, etc). Some additives have been studied in detail to secure stability for the solution.

A sulphamate electrolyte for lead-tin alloy plating has been proposed as a combination of the already developed tin solution and a lead sulphamate solution developed previously (see MSc dissertation, 1981). This solution has been used to electrodeposit four types of alloys of composition 90, 80, 70 and 40% lead (remainder tin). The effects of the more important parameters for the alloy solutions have been investigated to achieve the optimum condition for alloy electrodeposition.

As an application of the alloy of composition 90% lead (remainder tin), a set of bearings of a motor car engine has been plated for the purpose of examining the suitability of the alloy for such applications. Preliminary indications are of general acceptance.

## ACKNOWLEDGEMENTS

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## PREFACE

The practical importance of electrodeposited alloys has grown during recent years and the use of electroplating techniques has been adopted by many firms over the world for a variety of applications in many industrial areas. In addition to the superior properties exhibited by electrodeposited alloys, the importance of the technique is also due to some possible technical advantages of them including the following:

- the composition of the alloy may be tailored to meet certain surface properties.
- an economical coating can be electrodeposited if one of the parent metals is expensive
- metals with good surface properties which cannot be electrodeposited alone such as W, Mo, etc. can be codeposited with other metals.

The main drawback to electroplating in alloys is the difficulty in controlling the plating process stemming from a lack of knowledge and incomplete understanding of the process. This may limit its use. A large number of binary and ternary alloys have been electrodeposited under laboratory conditions but only a few have been used for industrial applications.

Tin-lead alloys are one of the few alloys which have been well studied and found many applications, especially in motor cars and the electronics industry.

An alloy with composition of 8, 10% Sn-remainder lead is widely used as an overlay upon the hard bearing material to improve its bearing properties and to confer greater corrosion resistance and better load distribution. An alloy with composition of 63% Sn - 37% Pb has the advantage of low melting point (183°C). It is widely used as a solderable coating upon many electronic articles, especially printed circuits and connectors.

Tin-lead alloys may be electrodeposited from many different solutions, but the fluoborate solution is commercially dominating. In recent years, new stricter regulations have been introduced in some industrial countries (Japan) from a standpoint of pollution. Keeping the established solutions which are in common use (fluoborate) within these new regulations requires the installation of a high cost plant and equipment, consequently higher plating costs arise. This necessitates research for alternatives to fluoborate. Many formulations have been proposed, some of them were known before but they require more study and better understanding, and the others are completely new. From them have come those which are based on sulphamate. Sulphamate solutions, in addition to their relative non-toxic property, have been used successfully in electrodepositing other metals and have shown many good features in the electroplating field (see Section 3.1.2, Section 4.3).

In this thesis, a brief mention of the history and the scope of tin and tin-lead alloy electrodeposition precedes the general principles for alloy electrodeposition and describes the roles of plating and operating variables in electroplating baths. The different

types of solutions which are in use for electroplating with tin and tin-lead alloys have been reviewed.

The practical experimental work reported consists of an investigation of many proposed methods for preparing a tin sulphamate solution for tin electroplating. An electrochemical method was developed and the different parameters of the solution prepared by this method were studied. It included current density, additive agents, conductivity, polarization behaviour, etc. Optimum conditions for plating with the solution have been defined. A sulphamate electrolyte for tin-lead alloy plating was investigated in particular, electrolytes with different tin-lead ratios were used to electrodeposit alloys with compositions of 90, 80 and 70%\*lead (remainder tin). The effects of current density and metal ratio in the bath on the composition of the obtained deposit were studied. Polarization data under the influence of some parameters were obtained and some electromicrographs of the electrodeposited tin and tin-lead alloys have been prepared.

The results of the work are discussed in terms of developing an industrial method by which a tin sulphamate solution could be produced for electroplating with tin. This solution, if combined with that of lead previously developed, could yield a tin-lead alloy suitable for many industrial purposes.

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\* In a later trial an alloy of 40% lead (remainder tin) was also electrodeposited

## P A R T   I

### LITERATURE REVIEW

This part of the thesis includes a brief mention of the history and the scope of tin and tin-lead alloy electrodeposition. It also describes the general principles of electrodeposition of alloys and the role of the different variables of electroplating baths. It reviews briefly the types of solutions which are in use for electroplating of tin and tin-lead alloys. A description of the most important applications of tin-lead alloys in the engineering industry is also included.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Historical Perspective

When and where tin was discovered is unknown, but there is a clear evidence that tin was one of the earliest metals known to mankind dating back to the period between 3200 and 3500 BC. A variety of discoveries proved that tin and its alloys were used by the old civilizations to produce some kind of weapons and tools; the Roman used tinned copper vessels but tinned iron vessels did not appear until the fourteenth century in Bohemia. Indeed there seems to be a paucity of very ancient objects made entirely of tin, in spite of pure tin ingots, possibly of Roman or even earlier origin, having been found in Cornwall, as well as objects substantially of tin, such as cups and scabbards, of Roman or medieval times which have been found in other parts of Britain. The idea that from earliest times tin was used for the benefit of other metals rather than being used pure is created by the discoveries of ancient objects bearing a tin coating, of others made of tin-lead alloy, and especially by the very early use of tin for hardening copper<sup>(1)</sup>. Bronze was so important an alloy in the old civilizations that the historians refer to a "Bronze Age" for one of the cultural development stages. Pewter was the main alloy widely used for manufacturing many articles for ordinary purposes of living; plates, mugs and wine vessels of the Dark Ages are to be found in many museums. One other ancient alloy of tin is that with lead which was used by Romans as solder; it was used in two compositions:

1 Sn:1 Pb    and    1 Sn:2 Pb

In the most recent history, the invention of tin-base bearing alloys was very important in developing fast-running machinery. It was introduced by Isaac Babbitt in 1839<sup>(2)</sup>. He claimed the invention of the bearing but he did not claim the alloy; this imposes doubt that the alloy probably was known before that date.

Tin as a coating over other metals had been used by the Romans but the tinplate industry is believed to have started in the fourteenth century<sup>(3)</sup>. It started in Bavaria where hammered sheets of iron were tinned; then it spread to other countries and has developed very rapidly since. Iron sheets were gradually replaced by rolls of steel strip and hot-dipping replaced by electrotinning after the production of electricity in 1877 and the invention of batteries in 1840. The production of electricity and the invention of batteries indeed created new directions in the modern industry which included the art of electrodeposition of metals. Tin alloys were also deposited with compositions similar to the earlier alloys. De Ruolz<sup>(4)</sup> deposited bronze from a bath containing copper complexes and stannate as early as 1842<sup>(5)</sup> but the theoretical knowledge at that time was limited and the extensive practice of the electrodeposition of tin and its alloys really commenced after the late 1920s when many investigators and researchers ran researches aimed at better understanding of the theoretical basis of the art and broadening the field of application and use of tin and its alloys.

Organotin chemicals are a new development and by their production a very important area for tin use has been established and has grown very rapidly in the last 30 years<sup>(6)</sup>.

## 1.2 The Scope of Tin and Tin-Lead Alloy Electrodeposition

If the amount of tin which is consumed in the tinsplate industry was omitted then the largest quantity of cast or wrought tin is used in an alloyed form rather than in a pure state. The variety of properties which can be obtained by alloying tin is wider than that obtained from the normally weak pure metal. This variety in fact, enables the metallurgist and the electroplater to tailor the alloy in a way by which most of the properties required from the manufactured products or the electrodeposits can be secured.

It was well recognised that the alloys which can be obtained by electrodeposition provide properties not attainable by the electrodeposition of pure metals. Relative to pure metal, alloy deposits tend to be denser and harder, tougher and stronger, more wear resistant and superior in anti-friction service.

In practice, there are two main reasons why alloy electroplating is not as widely used as one may expect: firstly, the greater difficulty faced in controlling the process of alloy electrodeposition and, secondly, the possibility of obtaining the required properties from any plated single metal by varying the conditions of the electrodeposition process. A large number of alloys have been electrodeposited (see Table 1), but only a few of them have attained real commercial

importance. Among them are tin-lead, tin-zinc, nickel-cobalt, etc. In the case of tin-lead alloy, the solution factors which may restrict the electrodeposition of the alloy have been thoroughly studied and the electrodeposition process of the alloy is reasonably well understood. Electroplating of the alloy from some types of solutions is fully controlled and the deposits obtained are superior to either tin or lead in some properties; for example, corrosion resistance (low tin alloys) and solderability (high tin alloys).

Tin-lead alloys have been electrodeposited to protect steel parts against corrosion (10-60% Sn), the deposit being claimed to be compact, suitable for use in seawater and other corrosive media<sup>(7)</sup>. Alloys with (5-6% Sn) were said to have better protection properties from corrosion than pure lead or tin-lead alloys with high tin content<sup>(8)</sup>. The so-called diffusion lead-tin coating obtained by electrodepositing lead and tin layers separately then heating the coating to temperatures of 220-230°C was found to have a good resistance for wear and abrasion<sup>(7)</sup> owing to the establishment of an intermetallic diffusion or alloy layer.

## CHAPTER 2

### ALLOY ELECTRODEPOSITION

The electrodeposition of metals may be considered to have developed in the middle of the nineteenth century, but it found no immediate applications because of the lack of substantial direct current sources. The early mention of the technique was by Jacobi, Jordan and Spencer<sup>(5)</sup> who have reported at the same time the value of electrodeposition for the production of surfaces and objects (electro-forming). The plating process in these early times was carried out by using an arrangement of galvanic cell in which an internal electrolysis process results in depositing the metal. Using an external electrical source only took place after 1840 when batteries were introduced by Mason.

The electrodeposition of alloys in the early stages was so bound up with that of pure metals that it probably took place at the same period of time. The development of plating with pure metals was much faster than plating with alloys because of the limited knowledge of alloy electrodeposition. Only 5% of the patents issued for plating in the USA were for alloys in the period between 1850 and 1883 and it was 9% in the UK.

Many investigators have investigated the process of alloy electrodeposition in the early years of this century, notably Spitzer<sup>(9)</sup>, Field<sup>(10)</sup>, Forster<sup>(11)</sup> and Kermann<sup>(12)</sup>, but unfortunately most of their work was either incomplete or dealt with the subject

in an empirical way without putting much emphasis on the theoretical aspects. The work of Kermann probably was the first work to study the process systematically and scientifically. The general principles and the important factors which influence the codeposition of two metals have not undergone a great change since that time in spite of the rapid developments in the field of alloy deposition since 1930. In recent work Faust<sup>(13)</sup>, Raub<sup>(14)</sup>, Lowenheim and Gore<sup>(15)</sup> and others have published general surveys for alloy deposition. Brenner<sup>(5)</sup> generalized and systemized the previous work in two volumed-book entitled "Electrodeposition of Alloys". A Russian study<sup>(21)</sup> has discussed the structure and properties of electro-deposited alloys but the theory is still imperfect. Up to now, no theory has been established which is able to state how an alloy with a required composition can be obtained from a known bath under definite conditions or to explain why so many metals disobey the main principles stated with that theory. Once such a theory has been found it would greatly decrease the amount of experimental work required to determine the relations between alloy composition, properties of deposits and the operating variables.

## 2.1 General Principles

Some investigators<sup>(12,18)</sup> reporting in the literature have confused the conditions necessary for the electrodeposition of alloys and the effects and the roles of some variables controlling the process, but some investigators<sup>(5)</sup> have separated and distinguished between the conditions required to achieve a useful codeposition of the alloy

components and the other factors which affect and control the composition of the alloy electrodeposited. Dealing with the article in the latter manner is more logical and more practical because the first step in alloy electrodeposition process is the investigation as to whether the codeposition of its components simultaneously is possible. Then, if so, to study the effect and the roles of the different variables on the composition of the deposits obtained. Whatever the method of investigation, two main conditions are necessary for securing a useful deposit from two metal components in solution:

- i) the deposition potentials of the two metals must be fairly close; and
- ii) at least one of the two metals must be capable of being individually deposited from aqueous solutions.

According to the first condition, the standard electrode potentials for metals (Table 2 )<sup>(16)</sup> can be considered a rough guide to give a superficial estimation of whether two metals may be electrodeposited from a simple salt solution or not, but the applicability of this table is limited because the data provided represents only a thermodynamic condition; real conditions require consideration of the kinetic factors (polarization) which represent the on-going codeposition process. The kinetic factors in fact result in a shift of the potentials to more negative values than the standard potentials.

The standard electrode potentials table has been successfully used to predict the possibility of electrodepositing easily many pairs of metals such as tin-lead, tin-nickel, nickel-cobalt, because their

standard electrode potentials are very close together (less than 100 mV apart), but on the other hand, it has failed to explain why the codeposition of silver and palladium or some other metals such as tungsten, molybdenum etc is rather difficult or probably impossible.

In many cases, the components of the alloy required to be deposited together, have standard electrode potentials far apart from each other. Two main options exist to bring the static potentials for two metals close together and are as follows:

- i) By complexing the solution the activities of the metal ions in that solution will alter and their electrode potentials will shift to more negative potentials. Table 2. The shift in potential is generally larger for the more noble metals and the difference between the potentials of two complex metals is less than that of the uncomplexed. This difference actually depends upon the complexing agent and the complexed ion; if a good complexing agent or agents are used, the electrode potentials will be brought closer together and their codeposition becomes more probable. In real practice, a large proportion of individual electroplated metals are obtained from complexed solutions which in addition to their good throwing power they secure smoother, brighter and finer-grained deposits. One complexing agent can be used for complexing the ions of both metals. "Single complex bath", or one or both metals are complexed, but with two different complexing agents "mixed complex bath". In both cases an excess of the complexing agent as "free agent" is required.

- ii) By altering the concentration of the more noble metal in the solution, the static electrode potential will change too.

According to the Nernst equation:

$$E = E_o + \frac{0.059}{n} \log a_m n^+$$

assuming the activity and the concentration of the metal ions in the solution are equivalent, a change of tenfold in the concentration of the metal ions will result in a change in potential of 59 mV for a monovalent metal and 29.5 mV for a divalent metal. This change in potential is really impracticable for adequate process control. (Figure 1. )<sup>(17)</sup> shows the variation of the electrode potential with the ion concentration for some metals.

In practice, the electrodeposition of metals occurs under the dynamic potentials of these metals; considering these potentials is more important than considering the static potentials. In fact the above discussion for bringing the static potentials for two metals closer together is correct for their dynamic potentials too in spite of the dynamic potentials being always more negative than the static potentials by the amount of polarization.

iii) The electrodeposition of two metals under the condition of limiting diffusion current is possible where a considerable shift in the deposition potential of the more noble metal is obtained but in practice such conditions are not used as rough and coarse deposits are formed.

## 2.2 Roles of the Variables in Alloy Electrodeposition Process

The composition, the rate of codeposition and the physical properties of the deposits in alloy electrodeposition processes are a function of many variables such as the metal ratio in the bath, current density applied, pH of the solution, agitation of the solution etc. No one of the variables has an exact effect on the composition and/or the nature of the deposits obtained and generalization is really difficult. A rough prediction for the effect is possible but the exact effect can be determined by experiment only. Many investigators have studied or briefly alluded to this effect. The results of the investigations have been systematized by Brenner, in more than 100 pages of his two volume book named "Electrodeposition of Alloys". It is not intended in this research to treat this subject in great detail, but a brief indication of the main effects of some variables must be relevant.

### 2.2.1 Plating Systems

To simplify the study, and for achieving better understanding of the effect of the different variables, Brenner divided the systems of alloy plating into five types as follows:

- i) Regular systems: in which the codeposition of the metals is under diffusion control, and the influence of plating variables can be predicted from diffusion theory. It occurs in baths containing simple metal ions with static potentials far apart but it may occur in complexed baths too.
- ii) Irregular systems: the codeposition in such systems is mainly controlled by the cathode potential and it mostly occurs in complexed solutions or in baths containing metal ions having static potentials close together.
- iii) Equilibrium systems: these consist of solution in chemical equilibrium with both of the parent metals. The codeposition of the metals by applying a low current density results in deposits having the same ratio of metals as in the bath.
- iv) Anomalous systems: the less noble metal in these systems deposits preferentially, and the bath may contain either simple or complex ions of the metals.
- v) Induced systems: in which the deposition of alloys is possible for metals which cannot be deposited individually. The effect of plating variables in such systems is unpredictable.

The first three systems are known as "normal" systems; and the last two are known as "abnormal" systems.

### 2.2.2 Effect of the Variables on Composition of the Deposits

Two categories of variables can be considered: the variables which are concerned with the bath (bath variables) and the variables which are concerned with the plating process (plating variables).

#### A. Bath variables

##### i) Metal ratio in bath:

In general, for baths of normal-system codeposition, any increase in the metal ratio in the bath results in an increase in its ratio in the deposit, but not necessarily to the same degree. A full range of alloy composition is obtainable if the metal ratio is altered, but there is a critical ratio (limiting bath composition) where a further increase results in depositing one of the components only. In anomalous-system codeposition, the behaviour of metals is not as consistent and in induced systems, the amount of the reluctant metal in the deposit increases with increasing its percentage in the bath, but there is a critical value of the reluctant metal in the deposit which cannot be surpassed even if its percentage in the bath was increased substantially.

The variation of the metal content in the bath at a fixed metal ratio affects the composition of the deposits in regular systems, but it has either a slight effect or no uniform trend in irregular, anomalous and induced systems.

ii) Complexing agents:

The effect of the complexing agents on the composition of the alloyed electrodeposits is derived from the fact that the deposition potential of one metal may be shifted to less noble values than the other, consequently the deposition of the former becomes reluctant. The concentration of the "free complexing agent" in the "mixed type" of plating bath markedly affects the composition of the deposit because the deposition of each parent metal responds to a different degree according to its particular complexing characteristic. Its concentration in "single type" baths is neither predictable nor has a very large effect<sup>(5)</sup>.

iii) Addition agents:

The effect of addition agents on the composition of the deposits is specific; certain agents affect the composition of the deposits of certain alloyed metals. Compared with complexed agents much smaller amounts of addition agent are required to perform the same change in the composition of the deposit and the amount of deposits rapidly approaches a limiting value above which any further increase in the addition agent concentration has no effect (see Figure 2. )<sup>(19)</sup>. It was reported that the addition agents in baths containing the metals as simple ions are most effective<sup>(5)</sup>.

iv) pH:

The variation in pH value mainly affects the physical properties of the alloyed deposits but it has some effect on the composition.

Ambiguous reports have been published<sup>(20)</sup> concerning these effects probably because of unintentional confusion between the effects of pH and some other variables. In general, variations of pH have little effect on the composition of deposits from baths of simple ions; however, they have large effects on the composition of deposits from baths of complexed ions.

## B. Operating Variables

### i) Current density:

The effect of current density on the composition of the alloyed deposit is usually the most important effect of all the plating variables, but it can be less consistent or predictable. In regular-type systems the content of the more noble metal in the deposit decreases with current density. However in other types an opposite relationship occurs and the content of one metal may go through a maximum or minimum as the current density varies. The above is true as long as the limiting current density is not surpassed. As soon as the limiting current for the deposition of one metal is approached any further increase in the current density has no additional influence on the electrodeposition of this metal.

### ii) Temperature:

A variation in the temperature of an alloy plating solution indirectly affects the composition of the deposit obtained through the change of many characteristics of the plating system such as polarization, equilibrium potential, and metal concentration in the

cathode diffusion layer. The most important is attributed to the change in metal concentration. An increase in temperature increases the concentration of the metal ions near the cathode, thus favouring the deposition of that metal which was already preferentially deposited. Polarization decreases with increasing temperature and the deposit potential of the metal becomes more noble. Whether the deposition of a metal is favoured depends upon which deposition undergoes the largest decrease in potential.

### iii) Agitation:

The agitation of an alloy plating bath brings fresh solution near the cathode and reduces the thickness of the diffusion layer; this results in an increase in the metal concentration near the cathode and the effect on the composition of the deposits from solutions of simple ions will be similar to that of temperature i.e. favours the deposition of the metal which was already preferentially deposited. In complexed solutions, the prediction of the effects is rather difficult because not only does the concentration of metal ions increase in the diffusion layer by agitation, but the concentration of the complex ions increases too; the latter may result in an opposing effect to the former. In general, the change in composition due to agitation may be large as in regular systems or it may be negligible as in some of the other systems. A sharp change in the composition is an indication that the codeposition took place under diffusion control, in which case increased rates of deposition may also be promoted.

## CHAPTER 3

### ELECTRODEPOSITION OF TIN

Tin is a soft, ductile and silvery white metal. It is rarely used in its unalloyed form except as a coating on other metals. Its resistance to corrosion and tarnish, non-toxic nature and its solderability properties give the metal a prime importance in the food industry. The largest use of tin (40% of the world production of tin in 1978) is for coating steel to produce tinplate. In the past most deposits were applied by a hot-dipping process but the electrolytic methods have gradually replaced the hot-dip method because of many advantages headed by the simplicity of controlling accurately the coating thickness over a wide range of thicknesses where the economy in using the metal is of great importance for economic survival. The great threat which is directed to tinplate market nowadays comes from the use of aluminium and tin-free steel in the food industry, but in "sanitary" packaging of food, tinplate is still preferable.

Tin as a coating on steel is cathodic with difference of 0.304V in their standard electrode potentials; this means that steel may corrode through the tin coating pores, but in the presence of the organic food acids (carboxylic acids), tin becomes anodic and protects steel. For other tin coatings on steel a non-porous coat must be secured and a thicker deposit is thus required.

Tin can be electroplated either matt or bright. Developing a solution for bright electrodeposits has been the most significant development in the past three decades. Aldehydeamine additive agents were developed as brighteners for tin deposits. The properties of both matt and bright deposits are actually similar, but bright tin deposits are somewhat harder probably because the codeposition of some additives with the metal. Matt tin can be brightened by a reflowing process: the deposits are heated slightly above the melting point of tin then quenched quickly in water or oil at 50-80°C. Specifying whether a matt or bright deposit should be electrodeposited depends on the eventual use of the coat. In electronic or food industries for example, where the codeposition of traces of brightener additive agents might harmfully affect the role of the coat and using reflowed matt deposits in such cases is probably preferable. The growth of whiskers or tin pests on tin deposits can be inhibited by codepositing with tin about 1% lead.

### 3.1 Types of Bath

Tin may be electrodeposited from alkaline or acid solutions and the choice depends on the individual requirements of each application. Alkaline solutions contain tin ions in the tetravalent state, but acid solutions usually contain the ions in the divalent state, thus the alkaline solutions require passage of double the amount of electricity required by acid solutions for yielding the same amount of deposit. Throwing power for alkaline solutions is excellent, but the cathode current efficiency is low. In acid solutions the cathode

current efficiency approaches 100% but the additive agents are essential for yielding good deposits, otherwise a treed, crystallized and non-adherent deposit will be obtained. Bright deposits from alkaline solutions can be obtained only by the reflowing process following the electrodeposition process, but it could be achieved easily from acid solutions by adding some organic brighteners. Table 3 shows a comparison between the properties of the two types of solutions.

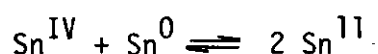
### 3.1.1 Alkaline Solutions

Probably the first solution for tin electrodeposition based on alkaline stannate was that one which was developed by Wernlund and Oplinges<sup>(22)</sup>. It contained sodium stannate and it yielded good deposits. By 1940 this solution had replaced all the older alkaline solutions which were known. Most of the work after that date was directed at studying and explaining the behaviour of the anodes in sodium stannate solutions in order to ease their control: this included the works of Hansel and Grevel<sup>(23)</sup>, Stout and Baum<sup>(24)</sup> and Heiman and Lucasse<sup>(25)</sup>. In 1942 Sternfels and Lowenheim<sup>(26)</sup> demonstrated the superiority of potassium stannate over sodium stannate and in 1949 Lowenheim<sup>(27)</sup> introduced the improved tin anode which contains a small amount of aluminium. In the late 1960s Jongkind<sup>(28,29)</sup> introduced an alkaline stannate bath based on potassium stannate. He used inert anodes and regulated the bath by tin oxide additions.

In general, the alkaline solutions contain alkaline stannate (sodium or potassium) and a free hydroxide. The hydroxyl ion is the

principal conducting medium in the bath. A soft ductile deposit has been obtained from such solutions and the appearance ranges from matt to slightly duller and greyer. Tin ions in alkaline solutions are usually present as stannate. If even a small amount of stannite was formed in the solution, a spongy rough deposit will be yielded.

Stannite ions may be developed in the solution due to an improper anode control<sup>(20)</sup>. Lainer<sup>(8)</sup> claimed that stannite ions formation is due to a cathodic not anodic process. The usual explanation of stannite formation is related to the disproportionation reaction



Stannate    Metallic    Stannite  
                 tin

Stannite can therefore form by reaction of stannate with tin anodes during non-operation periods and can subsequently disproportionately yield spongy tin deposits. Adding hydrogen peroxide to the solution in small amounts may oxidize the stannite to stannate but excess peroxide in the bath is harmful.

The critical factor in alkaline solutions is controlling the tin anode to ensure proper dissolution. It includes forming a suitable film on the anode capable of producing tetravalent ions and suppressing the formation of divalent ions. The film can be formed by passing a higher current than normal through the bath (see Figure 3). The colour of the film will be yellowish if a pure tin anode is used and an olive-green if the anode contains 1% aluminium. A black or brown film will be formed and the anode dissolution will stop when

the current passing becomes too high, but the film formed will dissolve and divalent ions may be produced if the current is too low.

Two types of alkaline stannate solutions are in commercial use: one is based on sodium stannate (Table 4 ) and the other on potassium stannate (Table 5 ), both of them yield a good deposit if the electrodeposition process is well controlled. The choice between them depends on the merits which may be gained when replacing one by the other. Potassium stannate solutions are usually used effectively when a thick deposit at high rate of deposition is required, but in smaller jobbing applications the sodium stannate solutions are still practicable. Table 6 shows a comparison between some features of the two solutions.

The use of inert anodes in alkaline baths has some advantages: no filming difficulties, no stannite ion formation and no change in the shape of the anode or limits in applied current density. The replenishment of tin ions in this case is by adding tin oxide to the solution.

### 3.1.2 Acid Solutions

Although the investigation of tin plating processes has included numerous stannous salt baths such as fluosilicate<sup>(30)</sup>, fluoride, fluoborate, perchlorate, oxalate, pyrophosphate<sup>(30,31)</sup> and sulphamate<sup>(32)</sup> only three types of solutions have gained commercial importance for general plating purposes. These solutions are: stannous sulphate, stannous fluoborate and a halogen formulation. Stannous sulphate

solutions have been investigated by many investigators<sup>(33,37)</sup>. Most of their work was to improve the quality of the deposits obtained from such solutions and many addition agents were suggested for this purpose. The sulphate bath suggested by Nachtman<sup>(38)</sup> is still in use today for plating steel strips with matt deposits. Until 1957 reflowing the electrodeposit was the only method for brightening the coat, but Harper et al<sup>(39)</sup> succeeded in obtaining a bright deposit by adding wood tar as a brightener to the bath.

Grasselli (Du Pont)<sup>(40)</sup> has developed the halogen bath formulated in 1942. It includes: stannous chloride, alkali, metal chloride and fluoride and a suitable addition agent. The bath was said to be more suitable for use with high current densities.

The research of Parkinson<sup>(41)</sup> and Carlson<sup>(42)</sup> led to the fluoborate solutions. It has been claimed that fluoborate baths yield a fine grained deposit.

More investigation has been carried out since 1960 with the aim of improving the quality of the known baths. Many additive agents<sup>(43)</sup>, brighteners<sup>(44)</sup> and surfactants have been developed.

In general acid baths must contain in addition to metal salt and free acid, some addition agents to produce sound deposits. The presence of antioxidants in the bath is necessary to prevent the oxidation of divalent tin ions to tetravalent ions. Although the latter ions have no harmful effect on the deposits, it depletes the former ions in the bath. A brightener agent may be added to the bath if bright deposits are required.

i) Stannous sulphate bath:

The stannous sulphate solutions were proposed for use in the electrodeposition process of tin many years ago, but the most satisfactory deposits from such solutions have been obtained only after developing a suitable addition agent to suppress the treed-dendritic growth of the deposits and to prevent the oxidation of tin ions in the solutions. Many different addition agents have been investigated by many workers for this purpose, but probably investigation of the use and the role of cresol sulphononic acid and some other similar addition agents by Hothersall and Bradshaw<sup>(45)</sup> was a turning point in the perfection of the stannous sulphate bath. Since then cresol sulphononic acid has been used as antioxidant for divalent tin ions in static sulphate baths which are usually used for general plating. In barrel plating a continuous electrotinning process, phenolsulphonic acid was preferred for essentially the same purpose.  $\beta$ -naphthol, gelatin and animal glue have also been used as addition agents to improve the quality of the deposit. The action of these sulphononic acids can only be satisfactorily explained if mild complexing takes place; if this is so, the solutions ought to be regarded as stannous phenol sulphanate etc. rather than stannous sulphate.

Bright tin deposits have been obtained from sulphate baths by adding some brightener additions to the bath. The first mention of such agents was in Schlotter's<sup>(36)</sup> report in 1936. He introduced a specific proprietary agent: if added to the bath a bright deposit would be obtained. Some other works based on using wood tar as a

brightener were carried out by Mathers and Discher<sup>(46)</sup> of the Tin Research Institute<sup>(47)</sup>, but there was some doubt about its stability. Recently many firms have claimed the production of bright tin deposits by using their own brightener agents which are still private and proprietary to them.

Some typical compositions for stannous sulphate baths are shown in Table 7. No sharp difference in the constituents of the different compositions are apparent, but there is a slight difference in the amounts and/or the operating conditions according to the purpose of the bath. Agitating the solution permits the use of a higher current density which makes the bath suitable for electrotinning or barrel plating, but a lower current density is suitable for general plating in still baths.

The main difficulty met in a stannous sulphate bath is controlling the addition agent amounts in the solution. As a general rule the addition agent should be added when a drop in the applied voltage occurs, the grain size of the deposit increases and the covering power becomes poor<sup>(48)</sup>. The Hull cell is used as the main process test method.

ii) Stannous fluoborate bath:

The high solubility of tin fluoborate salt in water permits the preparation of a solution with high tin content; this fact gives the fluoborate solutions one major advantage over the sulphates. The fluoborate solutions are able to operate at much higher current

densities, consequently giving a higher deposition rate and speed. The main objections to the bath are the high drag out loss, and the tendency to form sludge through slow chemical changes in the bath.

For many applications, such as barrel plating for small parts, plating of wire and narrow gauge strip, a satisfactory finish was produced from the bath but similar to sulphate addition agents are necessary in the bath. Gelatin and  $\beta$ -naphthol were previously used but some other alternatives such as hydroquinine, resorcinol etc. showed promising results. Typical compositions for the bath are shown in Table 8.

Bath (1) was suggested by ITRI. A smooth fine-grained white deposit was produced from the bath which can be operated at room temperature over a wide range of current densities. Bath (2) was proposed by Lowenheim. The agitation of the solution permits applying current densities up to  $12.5 \text{ A/dm}^2$  at  $20^\circ\text{C}$  and up to  $42.5 \text{ A/dm}^2$  if the solution<sup>is</sup> heated to  $40^\circ\text{C}$ . The throwing power of the bath is excellent and the deposit is satisfactory. The last three baths in the table were suggested by P. Davis (TRI, USA) to fulfil many different requirements.

### iii) Halogen bath:

The bath was essentially developed for use in the continuous electroplating process of steel strips. A plating speed up to 600 m/min is achieved. The bath usually contains the tin as stannous chloride, alkaline fluoride to suppress the hydrolysis of the salt and some

addition agents to secure a satisfactory deposit. The addition agents include naphthol sulphonic acids or polyalkalene oxides. The use of gelatin or peptone is also possible. A typical composition for the bath is shown in Table 9.

Tin ions in the solution tend to oxidise especially when aerated and the presence of even a small amount of iron or copper ions in the solution promotes the oxidation of tin. Adding some inhibitors is necessary to form insoluble sludge<sup>(49)</sup>. Lainer<sup>(8)</sup> said the so-called halide solution which contains chloride and fluoride of tin is not used in electroplating. The solution and its associated process was originally patented by Du Pont Co. in the USA and has been used primarily in the USA and more recently in Australia and South Africa.

A comparison between some features of the main acid baths is shown in Table 10.

#### iv) Sulphamate bath:

Although the sulphamate solutions are widely used for the electrodeposition of many metals such as nickel, using the solution for electrodeposition of tin is still very unusual. The attractive properties of the acid (very soluble in water, relatively non-toxic, non-volatile etc., see also Section 6.4.1) compared to those of other commonly used solutions <sup>have been</sup> still not <sup>exploited</sup> probably because the relatively low solubility of its salt in water and its difficulty to prepare.

A limited number of articles have been published in the literature concerning tin sulphamate solutions. The earlier work was carried out by Piontelli<sup>(32)</sup> and co-workers. In addition to tin they investigated the possibility of electrodeposition of many metals from the solution, but the results obtained concerning tin were not really promising. They prepared their solution by displacing copper metal from copper sulphamate solution by metallic tin by an electrolysis process. Many methods have been patented for plating tin single<sup>(50,51)</sup> or alloyed<sup>(51,52)</sup> with lead from sulphamate baths but the successful applications are in narrow areas; probably the most recent patent<sup>(53)</sup> is one concerned with a method for local plating with tin for the purpose of repairing military and other aircraft parts.

## CHAPTER 4

### TIN-LEAD ALLOYS

#### 4.1 Introduction

The process of electrodeposition of tin-lead alloys is one of the simplest processes of alloy plating. In addition to the closeness of their standard electrode potentials ( $-0.136\text{V}$  for  $\text{Sn}^{2+}$  and  $-0.126\text{V}$  for  $\text{Pb}^{2+}$ ), the metals have a high hydrogen overpotential which permits the codeposition of the two metals from acid solutions with a cathodic current efficiency of nearly 100%.

Tin-lead alloy deposits are superior to either metal alone in corrosion resistance and in solderability<sup>(59)</sup>. Thus the alloy is extensively used in bearings, electronic circuits, and many other industrial applications (see Applications).

The hot-dip methods have been used for a long time for applying the alloy to other metals, but two of the reasons why hot-dipping gave way later to the electrodeposition method are: the improvement in the electrodeposition process for alloys and the superior physical properties of the electroplated alloys.

Groff<sup>(54)</sup> was the first worker to patent a process for plating the interior of the air flasks of torpedoes by electrodeposition of tin-lead alloy using a fluoborate bath. One year later Chandler<sup>(55)</sup> patented a similar process but from a bath based on fluosilicate. Probably the two methods were suggested as an improvement to a former process for protecting the flasks with lead coatings, but the first

basic study for the electrodeposition of tin-lead alloys was carried out by Blum and Haring<sup>(56)</sup>.

A systematic study of the effects of the plating variables on the composition of the alloyed deposits was published 30 years later<sup>(57)</sup>. For such a study, although it has been involved in one type of solution (fluoborate), the results obtained can be considered a useful guide for the recent work dealing with other acid solutions.

An intensive research has been carried out in the last twenty years to develop new baths for the electrodeposition of tin-lead alloys for two reasons. Firstly, the strict regulations in some countries concerning the use of some chemicals from the standpoint of environmental pollution, and secondly the great demands imposed by the rapidly expanding electronics industry.

#### 4.2 Types of Bath

Tin-lead alloys may be electrodeposited from many different solutions. The literature includes different compositions for baths based on fluoborate, fluosilicate, sulphamate, pyrophosphate and chloride etc. but fluoborate baths are the only ones in common use for commercial purposes. Fairly recently attempts have been made by many workers to develop and market alternatives to fluoborate such as sulphamate, phenolsulphonate, alkanolsulphonate, and very recently alkylsulphonate. It has been claimed that good deposits have been secured from such solutions, but some doubts have limited their commercial spread.

i) Fluoborate baths

The first patent for electroplating with tin-lead alloys included a bath based on a fluoborate solution. It was in the early 1920s, and since then many formulations have been proposed for different fluoborate baths.

In general fluoborate solutions have many advantages over other solutions: they include its high stability, high deposition rates, high conductivity and the yield of fine-grained<sup>(58)</sup> deposits, but at the same time they have some disadvantages. On top of them are the high initial cost, the toxicity and the difficulty of preparing the solution. The difficulty in preparing the solution was actually overcome in practical terms by the availability of the so-called "solution concentrates" which contain the metallic fluoborate in a concentrated form and their use requires only dilution with water.

Fluoborate baths consist essentially of lead fluoborate, stannous fluoborate, fluoboric and boric acids and some addition agents usually glue, gelatin or peptone. The free acids in the bath are to minimise the hydrolysis of the fluoborate and to improve the stability and the conductivity of the solution. The additive agents are to suppress the tree or dendritic growths and to improve the quality of the deposits. The composition of the solution differs from one bath to another according to the composition of the alloy required. Table 11 shows the composition of some typical baths for electrodeposition of tin-lead alloys of different compositions<sup>(59)</sup>. The anodes used should be of the same composition as the alloy required. Air agitation should

be avoided as this will oxidise the stannous tin to stannic (II→IV) and cannot easily be reversed.

The tin-lead alloy electrodeposition system is of the regular type on the classification of Brenner and one expects a large variation in the composition of the deposits with the electroplating variables, but this is not the case. They show much smaller variations because the potentials of the two metals are so close together and probably brought closer by the addition agents. The study of the operating variables by Du Rose and Hutchison<sup>(57)</sup> showed that any increase in the current density increases the content of tin in the deposit but agitation and temperature have a negligible effect. The increase in metal content in the bath decreases the amount of tin in the deposit but increase in the addition agent concentration increases the tin in the deposit.

#### ii) Pyrophosphate baths

The pyrophosphate bath for electrodeposition of tin-lead alloys is the only alkaline or near-alkaline bath which has been well investigated by many workers<sup>(60,61)</sup> and promising results have been claimed. The bath usually consists of tin as stannous pyrophosphate, lead as lead nitrate and sodium or potassium pyrophosphate. The latter is usually added for the purpose of complexing the stannous ions. Adding some addition agents is necessary to yield smooth deposits; these agents are usually glue or gelatin and  $\beta$ -naphthol<sup>(62)</sup>.

Sree et al<sup>(60)</sup> have carried out the largest investigation concerning the pyrophosphate bath. They deduced a typical composition for a

bath (see Table 12). They claimed that if the bath operates under certain conditions the deposits obtained will contain from 2-15% tin and found that the performance of the bath is similar to that of fluoborate solution in its suitability for codeposition of tin-lead alloys. A more recent work by the same authors<sup>(63)</sup> has resulted in some modification in its composition to secure a wider range of tin content in the deposit. Campbell<sup>(61)</sup> and Von Fraunhofer<sup>(62)</sup> in a very recent work have stated that this type of solution gives adherent, smooth and fine-grained deposits.

Except for the effect of temperature, the variation of the composition of the deposits with respect to the plating variables is that of a regular alloy plating system. The amount of tin in the deposit increases with any increase in current density, addition agent and tin content in the bath<sup>(60)</sup>. Temperature has a slight effect on tin content, but agitation increases the lead content in the deposit.

#### 4.3 Recent Developments

Search for new types of solutions and attempts to improve some known solutions for electroplating tin-lead alloys have been intensified in recent years aiming to establishing optimum conditions for the process both technically and economically. Solutions based on fluoborate are at present commercially dominating. Many formulations have been proposed, some of them were known but they require more study and others are completely new. From them come those which are based on sulphamate, alkanolsulphonate, and alkylsulphonate.

### i) Sulphamate baths

Attempts to exploit the remarkable properties of sulphamic acid are not new, but it recalls the early thirties when Piontelli and co-workers<sup>(32)</sup> carried out a systematic investigation to examine the possibility of electrodeposition of many metals including lead and tin from sulphamate solutions. At the end of the forties they carried out another investigation<sup>(64)</sup> concerning the electrodeposition of many alloys including tin-lead alloy from sulphamate baths. The results of the latter as they have been reported were not promising and the solutions have had little practical importance even when using an excess of free sulphamic acid. They stated that the sulphamate salt hydrolysed after only two days, yet two years later, Clifton<sup>(51)</sup> patented a sulphamate solution and a method for electroplating a copper substrate with tin-lead alloy. He claimed that the solution is capable of yielding deposits containing up to 30% tin. Du Rose et al<sup>(52)</sup> at almost the same time patented the use of many addition agents in sulphamate baths to promote the deposition of tin. Indira and Udupa<sup>(65)</sup> showed in more recent work the effect of CTAB as an addition agent in sulphamate baths. They claimed that the presence of such an agent in the bath is sufficient to secure an excellent covering and throwing power: deposits of quality have been obtained.

The main constituents of sulphamate baths are: lead sulphamate, tin ions, free sulphamic acid to minimise the hydrolysis of the salts and addition agents to improve the quality of the deposits. In the literature no clear method has been mentioned for preparing such a solution. The composition of a typical bath is shown in Table 13<sup>(65)</sup>.

The effect of plating variables on the composition of the deposits was said to be similar to their effect on a fluoborate bath and the effect of temperature was not uniform. The effect of bath composition and current density on the composition of the deposits is shown in Figure 4<sup>(32)</sup>.

ii) Alkanolsulphonate baths

A very recent bath based on alkanolsulphonates was developed by Dohi and Obata<sup>(66)</sup>. The bath was developed for the purpose of replacing fluoborate and phenolsulphonate<sup>(67)</sup> baths because the effluent from these baths contains fluoride or phenol which came under legal control in some countries (in this case Japan). The bath was designed originally to yield deposits of 90% Sn:10% Pb composition which are widely used in the electronic and electrical manufacturing fields.

In addition to the metal ions, the bath contains free acid and some addition agents as brightener and surfactants. The solution is usually prepared by dissolving stannous oxide and lead oxide in alkanolsulphonic acid then adding the free acid and the additives to the solution. The optimum composition for this bath is shown in Table 14. It was claimed that the bath is applicable for still or barrel plating and bright deposits resisted whisker formation when produced at low current densities. The tin-lead ratio in the deposits was said to be equal to that in the solution over a wide range of plating conditions, but the cathode efficiency was relatively low at higher current densities. Luke<sup>(68)</sup> has stated that such solutions have not been commercially successful.

### iii) Alkylsulphonate bath

The bath was developed in the last year by D.A. Luke<sup>(68)</sup> of Lea Ronal (UK) Limited to replace the fluoborate bath in electro-depositing of (tin-lead) alloys mainly with a composition of 60% Sn, 40% Pb. Such an alloy composition is widely used as a solder in the electronics industry. The bath basically consists of tin and lead ions, free acid and addition agent. The addition agent is covered by patent (to Lea Ronal)<sup>(68)</sup>. The typical composition for the bath is shown in Table 15.

A comparison between this bath and that one based on fluoborate was carried out by Luke<sup>(68)</sup> to show the merits of the bath. He claimed that a bath based on alkylsulphonate is superior to that based on fluoborate in the ability of the former to operate at lower metal contents, the ability to operate with inert anodes, it eases effluent treatment and yields deposits with lower levels of organic impurities. He forecasts that this bath may eventually replace the fluoborate bath if better addition agents are developed to yield deposits with superior properties.

### iv) Other baths

The electrodeposition of tin-lead alloys from many other solutions has been investigated by many investigators. Kudryavtsev et al<sup>(7)</sup> claimed that a bath based on p.phenolsulphonic acid can replace the fluorobate bath for the codeposition of tin-lead alloys. The main constituents of the bath are: lead and tin as salts of p.phenolsulphonic acid, free p.phenolsulphonic acid to prevent the hydrolysis of

the metal salts and an organic addition agent to improve the quality of the deposits. It was said that the bath is suitable for the electrodeposition of both low and rich tin alloys. By changing the plating variables two main and different compositions were obtained: 8-12% Sn to be used as an antifriction coating and 20-60% Sn to be used as a protective coating mainly for steel substrates. Low tin content electrodeposition was claimed to be similar in properties to a heat-treated coat of two individual layers of tin and lead electrodeposited separately. The composition of the bath is shown in Table 16.

Dohi and Obata<sup>(67)</sup> in recent work on the phenolsulphonate bath concluded that bright tin-lead alloys containing 50-100% Sn can be electrodeposited from such a bath. They used a condensation product of acetaldehyde with o-toluidine as a brightener, acetaldehyde as an additive agent and polyethylenglycol nonylphenyl ether as a surfactant. They claimed that the composition of the electrodeposited alloy was nearly that of the bath over a wide range of current densities (0.25-10 Amp/dm<sup>2</sup>). The throwing power of the bath was said to be the same as that of a fluoborate bath.

Melnikov and Sizov<sup>(107)</sup> patented a bath based on chlorides. The bath contains the metals as chloride salt, ammonium chloride, hydrochloric acid, boric acid and glue (see Table 17). It has been claimed that if the bath operates under current conditions of 0.5-1 Amp/dm<sup>2</sup> at room temperature, a good alloy deposit can be obtained.

Narayan and Devraj<sup>(88)</sup> in their study of the bath stated that this bath is not capable of producing an adherent bright deposit in

its patented form. They recommended a bath containing lead, tin chloride salts, boric acid and gelatine (see Table 18). They claimed that gelatine as an additive agent can secure a good quality deposit with tin contents up to 60%. The optimum amount of gelatine was said to be 1.11 g/l. The bath was said to be of regular alloy plating system, and the plating variables have a similar effect on the composition of the deposit as that of fluoborate bath. An increase in current density and temperature will be accompanied by an increase in tin content in the deposit and decrease in grain size. The effect of temperature was more pronounced on a bath of high tin content.

#### 4.4 Other Tin Alloys

Although most of the work on the electrodeposition of tin alloys has been concerned with the tin-lead alloys because of its importance, the literature contains very many papers concerning the possibility of codeposition and the importance of many other tin alloys. Alloys of tin with copper and nickel are commercially important. Alloys of tin with zinc and cadmium find some applications. Tin-bismuth and tin-antimony are known with their special property of inhibiting the transformation of white tin to a powdered grey tin - "tin pest" - at lower temperatures.

The most important tin alloys, other than tin-lead alloys, are the following:

##### i) Tin-copper alloys

The alloy is one of the oldest alloys used by human beings and is still in use as bronze or speculum. It has many useful characteristics: hard, strong, pleasing colour, resistance to corrosion even

in salt environments.

The alloy can be electrodeposited at any desired composition: however, the alloy which is in common use contains 10-15% or 40-45% tin. The increase in the tin content in the alloy tends to change its colour from red-like copper to white-like silver.

The standard electrode potentials of tin and copper differ by almost 0.5V and the codeposition of the two metals from simple acid solutions is rather difficult. Complexing the metal ions in the solution brings their deposition potentials closer together and their codeposition becomes possible. The baths which are in commercial use are of a mixed type. Copper ions are usually complexed by cyanide and tin ions are used in a simple state or complexed by a different complexing agent. One of the typical baths has the composition which is shown in Table 19<sup>(1)</sup>. It can be regarded as a mixture of a sodium stannate tin-plating solution with a cuprous cyanide copper-plating solution. Separate tin and copper anodes are usually used for the electrodeposition of high tin content alloys but for lower tin content alloys cast bronze anodes may be used but with some restriction concerning the current density.

The baths of tin-copper alloys are of the irregular type. The concentration of the complexing agents (free cyanide and sodium hydroxide) play a more important role in determining the composition of the deposits than any diffusion phenomena. Any increase in free cyanide tends to increase the tin content in the deposits and a reverse result would be obtained if the free hydroxide was increased<sup>(1)</sup>.

Non-cyanide tin-copper alloy plating baths such as oxalate<sup>(69)</sup>, sulphate<sup>(70)</sup>, pyrophosphate<sup>(71)</sup>, fluoborate<sup>(72)</sup> and cyanide-pyrophosphate<sup>(73)</sup> have been investigated by many workers: but only the last one has found a commercial outlet.

Tin-copper alloys with low tin contents (10-15% Sn) have a pleasing colour, with two special applications: one as an undercoat in decorative chromium plating and the other as a stop-off in the nitride hardening of steel parts especially gears for engines. In some other applications the deposits must be lacquered to prevent tarnishing or wearing.

Alloys with higher tin contents (40-45% Sn) known as speculum find many decorative applications especially as articles for indoor service. They have an excellent tarnish resistance, but a phase change in the alloy structure may take place with time and blacken the coat<sup>(74)</sup>.

## ii) Tin-nickel alloys

Both tin and nickel have a good corrosion resistance but alloying the two metals together results in an alloy having a special interest to the industry. The alloy has a high corrosion and tarnish resistance, good bearing properties and it is solderable. An alloy of 65 Ni:35 Sn is said to have a high etch-resistance and it is used successfully in the electronics industry<sup>(75)</sup>. It has a special importance because it can be obtained only by electrodeposition. It is of a single-phase nature and has a composition very near to NiSn.

The metals tin and nickel have a difference in their standard electrode potential of  $\approx 0.1V$ , but in simple salts the nobility of the cathode increases rapidly as the concentration of tin increases in the solution and tin alone may be deposited. Thus codeposition of the two metals requires the maintenance of a low level of tin ions in the solution, and complexing of the solution may be necessary to suppress the deposition of tin. One of the complexing agents which has been used is fluoride. An early bath to electrodeposit the alloy was based on chloride and contained fluoride as additive agent<sup>(76)</sup>. Insoluble salts were formed and rough deposits were obtained occasionally from the bath. Davis<sup>(77)</sup> modified the bath and replaced sodium ions by ammonium ions to prevent the formation of the insoluble salt. Dillenburg<sup>(78)</sup> suggested the addition of an amine to the bath; he claimed that the amine will enable the bath to operate at lower temperatures and more neutral pHs. The deposit obtained was said to be bright. A typical composition of the bath is as shown in Table 20<sup>(79)</sup>.

Nickel anodes are usually used to supply the solution with nickel ions and stannous ions are supplied by adding stannous chloride. The fluoride content of the bath should be maintained at the same level as tin to fully complex the latter.

Alternatives to the bath including pyrophosphate<sup>(80)</sup>, fluoborate<sup>(82)</sup>, and organic<sup>(81)</sup> solutions have been proposed but none of them has a sufficient commercial interest.

An alkaline bath based on  $Na_2SnO_3$  and  $NaNi(CN)_4$  was suggested by Kudryavtsev et al<sup>(83)</sup> who claimed that the bath yields a uniform

thickness even on intricate parts but with low cathode efficiency.

### iii) Tin-cadmium alloys

The interest in the electrodeposition of tin-cadmium alloys is of recent origin. It was due to the need to find a substitute for cadmium metal used as a corrosion-resistant coating for the protection of steel parts for the aircraft and specific electrical components. It was said that the alloy was superior in this field to other coatings such as zinc, cadmium and tin-cadmium diffused coating especially in humid<sup>(8)</sup> and salt water environments<sup>(101)</sup>; but its superiority to cadmium in other environments has been questioned<sup>(84)</sup> and the relative merits of cadmium and tin-cadmium alloy depend on <sup>the</sup> conditions involved<sup>(85)</sup>.

The standard electrode potentials for tin and cadmium are close enough together ( $-0.136\text{V}$  and  $-0.403\text{V}$  respectively) to permit their codeposition even from simple ions. Many baths, acidic or alkaline, have been proposed to yield deposits with various compositions. They include sulphate<sup>(86)</sup>, fluoborate<sup>(87,89)</sup>, fluosilicate<sup>(90)</sup>, chloride-fluoride<sup>(91,92)</sup> and cyanide-stannate<sup>(93)</sup>. Commercially the alloy was deposited only from acidic baths mainly fluoborate. The acidic bath usually needs addition agents to secure good deposits and excess acid to prevent the hydrolysis of the tin components. The composition of a typical fluoborate bath is as shown in Table 21<sup>(89)</sup>. The tin content in the deposit is 27%.

The alkaline bath which was recommended by Lowenheim has the composition which is shown in Table 22<sup>(20)</sup>. The anodes should have the same composition as the deposit required.

The effects of the different variables of acid baths on the composition of the deposits are predictable from the simple diffusion theory; the baths being of a regular-type. According to Davis et al<sup>(94)</sup> any increase in metal content of the bath, temperature, pH, and agitation will cause increases in the tin content of the deposits, and any increase of current density or addition agent will cause a decrease in the amount of tin in the deposit. Alkaline baths behave as an irregular system in contrast to the acid baths. The plating variables in such baths affect the composition of the deposits indirectly through changing the cathodic efficiencies of the metal deposition reactions.

#### iv) Tin-zinc

The interest in the electrodeposition of tin-zinc was stimulated after World War II, because of the shortage of cadmium which was usually used as a coating for protection of steel. The codeposition of the two metals is possible in any composition but an alloy of 80 Sn:20 Zn has been mostly used. Such an alloy offers superior corrosion protection for steel and has an excellent solderability<sup>(95)</sup>.

The standard electrode potentials of tin and zinc are -0.136V and -0.763V respectively. The codeposition of the two metals from simple acid ions is rather difficult. In alkaline solutions the deposition potentials of the metals are much closer together and the commercial baths are based on a mixed type, in which the bath contains tin in the form of stannate and zinc as zincate ( $\text{ZnO}_2$ )<sup>2-</sup> and/or complex cyanide  $[\text{Zn}(\text{CN})_4]^{2-}$ .

Vaid and RamaChar studied the possibility of electrodepositing the alloy from a pyrophosphate bath; Davies et al<sup>(94)</sup> have developed a cyanide-free bath based on using an organic agent instead of cyanide but both baths have no commercial interest to any extent.

Sodium or potassium salts are used in cyanide solutions to provide the stannous ions. Lowenheim<sup>(96)</sup> claimed that potassium salts are preferable because their use enables the bath to be operated with higher current efficiencies at high current densities. Table 23 shows a typical composition for a cyanide bath containing tin as potassium stannate. The anodes should be filmed and have a composition of 80 Sn:20 Zn. The composition of a cyanide bath containing tin as sodium stannate is shown in Table 24.

Stannate-cyanide alloy plating systems are of the irregular type probably because the deposition potentials of tin and zinc are close together<sup>(5)</sup>. In general the zinc content in the deposit decreases with current density but there are some exceptions, and increasing the temperature increases the tin content in the deposit.

#### v) Tin-cobalt

Tin-cobalt alloys have gained much commercial interest recently as an alternative to chromium metal especially in decorative finishes. The electrodeposition of chromium from the known baths has many disadvantages including poor throwing power, high current densities, toxicity and corrosiveness. This makes the process rather difficult and the barrel plating process hazardous to both the users and the environment.

The appearance of tin-cobalt alloys is similar to that of chromium but its hardness and wear resistance are significantly lower. This limits the usage of the alloy in engineering applications, but it is preferably used in the domestic products industry. The alloy, unlike chromium metal, is solderable.

Very little has been published in the literature concerning the electrodeposition of tin-cobalt alloys and the baths are still a subject of patents. The earliest reference to the alloy was in a patent issued to the Du Pont Company<sup>(102)</sup> in Germany. The possibility of electrodepositing the alloy from fluoride-based solutions was claimed by Cuthbertson<sup>(103)</sup> and Sree and Rama Char<sup>(104)</sup> have suggested a pyrophosphate bath. Miyashita and Kurihara<sup>(97)</sup> have claimed the production of an alloy composed of 20% Co:80% Sn; they state that the alloy exhibits good environmental resistance which results from passivation of the alloy. The passivating film has been studied by Thomas and Sharma<sup>(105)</sup> who deduced that the film is of an hydrated tin (IV) oxide nature. Clarke et al<sup>(98)</sup> in the United Kingdom reported the electrodeposition of an alloy containing 33% cobalt from a fluoride/chloride based solution. The alloy was said to exhibit passivating properties too and the deposit obtained was an intermetallic compound. Hemsley and Roper<sup>(100)</sup> carried out a detailed study on the codeposition of an alloy containing 20% Co from a mildly alkaline sulphate-based solution. They showed that the alloy is competitive with chromium as a coating for indoor use. Beer<sup>(99)</sup> of Alkan Ltd. has compared the properties of the deposits which were obtained from fluoride and sulphate based systems: he concluded that there is a difference in colour,

hardness and wear-resistance but the other properties are broadly very similar. The corrosion behaviour of the alloy from sulphate baths has been studied by Spanchak and O'Grady<sup>(106)</sup>; they showed that an amorphous mixture of the elements is produced from the solution. The corrosion properties for such a structure are similar to the individual metals concerned. Thus the alloy offers a good alternative to chromium for small complex articles where chromium may be difficult to apply.

## CHAPTER 5

### APPLICATIONS

It has been relatively easy for electrodeposited tin-lead alloys to find many applications and to be very popular especially in the engineering industry because: firstly the alloy is one of the few electrodeposited alloys to have been almost fully understood, and secondly because of the many competitive properties possessed by the alloy such as solderability, corrosion resistance, softness, low melting point etc. The properties and the use of a tin-lead alloy are very dependent on its composition; alloys with a variety of composition have been electrodeposited in many applications. It is well known that tin-lead alloy containing 7-15%Sn has good resistance to outdoor corrosion, and an overlay containing 8-10% Sn is widely used in plain bearings manufacture as anti-friction and high corrosion resistance coating. As a solderable coat, an alloy with  $\lambda^a$  content of 10-60% Sn is commonly used in the electrical and electronic equipment; alloys with nominal composition of 63% Sn, 37% Pb was said to be a substitute for gold as a finish on connector contacts<sup>(74)</sup>.

The tremendous growth and development in both the automotive and electronic industries in the last two decades has been accompanied by an enormous growth in the popularity of tin-lead alloys. In the first area, the use of higher performance engines required an improvement in bearing properties of many bearing alloys; and in the electronics area the use of printed circuits required a good solderable alloy capable of retaining this property for a long shelf life. The use of tin-lead alloys in these two areas will be discussed below.

## 5.1 Bearings

Bearings are those elements of machines in which forces are transmitted between solids which are moving relative to each other<sup>(108)</sup> and while there is a relative motion between two parts friction and wear occur and their effect must be minimised.

In engines, bearings are essential parts like pistons, rings and valves and special attention is given to them which stems from fear of breakdown. Their design and metallurgical composition should be given some care because their behaviour directly affects the life span of the engine and its running.

Many types of bearings are known but plain bearings are the common type used in engines. The essential function of this bearing is to allow surfaces to slide relative to each other in conditions of hydrodynamic lubrication whilst providing some type of location between them. Some authors like to divide plain bearings into two types: soft and hard according to the bearing material used.

### 5.1.1 Bearing Material Requirements

For perfect performance, the bearing material must have the following properties<sup>(109)</sup>:

- a) Sufficient mechanical strength to resist the high fluctuating pressure.
- b) High enough melting point to resist damage at high temperatures of operation.

- c) High corrosion resistance.
- d) Good embeddability to absorb dirt particles.
- e) Good conformability so as to yield easily when the shaft is mis-shaped.
- f) Sufficient hardness to resist abrasion, wear and cavitation erosion.
- g) Excellent boundary properties to resist seizure when the bearing is loaded at speeds not high enough to provide<sup>a</sup> a thick hydrodynamic film.

Additional to these, bearing materials should be capable of being produced by economic manufacturing processes.

No one of the bearing materials known offers all these properties. Lead Babbitt alloy, as an example, has excellent resistance to seizure and excellent deformability and ability to embed, but it should not be used at temperatures over  $115^{\circ}\text{C}$ ; also it has poor fatigue resistance. Tin Babbitt alloy has better corrosion resistance than lead Babbitt but its hardness and compressive strength decreases rapidly with increasing temperature. Cadmium alloys are better than Babbitts in fatigue resistance, but do not have as good surface behaviour or corrosion resistance; the same is true for copper-lead and leaded bronze alloys. Solid aluminium has better fatigue resistance than Babbitts, corrosion resistance is good but<sup>it</sup> has poorer surface behaviour because it shows a tendency to seizure.

In order to optimise the above conflicting requirements a compromise consisting of two layers was proposed: a lining layer of high

strength material electroplated with a material of good bearing properties: the latter is normally a lead alloy.

#### 5.1.2 Overlays

The overlay is a binary or ternary lead alloy electrodeposited in a thickness, upon bearing surfaces sufficient to overcome the problems posed by the hard bearing materials. It was first applied upon the bronze bearings in the late 1930s, but nowadays its use has become essential with the increase in demand for bearings of high quality to match the large developments and improvement in the engine industry. Overlays now are electrodeposited on copper-lead, aluminium-tin, and more recently on tin and lead base alloys<sup>(111,112)</sup>.

#### 5.1.3 Overlay Functions and Design Considerations

The overlay has two main functions:

1. Protecting the lining material layer from the corrosion attack caused by the oxidised lubricating oils, and
2. Reducing the tendency towards seizure caused by any foreign particles which might be suspended in the oil film between the sliding surfaces. The latter function is guaranteed by improving the embeddability, conformability and compatibility of the bearing.

Good quality overlays must also have a sufficient fatigue strength and wear resistance to enable the bearing to survive for the life of the engine. In general, a plain bearing with plated overlay should be able to:<sup>(110)</sup>

- a) Withstand fatigue loads in the order of  $100 \text{ MN/m}^2$ .
- b) Withstand these loads at temperatures in the order of  $100^\circ\text{C}$ .
- c) Operate with a limited oil supply without damaging the journal, especially during starting and stopping.
- d) Absorb any foreign particles from the lubricant.
- e) Resist the possibly corrosive action of the lubricant, and
- f) Be capable of manufacture to close tolerances.

Heavy fatigue loads require thin overlays because the fatigue strength of an overlay decreases as the thickness increases<sup>(112)</sup>, but extremely thin overlays have too short a life. In plain bearings the lining layer and the steel backing usually cope with heavy fatigue loads, but a balance between the limits of these loads and the overlay thickness must be considered.

Under normal conditions most overlays operate at temperatures of about  $100^\circ\text{C}$ . A momentary rise in this temperature is no risk for the overlay but a sustained rise (for example, lack of oil, failure in oil cooling system) will cause a complete bearing seizure if the overlay has a relatively high melting point. In addition, hot oil is more liable to deterioration than cold oil, consequently, deterioration products may cause corrosive attack to the overlay.

#### 5.1.4 Overlay Composition and Properties

Overlays of different composition have been electrodeposited but the nominal compositions of the overlays in common use are<sup>(113)</sup>:

Lead - 10-12% tin  
Lead - 5- 8% indium  
and Lead - 10% tin - 2% copper.

Lead-tin and lead-tin-copper overlays are normally electrodeposited from single solutions but lead-indium overlay is electrodeposited as two separate layers of lead and indium, then alloyed by heat treatment. (An alloy electrodeposit is technically possible but not used in practice).

The thickness of the overlay ranges between 17 and 75  $\mu\text{m}$  depending upon bearing loading and bearing type and size. A thickness of 25  $\mu\text{m}$  for passenger-car engines is most common.

The fatigue strength of the overlay depends on the thickness and composition. Thinner overlays have higher fatigue<sup>(114)</sup> strength (see Figure 5) and the strength of lead-indium overlays is 20% higher than that for lead-tin overlays<sup>(115)</sup>.

Fatigue strength for lead-tin overlays is the same as that for lead-tin-copper overlays.

The wear resistance of lead-tin overlays is higher than that for lead-indium, although they have the same as-plated hardness (8-10 HV). Both hardness (13-15 HV) and wear resistance for lead-tin-copper overlays are higher than those for the other overlays. The copper tends to behave as an improving factor, but the extreme increments in copper amounts reduce the strength. An optimum amount of copper is said to be (1-3%)<sup>(2)</sup>.

Corrosion resistance of lead-tin overlays is higher than that of lead-indium<sup>(116)</sup>. The attack does not occur until the content of tin or indium falls below a critical level (3% for tin and 5% for indium)<sup>(115)</sup>. The fall in the content of tin or indium is generally due to a diffusion process taking place if the engine runs under high temperature conditions (see Figure 6). For the purpose of preventing such diffusion electrodepositing a nickel barrier under the overlay can be adopted, but more recent studies showed that diffusion occurs even with the existence of a nickel barrier to form intermetallic compounds of one of the forms  $\text{Ni}_3\text{Sn}_4$  or  $(\text{Cu}_8\text{Sn}_5 + \text{Cu}_3\text{Sn})$ <sup>(117)</sup>. A cobalt barrier was suggested by others<sup>(118)</sup>, but its effectiveness has not been proved yet. A beneficial role for nickel barriers is to stop loss in adhesion between the overlay and the cast lead-copper lining layer in steel-backed bearings due to formation of a Cu-Sn-Fe compound.

Failure of overlays by cavitation erosion is possible due to bubbles forming and collapsing at the metal-oil interface. Overlays of lead-tin-copper have been claimed to show the best resistance for this type of failure<sup>(112)</sup>.

#### 5.1.5 Selection of the Overlay

Three main factors must be considered for appropriate selection of overlay type and composition:

- a) The service conditions under which the bearing will operate.
- b) The service life required from the bearing, and
- c) The cost of the overlay.

Ideally, bearings must survive for the life of the engine, but large numbers of them are scrapped long before they reach the end of their useful service life because of incorrect selection of the bearings.

Lead-tin-copper overlays introduce better fatigue strength and wear/corrosion resistance properties, so their plating upon the large bearings of medium speed diesel engines is essential because service conditions in this type of engine are severe and the required service life is long.

Tin-lead and tin-indium overlays are relatively softer than lead-tin-copper overlays. Their use may be preferred in automotive applications. However, the real case is that improvement in surface properties and service life gained by electroplating bearings with overlays must offset the increment in the cost which may approach 30%; this increment which is not necessary due to the cost of materials alone, but mainly to the necessity of applying the overlay in a precise prescribed limit of thickness and composition for the purpose of insuring optimum compromise of surface properties.

## 5.2 Printed Circuits and Connectors

The second main use of electrodeposited tin-lead alloys is in the electronics industry as a solderable and protective coating mainly in printed circuits and connectors manufacture.

The electronics industry in fact has shown a large expansion in the last decade by introducing the so called "dry circuits". One main advantage for such circuits is the operation at low levels of volts ( $\approx 20$  mV) and currents ( $\approx 10$  mA). It was necessary with this achievement to use a component of high quality properties such as high conductivity and wear and corrosion resistance. In the early times, precious metals such as gold and silver have been used extensively as solderable protective coatings upon copper substrates, but later for competitive reasons, alternatives were required especially with the sharp increase in the price of gold and silver. Many metals and alloys have been considered, but the right choice and the final decision is a compromise between the cost of material and the equipment function. Tin-lead alloy was one of the best alternatives in this area. In addition to its low cost compared with gold, it has many competitive properties.

#### 5.2.1 Printed Circuits

In principle, the "printed circuit" consists of a non-conductive plastic board on which is laid a conductive pattern or circuit track of metallic lines<sup>(119)</sup>. Copper is regarded as the best metal in terms of conductivity and cost<sup>(120)</sup>. In assembly the components are mounted on the other side of the board and connected to the circuit by connecting wires through special holes punched at selected points on the track. The wires are soldered to the circuit by immersing the circuit side with the surface of a molten solder to ensure that all the joints are firmly soldered. For a successful soldering

process, the conductive track must exhibit a good solderable surface but, because the boards are normally stored for a long period of time before use, the copper tracks tend to oxidise and become poorly wetted by solder. Electroplating the tracks with a thin layer (5-7  $\mu\text{m}$ ) of tin-lead alloy protects the copper surface and secures good solderability. An alloy with a composition of 60 Sn:40 Pb not only provides a good solderable surface, but it is not prone to whisker growth<sup>(121)</sup>, in addition, by having a relatively low melting point ( $183^{\circ}\text{C}$ ), it maintains the non-conductive board safe; this board might deteriorate if molten solders of higher temperature were used. Hot-dipping may be used for plating the track, but the electroplating method has many advantages<sup>(119)</sup>; the uniform thickness of the coat, and the ability to provide a consistent coat inside the holes which enables the solder to penetrate readily through the holes.

### 5.2.2 Connectors

Connectors have been defined as "components normally attached to a cable or to a piece of apparatus for the purpose of providing connection(s) through a suitable mating part between cables and/or pieces of apparatus"<sup>(122)</sup>.

Many types of connectors have been designed to suit a diversity of applications which include: household and domestic products, computers, telecommunications equipment, space vehicles etc. Some of the connectors are separable and some of them are permanent, but all of them have the same function, conducting an electrical current of a specified rating mainly in low quantities.

The most important area in the connector is the contact area which must be of high conductivity to maintain the stability and continuity of the electrical current flow. Using copper or copper alloys in connector manufacture can be satisfactory. They have a high conductivity but their corrosion products in many environmental conditions, result in a reduction in the interface conductivity due to imperfect metal to metal contact, consequently a reduction in current flow will occur. To minimise the problem, plating the basic metal with a suitable coating is necessary. The choice of this coating depends on many factors<sup>(123)</sup> which include: the expected life of the equipment, the number of inserts and withdrawals to be made during that expected life, the environment in which the connector will operate and the necessity for competitive prices.

Gold was dominant until the last decade, but its high cost and the fluctuating price, necessitated alternatives. Tin-lead alloy is one of these alternatives which may prove to be an adequate contact material for relatively few matings<sup>(121)</sup>. The remarkable advantage of gold over an alloy of 60% Sn:40% Pb is that gold is relatively inert and is not affected by atmospheric pollutants. Waine and Sollers<sup>(124)</sup> reported a strong similarity in contact resistance behaviour between tin-lead alloy and gold coating until wear through the tin-lead overlay coating occurs.

The main objection to the use of tin-lead alloy is the formation of oxide films<sup>(125)</sup> on the surface of the connector which could lead to a serious failure in the connecting process; this fact limited the use of the alloy in certain applications mainly in military and

aerospace equipments. For the purpose of reducing the cost of plating materials and making use of the inert property of gold, a selectively gold plated connector was produced. The rest of the substrate is electroplated with tin-lead alloy.

The so called Gas-Tight High Pressure Contact is a specially designed connector electroplated with tin-lead alloy finish. It was claimed that this design reduces 33% of the cost compared with gold plated connectors<sup>(126)</sup>. It showed stable contact resistance under extreme environmental conditions which included the exposure in concentrated nitric acid fumes followed by ammonium sulphide.

### 5.3 Other Applications

Electrodeposited tin-lead alloys have been used in many other applications derived from the variety of properties exhibited by them. In the template industry, an alloy containing 7-15% tin has been electroplated on steel sheets and strips. Du Rose<sup>(19)</sup> deduced from his studies that an alloy containing 6% Sn has superior corrosion resistance, but the use of electroplating in this area is still limited probably because the lack of achieving competitive advantages over the well known methods: hot-dipping. Narrow tin-lead plated strips are commonly used in the manufacture of brake-fluid pipes for automobiles, cable sheathing and heat exchangers.

High-speed plating of copper wires with tin-lead alloy is another area of application. Wires with diameters of 0.41-1.29 mm have been electroplated with coating thicknesses ranging from 7.6 to 12.7  $\mu\text{m}$ .

In the radiator industry, the deposition of 5-20  $\mu\text{m}$  of tin-lead alloy on radiator tubes was reported by Russian publications<sup>(127)</sup>.

As a self-lubricant coating, the alloy was applied to pistons, piston rings, and on threaded parts of stainless steel to prevent their seizure.

One more use for the alloy is in the printing industry; the alloy was electrodeposited on the electroformed copper printing blocks to facilitate the adherence of copper with the "type metal" alloy.

## PART II

### EXPERIMENTAL WORK - I

This part of the thesis describes the experimental work carried out to develop a solution based on sulphamate for electroplating tin. A solution has been developed and its important parameters (addition agents, current density, conductivity, polarization behaviour etc) were investigated. It also includes the results of the work which was discussed in view of the suitability of the solution developed for electroplating with tin. Some conclusions are briefly mentioned.

## CHAPTER 6

### ELECTRODEPOSITION OF TIN

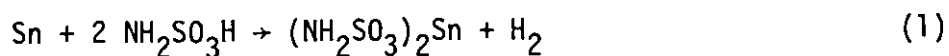
#### 6.1 The Development of Tin Sulphamate Solution

In the literature no clear method has been described for preparing a sulphamate solution for electrodeposition of tin, all the published articles discuss only the results. These results if they were positive, are only practicable if a stable solution can be satisfactorily prepared and maintained over a long period of time. Experimental work was therefore carried out in order to prepare a tin sulphamate solution able to yield satisfactory tin deposits: this solution, combined with that which was previously developed for lead<sup>(128)</sup>, will form the basis for further work for electrodeposition of lead-tin alloys.

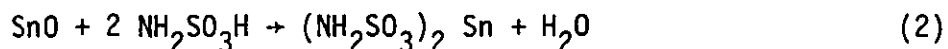
##### 6.1.1 Initial Proposals

Three possible methods for preparing tin sulphamate solution have been studied:

1. Dissolving solid sulphamic acid in distilled water, then dissolving tin metal in the acid solution chemically according to the chemical equation:



2. Dissolving sulphamic acid in distilled water, then dissolving stannous oxide in the acid solution chemically according to the chemical equation<sup>(129)</sup>:



3. Dissolving tin metal electrochemically (Faradaic method) using an electrolysis cell containing sulphamic acid solution, a tin anode and an inert conducting cathode. In each case the salt,  $(\text{NH}_2\text{SO}_3)_2 \text{Sn}$ , will be produced ready dissolved in water to yield the electroplating solution. Precise composition will be adjusted by dilution and addition of other salts and additives as necessary.

#### 6.1.2 Tin-acid Chemical Reaction Method

The solid sulphamic acid used in this method and the other two methods was obtained as Fison Laboratory Reagent. This solid acid was dissolved in distilled water to produce solution of the required concentration.

In this method three pieces of pure tin (BDH 99.99 purity) were fully pre-treated and weighed. Each one was dropped in a flask containing 250 ml of sulphamic acid solution. The concentration of the acids was 200, 100 and 50 g/l. The loss in the weight of each tin piece was defined after periods of 27, 98 and 140 hrs. The concentration of tin in the solution obtained was then calculated.

#### 6.1.3 SnO-acid Chemical Reaction Method

An approximate estimation of the reacting components was done according to the chemical equation (2) of the chemical reaction between these components. The solubility limit of tin in water was

also considered<sup>(130)</sup>, that is to make sure that all the added stannous oxide would react. Stannous oxide was added to sulphamic acid solution of concentration 100 g/l. The solution was stirred and heated to about 40°C to activate the reaction but generally resulted in a quantity of a black stannous oxide being undissolved and precipitated at the bottom of the flask.

#### 6.1.4 Faradaic Dissolution Method

Sulphamic acid solution with a concentration of 100 g/l was prepared for use in the method. The electrolysis cell used in the early stage was a 500 ml flat bottomed culture vessel containing 250 ml of the solution and the electrode components. The cell electrode components consisted of a cylindrical tin anode (diameter 65 mm) made from a pure tin sheet and a cathode of a narrow strip copper sheet. Both of them were fully pre-treated and weighed. The electrical current was supplied to the cell from a Farnell L10-3C power unit. Current was maintained at 100 mA and the quantity of electricity passed was monitored by a (Kemitron) coulometer.

Later the culture vessel cell was abandoned and replaced by a two-compartment cell (see Figures 7, 7a). This cell was designed especially to produce uncontaminated solution with the material of the cathode. It consisted of two glass made cylindrical compartments, the larger compartment contained the anode and the anolyte (solution to be prepared) and the smaller one to contain the cathode and the catholyte. The two compartments are connected by a glass made horizontal tube.

A glass filter disc in the middle of the tube permits the electrical contact between the anolyte and the catholyte but prevents any mixing for them<sup>(131)</sup>. The electrodes used with this cell were a rod of cast tin of 10 mm diameter as anode and a strip of stainless steel with dimensions of 95 x 15 mm as a cathode (Figure 8). The strip was cut from a sheet of 1.0 mm thickness. The immersed area of the anode was kept equal to 15 cm<sup>2</sup> by masking the remaining area with PTFE tape. The cell was partially immersed in a water bath thermostatically controlled at 20°C during the trials. Samples of 2 ml size were withdrawn from each compartment every 2.5 hours, diluted with 1:9 HCl solution to 100 mls and kept for analysis. The reading of the coulometer was recorded with each sample. This procedure of preparing the solution was stopped when the solubility limit of tin was approached or where a precipitation of some tin compounds was noticed in the anolyte compartment.

Further trials were carried out to investigate the effect of temperature on the solubility limit of tin in sulphamic acid. A saturated solution with tin ions was heated to 70°C while feeding with electrical current continued until a renewed precipitation of tin compounds was noticed at the bottom of the cell. The solution was then cooled gradually in steps of 5°C, the temperature being kept constant for 30 minutes in each step, and samples of 2 ml were withdrawn and diluted to 200 ml with 1:9 HCl solution and kept for analysis.

## 6.2 Studies of the Developed Solution

Further experimental work has been carried out to examine the various operating parameters of electroplating baths based on tin sulphamate solution prepared by the Faradaic method in particular, i.e. additive agent, current density and conductivity. The polarization characteristics of tin deposition on tin cathodes were also studied by a linear sweep potentiostatic technique.

The electrolyte chosen for this work contained tin with a concentration of 10 g/l. The additive agents were added to the bath when required.

The cell used for plating trials and polarization studies consisted of a 500 ml flat bottomed culture vessel equipped with a five-necked socket lid (Figure 9). The lid carried the electrode assemblies via PTFE sleeve adaptors. A glass tube was fitted with diffuser block for nitrogen gas agitation of the solution when required and a saturated calomel electrode was inserted when needed. A standard Hull-cell of volume 267 ml was used to study the effect of additive agents and to define the range of current density for good plating.

### 6.2.1 Additive Agents

The preliminary trials for electroplating with tin sulphamate solution showed inferior deposits when the solution was used without additive agents. The standard Hull-cell was used to examine the effect of the additives on the quality of the deposits obtained by applying different current densities. The anode in the cell was a squared piece

of rolled tin with dimensions of 60 x 70 mm and 1 mm thick. The cathodes were cut pieces of 65 x 100 mm from a 0.25 mm thick sheet of polished copper. The anode and the cathodes were adequately pre-treated to secure a clean, smooth surface.

A selection of additive agents was investigated; it included: phenolsulphonic acid, peptone, gelatin, pyrogallol, resorcinol, polyethylene oxide and polyethylene glycol. The additives were tried individually at first then as groups. Three groups of additives were formed based on those additives showing the best results as individuals. The groups were:

GROUP I	Phenolsulphonic acid	2.5 g/l
	Peptone	5 g/l
	Gelatin	2.5 g/l
GROUP II	Phenolsulphonic acid	2.5 g/l
	Peptone	2.5 g/l
	Pyrogallol	2.5 g/l
GROUP III	Phenolsulphonic acid	2.5 g/l
	Peptone	2.5 g/l
	Polyethylene oxide	2.5 g/l

A 267 ml of freshly prepared tin sulphamate solution was used in each trial. The additives were added to the solution in the cell as required after being dissolved in sulphamic acid.

A constant current of 1 Amp was applied to the cell from a Farnell L10-3C power unit for 10 minutes in each trial. The current applied and voltage were monitored by two Sinclair digital multimeters and adjusted manually.

### 6.2.2 Plating Trials

The plating trials were carried out with solutions containing the additives as groups. The required additives were dissolved in sulphamic acid and added to the solution. A 250 ml of the solution was used in each trial. It was contained in the flat-bottomed vessel described before. In the early trials cylindrical anodes of tin were used, but this type of anode was replaced by a rod of cast tin later. The rod of tin was of 10 mm diameter. It was pre-treated before use to secure a clean surface. The exposed area of the anode was controlled to 8 cm<sup>2</sup> by masking the upper immersed part of the anode and the anode then located at one of the side sockets.

The cathodes were prepared by cutting 70 x 10 mm strips from a 0.25 mm thick sheet of polished copper. The cathodes were pickled in a solution of 50% nitric acid for 20 seconds, rinsed with distilled water, then acetone and dried and weighed. The upper end of the cathode was held in a slot on a stainless steel rod by a grub screw and the rod was located in the central socket of the cell lid. The plated area on the cathode was kept equal to 4 cm<sup>2</sup> by masking the remaining area with PTFE tape. Constant current was applied to the cell and was manually adjusted to the required values. It was monitored by a digital multimeter connected in series with the cell. Each plating run lasted for 20 minutes. After each run the cathode was demasked, rinsed in distilled water, acetone, then dried and weighed. The cathode current efficiency was then calculated from the weight of deposit and the quantity of electricity passed using Faraday's law:

$$W = W_e I t$$

where  $W$  = weight of deposit (g)

$W_e$  = electrochemical equivalent and equal to 2.213 (g/hr) for  
the reaction  $\text{Sn}^{2+} + 2e \rightarrow \text{Sn}$

$I$  = current passed (Amp)

$t$  = time (hours)

### 6.2.3 Polarization Studies

The equipment used in the polarization studies is shown in Figure 10. An identical cell to that used in later plating trials was used in these trials too. The cell was contained in a "Tecam" temperature-controlled water bath. The temperature was controlled to  $\pm 0.05^\circ\text{C}$ .

The potentiostat used was a '6A Kemitron' with a built-in digital sweep generator (Kemitron SG2) and volt-amperemeter (Kemitron LCV-2). The sweep generator could sweep at rates from 0.1 mV/sec to 10 V/sec in decades with a multiplication factor from 1 to 10. The maximum output of the generator is 2V. The output of the potentiostat was delivered to the input of a 'Bryans 28000' chart recorder as a potential by using a standard resistance ( $1\Omega$ ) connected between the output terminals of the potentiostat. The electrode potential vs the current density were replotted manually from the recorder chart on semi-logarithmic paper so that some expansion of the lower current densities could be obtained.

In cathodic polarization studies, the cathode was a narrow copper strip with similar dimensions for that which were used in plating trials. The exposed active area was kept equal to 4 cm<sup>2</sup>. The remaining area was masked with PTFE tape. The anode was a rod of pure tin with diameter of 1 cm and the exposed area was equal to 8 cm<sup>2</sup>.

In anodic studies, both the anode and the cathode were narrow strips. The anode was a strip of tin and the cathode was a strip of copper. The active area for each of them was kept equal to 4 cm<sup>2</sup>.

The reference electrode used was a saturated calomel electrode with an extended ceramic tipped luggin probe. The tip of the luggin was placed very near to the cathode. All potentials quoted are on the SCE-scale of potential.

The polarization curves were plotted as the following. The electrodes after being pre-treated properly and the relevant areas were masked and were then located in their positions in the cell which was filled with 250 ml of the solution and placed in the water bath. The reference electrode was positioned in the cell and the electrodes were connected to the appropriate sockets in the potentiostat. The cathode was pre-plated with a thin layer of tin by passing a constant current of 20 mA for 3 minutes and the static potential was measured. The sweep potential was then applied and swept cathodically or anodically as required. Several sweep rates were used; however, for most of the polarization data a sweep rate of 30 mV/min was used.

#### 6.2.4 Conductivity Measurements

The conductivity of the solution was measured by using a direct read-out Philips conductivity meter, type PW 9501/01 (Figure 11). This meter measures the conductivity with the aid of a precalibrated cell (Figure 12) which had a cell constant of  $28.3 \text{ cm}^{-1}$ . It is constructed from Pyrex glass with cylindrical platinized electrodes. It can be operated with a minimum sample size of  $4 \text{ cm}^2$  over a range of  $1\text{-}1000 \text{ ms cm}^{-1}$ . The conductivity meter itself consists basically of an impedance bridge fed by an a.c. signal from an oscillator able to supply it with frequencies of 200 or 2000 Hz according to the value of cell constant/conductivity ratio; a low frequency should be selected for high ratio values and vice versa.

The measuring trials were carried out on a solution prepared by the 'Faradaic dissolution method' containing originally 10 g/l tin. This solution was diluted when required. Samples of  $5 \text{ cm}^3$  volume with different concentrations of tin were held in a series of boiling tubes enclosed in a water bath thermostatically-controlled by a thermostat/stirrer. The cell was soaked in distilled water for several hours before use. The conductivity for each sample was determined by immersing the cell into the sample ensuring that the system came to thermal equilibrium for each reading.

#### 6.2.5 Analysis and Thickness Measurements

The analysis of the samples withdrawn from prepared solutions was performed using atomic absorption spectrophotometry. An instrument produced by Instrument Laboratories Inc. was employed - type IL 151.

The samples of 2 ml of tin solution after dilution with 1:9 HCl solution to 100 ml using a volumetric flask of grade A were analysed using the 'direct calculation' method and providing a linear calibration of concentration versus absorbance. This method is easy and allows fast results with practical accuracy.

A nitrous oxide-acetylene flame was used in the earlier stages, but it was replaced with air-acetylene flame later after consultation with the International Tin Research Institute.

The thickness of deposits of some samples was measured by a direct calculation method, i.e. from the knowledge of the weight of deposit and the dimensions of the sample considering the density of tin equal to 7.3 gm/cc.

## 6.3 Results

### 6.3.1 Development of Solution

The solution which was obtained by direct chemical reaction between tin and sulphamic acid solution was diluted in tin ions. The acid concentration had little effect on the amount of tin dissolved, but a solution with a concentration of 100 g/l sulphamic acid gave the best results (Figure 13). The effect of time is negligible too (Figure 14).

The trials for preparing the solution by chemical reaction between stannous oxide and sulphamic acid solution resulted in a large quantity of black stannous oxide being precipitated at the

bottom of the flask unreacted with the acid. This meant that a dilute solution of tin ions was produced. The cathodic electrodeposits from such solutions were only moderately acceptable.

The solution prepared by the Faradaic dissolution method was more concentrated with tin ions and much more suitable for electroplating with tin. The earlier trials in which a cylindrical tin anode and a narrow strip of copper cathode were used, produced a solution contaminated with copper ions, monitoring the weight of the cathodes used showing a decrease in their weights in the earlier stages of the trials. Replacing the copper cathodes with stainless steel and using the two-compartment cell produced uncontaminated solution. The relation between the quantity of electricity passed in the cell and the concentration of tin in the solution prepared is shown in Figure 15. The solubility limit of tin in the acid was found to be  $\approx 20$  g/l. The effect of temperature on this limit is shown in Figure 16. Heating the solution up to  $70^{\circ}\text{C}$  increased this limit to  $\approx 24$  g/l. The efficiency of the process is shown in Figure 17. It was low at the earlier stages, then it increased gradually to approach a maximum value of  $\approx 97\%$ . The analysis for samples from the catholyte solution showed that a small amount of tin was transferred through the porous disc; this amount was really negligible.

#### 6.3.2 Additive Agents (Hull-cell)

Table 25 shows the data obtained from Hull-cell trials for solutions containing 10 g/l tin and additive agents as individuals. The best results were for solutions containing phenolsulphonic acid,

peptone or gelatin. Good semi-bright deposits were obtained for a range of current densities up to 2 Amp/dm<sup>2</sup> from solutions containing peptone and up to 1.5 A/dm<sup>2</sup> from solutions containing gelatin. The range of good deposits from solution containing phenolsulphonic acid was found to start from 1.5 A/dm<sup>2</sup> up to 3 A/dm<sup>2</sup>, but such additives showed inferior throwing power to that obtained from solutions containing peptone. Other additive agents such as polyethylene oxide, polyethylene glycol, resorcinol and pyrogallol showed a narrower range of current densities for good deposit but superior throwing power to other additive agents. The remarkable feature in the results was that the amount of additive had little or no effect on the width of the range of current density for good deposition; 2.5 g/l of peptone showed approximately the same effect as 10 g/l but 5 g/l of gelatin extended the range of good semi-bright deposit by only 0.05 A/dm<sup>2</sup> over that of 2.5 g/l. Increasing the amount of gelatin up to 10 g/l reversed the result.

The data obtained from the trials on solutions containing the additive agents as groups is shown in Table 26. Two main areas were noticed, one of good semi-bright deposit and the other burned and/or dark. No remarkable improvement was found by using the additive agent as groups on the width of range of current density but there was a slight extension in the direction of low current densities. A group of additive agents, consisting of 2.5 g/l phenolsulphonic acid, 2.5 g/l peptone and 2.5 g/l pyrogallol, secured the best results. Matt and/or semi-bright deposits were obtained for current density range of 2 A/dm<sup>2</sup>.

### 6.3.3 Efficiency Measurements

The plot in Figure 17 shows the efficiency of the process of developing tin sulphamate solution by the Faradaic method. The efficiency calculated as a ratio between the actual amount of tin dissolved in the solution and the theoretical amount presumed to be dissolved according to Faraday's law. The efficiency was low at the earlier stages of the process ( $\approx 18\%$ ), then it increased gradually to approach  $\approx 97\%$ . It dropped sharply after approaching the solubility limit of tin in the acid.

The cathode current efficiency of electroplating from this tin solution was found to be high for the range of currents which produce useful deposits. The effect of current density on the cathode current efficiency for solutions containing the additive agents as groups is shown in Figure 18. At low current densities, the efficiency was high (90-100%), but as the current density increased the CCE decreased. The solution containing group 2 of additives showed a slightly higher CCE than solutions containing the other groups. The effect of temperature was found to maintain the CCE at the higher limits i.e. above 95%.

### 6.3.4 Anodic Polarization

The anodic behaviour of tin electrodes immersed in solution containing 10 g/l tin is shown as curve (1) in Figure 19. The effect of phenolsulphonic acid as additive agent is to displace the curve to more base potentials (i.e. to depolarize). This displacement was small

at low current densities (Figure 19) but it was larger for higher current densities. A displacement of 7.5 mV was obtained from solutions containing 2.5 g/l additives for a current of 0.1 A/dm<sup>2</sup> (see curve 2); it increased to 37 mV when the current became 1 A/dm<sup>2</sup>, and it was 9 mV from solutions containing 5 g/l additives for a current of 0.1 A/dm<sup>2</sup> (see curve 3); it further increased to 45 mV when the current became 1 A/dm<sup>2</sup>. The rest potential kept its value at  $\approx -440$  mV (SCE-scale).

The effect of pyrogallol is shown in Figure 20. Pyrogallol polarizes the reaction at less base potentials—curves 2 and 3 in Figure 11. A 2.5 g/l pyrogallol addition to the solution lowered the polarization by 60 mV for a current density of 1 A/dm<sup>2</sup> (see curve 2); it became 70 mV when the amount added was increased to 5 g/l.

Unlike phenolsulphonic acid and pyrogallol, gelatin showed no or little effect on the anodic behaviour even when it was added in large quantities (Figure 21).

The effect of addition agents as groups on the anodic behaviour is shown in Figure 22 - curve 1 is for a solution containing 2.5 g/l of each of the additives, phenolsulphonic acid, gelatin and 5 g/l of peptone. Curve 2 is for a solution containing 2.5 g/l of each of the additives phenolsulphonic acid, peptone and pyrogallol and curve 3 for solutions containing 2.5 g/l of the additives, phenolsulphonic acid, peptone and polyethylene oxide. Curve 4 is the anodic behaviour for a solution without additive. The effect of the group of

additives shown in curve 3 is to shift the curve to more base potentials but the group shown in curve 1 has the effect of shifting the curve to less base potentials while the group shown in curve 2 maintained the curve approximately as if no additive was used up to a current density of  $1.5 \text{ A/dm}^2$ , and then shifted the curve to more base potential values.

Figure 23 shows the effect of temperature on the anodic behaviour, higher temperatures result in shifting the curve to higher base potentials.

The effect of additive agents on the rest potential is negligible but the effect of temperature is to decrease the potential slightly in a negative direction.

#### 6.3.5 Cathodic Polarization

The cathodic polarization curves were plotted for solutions containing 10 g/l tin. In preliminary trials sweep rates of 30 mV/min, 60 mV/min and 120 mV/min were used but later the sweep rate of 30 mV/min was used for most of the work.

Figure 24 shows the effect of the sweep rate on the shape of the curve. At low current densities, increasing the sweep rate shifts the curve slightly to less base potentials but at higher current densities the situation is reversed. Without addition agents the solution was found to have a rest potential of  $\approx -440 \text{ mV}$  and a limiting current density of  $\approx 1 \text{ A/dm}^2$ .

The effect of temperature on cathodic behaviour is shown in Figure 25. Heating the solution shifts the curve to less base potentials (depolarize) with smoother transformation to hydrogen evolution. The rest potential was found to decrease in negative value as the temperature increased.

Gelatin as additive showed negligible effects for very low potentials (Figure 26) but at higher potentials a pronounced fall-back was apparent and the curves were shifted to more base potentials. The shift was increased with the increase in gelatin concentration in solution.

The effect of adding different amounts of peptone to the solution is shown in Figure 27. The limiting current density range of potential was increased and the curve at low potentials was slightly shifted to less base values; the amount of shift decreased with the increase in the amount of peptone. Increasing the amount of peptone shifted the limiting current density slightly for higher values of current.

Resorcinol, similar to peptone, had the effect of shifting the limiting current density to higher values (Figure 28) but the amount of shift was more than that for peptone. Increasing the amount of resorcinol maintained the limiting C-D almost constant but it shifted the potential to higher base values for current densities higher than  $0.75 \text{ A/dm}^2$ . The trend for current densities less than  $0.75 \text{ A/dm}^2$  was variable.

The effect of pyrogallol is shown in Figure 29. It showed no increase in limiting current density. The only apparent effect is displacing the curve to more base potentials. Increasing the amount of pyrogallol increased this displacement.

Phenol-sulphonic acid gave a decrease in the limiting current density (Figure 30), but it increased the related potential. A small fall-back was seen in the curve; it became clearer for solutions containing 10 g/l additive (curve 4, Figure 30) and pronounced for solution containing in addition to phenolsulphonic acid 5 g/l gelatin. Adding gelatin reduced the limiting current density remarkably (curve 5).

The effect of addition agents as groups on the cathodic behaviour is shown in Figure 31. The three groups of additives showed a tendency to polarize the curve to less base potentials but to different extents. One group of additives consisting of 2.5 g/l phenol-sulphonic acid, 2.5 g/l peptone and 2.5 g/l polyethylene oxide caused a major shift in potential. It also showed a peculiar effect on the limiting current density (Figure 31, curve 2). In addition to reducing this current, two fall-backs were formed; one at potentials about -600 mV and the other at potentials about -900 mV. A group of additives consisting of 2.5 g/l phenolsulphonic acid, 2.5 g/l peptone and 2.5 g/l pyrogallol showed a lower shift in potential but slightly increased the limiting current (Figure 31, curve 3). A group of additives consisting of 2.5 g/l phenolsulphonic acid, 5 g/l peptone, and 2.5 g/l gelatin showed a moderate shift in potential to less base values and limiting current density between that of the other groups.

#### 6.3.6 Stability of the Solution

Some attempts were made to study the stability of solutions containing additives by detecting any change in the cathodic behaviour with time and also by plating some samples with these solutions.

Figure 32 shows the effect of time on the cathodic behaviour of solution containing 2.5 g/l phenolsulphonic acid, 2.5 g/l peptone and 2.5 g/l pyrogallol. A slight depolarization in the region of hydrogen evolution resulted from re-plotting the curve after 30 hours (curve 2).

Solution containing 2.5 g/l phenolsulphonic acid, 2.5 g/l peptone and 2.5 g/l polyethylene oxide showed more change in the cathodic behaviour with time (Figure 33). Curve 3 in the figure is for fresh solution and curve 2 is for the solution after 30 hours.

A fluctuating effect of time was obtained from solution containing 2.5 g/l phenolsulphonic acid, 5 g/l peptone, and 2.5 g/l gelatin (Figure 34). At range of potential - 525 mV to  $\approx$  - 750 mV a shift for lower currents was noticed with increasing time, but for potentials higher than that the effect was fluctuating.

#### 6.3.7 Conductivity

The results of the conductivity measurements for the solution are shown in Figure 35. Concentrated solutions with tin showed higher conductivity values, for example, at 25°C solution containing 10 g/l tin showed a conductivity value of  $88 \text{ mS cm}^{-1}$  but a solution

containing 1.2 g/l tin showed a conductivity value of  $29 \text{ mS cm}^{-1}$ .

The effect of increased temperature was to increase the conductivity in an approximately linear fashion. The conductivity of solution containing 10 g/l increased to  $105 \text{ mS cm}^{-1}$  when the solution was heated to  $40^{\circ}\text{C}$  and became  $\approx 130 \text{ mS cm}^{-1}$  when the solution was heated to  $55^{\circ}\text{C}$ . The rate of the increment was increased as the concentration of tin was increased.

#### 6.3.8 Electromicrography Studies

Electromicrographs were taken for deposits electroplated from solutions containing different types of addition agents. Some of them are shown in Figures 36, 37 and 38. Using different types of additives resulted in deposits of different crystal size and roughness grades. Solution containing 2.5 g/l peptone produced a relatively smoother deposit with larger active area than deposits obtained from solution containing 2.5 g/l resorcinol; the deposits from the latter were coarse with small active area. The deposits from solution containing gelatin in the same amount were of pyramidal shape. Traces of the additive were deposited with the metal but the surface was relatively smooth. Pyrogallol in the solution produced rough deposits but of interlocked crystals; this may provide good mechanical properties. Polyethylene oxide, with quantities of 2.5 g/l in the solution, produced rough surfaces. Traces of the additive were deposited with the metal but deposits from solution containing 2.5 g/l polyethylene glycol were smoother.

## 6.4 Discussion

Looking for new types of electrolytes for plating or attempting to improve known electrolytes is a continuous process as long as we always seek optimum conditions for any process, both technically and economically. Electroplating tin and tin-lead alloys are both processes which are well studied and reasonably well understood. Many electrolytes for their plating have been established, but solutions based on fluoborate are generally used for alloy deposition. A new stricter regulation, from the standpoint of pollution, has been introduced by Japan in recent years; these strict regulations are expected to be extended in the near future for the other industrial countries which might result in limiting the spread of the common solutions and provide added extra costs for the solutions which are already established. This necessitates a search for alternatives to the commercially dominating solutions. A variety of formulations has been proposed; amongst them are those based on sulphamate.

### 6.4.1 Why Sulphamate Solution?

Sulphamic acid solutions are based on an ideal simple acid which has an ideal property to form an electrolyte suitable for electroplating processes. The acid is solid, crystalline, non-volatile, relatively non-toxic and very soluble in water. Its solution in water is highly acidic and quite stable at room temperature. It hydrolyses very slowly at low temperatures but much more rapidly at higher ones to produce ammonium bisulphate.

Its complexing tendency is low.

Sulphamate baths have been chosen for this project for many reasons including:

- a) Sulphamate baths have been used successfully for commercial electroplating of many metals, notably nickel, cobalt and indium.
- b) The deposit from sulphamate solution is generally low stressed.
- c) The deposit from sulphamate solution is chemically more pure than deposits from other solutions, nickel deposits as an example have the best thermal stability.
- d) The mechanical properties of the deposit can be controlled by proper choice of operating conditions.

The literature published concerning the suitability of tin sulphamate solutions for electroplating tin or tin-lead alloys is not only very limited but it includes some confusion in the results. Some investigators claim that a satisfactory good deposit was obtained from such solutions and support their claims with some commercial patents, and some others state that such solutions are of no practical importance. This conflict in results created some kind of uncertainty about the suitability of tin sulphamate solutions for electroplating purposes and is consequently a limitation in this use and a block for any improvements in their properties. The claims of the latter team are probably based on two facts:

- a) The low solubility of tin sulphamate salt in water (214 g/l as tin sulphamate  $\approx$  80 g/l as tin-metal) and
- b) The moderate stability of the solution especially at higher temperatures.

In real practice, both of these drawbacks are hardly acceptable as reasons to sacrifice the many advantages possessed by the solution. In addition, there are many other solutions showing similar drawbacks but they have been commercially used for a long time; sulphate solutions as an example are based on tin sulphate salt which has a solubility in water (87 g/l) not far from that of tin sulphamate. Concerning the stability, it is well known that this drawback is the main problem for all electrolytes; even those which are in common use (fluoborate solution as an example) have some sort of instability and hydrolyse with time.

The remedy for these tin sulphamate solution drawbacks may be attained if these solutions are subjected to sufficient study, and the use of them found a real industrial outlet.

#### 6.4.2 Development of the Solution

It could be claimed, with some justification, that tin is outstandingly a chemically resistant metal. This fact makes preparing a solution for plating tin based on unfamiliar acids (sulphamic) rather difficult. The trials which have been carried out to prepare such a solution chemically were dependent on the little knowledge published which includes an uncertain understanding of

the nature and characteristics of the chemical reactions between the components. The results which have been obtained from methods based on chemical proposals were of no practical importance to exploit. The only choice was to adapt and improve the method based on electrochemical principles, i.e. the Faradaic dissolution method.

i) The chemical methods

It was expected that the strong sulphamic acid would simply react with tin to produce tin sulphamate salt because it is known from the literature<sup>(132)</sup> that sulphamic acid can readily react with oxides, hydroxides, carbonates, and active metals to form salts. However, it was not the case with tin, the results obtained were completely different from those which were expected and only a small amount of tin was dissolved on immersing tin metal in sulphamic acid solutions. In the best circumstances, the solution obtained contained less than 0.2 g/l tin (Figure 14) and the effect of time and/or the acid concentration to increase this amount was negligible. This concentration is too small to secure good electrodeposits and the plating trials which were carried out using this solution proved and confirmed that such solution is not really viable.

The large quantity of black stannous oxide precipitated at the bottom of the flask is an indication that the chemical reaction between stannous oxide and sulphamic acid was incomplete. Preparing the solution by this method depends primarily upon the chemical reaction between the components and upon the solubility of tin

sulphamate salt. The quantities of the reacted components were calculated using the chemical equation (2) shown previously (Section 6.1.1) that suggests a complete reaction between these components takes place. The solubility of tin sulphamate was taken as 214 g/l of water at room temperature. No doubt the solubility of tin in sulphamic acid solution should differ from the value considered, but unfortunately it was the only value available as a guide after an extensive search of the literature concerning the properties of such compounds. Whatever the reason for precipitation of the oxide, the solution obtained using this method was normally dilute in tin and the plating trials carried out using such a solution were only moderately acceptable. If the high cost of stannous oxide was also considered, this is another important reason to justify using the Faradaic method of preparation.

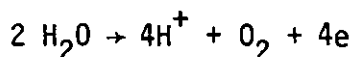
#### ii) The Faradaic dissolution method

A variety of components (cell, power unit, connection, etc) (Figure 8) were required for preparing the solution in the Faradaic dissolution method and the process was more difficult than the methods which were based on the chemical reaction process, but it was the only choice available to produce solutions containing sufficient amounts of tin able to secure good deposits. Controlling the concentration of tin in the solution prepared was another difficulty because the process can be controlled by electrochemical parameters, i.e. it depends on the quantity of electricity passed in the cell, and the behaviour of the electrodes in the acid solution.

The early trials which were carried out in a flat-bottomed flask were essentially a preliminary trial to investigate whether useful solutions could be produced or not. The copper cathodes used in this trial were an attempt to simulate the same conditions as those in the real use of the solution. Replacing these cathodes was necessary after the discovery of their dissolution by a chemical reaction and the production of solution contaminated with copper ions. The use of stainless steel cathodes might minimise contamination, but preventing contamination completely was achieved by the separation of the catholyte from the anolyte. The use of the two-compartment cell was essential if such uncontaminated solution was to be produced. The glass filter diaphragm used to separate the anolyte from the catholyte prevented mixing of the solutions in the two compartments, but permitted electrical contact between them. This resulted in transportation of only slight amounts of tin to the catholyte. The amount was originally considerable (20%) at the earlier stages, but it dropped to a negligible level (1.2%) with the effective use of the diaphragm.

The plot in Figure 15 shows the relation between the quantity of electricity passed in the cell and the related concentration of tin ions in the solution produced. The importance of such a curve depends upon the ability to use this curve for further preparation processes. The curve indicates that a small amount of tin was dissolved in the earlier stages resulting in dilute solution with tin (0.1 g/l for 2.7 KC ). The amount of tin dissolved increased gradually to approach the solubility limit ( $\approx 20$  g/l for 17.1 KC). The trend of increasing dissolution is not linear as one may expect; this indicates that an

electrochemical or chemical reaction other than simple tin dissolution took place. The most probable reaction is oxygen evolution according to the equation:



This reaction consumed a large quantity of electricity in the earlier stages of the process when the solution was depleted or diluted in tin ions, but became small when the concentration of tin ions in the solution increased later. This behaviour is probably due to a change in the overpotential of oxygen with respect to the tin concentration in the solution. Such change indicates that the overpotential of oxygen on tin oxide in sulphamic acid decreases as the tin concentration in the solution increases, i.e. tin ions in the solution may inhibit the effect of oxygen overpotential. It should also be noted that initially the pH is very low and increases as tin dissolves forming tin sulphamate; this also will lead to a decreased tendency for hydrogen to evolve and would be observed as a polarization effect with respect to the hydrogen evolution reaction.

The solubility limit obtained for tin in sulphamic acid was  $\approx 20$  g/l tin. It is much lower than that of tin in water (80 g/l) which was claimed by some workers<sup>(130)</sup>.

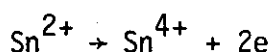
The change in the solubility limit produced by heating the solution was  $\approx 4$  g/l (Figure 16). Deciding whether it is beneficial to heat the solution, needs more investigation especially in relation

to preparation of commercial quantities for plant trials. This could be a significant disadvantage in initially installing such a process.

#### 6.4.3 Selection of the Additive

It is well known that the key to satisfactory electrodeposited tin from acidic solutions is the addition agents. The preliminary trials of plating with the sulphamate solution developed confirmed this fact; the deposits obtained from these trials even when freshly prepared solutions were used, were rough, treed and macrocrystallized. In the best circumstances the deposits were covered with a light non-adherent or "dusty" layer easily removed by gentle rubbing or buffing. The use of the additives was thus necessary and essential for producing satisfactory deposits.

The use of additives was also necessary for improving the stability of the solution by suppressing the oxidation of stannous ions ( $\text{Sn}^{2+}$ ) to stannic ions ( $\text{Sn}^{4+}$ ) according to the equation



which is very common in acid tin solutions. The claim that the presence of the stannic ions in acid solution does not affect the electrodeposition process itself is probably true, but the transformation of some useful ions (stannous) to some immune ions (stannic) results in reduction in the concentration of the active tin ions in the solution consequently extra cost for unnecessary processing.

The use of the additives with the solution may have two main drawbacks: firstly, the breakdown of the additives with use and/or time, and secondly the deposition of some of the additive molecule

residues with the deposits obtained. Increasing the amount of the addition agent in the solution is the only way to compensate for the quantity broken down, but the deposition of some additive molecules is hardly avoidable. The risky level of its presence in the deposit depends on the practical uses of the surface obtained.

The Hull cell used was an easy means to test the suitability and the effect of many additives for use with the solution developed. They were selected from the additives being reported as good additives for other acid solutions. This was the best way to start in spite of the fact that each addition agent may often be suitable only for a specific solution in a specific condition.

The use of peptone as an addition agent with acid tin solution is very rarely reported in the literature but its use with tin-lead fluoborate solutions is well documented and recommended for optimum performance. Its use with the sulphamate solution was very effective. It promoted the formation of fine-grained deposits over a range of current density up to  $2 \text{ A/dm}^2$ . This range virtually was the best range obtained from the additives tested. The throwing power for the solution was good.

The results of using gelatin are approximately consistent with the results reported by some workers<sup>(133)</sup> concerned with the use of gelatin in solutions based on tin sulphate. The deposits from sulphamate solution were similar in quality to those obtained from sulphate solutions, i.e. compact, adherent and without dendrites, but the throwing power of tin sulphamate solution unlike that for tin sulphate

was moderate. The excellent throwing power for sulphamate was secured by solutions containing polyethylene oxide or pyrogallol. Unfortunately pyrogallol and polyethylene oxide gave a narrow range of current density for good deposits (up to  $0.75 \text{ A/dm}^2$  only). The surface of the deposits obtained was relatively rough. Compared with peptone, the range of current density for good deposits for solutions containing gelatin is lower; it was up to  $1.5 \text{ A/dm}^2$ .

Resorcinol is recognised by some authors<sup>(87)</sup> as a good addition agent for lead plating from fluoborate solutions but in contrast to that, the results obtained by the author<sup>(134)</sup> for resorcinol showed poor deposits when used with lead sulphamate solutions. Its use with tin sulphamate was considered because it is a relatively simple chemical compared with peptone or gelatin and it could be obtained in a reasonably pure form which eliminates the possibility of leaving or forming any undesired impurities which may have more effect on the process than the additive itself. The trials with resorcinol showed a narrow range of current density for good deposition, similar to that shown by polyethylene oxide and pyrogallol (i.e. up to  $0.75 \text{ A/dm}^2$ ). The surface of the deposits obtained was relatively rough compared with that obtained from solutions containing peptone or gelatin in the same levels.

The results obtained from using polyethylene glycol with sulphamate solution was moderate compared with the results of other additives. Unlike the other additives examined, the amount of polyethylene glycol in the solution did affect the range of good deposits (see Table 25).

This additive in particular was investigated as one of the polyethers which have a large molecular weight, and showed similar results to gelatin when used with tin sulphate solutions and secured a very marked improvement when used with silver sulphamate baths. Its use decreased the size of grain, suppressed the dendritic growth and increased the throwing power of the bath<sup>(133)</sup>.

Phenolsulphonic acid was recommended as one of the most effective anti-oxidant agents, inhibiting the oxidation of stannous ions in tin sulphate solutions. Compared with other additives examined, it shifted the range of good deposits of sulphamate solutions to higher values of current density (up to 3 A/dm<sup>2</sup>). This may be considered as an advantage because it allows plating with higher rates but unfortunately the throwing power of the solution was poor. Plating with solutions containing this additive at current densities less than 1.5 A/dm<sup>2</sup> showed black, poor deposits.

The investigation of the additives as groups was carried out to see if any improvement in the range of good deposits and throwing power of the solution can be attained.

It was found that the best result was obtained from a group consisting of

2.5 g/l phenolsulphonic acid  
2.5 g/l peptone  
2.5 g/l pyrogallol

There was no great improvement in the width of the range itself by using this group; only a slight extension in this range for low current density was obtained, but the main improvement secured was in the throwing power of the solution. This improvement in throwing power was probably due to the inclusion of pyrogallol in the group; pyrogallol in fact was included in the group for this purpose. Both gelatin and polyethylene oxide showed a reduction in the range when they replaced pyrogallol in the group (see Table 26); the reduction was lower for gelatin than for polyethylene oxide.

Phenolsulphonic acid was included in all the groups tested because of the recommendation for its use as antioxidant for tin ions in acidic solutions. This role was not fully investigated in this study but only through some plating trials carried out with solutions containing the additive at different periods of time. Inferior deposits were obtained when old solution was used even when it contained the additive. This result indicated that the solution became poorer with tin ions with time because of either an oxidation or a hydrolyzation process.

#### 6.4.4 Polarization Studies

The main purpose of these studies was to establish the basic polarization characteristics of the electrodeposition of tin from sulphamate solutions.

The equipment and method used to obtain the data were reliable for obtaining quick results of practical accuracy. The potentiostat worked well during the stages of the work and proved to be suitable

for such a project. Its size and the level of the readings were just what is required for obtaining reliable results.

Use of the flat-bottomed cell with its five necked lid was very convenient. It enabled positioning or replacing the electrodes in their places easily and accurately for each trial. The only drawback for using this cell was the non-uniform distribution of current over the plane parallel electrodes. The current density at the edges of the electrodes were probably higher than that at the centre. <sup>More</sup> accurate results might be obtained if concentric cylindrical electrodes had been used but the use and the geometrical adjustment of such electrodes are more difficult.

The increase in current density at the edges of the electrodes might result in an excess dissolution or (deposition) on the electrode in these areas. Consequently an increase in the electrode surface area may occur and cause a fall in the total current on the electrode. A constant surface area of the electrode is more desirable but practically is very difficult to achieve. For practical study a small change in the area of the electrode must be of little importance.

A quick yield of polarization plots can be obtained if very fast scanning rates ( $> 120$  mV/min) were used but such rates may result in losing some necessary fine detail of the plot. In contrast a very slow scanning rate is time-consuming. The scanning rate used (30 mV/min) was very reliable and the necessary details within the practical limits of current density were obtained.

The study of the anode behaviour for the solution formed a minor but important part of the work. It was important and necessary because the anodic dissolution in the electrodeposition process has a vital role; it supplies the solution with metal ions and any suppressing or delaying in the dissolution of the anode for any reason (passivity for example) may affect the electrodeposition process.

The study was carried out for solutions without and with additives (individuals and groups). It showed smooth and free dissolution at the anodes without any trouble even when no additives were added to the solution. All the types of additives used, except phenolsulphonic acid, polarized the dissolution of tin but to different amounts (Figures 16-18). The polarization was probably because the accumulation of the additives near the anode which may result in reduction of the active anodic area available for dissolution and transferring ion metals to the solution.

Phenolsulphonic acid, unlike other addition agents, showed some depolarization of the reaction for tin dissolution, i.e. phenolsulphonic acid enhances the dissolution of tin possibly by chemical reaction.

The use of additives as groups was found to reflect the effect of the individual components of each group but it did not change the general trend of the dissolution reaction of tin i.e. the free, smooth dissolution of the anode. The group consisting of phenolsulphonic acid, peptone and gelatin polarized the dissolution reaction (Figure 19)

but replacing gelatin with polyethylene oxide in this group caused depolarization of the reaction. Replacing gelatin with pyrogallol depolarized the reaction too but only for high current densities ( $> 1.6 \text{ A/dm}^2$ ).

Generally speaking, it was not required of additives in the solution to have a major role in the anodic dissolution process; they were virtually added only to control the cathodic process and to improve the quality of the deposit. The study of their effect on the anodic dissolution was to ensure that their existence in the solution had no side effects which may damage the continuity of the dissolution process.

Heating the solution to higher temperatures did show the expected effect i.e. depolarizing the dissolution reaction of tin (Figure 20).

The results obtained from the cathodic study showed a limiting current density of  $1.1 \text{ A/dm}^2$  and low polarization ( $\approx -550 \text{ mV}$ ) for the deposition reaction of tin from a solution without addition agents. The low polarization noted is desirable practically for economic reasons, but the deposits obtained under this condition (no additives) were virtually unusable. To obtain good deposits, the use of additives is essential. The normal effect of the additives on cathodic deposition is to increase the polarization reaction. However, additives which decrease this reaction do exist but very rarely. All the additives used affected the cathodic deposition of tin from the solution developed in like manner; the polarization increased but in different

amounts according to the addition agent in the solution (Figures 23 to 27).

In addition it was noticed that some addition agents (peptone in particular) caused an increase in the range of potential for the limiting current density (i.e. the hydrogen evolution reaction was suppressed and the cathodic current efficiency kept high over this range of potential). Such a result is very desirable in electrodeposition of metals because good deposits can be obtained at high process efficiency. The probable reason for such behaviour is a thin film formation probably of the additive near the cathode; this film breaks down at certain potentials.

The results obtained by using peptone (Figure 24) showed that the limiting current density of  $\approx 0.9 \text{ A/dm}^2$  remained constant over a range of potentials from  $\approx -475 \text{ mV}$  up to  $\approx -850 \text{ mV}$ , when  $2.5 \text{ g/l}$  of peptone was added to the solution. Increasing this amount was found to increase the current slightly. In some plating trials under these conditions, similar behaviour for the solution was noticed; the limiting current density remained constant at approximate value of  $1 \text{ A/dm}^2$  when the potential increased from  $\approx -500 \text{ mV}$  up to about  $-800 \text{ mV}$ . The deposits obtained from these trials were good. Any further increase in potential was accompanied by an increase in current density and rough deposits were obtained.

Unlike peptone, gelatin showed a fall back in the curve resulting in a decrease in current density at a potential of about  $-550 \text{ mV}$  (Figure 23). The fall back ended with gradual return to the original current

density. The probable reason for the fall back is slight film forming and a gradual vanishing as the potential increases.

The other additives showed a normal behaviour for cathodic polarization except phenol sulphonic acid (Figure 27), which showed two fall backs before approaching the limiting current density.

The effect of using the additives as groups was found to be a combination of the individual effects of the components. A reduction in the limiting current density but an increment in the range of potential for this limiting current.

Heating the solution for higher temperatures reduced deposition polarization (Figure 25) but did not improve the quality of the deposits.

Detecting the change in the cathodic behaviour of solution containing the additives as groups with time was a rough guide to the stability of the solution. The cathodic plots plotted for solution of 30 hours age were found to differ slightly from those plots for freshly prepared solutions (Figures 29-30). It is very difficult to justify whether this slight difference was due to the ageing or to the unreproducibility of the experiments which happens to be very similar. The more probable explanation is to be a combination of both. The difference between the plots becomes significant after 78 hours (Figure 31); this means that a continuous use of the solution is required if an acceptable degree of stability is to be maintained; the stability of most solutions in commercial use is maintained in this way.

No attempt has been made to relate the stability of solutions containing additives individually with cathodic plots.

#### 6.4.5 Optimum Conditions

The method adopted for preparing the tin solution (see 6.4.2) showed that an optimum efficiency for the process could be achieved if a solution containing  $\approx 17$  g/l of tin was prepared (Figure 14). Using such a solution, having a concentration very near to the solubility limit of tin in sulphamic acid ( $\approx 20$  g/l) in plating may offer the risk of a fast precipitation of tin even at ambient conditions. Heating the solution during the process of preparing the solution does not substantially affect this limit, only an increase of 4 g/l occurred. In addition, it imposes the risk of hydrolysing the solution, a phenomena discussed repeatedly in the literature and which was noticed during the course of this work. On the other hand, the use of dilute solution of tin produced poor deposits which were virtually unusable. The use of a solution containing 10 g/l was found to be reliable for all the plating trials.

The effect of the acidity of the solution was not subject to a real study in this work because the solution already has a high acidity ( $\text{pH} \approx 0.7$ ) and no marked effect on the deposits being expected for this variable. In addition, modifying such high acidity with other components requires a considerable amount of the component which, its presence in the solution, might cause other effects. It will be difficult in such circumstances to define whether the resulting change was due to the

new pH value or to the component itself.

Increasing the temperature of the solution may have a little advantage, improving the conductivity of the solution (Figure 32) and keeping the cathode current efficiency at high values, but it imposes the risk of enhancing the hydrolysis of the solution which practically may start at ordinary temperatures. Another point must be accounted for on heating the solution: the extra cost of power!

The deposits obtained from the solution without additives were poor in quality even when they were plated at low current densities. The search for the most suitable addition agent showed that the use of a combination of addition agents is more effective (see 6.4.5). Good, smooth deposits might have been obtained by adding 2.5 g/l of peptone to the solution over a range of current densities up to 2 A/dm<sup>2</sup> but the throwing power for solutions containing peptone was found to be moderate. Such a solution might be useful for plating uncomplicated articles for protection purposes where the throwing power is a minor factor but for plating articles where the thickness and covering power is important, throwing power must be considered. Such throwing power was obtained by using pyrogallol and gelatin, but unfortunately both of them showed a narrow range of current density for good deposition. Solutions containing pyrogallol or gelatin may be suitable for plating articles at low current densities only. Phenol sulphonic acid was included in the combination of the additives because the well-reported role of this additive as antioxidant agent.

The current density, when plating from solutions containing additives individually, was found to have little effect on the cathode current efficiency which was normally higher than 90%. For solutions containing the additives as groups (Figure 15), the group which showed the wider range of current density for good deposits showed a slightly better cathode current efficiency.

The best results of good smooth deposits could be obtained from solutions containing 10 g/l tin over a range of current density up to 2 A/dm<sup>2</sup> if a group of additives composed of:

	2.5 g/l peptone
	2.5 g/l phenol sulphonic acid
and	2.5 g/l pyrogallol

was used. The cathode current efficiency at low current density is ≈98%. It drops slightly for high current densities.

## 6.5 Conclusions

The production of a tin sulphamate solution for electroplating with tin is possible. The Faradaic dissolution method was found to be the most suitable one for this purpose.

The efficiency of such a method is low in the earlier stages probably because a considerable amount of electrical power is consumed by secondary reactions. It increases later to approach an optimum value of  $\approx 97\%$ .

The solubility limit of tin in sulphamic acid was found to be equal to  $\approx 20$  g/l. It increases to 24 g/l by heating the solution up to  $60^{\circ}\text{C}$ .

The deposits of tin obtained from such solution are in general similar to those deposits obtained from other acid solutions, i.e. not adherent and dendritic. The use of additives is essential for suppressing the dendritic growth, improving the quality of deposits and stabilizing the solution.

No one of the additives examined fulfilled all the requirements adequately when used alone. The optimum results were achieved when a combination of additives was used.

Recommended solution for good plating is as follows:

Tin content	10 g/l
Peptone	2.5 g/l

Pyrogallol	2.5 g/l
Phenol sulphonic acid	2.5 g/l

It operates under the conditions of

Cathode current density	up to 2 A/dm <sup>2</sup>
Temperature	20-25°C
Cathode current efficiency	>90%

Heating the solution can maintain the cathode current efficiency at high levels, but it imposes the risk of fast hydrolysis of the solution.

The solution is liable to slow hydrolysis even at ambient conditions if it is left without use. The continuous use of the solution is necessary for maintaining reliable stability.

### PART III

#### EXPERIMENTAL WORK - II

This part of the thesis includes the experimental trials for electrodepositing lead-tin alloys from a sulphamate solution. The solution was based on the solutions developed initially for lead and tin. Lead-tin alloys of different compositions were electrodeposited and the effect of the main variables on the composition was studied.

As an industrial application of the alloy, a set of bearings for a motor car engine was plated with an alloy of 90 Pb:10 Sn composition. The main properties of the plate were examined in cooperation with the Glacier Metal Company Limited.

The results of the work were discussed in view of the suitability of the alloy for industrial applications.

## CHAPTER 7

### ELECTRODEPOSITION OF TIN-LEAD ALLOYS

The experimental work in this part is complementary work to that carried out previously on lead to develop a solution for electroplating with lead<sup>(128)</sup> and on tin (previous chapter) to develop a solution for electroplating with tin. Now, after developing the two solutions mentioned, the experimental work is continued to investigate the possibility of developing a solution based on the two solutions developed for electroplating tin-lead alloys from sulphamate solutions.

Most of the work concentrates on studying the polarization behaviour of the solution, the effect of current density, temperature and tin content in the bath on the composition of the alloyed deposit. The effect of current density and temperature on cathode current efficiency was also investigated. The work also includes the selection of suitable addition agents and the effect of the presence of free acid on the range of good deposits. Further work included some analysis of the deposit and its structure.

The alloys which have been considered in the work have the compositions of 90%, 80%, 70% and 40% lead, the remainder being tin.

For practical industrial applications, the alloy has the composition 90% Pb, remainder tin. Some plating trials were carried out at the end of this project to plate some car engine bearings supplied by the Glacier Metal Company Ltd.

## 7.1 Solution Preparation

Because no one of the two components forming the solution (lead and tin) is available as laboratory reagent, preparing the solutions used was based on first preparing tin and lead solutions separately in the laboratory and then mixing the two solutions together. Preparing lead sulphamate solution was based on the method described briefly in the previous work on lead, i.e. by neutralizing the basic lead carbonate  $2 \text{ Pb CO}_3 \text{ Pb(OH)}_2$  with sulphamic acid ( $\text{HSO}_3\text{NH}_2$ ) solution in water to produce lead sulphamate salt dissolved immediately in water. The concentration of lead in the solution prepared in this method depends on the concentration of sulphamic acid solution used; sulphamic acid solution with concentration of 50 g/l lead when completely neutralized with lead carbonate. Acid solution of higher concentration produces lead solution with higher lead content.

Preparation of the tin sulphamate solution was based on the results of the work described in the previous chapter (see Chapter 6). Solutions containing 10 g/l tin can be produced by passing a quantity of electricity equal to 8300 Coulomb through the cell described in the Faradaic dissolution method. Indeed, preparing a tin solution with this concentration was used for preparing the alloyed solution for all the trials.

To facilitate the process of preparing the alloyed solution of required percentage of tin and lead and to ease the calculation of the quantities of tin and lead sulphamate solutions of known concentrations, the following two formulae were derived:

$$Y = \frac{A.Q}{A + B.C} , \quad X = \frac{C.B.Q}{A + B.C}$$

where: Q = the quantity of tin-lead solution to be prepared in ml

X = the quantity of lead sulphamate solution required in ml

Y = the quantity of tin sulphamate solution required in ml

A = lead content in lead sulphamate solution g/l

B = tin content in tin sulphamate solution g/l

and C = lead:tin wt. ratio of the solution prepared.

Preparing 275 ml of solution with a lead/tin ratio of 90:10 required the mixing of 125 ml of lead sulphamate solution containing 108 g/l lead with 150 ml of tin sulphamate solution containing 10 g/l tin. The total metal content for the produced solution is 54.5 g/l.

Similarly, preparing 275 ml of solution with lead/tin ratio 80:20 required the mixing of 74 ml of lead solution containing 108 g/l lead with 201 ml of tin solution containing 10 g/l tin. The total metal content for the produced solution is 36.5 g/l.

For a solution with lead/tin ratio of 70:30 the lead and tin solutions required were 49 ml and 226 ml respectively and the produced solution has the metal content of 27.4 g/l.

Finally, a preparation of 275 ml of solution with lead/tin ratio of 40:60 required the mixing of 260 ml of tin and 16 ml of lead. The total metal content for the obtained solution is 15.6 g/l.

All the chemicals used for preparing the solutions were supplied from Fisons Laboratory Reagents.

All liquid measurements were performed using measuring cylinders and all solid chemicals were weighed using a "Oertling" three figure balance.

## 7.2 Anodes

The anodes of high lead content were prepared by melting pieces of lead sheet of 99.9% purity and pieces of tin stick of the same purity by the following procedure.

- a) The required amounts of tin and lead to obtain the alloy of the anode with specific composition were calculated, then the metals were weighed.
- b) The metal pieces were then heated to melting using an air acetylene flame.
- c) The molten alloy was then cast either in a cylindrical mould of 10 and 20 mm diameter or in a rectangular one of 30 x 70 mm dimensions.
- d) The rectangular casts were then cold rolled to a suitable thickness according to the end use of the anode; to thickness of 5 mm for polarization trials and to 2.5 mm for Hull-cell trials. The rod casts were cut into pieces 45 mm long to be used with plating experiments. One rod cast with composition of 90 Pb:10 Sn with

diameter of 20 mm was kept at lengths of 110 mm for using in bearing plating trials. A stainless steel rod of 5 mm diameter was fixed in the top of the rod cast to connect the current.

- e) The cold rolled sheets were then cut to the required dimensions; strips of 10 x 70 mm (anodes for polarization trials) and 62 x 70 mm (anodes for Hull-cell trials).
- f) A copper wire was soldered to the top of the anodes for plating and polarization trials; this wire was, after soldering, covered with a glass tube and the junction point of the glass and the top of the anode was glued with 'Lacomit' (a proprietary stopping off medium obtained from W. Canning Ltd).
- g) The composition of each anode was then engraved on a suitable site on the anode to avoid mixing the anodes between each other.

The anodes of high tin content (60% tin) were cast to dimensions from the beginning because it was difficult to form them in cold roll process. The other stages were similar to that of high lead content anodes.

### 7.3 The Cell and Other Equipment

The cell and the other equipment used for running the trials on tin-lead alloy solutions were similar to those which were used for running the trials on tin solution. The flat-bottomed vessel described in article 6.2.2 was used to contain the solution required for all plating and polarization trials. It was also used to plate a set of car engine bearings. A special bearing holder was used (see Figure 39); it consisted of a cylindrical copper ring made of copper sheet so as its inner diameter was equal to the outer diameter of the bearing. Two copper wires were soldered to the upper end of the ring to connect current to the bearing; these wires and the outer surface of the ring were isolated by PTFE and Lacomit.

A larger vessel (2500 ml size) was used to plate another set of bearings. A special jig for holding the bearings of these trials was supplied by the Glacier Metal Company Ltd (see Figure 40). It consisted of four semi-circular shaped pieces of perspex which could be clamped together to hold between them a two half shell bearing. The anode can be positioned in the centre of the bearing. Several holes were contained in the perspex pieces to allow circulation of solution between the anode and the cathode (bearing). The 'Tecam' water bath described before (see 6.2.3) was used to contain the cells and to heat the solutions when required.

The "6A Kemitron" potentiostat with its built-in digital sweep generator described in Section 6.2.3 was used for the polarization studies where its output was received by a "Bryans 28000" chart

recorder as a potential monitor.

The agitation of the solution was provided by bubbling nitrogen gas into the solution when required, through a gas bubbler connected to a cylindrical nitrogen gas container. The flow rate was monitored using the subsidiary valve attached to the cylindrical gas container.

The conductivity of the solution was measured by using the Philips conductivity meter type PW 9501/01 described before (see 6.2.4) with the aid of the pre-calibrated cell which had a cell constant of  $28.3 \text{ cm}^{-1}$ .

#### 7.4 Hull-Cell Trials

These trials were carried out to examine the current density range for good plating with the solution and to select the suitable addition agent(s) to be used. All trials were performed using the standard Hull-cell of 267 ml size.

The anodes were prepared as described in Section 7.2, then pickled with a mixture of concentrated  $\text{HCl} + \text{HNO}_3$  (1:1) for 1 min, rubbing the surface with emery paper (600 grade) and rinsing in distilled water, then acetone and dried by hot air steam and kept in a desiccator ready for use.

The cathodes were cut pieces of copper sheet with dimensions of 65 x 100 mm pickling by immersion in nitric acid of 30% concentration for 20 seconds, then rinsed in distilled water and acetone, and dried by hot air steam.

The solution used in the trials was prepared as described in Section 7.1. The appropriate quantities of lead sulphamate and tin sulphamate solutions were mixed to produce solutions with four different lead-tin ratios i.e. 90, 80, 70 and 40% lead, remainder tin. A quantity of solution equal to 267 ml was used in each trial.

The addition agents used were selected from those additives which showed the best results with individual lead and tin solutions i.e. gelatin for lead, and a group of additives consisting of phenol-sulphonic acid, peptone and pyrogallol for tin. Phenolsulphonic acid was abandoned later. The additives were added to the solution after being dissolved.

Some trials were carried out without free acid and some of them after adding a 50 g/l sulphamic acid aliquot.

Most of the trials were performed by applying a total constant current of 1 amp for 20 minutes supplied by a power unit (type Farnell L10-3C) but some of them were performed with lower current to obtain clearer results.

### 7.5 Plating Trials

Solutions with compositions similar to those used in the Hull-cell trials were prepared as described before. 250 ml of the solution were used in each plating trial carried out using the 500 ml cell but 900 ml were used in each trial carried out using the 2500 ml cell. A group of additives consisting of peptone, pyrogallol and gelatin with a level of 2.5 g/l each was added to the solution. 50 g/l of

sulphamic acid as a free acid was added to the solution in some trials.

The anodes used in the plating trials were of the same composition as the solutions and prepared as described in Section 7.2. They were pretreated in a similar method to that mentioned in Section 7.4. The anode used in the large cell plating trials was covered with acid-resistant bag to suppress any transfer of metallic slime to the cathode.

The cathodes were of copper. The majority of them were strips with dimensions of 10 x 70 mm and pretreated simply by pickling in nitric acid then weighed, but a few of them, in the early stages of the project, were cylindrical to simulate the conditions of one of the practical applications of the alloy (bearing). The cylindrical cathodes were prepared by the following method: a rectangular piece of copper was cut to the dimensions of 210 x 65 mm from a rolled copper sheet with thickness of 0.25 mm. The shorter sides of the piece were soldered together to form a cylinder with diameter of  $\approx 60$  mm. A copper wire was then soldered to the upper edge of the cylinder, this wire and the soldered edges were painted with 'Lacomit', then the cathode was pretreated as mentioned above and its outer surface was covered with 'Lacomit', or adhesive paper to prevent the unnecessary plating of this surface.

The bearings before they were plated, were pretreated simply by degreasing using hot 'Genklene' bath, soaking in dilute HCl solution for 10 minutes, rinsing in distilled water and acetone, then drying

and keeping them in a desiccator ready for use. The solution used in plating the bearings had the lead/tin ratio of 90 Pb:10 Sn. All the bearings were plated with an overlay of an approximate thickness equal to 25  $\mu\text{m}$ ; this thickness was assumed to be obtained by passing 1100 Coulombs through the plating cell.

The constant current was supplied to the plating cell from the potentiostat and each trial lasted for 15 minutes (except the trials of plating the bearing where different times were required for each trial). The cathode was washed after each trial, dried and weighed.

The solutions were heated using the temperature controlled water bath when required.

The cathode current efficiency was calculated for some trials from the actual weight of the alloyed deposit and the theoretical weight obtained by using the following formulae:

$$W = (w_e)_{\text{alloy}} \cdot I \cdot t$$

and

$$(w_e)_{\text{alloy}} = \frac{w_1 \cdot w_2}{f_1 \cdot w_2 + f_2 \cdot w_1}$$

where: I = total applied current (amp)  
t = time (hours)  
W = weight of deposit (grams)

$(w_e)_{\text{alloy}}$  = the electrochemical equivalent of the alloy at 100% cathode efficiency (g/A.hr)

$f_1$  = weight fraction of tin in alloy

$f_2$  = weight fraction of lead in alloy

$w_1$  = the electrochemical equivalent of tin and equal to (2.213 g/A.hr) for the reaction  $\text{Sn}^{2+} + 2e \rightarrow \text{Sn}$

$w_2$  = the electrochemical equivalent of lead, and equal to (3.865 g/A.hr) for the reaction  $\text{Pb}^{2+} + 2e \rightarrow \text{Pb}$ .

All weight measurements for calculating cathode current efficiency were carried out using a 'Sauter' five figure balance.

## 7.6 Polarization Studies

All the equipment used in the polarization studies of alloyed solutions were described previously when similar studies were carried out on tin solution (see 6.2.3). The only difference in the present work is the use of alloyed anodes having a composition the same as that of the solution used in the trials.

The anodes were prepared with the required compositions from tin and lead metals of high grade purity (99.9%) using the method mentioned in Section 7.2. They were pretreated in the same way as that used for pretreating the anodes used in the Hull-cell and plating trials and they were also cleaned and smoothed after each run using emery paper to ensure a smooth anodic surface. The anodic area was kept equal to 4 cm<sup>2</sup> in all the trials.

The cathodes used, which were strips of copper, after insertion in the cell, were preplated with a thin layer of the alloy before each trial and the rest potential was recorded before the potential scan started.

For most of the trials a scanning rate of 30 mV/min was used but in a few runs higher or lower scanning rates were tried.

Most of the work on polarization included plotting the anodic and cathodic curves mainly for solution of lead/tin ratios of 90, 80 and 40 lead, remainder tin, and the effect of some parameters including temperature, free acid and agitation on these curves assessed. 250 ml of the solution was used in each trial and the additives used with the solution were:

	2.5 g/l peptone
	2.5 g/l gelatin
and	2.5 g/l pyrogallol

A few trials were carried out with solutions containing peptone and pyrogallol only in the same levels and two trials were made to plot the cathodic behaviour of the electrodeposition on the bearing.

### 7.7 Analysis and Thickness Measurements

In the analyses of the alloyed electrodeposits were performed using the atomic absorption spectrometry technique, except one trial where the analysis was carried out using the microprobe (see Section

7.8) with the aim of comparing the results obtained from the two methods.

Small pieces of  $0.25\text{ cm}^3$  area were cut from the plated cathodes and dissolved in acidic mixture consisting<sup>(135)</sup> of:

500 ml of HCl 1:1  
400 ml of  $\text{HNO}_3$  concentrated  
50g tartaric acid  
and 10 ml of distilled water.

Preparing tin samples for the analysis was carried out by the following procedure:

- a) The small cut pieces were dissolved in 10 ml of the acidic mixture contained in a 100 ml volumetric flask grade (A).
- b) The solution obtained was covered and heated gently to ensure complete dissolution to the alloyed deposit.
- c) The solution was then diluted to 50 ml with distilled water and kept for analysis.

Further dilution was carried out for the samples of composition of 60 Sn:40 Pb because they were rich in tin and their dilution is necessary to bring the level of tin in the solution to or very near to the linear limits of the absorbance of tin in the atomic absorption spectrometer.

Preparing lead samples for analysis was carried out by the following procedure:

- a) A 5 ml of the tin sample previously prepared was contained in a 100 ml volumetric flask of grade (A).
- b) The solution was then diluted to 15 ml by adding 10 ml of HCl 1:1.
- c) The solution was then diluted to 100 ml with distilled water and kept for analysis.

The standard solutions of tin and lead used for the analysis procedure were prepared by diluting commercial standards containing the metals in concentration of 1 mg/ml supplied by Fisons Laboratory Reagents. The diluting was in order to produce new standards containing the metals within the linear absorbance limits, i.e. 100  $\mu\text{g/ml}$  for tin and 15  $\mu\text{g/ml}$  for lead.

In order to minimise the risk of any background interference, 400  $\mu\text{g/ml}$  of copper was added to the prepared standards.

A wavelength of 224.6 nm was used for tin and 217 nm for lead analysis. The flame used was a mixture of air-acetylene.

From the analysis, the ratio of lead to tin in the solution was determined and hence the alloy composition.

The thickness of the deposit was measured by a direct measurement method, i.e. from the knowledge of the weight of deposit on the sample and its area considering the densities of lead-tin alloys with various compositions, as follows<sup>(135)</sup>:

The density of alloy of composition 90 Pb:10 Sn = 10.5 g/cc

The density of alloy of composition 80 Pb:20 Sn = 10.2 g/cc

The density of alloy of composition 70 Pb:30 Sn = 9.66 g/cc

#### 7.8 SEM and Microprobe Work

The topography of the surface of the alloyed deposits was examined, and the effect of the current density on the shape and the size of the deposits of some samples was studied using a scanning electron microscope (Cambridge Stereoscan Mark 2A). Micrographs for alloys with different compositions were produced.

A Jeol JEM-100CX series scanning transmission electron microscope was used to study the structure and the composition of selective samples of the electrodeposits. These electrodeposits were of presumed composition of 90, 80 and 70 lead, remainder tin.

#### 7.9 Mechanical Properties and Corrosion Resistance

Fatigue and wear resistance tests for alloyed deposits of an approximate composition of 90 Pb:10 Sn were carried out by the research

and Development Department at Glacier Metal Co. Ltd. The deposits were electroplated as overlays with an approximate thickness of 25  $\mu\text{m}$  upon bearings of steel backed Cu Pb 30 of a special size (used for a Saxon fatigue test machine at the company). The machine was designed and developed by the Company specifically for testing bearings. In one test, a cyclic load of 34 MN/m<sup>2</sup> was applied to the bearing for 20 hours. In a second test a load of 51 MN/m<sup>2</sup> was applied.

A simple adhesion test was carried out at Glacier's laboratories according to their standards. In one test the adhesion of an "as plated" deposit was carried out by making deep intersected scratches in the plate, then trying to peel it using a piece of insulating tape (one side of which was adhesive). A similar test was carried out but after diffusion-annealing the sample in an oven at 160°C for one hour.

Corrosion tests were carried out by immersion of pieces of 1 cm areas of the plated bearings in different types of oil for 240 hours, then measuring the loss in the deposit. The types of test oil included:

- Medicinal white oil (contains no inhibitor)
- 10W/40 used oil for 3000 miles run
- and 20W/50 oil brand new

## CHAPTER 8

### RESULTS

#### 8.1 Hull-Cell

The earlier trials of Hull-cell were carried out with solution containing, in addition to lead and tin metals, a group of additives consisting of: 2.5 g/l phenolsulphonic acid, 2.5 g/l peptone and 2.5 g/l pyrogallol. This group of additives in fact is the group which secured the best results when used with tin solutions, but when this group was added to a mixture of lead and tin sulphamate solutions, an emulsion-foamed solution was obtained indicating that a chemical reaction took place between the components of the solution. Investigation of the reasons showed that phenolsulphonic acid when added to the mixture of lead and tin sulphamate reacted with lead to produce an insoluble lead compound. According to this observation, phenolsulphonic acid was discarded and replaced with gelatin which had been recommended as an addition agent with lead sulphamate solutions. The Hull-cell trials then continued in alloyed solutions containing the following addition agents:

	Peptone	2.5 g/l
	Pyrogallol	2.5 g/l
and	Gelatin	2.5 g/l

The results obtained from the trials are shown in Table 27. Three main ranges were noticed on the cathode; a dark range at very low

current density, a good deposit range and a burnt range at high current density. The current density range of good deposit only is shown in the table. It starts from 0.75 A/dm<sup>2</sup> up to 2 A/dm<sup>2</sup> for solution of lead/tin ratio equal to 90 Pb:10 Sn\*, but it starts from 0.2 A/dm<sup>2</sup> up to 2 A/dm<sup>2</sup> for solution of ratio equal to 70 Pb:30 Sn. The range for solution of lead/tin ratio equal to 80 Pb:20 Sn starts from 1 A/dm<sup>2</sup> up to 2.5 A/dm<sup>2</sup> and for solution of ratio equal to 40 Pb:60 Sn, starts from 0.3 A/dm<sup>2</sup> up to 3 A/dm<sup>2</sup>. It is clear that as tin content in the solution increases, the width of the range of good deposit increases.

The effect of adding 50 g/l sulphamic acid to the solution (free acid) maintained the upper limits of the ranges constant for the solution (all compositions) but it extended the lower limit for lower current density values. There was no clear trend for this extension, but solution of lead/tin ratio equal to 40 Pb:60 Sn showed the largest extension; good deposit obtained at very low current densities.

## 8.2 Plating Trials

The observations and results obtained from Hull-cell trials showed that on adding phenolsulphonic acid the alloyed solution deteriorated. The plating trials with solution containing peptone

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\* Whenever the expression 90 Pb:10 Sn solution occurs, it means a solution containing 49 g/l lead and 5.5 g/l tin. Similarly 80 Pb:20 Sn solution contains 29 g/l lead and 7.5 g/l tin, 70 Pb:30 Sn solution contains 19.2 g/l lead and 8.2 g/l tin and finally 40 Pb:60 Sn solution contains 6.2 g/l lead and 9.4 g/l tin.

and pyrogallol produced moderate deposits, and all the plating trials were then carried out with solution containing the group of additives mentioned in Section 8.1. Good deposits were obtained from solutions with different lead/tin ratios by applying current densities within the range of current densities obtained from Hull-cell trials, but plating with current densities near the limits of the range produced slightly inferior deposits, i.e. at very low current densities the deposits were dark, and at very high current densities the deposits were dark or matt but rough (see Tables 28, 29, 30 and 31). The effect of temperature on the appearance of the deposit was to maintain the good quality of deposit with more rough appearance.

The deposits on circular cathodes were very smooth when a fresh solution was used but they were relatively rough from solution aged for one week.

The plating trials of the bearings produced satisfactory deposits, i.e. smooth, adherent and compact (see Figure 41), but the deposits plated from the small cell (500 mls size) showed a gradual change in colour from matt to semi-bright: this change in colour is probably due to non-uniform distribution of the current over the cathode. Such a change in colour was not shown by the deposit obtained from the large cell where the current distribution is more uniform. Fine particles were noticed on the plated surface of some bearings, these particles were probably from the paint 'Lacomit' covering the immersed parts of the bearing holder or jig.

The conductivity of the solution was measured as a matter of course during some plating trials; it was found to increase with temperature in the usual way.

### 8.3 Cathode Current Efficiency

The cathode current efficiency of some plating trials from solutions with different compositions is shown in Tables 28, 29, 30 and 31. In general the deposition of the alloy took place at very high efficiency (about 100%). In Tables 28, 29 and 30, there are some values of the efficiency at temperatures above 40°C which are actually higher than 100%. This is virtually impossible, but the reason for this (if the experimental error is regarded as improbable) is ignoring the effect of temperature on the composition of the alloyed deposits and considering the composition of the alloy deposited at 40, 55 and 70°C equal to the composition of the alloy deposited at 25°C which proved to be untrue. Calculation of the efficiency for deposition from solutions of lead/tin ratio equal to 40 Pb:60 Sn in different temperatures was based on the real values of composition obtained from the analysis; this efficiency was realistic.

No effect for the current density or temperature on the cathode current efficiency was found.

### 8.4 Polarization Studies

The polarization studies included the anodic and the cathodic behaviour of alloyed electrodes of different compositions in solutions

of matched compositions and containing the group of additives mentioned before.

i) Cathodic polarization

Sweep rates of 18, 30 and 60 mV/min were tried at the beginning for solution of metal ratio equal to 90 Pb:10 Sn (see Figure 42), but sweep rate of 30 mV/min was used for most of the work.

The rest potential for mixtures of solutions of different compositions was found to be equal to  $-430 \pm 6$  mV. It differed slightly from that of lead (-414 mV) and that of tin (-440 mV). The change in rest potential values with temperature and the presence of the free acid in the solution was negligible and of the order of 10 mV. All the cathodic polarization curves of solutions with different compositions showed a limiting current density, Figure 43. The limiting current density decreased as the percentage of tin in the solution increased; it was slightly more than 4 A/dm<sup>2</sup> for a solution of metal ratio equal to 90 Pb:10 Sn. Curve 4 in the figure decreased to 2.7 A/dm<sup>2</sup> when the ratio became 80 Pb:20 Sn, curve 3 to  $\approx 2$  A/dm<sup>2</sup>, curve 2 when the ratio became 70 Pb:30 Sn and to  $\approx 1$  A/dm<sup>2</sup> when the ratio dropped to 40 Pb:60 Sn, curve 1.

The effect of the free acid on the cathodic deposition from solution having the metal ratio of 90 Pb:10 Sn is shown in Figure 44. The free acid depolarized the codeposition reaction markedly at low potentials but very little at high potentials near the limiting current density.

The effect of temperature on the cathodic reaction was in general to depolarize the codeposition reaction. The trend of this effect was followed by solution having metal ratio of 90 Pb:10 Sn (Figure 45). Heating such a solution up to 70°C depolarized the reaction (approximately 150 mV) at a current density of 2 A/dm<sup>2</sup>. The amount of depolarization decreased to ~ 100 mV for the same current when 50 g/l free acid was added to the solution (Figure 46). This effect of free acid is the reverse of what one may expect where the free acid usually depolarizes the reaction, but this effect for the free acid is not absolute because at 4 A/dm<sup>2</sup> depolarization for solution without free acid was  $\approx$  -275 mV and -375 mV for solutions with free acid at temperature of 70°C.

Similar results for the effect of temperature were obtained from solutions of metal ratio equal to 80 Pb:20 Sn when the solution was heated to 55°C but further heating polarized the reaction at potentials higher than -550 mV (see Figure 47).

Heating solution of metal ratio equal to 70 Pb:30 Sn up to 40°C depolarized the reaction; heating the solution further up to 55°C polarized the reaction for potentials between -550 mV and -650 mV but depolarized the reaction for the remaining potentials.

The effect of temperature on the polarization reaction of solutions having metal ratio of 40 Pb:60 Sn followed the general trend, i.e. depolarizing the reaction on heating the solution (see Figure 49).

Mildly agitating the solution using nitrogen gas showed similar effects on the cathodic reaction as that of temperature or free acid. Depolarizing the reaction by some 50 mV occurred at a current density of 2 A/dm<sup>2</sup> for solutions of lead/tin ratio equal to 90 Pb:10 Sn (see Figure 50).

The cathodic behaviour of the deposition from a solution of 90 Pb:10 Sn ratio showed a slight shift in the curve for less base potentials, see Figure 51, when the large cell was used.

ii) Cathodic polarization for lead, tin and lead-tin

The relationship between the deposition reactions of lead, tin and lead-tin alloy are shown in Figure 52. Curve 1 represents the deposition of lead from solution containing 54 g/l lead and 50 g/l sulphamic acid (free). Curve 3 represents the deposition of tin from solution containing 10 g/l tin and a group of additives consisting of phenolsulphonic acid, peptone and pyrogallol (2.5 g/l each) and curve 2 represents the deposition of lead-tin alloy from solution containing 49 g/l lead, 5.5 g/l tin, 50 g/l free acid and a group of additives consisting of peptone, gelatin and pyrogallol (2.5 g/l each). Relating the curves in Figure 52 to each other, to examine if there is any relation between the deposition of the alloy and the deposition from the parent metals, is not realistic because there is no relation between the level and type of constituents in the alloyed and parent solutions. More realistic results might be obtained from the curves in Figure 53 where curve 2 representing

the deposition of the alloy from solution obtained by mixing the solutions which their deposition is represented by curve 1, lead, and curve 3, tin. The lead solution in this case contains 49 g/l lead and 2.5 g/l gelatin, the tin solution contains 5.5 g/l tin, 2.5 g/l peptone and 2.5 g/l pyrogallol, and the alloyed solution contains the constituents of the two parent solutions.

In both figures, the position of the curve representing the deposition of the alloy is between the curves of lead and tin. This is the most usual position for alloy curves. It was hoped that a simple relationship between these curves might be deduced by which the prediction of the composition of lead-tin alloy from sulphamate solutions becomes possible, but the results were disappointing.

### iii) Anodic polarization

The polarization curves for the anodic behaviour of solutions with different compositions and containing the group of additives mentioned before, showed continuous dissolution of the anodes over a wide range of current density (up to 7 A/dm<sup>2</sup> in some conditions) and no limiting currents were attained.

It was noticed that increasing the amount of lead in the solution increases the rate of dissolution (Figure 54). For a potential of -200 mV the current density was equal to 1.2 A/dm<sup>2</sup> for solutions of lead tin ratio of 40 Pb:60 Sn, 1.9 A/dm<sup>2</sup> for solutions with ratio of 70 Pb:30 Sn, 2.6 A/dm<sup>2</sup> for solutions with ratio of 80 Pb:20 Sn and 5 A/dm<sup>2</sup> for solutions with ratio of 90 Pb:10 Sn.

The effect of temperature was to depolarize the dissolution reaction. The anodic dissolution of solutions having metal ratio equal to 90 Pb:10 Sn was depolarized by some 80 mV at 2 A/dm<sup>2</sup> when the solution was heated from 25°C to 70°C (see Figure 55), this amount was equal to ~ 50 mV for a solution of metal ratio equal to 80 Pb:20 Sn and contains 50 g/l free acid (see Figure 56). For solution of lead/tin ratio equal to 70 Pb:30 Sn, a depolarization of ~ 75 mV at current density of 2 A/dm<sup>2</sup> was obtained when the solution was heated from 25°C to 40°C (Figure 57). A solution with high tin content showed a high depolarization with heating, it was equal to about 150 mV at 2 A/dm<sup>2</sup> when the solution was heated from 25°C up to 55°C (Figure 58).

#### 8.5 Composition of the Deposit

The results of the analysis of the electrodeposits obtained from some plating trials showed that the codeposition of lead and tin in different percentages is possible if the metal ratio in the solution used and the current density applied are controlled to certain conditions. Lead-tin alloy with composition of 90.2 Pb:9.8 Sn was produced from solution containing the two metals in the ratio of 90 Pb:10 Sn when applying current density at 0.5 A/dm<sup>2</sup>. Thus the composition of the deposit obtained is in general approximately equal to that of the solution used. Similarly, lead-tin alloy with composition of 79.8 Pb:20.2 Sn which is nearly that of the composition of the solution electrodeposited from (80 Pb:20 Sn), was obtained by applying a current density of 1 A/dm<sup>2</sup>. Further alloyed deposits with composition

of 69 Pb:31 Sn were obtained from solution having a metal ratio of 70 Pb:30 Sn by applying a current density of 1.5 A/dm<sup>2</sup>.

In the electrodeposition of alloy with high tin contents, i.e. 60 Sn:40 Pb, alloyed deposits with tin percentages higher than that of the solution were obtained even at low current density; for example, a deposit containing 62.5% tin was obtained from solution of metal ratio equal to 40 Pb:60 Sn which means that tin electrodeposited preferentially.

Deposits with other compositions of lead and tin may be obtained by controlling the applied current and the metal ratio in the bath for certain amounts. Such variables in fact are the most important variables affecting the composition of the electrodeposited alloys.

i) . Current density

The effect of current density on the composition of the electrodeposited alloy of high lead content is shown in Figure 60 and that for alloy of low lead content, i.e. 40 Pb:60 Sn is shown in Figure 59. These effects were obtained for solutions of metal ratios equal to 90, 80, 70 and 40 Pb, the remainder being tin. The results of the effect were similar for the different metal ratios, i.e. increasing current density applied increases the percentage of the less noble metal (tin) in the deposit, but the rate of the increment is different and in general increases with increasing tin content in the bath. Solutions of metal equal to 40 Pb:60 Sn ratio showed the highest rate of increment in tin content in the deposit; increasing current density from 0.5 A/dm<sup>2</sup> to 1.5 A/dm<sup>2</sup> increased the tin content in

deposit from 62.5% to 79.3%. For the same increment in current density, solution of ratio 70 Pb:30 Sn increased the tin content from 23% to 31%; solution of ratio 80 Pb:20 Sn increased the tin content from 17.8% to 22.5% and finally solution of ratio 90 Pb:10 Sn increased the tin content from 9.8% to 15.7%.

There was a deviation in the composition of the deposit obtained from that of the solution used; this deviation is negligible for alloys of very low tin content (90 Pb:10 Sn) obtained at low current density ( $0.5 \text{ A/dm}^2$ ), but the deviation increases to higher values as the current density increases. The deviation of alloys from solution of 80 Pb:20 Sn is negligible at current density equal to  $1 \text{ A/dm}^2$  but it is notable for lower and higher current densities. For alloys of 70 Pb:30 Sn, the deviation was negligible at current density of  $1.5 \text{ A/dm}^2$ , but it was considerable at lower currents. Finally, the composition of the deposit from solution of 40 Pb:60 Sn differs from that of the solution, the deviation was small at current density equal to  $0.5 \text{ A/dm}^2$  but it increased for high values as the current density increased.

ii) Metal Ratio

The effect of tin/lead ratio in the solution on the percentage of tin in the deposit is shown in Figure 61. Similar to the effect of current density, increasing the tin/lead ratio in the solution increases the percentage of tin in the deposit. The rate of the increment was higher at high current densities; it was 13% for current density of  $0.5 \text{ A/dm}^2$ , 14% for current density of  $1 \text{ A/dm}^2$  and 15% for current density of  $1.5 \text{ A/dm}^2$  when the percentage of tin in the solution

was increased from 10 to 30%.

A presentation of the effects with respect to the more noble metal (lead) is shown in Figure 62. The dotted line in the figure represents the composition reference line (points above this line represent deposits containing a larger ratio of lead/tin than that in the bath and vice versa). Theoretically, because lead is the more noble metal and must be electrodeposited preferentially, the deposits with all compositions must lie over the reference line but, it was not the case; only the deposit obtained at low current density ( $0.5 \text{ A/dm}^2$ ) and part of the deposit obtained at  $1 \text{ A/dm}^2$  lay over the reference line, this was probably because the composition of the obtained deposit is subjected not only to the composition of the solution but to many variables headed by current density. In this case current density promotes the deposition of the less noble metal (tin) preferentially. Thus the composition of the deposits is a compromise of the effects of current density and lead/tin ratio in the solution.

### iii) Temperature

The effect of temperature on the composition of the deposits was studied for alloys of high tin content only, i.e. alloys electrodeposited from solution of lead/tin ratio equal to 40 Pb:60 Sn (see Figure 59). Increasing the temperature of the solution decreased the amount of tin in the deposit. The amount of decrement was increased as the current density increased up to  $40^\circ\text{C}$ . The percentage of tin as example decreased by 1.3% by heating the solution up to  $40^\circ\text{C}$  at

0.5 A/dm<sup>2</sup>, 3.4% at 1 A/dm<sup>2</sup> and 7.3 at 1.5 A/dm<sup>2</sup>. At temperatures higher than 40°C, the amount of decrement apparently is independent from the current density applied.

#### 8.6 Microprobe and Electron Micrography Work

Electron micrographs were taken for deposits obtained from solutions with different metal ratios of lead/tin and containing the group of additives mentioned before. The ones shown in Figure 63 are for alloys electrodeposited from solution of lead-tin ratio of 90 Pb:10 Sn and those which are shown in Figure 64 are for alloys electrodeposited from solution of metal ratio of 80 Pb:20 Sn. The deposits were obtained by applying different current densities. The effect of current density was to increase the size of the crystals. The orientation of the crystallization of the deposit is clear.

The micrograph shown in Figure 65 is for alloy electrodeposited from solution of metal ratio equal to 70 Pb:30 Sn at a current density of 1.5 A/dm<sup>2</sup>. The real composition of the alloy as found by the analysis was 69 Pb:31 Sn. The surface of the deposit is very smooth and secures a large active area.

The analysis of selected samples of the deposit using STEM showed different results of the composition from that obtained using an atomic absorption spectroscopy technique, but it maintained the general trend of the effect of current density; i.e. the increase in the amount of tin as the current density increases. The difference in the results was expected because the analysis carried out by STEM

was for as-plated not polished samples. Using polished samples might give more accurate results but in industry most of the analysis is usually carried out on plated samples which offer the real properties of the deposit.

The scan of  $\approx 1 \mu\text{m}$  area from the deposit of a selective sample with composition of 90.2 Pb:9.8 Sn electrodeposited at current density of  $0.5 \text{ A/dm}^2$  is shown in Figure 66. The figure demonstrates the regular distribution of the two metals in the alloy, this indicates that the electrodeposits are of a homogenous solid solution nature.

### 8.7 Mechanical and Corrosion Resistance Properties

The deposits obtained without using solution additives were virtually useless. Adding the additives to the solution (see Section 8.2) resulted in a compact, fine-grained structure. The size of the crystals, as shown in the micrographs, was found to increase with increasing the applied current density.

The adhesion test for the coatings (90 Pb:10 Sn) on actual bearings showed good adhesion properties in both tests, i.e. as plated and for annealed deposits.

It was found in the fatigue tests that fatigue was initiated in one half-bearing after a run of  $3 \times 10^6$  cycles. The remaining halves tested showed good performances. The wear rate ranged from  $5\text{--}8 \mu\text{m}$  for the same test period.

The deposit showed a good corrosion resistance. Immersing the coating in new motor oil (grade 20W/50) showed negligible dissolution but the immersion of samples in medicinal white oil (without inhibitor) or used motor car oil (the inhibitor deteriorated) showed a rate of dissolution equal to 0.2-0.26  $\mu\text{m}$  (from weight loss calculations).

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## CHAPTER 9

### DISCUSSION

The idea of electrodepositing tin and tin-lead alloys from sulphamate solutions is not new; it returns back to the early thirties when Piontelli and co-workers<sup>(32,64)</sup> studied the possibility of depositing many metals and alloys from sulphamate solutions including tin, lead and tin-lead alloy. The only metal deposited successfully was lead, the results concerning tin and tin-lead alloy were not promising, consequently the use of sulphamate in the electro-deposition of tin or tin-lead alloy was negligible.

Theoretically two metals such as tin and lead can be codeposited easily from simple acid solutions because firstly the standard electrode potentials of the metals are very close together (only 10 mV apart) and secondly, lead has been successfully electrodeposited from many acidic solutions including sulphamic acid. The key question is why were the results of the early trials for codepositing the two metals from sulphamate solutions unsatisfactory? The probable reasons are as follows:

- i) Insufficient theoretical knowledge and publications, at that time, concerning the art of electrodeposition of metals and alloys; most of the published work was based on an empirical foundation for definite alloys and generalisation was impractical.

- ii) The equipment available for running experimental work or for establishing baths for electroplating were so primitive and had limited efficiency and variety.
- iii) Chemicals available were at a low grade of purity and were incapable of forming pure, stable solutions.

Nowadays, after the vast improvements achieved in electroplating, even the codeposition of the so-called reluctant metals such as tungsten with the iron group (e.g. Co, Ni) is possible. Thus it might be prudent to reconsider the possibility of using sulphamate solutions in electrodepositing tin and tin-lead alloys from sulphamate solutions. One other important reason to be considered in this aspect is the need for the use of chemicals with a lower degree of toxicity in order to keep the pollution of the surroundings within the new stricter regulations introduced by some industrial countries.

### 9.1 Experimental Technique and Equipment Used

It was obvious that any suggested technique for completing this work should consider two factors: the purpose of the project and the time available for achieving this purpose. If the factor of time was ignored, then the purpose must be the more important aim.

The final purpose of the project was to develop an alloy solution based on sulphamate for electrodepositing lead-tin alloys, then to examine the possibility of using this solution in some applications in industry.

The technique considered for completing the work was based on: firstly developing a sulphamate solution for electroplating with tin; secondly using this solution mixed with that solution developed previously for lead<sup>(128)</sup> to produce an alloyed solution for electroplating lead-tin alloy, and finally electroplating sets of car engine bearings as one of the lead-tin alloy applications widely used in industry.

The use of simple equipment, easy to set up and operate, was considered, thus simulating the situation in electroplating industry where the use of sophisticated equipment is inapplicable. The electroplating process is very often carried out in a relatively coarse, imprecise way and run by people of some experience but of no or little theoretical knowledge.

The two-compartment cell designed for producing the tin solution proved to be very practical during the work. Its use was easy and simple but needed some care. The size was very convenient for producing a sufficient fresh quantity of the solution for each trial. The concentration of tin in the solution was well monitored using the curve shown in Figure 15. The quantity of coulombs needed for producing the solution in any required concentration (usually 10 g/l tin) was easily defined using this curve. Any deviation in this concentration was within the experimental error. The only difficulty with the use of the cell was the process of evacuating the solution produced from the anolyte compartment, this was often carried out using a pipette. In an industrial process, where the solution is

required in bulk, the use of such a small cell for preparing the solution is impractical. A cell with a larger anolyte compartment must be used and evacuating the solution using a pipette is not suitable. Fixing a tap in the anolyte compartment near the bottom can facilitate the process of evacuating the solution.

The equipment and method used for plotting the polarization curves were convenient and reliable. However, the use of the potentiostat in a chemical atmosphere caused corroding of the earth terminal, this resulted in a noisy signal appearing in the curves at certain currents. It was difficult at the beginning to discover the source of this problem. Otherwise the potentiostat worked very well throughout all the project work.

The use of a small cell with a five necked lid was useful; the size was very convenient, positioning the electrodes and replacing them could be performed accurately for each trial but the use of plane parallel electrodes in such a cylindrical cell, did not give a uniform distribution of current over the cathode and the anode. The non-uniformity of current distribution over the anode might cause an excess dissolution at the edges; this results in variations in the total active area culminating in inaccurate polarization data. The use of large anodes with larger anodic areas might minimise the error causing the problem.

The Hull-cell proved to be useful, not only for studying the effect of the additives on the morphology of the deposit, but also for a quick examination and estimation of the range of current densities for good plating.

The use of plane cathodes in some plating trials posed similar difficulties as with the anodes; thicker deposits were noticed on the edges. Using a cylindrical cathode and a rod anode proved to be more realistic; a uniform current density distribution was thus achieved.

The use of the jig supplied by the Glacier Co. (for plating sets of car engine bearings) in the large cell, was found to have advantages over the simple bearing holder used in the small cell (see Figures 39 and 40). This jig, in fact, is a small prototype for a larger jig used in the industry for electroplating bearings, but for plating several bearings at a time. Using this jig secured uniform distribution of current and maintained uniform anode-cathode spacing. It was noticed that some care must be taken for centralising the bearing halves on the jig and some experience is required for matching the two halves of the jig together so as to form a perfect cylinder.

## 9.2 The Solution

Preparing a solution for electroplating with lead-tin alloy might be very easy if the so-called "*solution concentrates*" for lead and tin were commercially available as it is the case in solution based on fluoborate. The preparation of the solution in such cases is more a matter of diluting the concentrates of lead and tin to the required concentrations then mixing the proper quantities of the diluted solutions to obtain the alloyed solution in the required

metal ratio. Unfortunately, it was not the case in preparing lead-tin sulphamate solution; neither lead, nor tin, is commercially available in aqueous state probably because the low solubility of tin and the lack of good stability for both. Further, none of them is available in a pure solid form (as salt to the acid) which if so, probably the process would be more convenient.

The preparation of lead-tin sulphamate was dependent upon the preparation of its components in the laboratory. Lead solution was easily prepared by neutralising basic lead carbonate salt with sulphamic acid solution in water by chemical reaction. However, the preparation of a tin solution was more difficult. The use of chemical methods produced unsatisfactory solutions and the only choice was the use of an electrochemical method. The two-compartment cell was designed for this purpose and it worked well during the project work.

In the practical work lead and tin solutions were prepared freshly for each trial. They were mixed in proper amounts to produce the alloyed solution in the required lead-tin ratio.

It was obvious from the previous experience gained from the work carried out with lead and tin that the use of additives is essential for good plating; this was confirmed by the results obtained from the few preliminary trials carried out without adding additive to the solution, nodular dendritic and non-adherent deposits were obtained.

It was clear that there was no need for the use of complexant agents because of the relatively similar behaviour of lead and tin in sulphamate solution and the closeness of their standard potentials. The need was only for additives to improve the quality of the deposit and to maintain reasonable stability for the solution.

The work performed with tin solution suggested a group of additives including peptone, pyrogallol and phenolsulphonic acid as best additives with optimum amounts of 2.5 g/l each. The latter was included by being recommended as an antioxidant for tin ions in the solution, but its replacement was necessary because it reacted with lead ions in the solution. Gelatin was chosen because it secured the best results when it was used with lead sulphamate solution. Thus, all the experimental work with alloyed solutions was performed after adding a group of additives consisting of peptone, pyrogallol and gelatin at a level of 2.5 g/l each. No trials have been done to investigate these levels because the deposit obtained from the solution was satisfactory.

The results obtained from Hull-cell trials for solutions containing the group of additives, showed, in general, similar ranges of current density for good deposits to that obtained for tin but lower than that for lead. One exception was for the high tin-lead solutions.

The composition of the deposits obtained roughly covered the required compositions, i.e. by using the appropriate lead/tin ratio and applying the suitable current density, deposits of composition of 90, 80, 70 and 40% lead, remainder tin were obtained.

Adding free sulphamic acid solution to the alloyed solution extended the range for lower current density probably because of an increase in tin percentage in deposit or the conductivity of the solution.

The conductivity of the solution was found to be  $\approx 72 \text{ mS cm}^{-1}$ . It is lower than that of tin ( $\approx 95 \text{ mS cm}^{-1}$ ) and higher than that of lead ( $\approx 55 \text{ mS cm}^{-1}$ ). It varies slightly with respect to lead/tin ratio in the solution, such high conductivity is actually expected from highly acidic solutions based on sulphamic acid.

Improving the range of good deposits by heating the solution was not investigated because temperature enhances the hydrolysis of the solution and thence metal ion losses from active ion states.

### 9.3 Polarization Studies

It is well known for two metals to codeposit simultaneously, the conditions must be such that the more negative (less noble) potential of the less noble metal can be attained without employing an excessive current density. This can be achieved if the standard potentials of the two metals are close together. The importance of this condition follows from the fact that the more noble metal deposits preferentially.

Few pairs of metals actually satisfy the above mentioned condition. However, several ways can be used for bringing the potentials of two metals closer together (see Section 2.1).

Lead-tin is one of the few pairs which have very close standard reduction potentials, the potential of lead in acidic solution is -126 mV and the potential of tin is -136 mV with a separation of 10 mV only on the hydrogen scale. The closeness of their potentials makes their codeposition one of the simplest alloy plating processes. Further, because the potentials of both lead and tin are slightly less noble than that of hydrogen and since the two metals have a high hydrogen over-voltage, their alloys can be deposited from acid solution with  $\approx 100\%$  cathode current efficiency.

The rest potential was found to be -414 mV and -440 mV (saturated calomel electrode scale) for lead and tin sulphamate solutions respectively. The separation between them is thus 26 mV which is not far from 10 mV the separation between their standard potentials. The effects of the most essential variables, such as temperature, additions etc. on the rest potential were negligible and at the level of 10 mV. Such stability in the rest potentials of the two metals indicates that sulphamate solutions contain lead and tin metals essentially as simple ions.

In general, cathodic reactions for lead, tin and lead-tin sulphamate solutions were depolarised as the temperature of the solutions increased, but a fluctuation in the reaction was observed at high temperatures for solutions of particular lead/tin ratios. By heating the solution a great saving in power consumption could be achieved, but on the other hand, the extra cost of heating the solution must be considered. The fluctuation in the cathodic polarization shown at high temperatures is probably due to hydrolysis phenomena in the

solution which is widely reported in the literature. This was also noticed during the course of work by the precipitation of white-yellow compounds at the bottom of the cell.

The addition of sulphamic acid to the solution resulted in depolarising the reaction markedly at low potentials, but slightly at high potentials. This depolarization was accompanied with an improvement in the quality of the deposit. The range of current density for good deposition was slightly extended to lower current densities (see Table 27). This improvement was more likely caused by an increase in the content of tin in the deposit and/or a slight improvement in conductivity of the solution.

Mildly agitating the solution showed the same effect as the use of the large cell; both of them caused a slight depolarization to the cathodic reaction. This depolarization may be related to the decrease in the thickness of diffusion layer when agitation was used and with better current distribution in the case of the large cell.

A continuous smooth dissolution of the anodes was noted over a relatively wide range of current densities. This indicated that regular replenishment in lead and tin ions occurred during the plating process.

The effect of increasing the temperature was to depolarise the dissolution reactions as was the case in cathodic deposition reactions. Such similarity in the effect of temperature is necessary for maintaining constant metal ratios in the solution, otherwise segregation or depletion of the solution with metal ions could occur.

The relative similarity in the cathodic behaviour of lead and tin in sulphamate solution and the results drawn from the effect of the main variables on the composition of the alloyed deposits could make the lead-tin solution a model alloy solution. This may attract the researchers to relate the individual behaviour of lead and tin solutions to that of lead-tin and to investigate whether there is any possibility of relating the composition of the alloy deduced from the curves to that obtained experimentally. The result of such an investigation showed that there was no simple relation between the curves that could be established to serve this purpose. The polarization curve for the alloy lies between the curves of lead and tin. This eliminates the possibility of using the additivity concept of polarization behaviour for the individual metals. Such a result is not surprising because application of this concept implies that the electrochemical relation between tin and its ions in the solution are independent of the presence of lead and its ions which is not necessarily the case. In an electro-deposition process, the metals and their ions at the cathode-solution interface have a tendency to mutual chemical equilibrium. This means that the concentrations of metal ions at the cathode-solution interface during the codeposition are different from the concentrations at the interfaces when the metals are individually deposited. The precise 'interference' effect between such ions cannot be predicted although experience in analogous situations can give a useful guide.

#### 9.4 Plating Variables and Deposit Composition

Applying the diffusion theory for explaining the effect of the plating variables on the composition of the alloyed deposit is difficult and is only possible under certain conditions.

Metal deposition actually occurs at the cathode-solution interface and metal ions are continuously removed from the solution adjacent to the cathode and replenished from the body of the solution by diffusion, convection and electrical migration. The composition of the alloyed deposit basically depends on the relative concentration of the metal ions of the alloy components in the cathode-solution interface. Any change in the relative concentration of the metal ions for any reason (change in plating variables) will result in a change in the composition of the deposit.

According to the diffusion theory, the depletion of the more noble metal ions of a regular plating system is given by:

$$\Delta C = \frac{\delta I (1 - t)}{D}$$

where  $\delta$  is the thickness of the diffusion layer,  $I$  is the current density,  $t$  is the transference number and  $D$  is the diffusion constant.

$\Delta C$  can be related to the concentration of the depositable metal ions at the cathode-solution interface with the relation:

$$\Delta C = C_0 - C$$

where  $C_0$  is the concentration of the metal ions in the body of the solution.

From this relation it is obvious that the metal ion concentration  $C$  increases as  $\Delta C$  decreases, consequently all the plating variables causing an increment in  $\Delta C$  will cause decrement in the percentage of the more noble metal in the deposit and vice-versa.

Brenner<sup>(5)</sup> in his classification of alloy plating systems considered lead-tin alloy acidic solutions to be of a regular type as long as the tin content in the solution is less than 70%, and he further expected a large variation in the composition of the deposits from such a solution by varying the plating variables, particularly current density, temperature and agitation.

All the experimental work of this research programme was carried out using solutions of tin content less than 70%, and results were expected from these trials to be consistent with that of a regular alloy plating system. In fact the results obtained from the work approximately followed the trend expected, but at a lower level.

Increasing the lead/tin ratio in the solution showed a direct effect in the composition of the deposit, i.e. the higher lead percentage in the solution, the higher the lead percentage in the deposit (Figure 62). The curves shown in the figure however are not completely consistent with the characteristics expected from a *regular* plating system. The curve of 1.5 A/dm<sup>2</sup> is slightly below the reference line AB; this is somewhat unusual because the expected behaviour for

the more noble metal (lead) is to electrodeposit preferentially and the curve must therefore be above the reference composition line. The curve of 1 A/dm<sup>2</sup> is probably more significant because it cuts the reference composition line at point C. This point in fact represents an *equilibrium* codeposition system for lead and tin. The percentage of lead in the deposit at this point is the same as that in the solution (~80%). The more probable reasons for such behaviour are: (a) the closeness of the deposition potentials of lead and tin, and (b) similar effects of the additive agents used on both metals. The deposits from baths having a lead/tin ratio higher or lower than 80% Pb (remainder tin) should belong to another codeposition system, most likely *regular*. The curve of 0.5 A/dm<sup>2</sup> is completely above the reference line, this curve represents the typical behaviour of the more noble metal in a regular plating system.

The results obtained from changing current density did affect the composition of the deposit with the expected trend for a regular plating system. Increasing the current density increased the percentage of the less noble metal (tin) in the deposit but at a lower scale than that predicted by Brenner. Tin was electrodeposited with lead even at low current densities. It should be appreciated that as the standard potentials for tin and lead are so close it may not always be clear which metal is the most noble in the regular solution concept.

The affect of temperature on the composition of the deposit was studied for a solution of higher tin content only, i.e. of lead/tin

ratio equal to 40 Pb:60 Sn. The results obtained are consistent with that of a regular plating system i.e. increasing the temperature decreases the tin content in the deposit. The composition of these deposits approaches that of the solution and becomes independent from current density as the temperature increases.

Heating the plating solution in industry can be economically attractive through improving the conductivity and lowering the power consumption. The conductivity of sulphamate solution is already high, thus a saving in power is the only advantage that can be gained by raising the temperature. On the other hand this increases the risk of a high rate of solution hydrolysis. An optimum solution temperature takes account of excessive heat losses and a value of 40-60°C is common if these are the main considerations.

## 9.5 Process Control and Some Practical Considerations

### Bath Compositions:

In the process of alloy plating, the ability to control the metal ion concentration in the solution is of the same importance as developing the process itself. If not, the capability of the process to survive may be greatly reduced.

The composition of deposits produced from alloyed solutions is essentially related to the composition of the solution. In practice, the composition of alloy plating solutions must be held constant over long periods of working the bath. To accomplish this, metal ions must

be added to the bath when required in the same ratio as they are deposited and roughly in the same amounts.

During the work on this project, soluble lead-tin alloyed anodes having the same composition as the solutions and the desired deposits were used, but several other means can be used to replenish the metal ions in alloy plating baths. They can be summarised as follows:

1. soluble alloy anodes;
2. soluble separate nodes of each metal;
3. inert anodes with chemical replenishment;
4. combination of (1), (2) and (3).

The soluble alloyed anodes were chosen because of their simplicity and reliability. In addition, the potentials of lead and tin are so close together in sulphamate solutions (26 mV apart) to make the non-uniform dissolution of the anodes unlikely, thus removing this main problem in the use of alloyed anodes.

In order to obtain a homogenous alloy anode, a rapid cooling of the molten alloy of lead and tin was carried out when the anodes were prepared. These anodes worked well during the project and no problems were faced in their pattern of dissolution.

The use of other methods for replenishing the solution with metal ions was not investigated because firstly, it is too difficult to replenish a solution prepared originally by an electrolysis method with the addition of chemicals and, secondly, because other methods have no obvious advantages over alloyed anodes. The only other method

which might be successfully applied is the use of dual lead and tin anodes, but since tin is slightly less noble than lead the latter may be deposited on the tin anode when the bath is not in operation. (The film thus formed is readily dissolved when the current is recommenced). The current supplied to the tin and lead anodes should be in the ratio required by the composition of the alloy being deposited.

#### Deposit Composition:

The composition of the alloyed deposit from a plating bath is influenced by many variables (see Section 9.4). Any change in one of them (which is often difficult to avoid) will require a compensatory change in one or more of the others in order to maintain a given plate composition.

Analysing the plated deposit obtained from the plating solution is necessary from time to time to keep the composition of the deposit within given limits. An approximate method was used by Haring and Blum<sup>(56)</sup> and its accuracy was discussed by Du Rose and Hutchison<sup>(57)</sup>. The approximate percentage of tin in the alloy can be calculated from the formula:

$$\text{Tin \%} = 518.2 \left( \frac{\text{amp-hour}}{\text{weight of alloy in grams}} \right) - 134.1$$

if the weight of the alloy and the coulombs passed were known.

The method is good for fast approximate analysis, but more accurate

results can be obtained by using other classical methods.

In this project, analysis of the deposit was carried out using the atomic absorption spectrometry technique. At the earlier stages, some difficulty was faced with dissolving the alloyed deposit for preparing samples for the analysis. Using a mixture consisting of concentrated hydrochloric and nitric acids in a ratio of 1:1 successfully dissolved the deposit but the use of such a solution was impractical due to the formation of excessive harmful acid fumes during analysing. After consultation with the International Tin Research Institute, the following was proposed:

	500 mls	HCl	1:1
	400 mls	HNO <sub>3</sub>	concentrated
	100 mls	distilled water	
and	50 g	tartaric acid	

The solution worked well and the analysis was carried out partly in the University laboratory and partly in the research laboratories of the ITRI.

#### Agitation:

Agitation of the solution was not used very often in the project in spite of the results deduced by many workers suggesting that the agitation of acidic lead-tin solutions does have some effect on the composition of the deposit. Three reasons why agitation of the solution in this project was limited can be cited. Firstly, because many reports

by other workers stated that agitating acidic lead-tin solutions will enhance the oxidation process of stannous ions in the solution they recommended the avoidance of agitation for such solutions. Secondly, because agitation enhances the oxidation process of stannous ions, it will be difficult to define whether any resultant effect is due to such oxidation or to the agitation itself; and finally, because of the lack of a precise measurement by which the type of agitation can be quantitatively expressed.

#### Stability:

It was noted that the sulphamate solution, in a similar manner to all other lead-tin alloy plating solutions, becomes cloudy and turbid with time because of the formation of insoluble tin compounds. The cause for that was attributed to the oxidation of stannous ions to stannic tin by atmospheric oxygen. This is not necessarily harmful as long as the quality of deposit is not affected. In order to minimise the oxidation process, an antioxidant additive must be added when required. Phenolsulphonic acid is recommended for tin solutions but its use with lead-tin solutions resulted in a chemical reaction with the lead producing an insoluble lead compound. Other antioxidants might give better results. This needs more investigation.

The breakdown of the additives in the solution and the sludge formed on the anode are another cause for the turbidity of the solution. Filtering the solution using filter paper or using activated carbon and nylon cloths on the anode was found to limit this problem.

#### pH:

Controlling the pH values of the solution was not attempted effectively because the solution had a high acidity ( $\text{pH} \approx 1.2$  at room temperature) and controlling such a highly acidic solution is very difficult. In addition, the variation of pH should have little effect on solutions containing the metals as simple ions as with sulphamate solutions.

The plating trials carried out with solutions containing 50 g/l of free sulphamic acid showed a slight improvement in the range of current densities for a good deposit. (The range was extended slightly for low currents). This improvement is probably due to a slight increase in tin percentage in the deposit and/or a similar improvement in the conductivity and throwing power of the solution.

#### Cathode Current Efficiency:

The lead-tin alloy was deposited at a cathode current efficiency of  $\approx 100\%$ . The composition of the solution and its temperature showed no effect on the efficiency. Such high efficiency is expected from highly acidic solutions containing the metals as simple ions. Another reason for obtaining high efficiency was because it was calculated only for current densities within the range of a good deposit, i.e. lower than the limiting current density. However, the efficiency should have dropped and the quality of the deposit would have been inferior if the plating was carried-out with currents higher than the limiting current because of hydrogen evolution. This idea in fact was evident when some bearings were plated by applying slightly higher current densities.

Dull vertical lines, wide at the lower end and narrow at the upper end of the bearings were observed. These lines could be the pathways taken by the hydrogen bubbles evolved at the cathode (bearing) as a result of applying a high current density. These lines are only apparent when the bearing is removed from the plating jig.

#### 9.6 Structure and Properties of the Deposit

The suitability of alloyed deposits for practical applications is closely linked to its structure and properties and it depends on the real service conditions.

The results obtained from the study of the structure of the deposit show that the deposits are most likely solid solutions. Further, the study of the electromicrographs of these deposits show that the crystal size was increased as the current density applied increased.

Deposits of a solid solution nature are very desirable in practical applications because the preferential dissolution of one component of the deposits (which is very usually in two-phase deposits) is improbable and consequently they must offer a good corrosion resistance and regular dissolution.

The size of the crystals of the deposit is the most important factor that controls their mechanical properties. Fine crystal surfaces (smooth) usually have better mechanical properties i.e. good wear and fatigue resistance etc. but smooth surfaces can only be obtained at low current densities, consequently slow plating process. On the other hand coarser crystal deposits are obtained by a faster plating process but with inferior mechanical properties.

The mechanical properties of the deposits were examined for an alloy having the composition of 90 Pb:10 Sn plated as an overlay upon the bearing surface at current density of 0.5 A/dm<sup>2</sup> (i.e. low C.D). The results of the tests were encouraging. The deposits showed a low wear rate, a good adhesion and a considerable fatigue resistance. The deposit also showed in the short assessment of corrosion resistance, a low corrosion rate. Such results in fact indicate that the alloy is suitable for use as an overlay in bearing manufacture. In real practice an alloy having similar composition or a ternary alloy contains in addition to lead and tin  $\approx$ 3% copper, are the best known alloys electrodeposited as overlays in the bearing industry.

The use of the deposits of other compositions for other applications such as solderable coatings for example, needs more practical investigation.

#### 9.7 Commercial Viability

In order to assess the suitability of a solution for use in an industrial process, two main aspects must be considered: technical and economical. The technical aspect is based on<sup>(136)</sup>:

- the stability of the solution
- the effluent problems associated with the solution
- the flexibility of the operating parameters (C.D., pH, temperature, etc)

- the consistency of the composition and structure of the deposit
- the capability of continuous replenishment of the solution in metal ions, and
- the applicability of the deposit produced to meet commercial purposes.

The economical aspect is based on:

- the continuous availability of the solution constituents
- the consistency of the price
- the extras imposed by using the solution (heating cost, operating costs, solution hydrolysis, effluent treatment, drag-out, etc), and
- the cost of any special equipment required.

In the first aspect lead-tin sulphamate solutions fulfil all the requirements which make such solutions ideal for commercial exploitation. No effluent problem is associated with the use of the solution. The replenishment of the solution by anodic dissolution for lead-tin anodes is smooth and continuous. The composition of the deposit obtained is consistent and can be well controlled by using a suitable current density and the required lead/tin ratio in the solution. The only drawback exhibited by the solution is the lack of long term stability. The stability of the solution is acceptable as long as the solution is being worked, but it falls when the solution is left idle for a period of time. Such a drawback in fact is not specific for this sulphamate solution, but it is shown even by the well-known and widely used solutions. Further research should find an answer for this problem unless it can be avoided.

The economical aspect has not been studied in depth at this stage, but the visible indications (i.e. no special equipment or complicated effluent treatment required) show that the use of such a solution might be more economical than other commercial solutions used at the present.

The main two areas for the use of the deposit are: in bearing manufacture (90 Pb:10 Sn alloy) and in the electrical and electronic industry as solderable coating (60 Sn:40 Pb). The use of (90 Pb:10 Sn) alloy as an overlay on bearing materials was the only application investigated in this work and the results obtained for the properties of the overlay (adhesion properties, corrosion and wear resistance and fatigue strength) are comparable with that obtained from other solutions.

The use of the alloy of 60 Sn:40 Pb as a solderable coating has not been studied at this stage but the quality of the deposit obtained (i.e. smooth and adherent) indicates that the suitability of the alloy for such use is likely. In general, solderable coatings require:

- a good resistance for any ageing changes in appearance, structure, etc
- a good corrosion resistance, and
- a good ability to fuse without any surface defects.

Such properties for the alloy have been claimed repeatedly in the literature for other solutions and the alloy was used successfully in printed circuits and connectors. Thus there is no reason to suggest that such an alloy is not suitable for this use if it was obtained from a sulphamate solution.

## 9.8 Suggestions for Further Work

It can be said that lead-tin alloyed deposits can be obtained from sulphamate solutions. These deposits are suitable for many industrial applications, particularly in bearing and printed circuit manufacture. Soldered coating is also another area worth considering.

It is too early to claim, without prejudice, that sulphamate solution can be considered as a definite alternative to other well-established and understood solutions such as fluoborate but the indications are promising. To do so, the stability of the solution must be subject to further investigation for the purpose of finding an additive(s) or means to maintain a long term stability to the solution which if so, the solution can be produced for commercial sale.

Other points of less importance but may be considered in any further study are, the effect of pH on the composition of the deposit and the agitation if precise standards for agitation measurement were established.

## CHAPTER 10

### CONCLUSIONS

Lead-tin alloy can be electrodeposited from sulphamate solutions with a variety of compositions. The required composition can be secured by using solutions containing a suitable lead/tin ratio and applying the appropriate current density.

Typical compositions of solutions for depositing alloy of different compositions are as follows:

Composition of Solution		Current Density A/dm <sup>2</sup>	Composition of Deposit
Lead:tin	Total Metal g/l		Lead:tin
90:10	54.5	0.5	90.2:9.8
80:20	36.5	1.0	79.8:20.2
70:20	27.4	1.5	69 :31
40:60	15.6	0.5	62.5:37.3

The use of addition agents is essential for producing good levelled deposits, otherwise rough, treed and non-adherent deposits will be obtained. The experiments showed that a group of additives consisting of:

2.5 g/l peptone

2.5 g/l gelatin

and

2.5 pyrogallol

is suitable for producing deposits of good quality over a range of current densities differs with the composition of the solution and of maximum value up to 3 A/dm<sup>2</sup>.

The effect of the plating variables on the composition of the deposit was such that increasing the percentage of tin in solution, current density and <sup>decreasing</sup> temperature increased the percentage of tin in the deposit. No attempt has been made at this stage to examine the effect of other variables such as agitation on the composition of the deposit. The effect of adding free sulphamic acid to the solution was to extend slightly the range of current density for good deposits at lower values.

The stability of the solution is good as long as the solution is working, but leaving the solution for a period of time (more than two days) requires the running of dummy plating before starting the real plating (this of course is not unusual).

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Binary alloys are indicated by a dot (.) at the intersection of a vertical and horizontal column. Ternary alloys are indicated by the rectangular enclosing the third element.

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Half Cell Reaction Complexed Ions	Potential Volts	Half Cell Reaction Simple Ions	Potential Volts	Difference Volts
$\text{Cr}(\text{OH})_2 + 3e \rightarrow \text{Cr} + 3(\text{OH})^-$	-1.3	$\text{Cr}^{3+} + 3e \rightarrow \text{Cr}$	-0.74	0.56
$\text{Zn}(\text{CN})_4^{--} + 2e \rightarrow \text{Zn} + 4(\text{CN})^-$	-1.26	$\text{Zn}^{++} + 2e \rightarrow \text{Zn}$	-0.763	0.50
$\text{H}_2\text{GaO}_3^- + \text{H}_2\text{O} + 2e \rightarrow \text{Ga} + 4(\text{OH})^-$	-1.22	$\text{Ga}^{3+} + 3e \rightarrow \text{Ga}$	-0.53	0.69
$\text{CrO}_2^- + \text{H}_2\text{O} + 3e \rightarrow \text{Cr} + 4(\text{OH})^-$	-1.2	$\text{Cr}^{3+} + 3e \rightarrow \text{Cr}$	-0.74	0.46
$\text{ZnO}_2^{--} + 2\text{H}_2\text{O} + 2e \rightarrow \text{Zn} + 4(\text{OH})^-$	-1.216	$\text{Zn}^{++} + 2e \rightarrow \text{Zn}$	-0.763	0.45
$\text{WO}_4^{--} + 4\text{H}_2\text{O} + 6e \rightarrow \text{W} + 8(\text{OH})^-$	-1.05	$\text{WO}_3 + 6\text{H}^+ + 6e \rightarrow \text{W} + 3\text{H}_2\text{O}$	-0.09	0.96
$\text{MoO}_4^{--} + 4\text{H}_2\text{O} + 6e \rightarrow \text{Mo} + 8(\text{OH})^-$	-1.05	$\text{Mo}^{3+} + 3e \rightarrow \text{Mo}$	-0.2	0.85
$\text{Cd}(\text{CN})_4^{--} + 2e \rightarrow \text{Cd} + 4(\text{CN})^-$	-1.03	$\text{Cd}^{++} + 2e \rightarrow \text{Cd}$	-0.403	0.63
$\text{HSnO}_3^- + \text{H}_2\text{O} + 2e \rightarrow \text{Sn} + 3(\text{OH})^-$	-0.91	$\text{Sn}^{++} + 2e \rightarrow \text{Sn}$	-0.136	0.78
$\text{Ni}(\text{NH}_3)_6^{++} + 2e \rightarrow \text{Ni} + 6\text{NH}_3$	-0.47	$\text{Ni}^{++} + 2e \rightarrow \text{Ni}$	-0.25	0.22
$\text{Hg}(\text{CN})_4^{--} + 2e \rightarrow \text{Hg} + 4(\text{CN})^-$	-0.37	$\text{Hg}_2^{2+} + 2e \rightarrow 2\text{Hg}$	0.789	1.16
$\text{Ag}(\text{CN})_2^- + e \rightarrow \text{Ag} + 2(\text{CN})^-$	-0.31	$\text{Ag}^+ + e \rightarrow \text{Ag}$	0.799	1.11
$\text{Cu}(\text{NH}_3)_2^+ + e \rightarrow \text{Cu} + 2\text{NH}_3$	+0.12	$\text{Cu}^{++} + 2e \rightarrow \text{Cu}$	0.337	0.22
$\text{AgCN} + e \rightarrow \text{Ag} + (\text{CN})^-$	+0.017	$\text{Ag}^+ + e \rightarrow \text{Ag}$	0.799	0.78
$\text{Ag}(\text{NH}_3)_2^+ + e \rightarrow \text{Ag} + 2\text{NH}_2$	+0.373	$\text{Ag}^+ + e \rightarrow \text{Ag}$	0.799	0.43

TABLE 2: Effect of Complexing Metal Ions on their Standard Electrode Potentials

PROPERTY	ACID	ALKALINE
Valency	Divalent	Tetravalent
Throwing power	Lower	Higher
Cathode C.E.*	Higher	Lower
Temperature	Room temperature	Elevated
Power consumption	Lower	Higher
Additive agents	Necessary	None
Bright deposit	Brightener	Reflowing
Plating speed	Faster	Slower
Anodes	Soluble	Inert (preferred)
Controlling bath	More critical	Easier
Permissible C.D. <sup>+</sup>	Higher	Lower
Quality of deposit	More ductile	Finer-grained

\* C.E. = Current Efficiency

+ C.D. = Current Density

TABLE 3: Comparison Between the Features of Acid and Alkaline Solutions

	Bath Constituents g/l			Working Conditions					Cathode Current Efficiency %	Notes
	Tin	Alkali (Free)	Additive	Tempera- ture °C	Applied Volts	Cathode CD A/dm <sup>2</sup>	Anode CD dm <sup>2</sup>	Anode Material		
1	40	12.5	-	80	3-4	1.6	2.16	Refined pure tin or alloyed	82-87	Still bath
2	80	22.5	-	70-80	3-4	0.8	2.16	"		Barrel plating
3	30-50	12-15	-	70-80	3-4.5	1.1-2.7	1.1-2.2	"		-
4	42	10	-	60-85		0.5-3		"		-

TABLE 4: Some Typical Sodium Stannate Baths for Tin Electrodeposition

	Bath Constituents g/l			Working Conditions					Cathode Current Efficiency %	Notes
	Tin	Alkali (Free)	Additive	Tempera- ture °C	Applied Volts	Cathode CDA/dm <sup>2</sup>	Anode CD A/dm <sup>2</sup>	Anode Material		
1	40	15	-	65-88	4-8	3.3-11	3.3-4.3	Refined tin pure or alloyed	85-90	Filmed condition
2	80	22.5	-	65-88	4-14	1-17	4.3	Alloyed 1% Sb	85-90	High-speed anodes
3	160	22	-	70-90		Up to 40		St. steel or nickel alloys	60-90	Inert anodes*

TABLE 5: Some Typical Potassium Stannate Baths for Tin Electrodeposition\*

\*The composition and the working conditions differ with about 10% in value according to the different references

Features	Potassium Stannate	Sodium Stannate
Quality of Deposit	Good	Good
Cathode C.E.*	Higher	Lower
Permissible C.D. <sup>+</sup>	Higher	Lower
Maximum temperature	90°C	75°C
Plating speed	Higher	Lower
Conductivity	Higher	Lower
Solubility of salt	Higher (increases with temperature)	Lower (decreases with temperature)
Sludge formation	More difficult	Easier
Cost of chemicals	Higher	Cheaper

\*C.E. = Cathode Efficiency

+C.D. = Current Density

TABLE 6: Comparison Between the Features of Potassium and Sodium Stannate Solutions

	Bath Constituents					Work Conditions					Cathode Current Efficiency %	Notes
	Tin g/l	Free Sulphuric acid g/l	Addition Agents g/l			Temperature °C	Applied Voltage V	Cathode CD A/dm <sup>2</sup>	Anode CD A/dm <sup>2</sup>	Anode Metal		
			Gelatin or glue	β-Naphthol	Others							
1	30-50	40-70	Gelatin 2	1	C.S.A. 30-60	Room to 20	0.4-0.8	1-10	1.1		100	-
2	30-40	40-70	1	2	70-120	"	"	1-10	2	Cast tin of high grade	100	-
2	30	50	5*	1	P.S.A. 40	"		10				Agitation
4	54 <sup>+</sup>	100	Glue 2	-	C.S.A. or P.S.A. 20-30	20-30		2-5				Still bath

\* Dihydroxydiphenylsulphone

+ As stannous sulphate

C.S.A. Cresolsulphonic acid

P.S.A. Phenolsulphonic acid

TABLE 7: Typical Compositions for Stannous Sulphate Baths

		Bath Constituents				Work Conditions					Cathode Current Efficiency %	Notes
	Tin g/l	Free Fluoboric acid	Addition Agents g/l			Temper-ature °C	Applied Voltage V	Cathode C Density A/dm <sup>2</sup>	Anode C Density A/dm <sup>2</sup>	Anode Metal		
			Gelatine	β-Naphthol	Hydro-quinone							
1	80	50-150	6	1	-	16-38	1-3	2.2-13.8		Refined tin	100	-
2	80	100-200	6	1	-	20-40	1-3	2.5-12.5 25-42.5		Pure tin	100	-
3	80	100	Peptone 5	1	1	16-38	-	2-20				Standard
4	120	200	"	1	1	16-38	-	2-20				High speed
5	30	300	"	1	1	16-38	-	2-20				High throwing power

TABLE 8: Typical Compositions for Stannous Fluoborate Baths

Bath Constituents	Quantity g/l
Stannous chloride	63
Sodium fluoride	25
Potassium bifluoride	50
Sodium chloride	45

TABLE 9: A Typical 'Halogen' Bath

(The bath operates at: Current density 45 A/dm<sup>2</sup>; pH 2.7).

Features	Sulphate	Fluoroborate	Halogen
Quality of deposit	Smooth	Fine-grained smooth	Smooth
Cathode C.D. A/dm <sup>2</sup>	Up to 10	Up to 42.5	45
Cathode C.E. %	100	100	100
Temperature °C	20-30	20-40	65
Conductivity	High	High	High
Deposition	Medium	High	High
Additive agents	$\beta$ -Naph <sup>(1)</sup> + Gel <sup>(2)</sup>	$\beta$ -Naph <sup>(1)</sup> + Gel <sup>(2)</sup> , Hyd. <sup>(3)</sup> Pe <sup>(4)</sup>	Gel <sup>(2)</sup> + Pe <sup>(4)</sup> , Polyalkylene oxide
Anodes	Pure tin	Pure tin Must be left in the bath	Pure cast tin
Application	Thin or heavy deposit	Heavy deposit	Rapid thin deposit

(1)  $\beta$ -Naphthol; (2) Gelatin; (3) Hydroquinine; (4) Peptone

TABLE 10: Comparison Between Some Features of the Main Acid Baths for Tin Electrodeposition

Sn% in Deposit	Solution Composition g/l				
	Sn	Pb	HBF <sub>4</sub> Free	H <sub>3</sub> BO <sub>3</sub> Free	Glue
5	5	85	100	25	0.5
10	10	90	100	25	0.5
25	25	65	100	25	1.5
40	40	45	100	25	3
50	50	35	100	25	4
60	60	25	100	25	5

Current Density = 3 A/dm<sup>2</sup>, Temperature = 25-30°C

TABLE 11: Fluoborate Solutions for Electrodepositing Tin-Lead Alloys

Component	Composition g/l		Notes
	Formula (1)	Formula (2)	
Stannous pyrophosphate or Tin	20 11.6	4.1-61.7 2.4-35.6	
Lead nitrate or Lead	17 10.6	3.3-33.1 2.1-20.7	
Potassium or Sodium Pyrophosphate	10 (sodium)	39.2-261.8	
pH	9.5	9-9.5	
Temperature °C	60	40-80	
Tin in anode %	50	10-50	
Cathode current density A/dm <sup>2</sup>	0.5-5.0	0.5-5.0	
Tin content in deposit %	2-15	0-90	
Cathode current efficiency %	94-98		
Addition agent	No mention	Increases tin in deposit	

TABLE 12: Typical Composition of Pyrophosphate Baths

Bath Constituents	Quantities g/l	
	Lead-rich alloy 18-12% Sn	Tin-rich alloys 20-60% Sn
Lead Sulphamate	97-138	42-110
Tin Sulphamate	24	60-120
Free sulphamic acid	51-80	70-120
C.T.A.B.*	2-10	1.5-10
Cathode current density A/dm <sup>2</sup>	1-2	1
Current efficiency %	100	-
Temperature °C	20-40	18-25

\*Cetyltrimethylammoniumbromide

TABLE 13: A Typical Composition for Sulphamate Baths for Tin-Lead Alloy

Bath Constituents	Quantities	Notes
Tin	18 g/l	
Lead	2 g/l	
Free acid (2-propanosulphonic)	100 g/l	$\text{CH}_2(\text{OH})(\text{CH}_2)_2\text{SO}_2\text{H}$
Surface active agent	20 g/l	Polyethyleneglycol- nonylphenylether
Brightener	20 ml/l	O-toluidine + acetal- dehyde
Formaline	8 ml/l	
Temperature, °C	20	

TABLE 14: Optimum Composition for Alkanosulphonate Bath to Yield 90% Sn Alloy

Bath Constituent	Quantities		Notes
	Normal speed plating	High speed plating	
Tin	18 g/l	30 g/l	
Lead	9 g/l	12 g/l	
Free acid	200 g/l	300 g/l	
Additive	20 ml/l	40 ml/l	
Temperature, °C	25	25	
Agitation	Moderate	Vigorous	
Current density A/dm <sup>2</sup>	2.5	10	

TABLE 15: A Typical Composition for Alkylsulphonate Bath

Bath Constituent	Quantities g/l		Notes
	For alloy of 8-12% Sn	For alloy of 20-60% Sn	
Lead (metal)	36-52	42-110	
Tin (metal)	12	60-119	
P.phenolsulphonic (free acid)	51-87	70-121	
Gelatin	2	1.5-3	
Temperature, °C	20-40	18-25	
Cathode current density A/dm <sup>2</sup>	1-2	1	
Anodes of composition corresponds to that required.			

TABLE 16: A Typical Composition for p.phenolsulphonate Bath

Bath Constituents	Quantities g/l
Lead chloride	5-10
Stannous chloride	15-20
Ammonium chloride	250-300
Hydrochloric acid	5-10
Boric acid	3-5
Glue	0.5-1
Current density A/dm <sup>2</sup>	0.5-1
Temperature	Room temperature

TABLE 17: The Composition of a Chloride-based Bath Patented by Melnikov et al

	Anode Composition %Pb	Bath Constituents g/l			Pb/sn Ratio in Deposit
		Lead Chloride	Stannous Chloride	Boric Acid	
1	46.1	8.5	.922	1.5	49.25
2	91.7	8.22	1.47	1.5	16.5
3	74.85	6.71	4.6	1.5	7.05
4	59.75	5.35	7.3	1.5	3.21
5	49.85	4.47	4.2	1.5	1.86
6	60.36	3.57	11.06	1.5	.99

Optimum conditions: Gelatin - 1.11 g/l; pH 1.5; Temperature 30°C.

TABLE 18: A Typical Composition of Some Chloride Based Baths

Bath Constituents	Quantity g/l
Tin as sodium stannate	40
Copper as cuprous cyanide	8
Free sodium hydroxide	15
Free sodium cyanide	16

The bath operates at conditions of:

Cathode Current Density: 1.5-2.5 A/dm<sup>2</sup>

Temperature 65 ± 2°C

TABLE 19: A Typical Composition of a Bath for the Electrodeposition of Tin-Copper Alloy

Bath Constituents	Quantity g/l
Stannous chloride	49
Nickel chloride	300
Ammonium bifluoride	56
Ammonium hydroxide	To adjust pH to 2.0-2.5

The bath operates under the conditions of:

Cathode Current Density: 1-3 A/dm<sup>2</sup>

Temperature 65-71°C

TABLE 20: A Typical Composition of a Bath for the Electrodeposition of Tin-Nickel Alloys

Bath Constituents	Quantity g/l
Cadmium Fluoborate	230
Tin fluoborate	49
Fluoboric acid (free)	60
Ammonium fluoborate	50
Boric acid	20
Sodium phenolsulphonate	2
Gelatin	2

The bath operates in the conditions of:

pH 3; Temperature 27°C; Cathode Current Density 3 A/dm<sup>2</sup>

TABLE 21: The Composition of a Typical Fluoborate Bath for Electro-deposition of Tin-Cadmium Alloys

Bath Constituents	Quantity g/l
Potassium stannate	105-132
Cadmium oxide	1.2-7
Total potassium cyanide	22-34
Free potassium cyanide	20-26
Potassium hydroxide	12-16

The bath operates in the conditions of:

Cathode Current Density 1-6 A/dm<sup>2</sup>; Temperature 65°C

TABLE 22: The Composition of a Typical Alkaline Bath for the Electro-deposition of Tin-Cadmium Alloys

Bath Constituents	Quantity g/l	
	Still	Barrel
Potassium stannate (tin)	45	36
Zinc cyanide (zinc)	6	8.3
Potassium cyanide	30	34
Potassium hydroxide	7.5	11.3

The bath operates in the conditions of:

Cathode current density 1-8 A/dm<sup>2</sup>; Temperature 65  $\pm$  2°C.

TABLE 23: A Typical Composition for a Cyanide-Potassium Stannate Bath for the Electrodeposition of Tin-Zinc Alloys

Zinc content in deposit %	8	22-25	47-50
Sodium stannate (tin) g/l	30	30	30
Zinc cyanide (zinc) g/l	1	2.5	8
Total cyanide g/l	20	28	4
Free sodium hydroxide g/l	2.5	4-6	5-6

The bath operates in the conditions of:

Cathode current density 1-3 A/dm<sup>2</sup>; Temperature 65  $\pm$  2°C

TABLE 24: A Typical Composition for a Cyanide-Sodium Stannate Bath for the Electrodeposition of Tin-Zinc Alloys

⑧

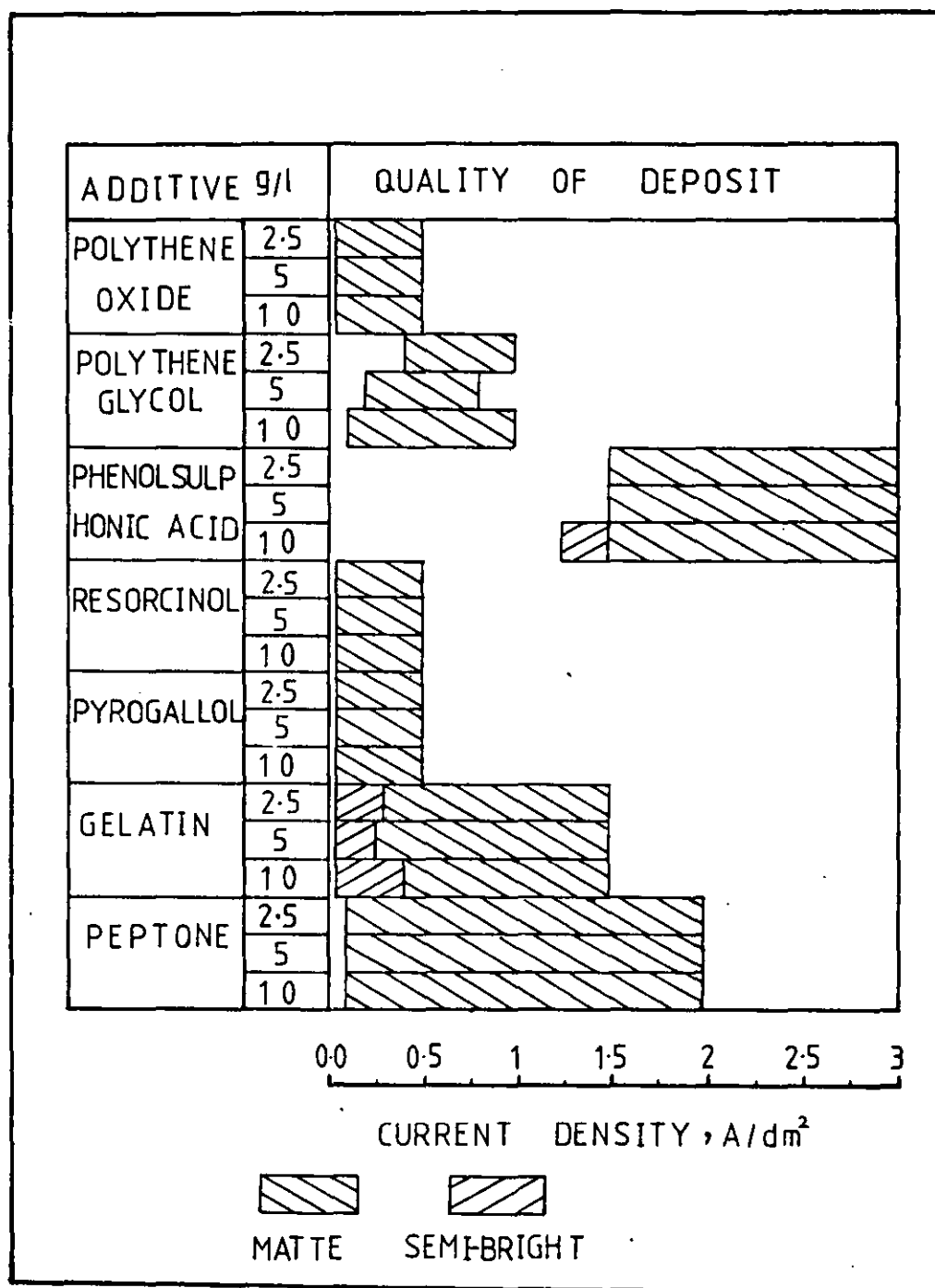


TABLE 25: THE EFFECT OF ADDITIVES ON THE CURRENT DENSITY RANGE OF GOOD DEPOSIT(TIN SOLUTION)

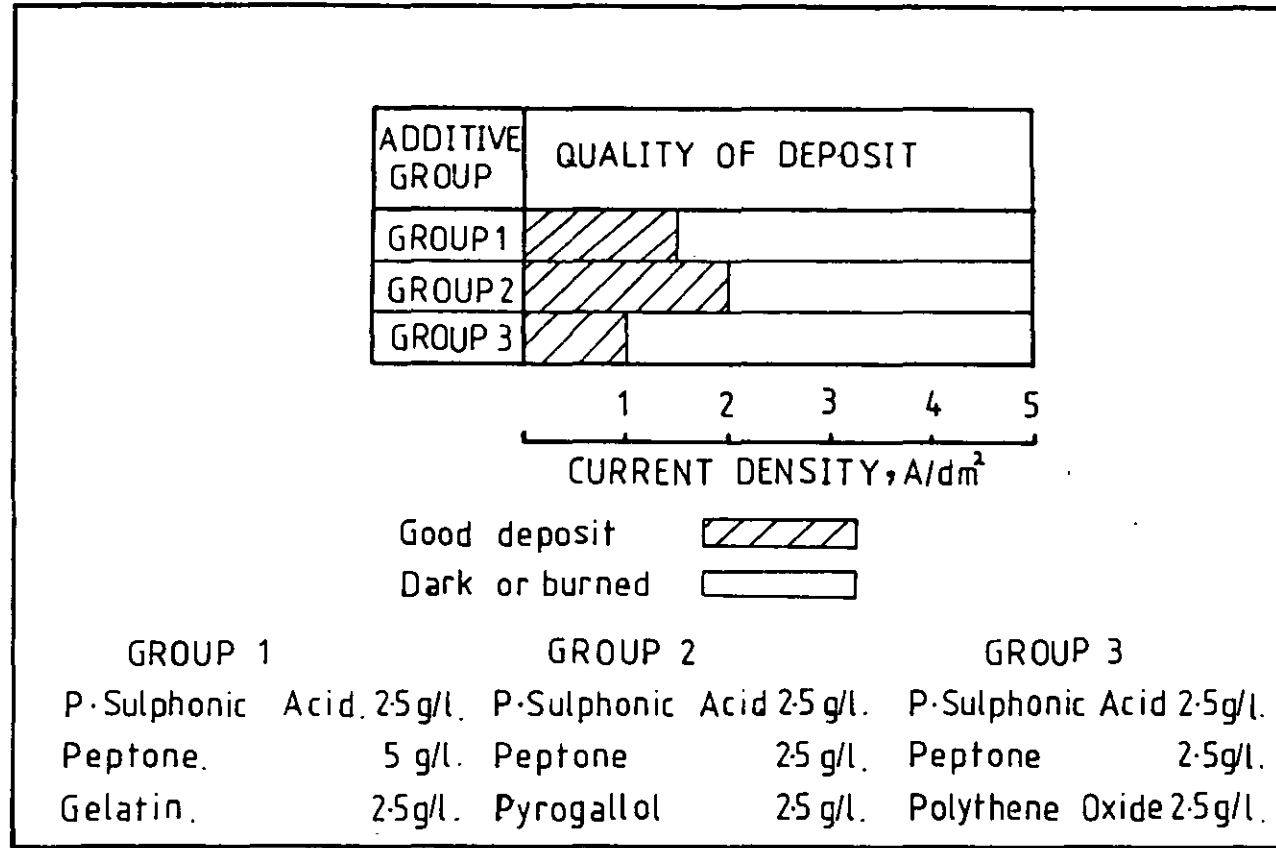


TABLE 26: EFFECT OF ADDITIVES (GROUPS) ON THE CURRENT DENSITY RANGE OF GOOD DEPOSIT(TIN-LEAD SOLUTION).

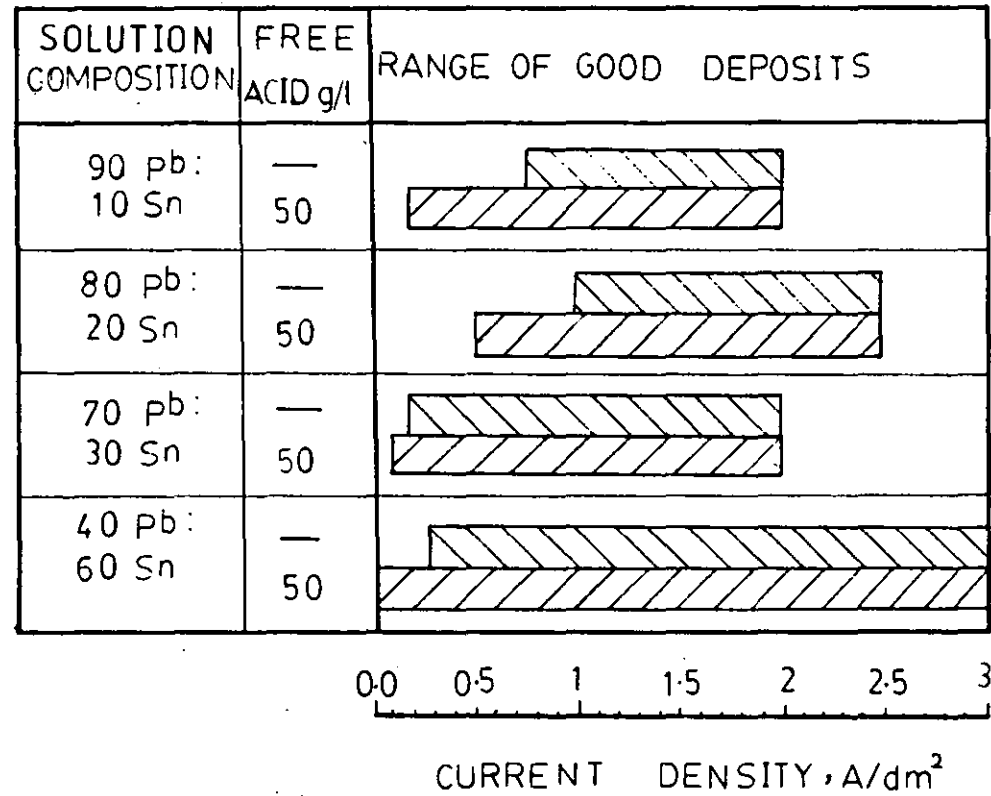


TABLE 27: THE EFFECT OF FREE ACID ON THE CURRENT DENSITY RANGE OF GOOD ALLOYED DEPOSIT (DIFFERENT SOLUTION COMPOSITIONS)

TABLE 28: Some features of deposits obtained from solution of lead/tin ratio 90 Pb:10 Sn, no free acid and with additives

Sample No.	Temperature °C	Current density A/dm <sup>2</sup>	pH	Conductivity mS cm <sup>-1</sup>	Weight of deposit gx10 <sup>-4</sup>	Average Thickness μm	Cathode Current Efficiency %	Quality of Deposit
1	25	0.75	1.25	71.5	270	6.5	99.99	Dark
2	"	1	-	-	351	8.5	99.67	Slightly dark
3	"	1.5	-	-	549	13	97.48	Good smooth
4	"	1.75	-	-	-	-	-	Good smooth
5	"	2	-	-	-	-	-	Good smooth
6	"	2.5	-	-	-	-	-	Good rough
7	"	3	-	-	-	-	-	Good rough
8	40	0.75	1.26	82	274	6.5	101.4	Good smooth
9	"	1	-	-	334	8	94	Good smooth
10	"	1.5	-	-	438	10.5	84.4	Good smooth
11	"	2	-	-	-	-	-	Good smooth
12	55	0.75	1.23	95	300	7	111	Good rough
13	"	1	-	-	390	9	110.8	Good rough
14	"	1.5	-	-	585	14	112.7	Good rough
15	"	2	-	-	-	-	-	Good rough
16	70	0.75	1.25	102	325	8	120	Good rough
17	"	1	-	-	415	10	117.82	Good rough
18	"	1.5	-	-	599	14.5	115.4	Good rough
19	"	2	-	-	-	-	-	Good rough
20	"	2.5	-	-	-	-	-	Good rough

TABLE 29: Some features of deposits obtained from solution of lead/tin ratio 80 Pb:20 Sn, no free acid and with additives

Sample No.	Temperature °C	Current Density A/dm <sup>2</sup>	pH	Conductivity mS cm <sup>-1</sup>	Weight of Deposit g x 10 <sup>-4</sup>	Average Thickness μm	Cathode Current Efficiency %	Quality of Deposit
1	25	0.5	1.2	66	168	4.5	99.84	Dark
2	"	1	-	-	335	8.5	99.54	Smooth, dark
3	"	1.5	-	-	491	12.5	97.3	Smooth, bright
4	"	2	-	-	-	-	-	Smooth, bright
5	"	2.5	-	-	-	-	-	Dark
6	40	0.5	1.3	-	172	4.5	100.8	Smooth good
7	"	1	-	-	335	8.5	99.6	Dark in middle
8	"	1.5	-	-	509	13	100.1	Smooth, good
9	"	2	-	-	-	-	-	Smooth, good
10	"	2.5	-	-	-	-	-	Smooth, good
11	55	6.5	1.22	-	182	4.5	108	Good, rough
12	"	1	-	-	360	9.0	107	Good, rough
13	"	1.5	-	-	545	13.5	108	Good, rough
14	"	2	-	-	-	-	-	Good, rough
15	"	2.5	-	-	-	-	-	Good, rough
16	70	0.5	1.2	-	187	5	111	Dull, rough
17	"	1	-	-	285	7	110	Dull, rough
18	"	1.5	-	-	553	14	109.6	Dull, rough
19	"	2	-	-	-	-	-	Dull, rough
20	"	2.5	-	-	-	-	-	Dull, rough

TABLE 30: SOME FEATURES OF DEPOSITS OBTAINED FROM SOLUTION OF LEAD/  
TIN RATIO 80 Pb:20 Sn, 50 g/l FREE ACID AND WITH ADDITIVES

Sample No.	Temperature °C	Current Density A/dm <sup>2</sup>	Weight of Deposit gx10 <sup>-4</sup>	Cathode Current Efficiency %	Average Thickness μm	Quality of Deposit
1	25	0.5	169	100.4	4.2	Matt
2	25	1	337	100.1	8.5	Matt
3	25	1.5	497	98.5	12.5	Very smooth
4	25	2				Matt, dark edges
5	25	2.5				Dark
6	40	0.5	181	106.1	4.5	Matt
7	40	1	353	105.7	9	Matt
8	40	1.5	512	103	13	Matt
9	40	2				Good, smooth
10	40	2.5				" "
11	55	0.5	192	112.6	5	" "
12	55	1	389	115.7	10	" "
13	55	1.5	557	112.5	14	" "
14	55	2				Dark at edges
15	55	2.5			4	Dark
16	70	0.5	161	94.4	6	Dull
17	70	1	238	84	13.5	Matt
18	70	1.5	546	110.3		Dull rough
19	70	2				" "
20	70	2.5				" "

TABLE 31: Some features of deposits obtained from solution of lead/tin ratio 40 Pb:6P Sn, no free acid and with additives

Sample No.	Temperature °C	Current Density A/dm <sup>2</sup>	Weight of Deposit gx10 <sup>-5</sup>	Cathode Current Efficiency %	Conductivity mS cm <sup>-1</sup>	Quality of Deposit
1	25	0.5	1780	100.6	60	Dull, smooth
2	"	1	3412	100.5	-	Good, smooth
3	"	1.5	4060	99.96	-	Good, smooth
4	"	2	6388	-	-	Good, smooth
5	"	2.5	7314	-	-	Dark
6	40	0.5	1794	101.4	70	Good, matt
7	"	1	3450	100.8	-	Good, smooth
8	"	1.5	5131	102	-	Good, smooth
9	"	2	6998	-	-	Dull, smooth
10	"	2.5	7695	-	-	Dark
11	55	0.5	1792	99.99	91.5	Good, smooth
12	"	1	3499	101.6	-	Good, smooth
13	"	1.5	5162	101.6	-	Good, dark edges
14	"	2	6810	-	-	Good, matt
15	"	2.5	7856	-	-	Dark

①

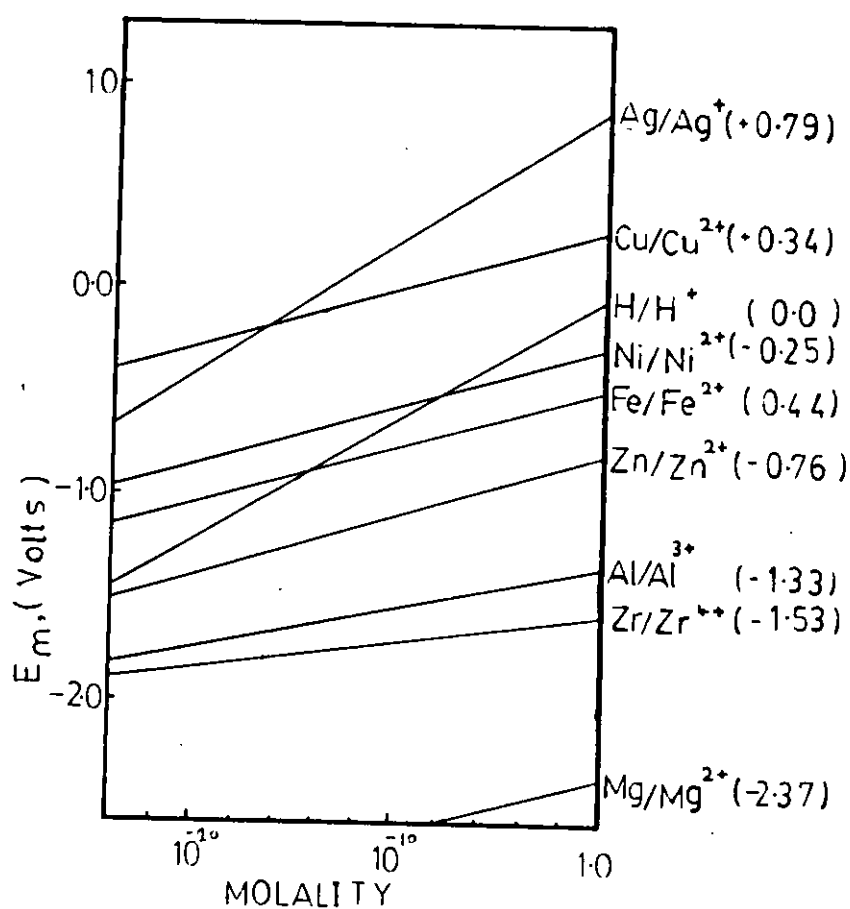


FIGURE 1: VARIATION OF ELECTRODE POTENTIAL WITH ION CONCENTRATION FOR SOME METALS (17)

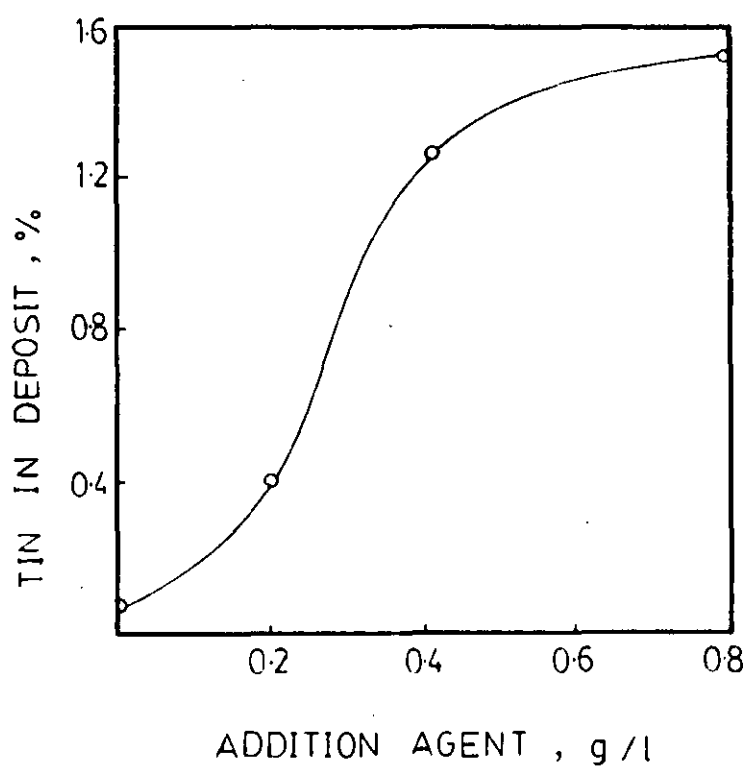


FIGURE 2: EFFECT OF ADDITION AGENT ON THE COMPOSITION OF ELECTRODEPOSITED LEAD-TIN ALLOY(SCHEMATIC).

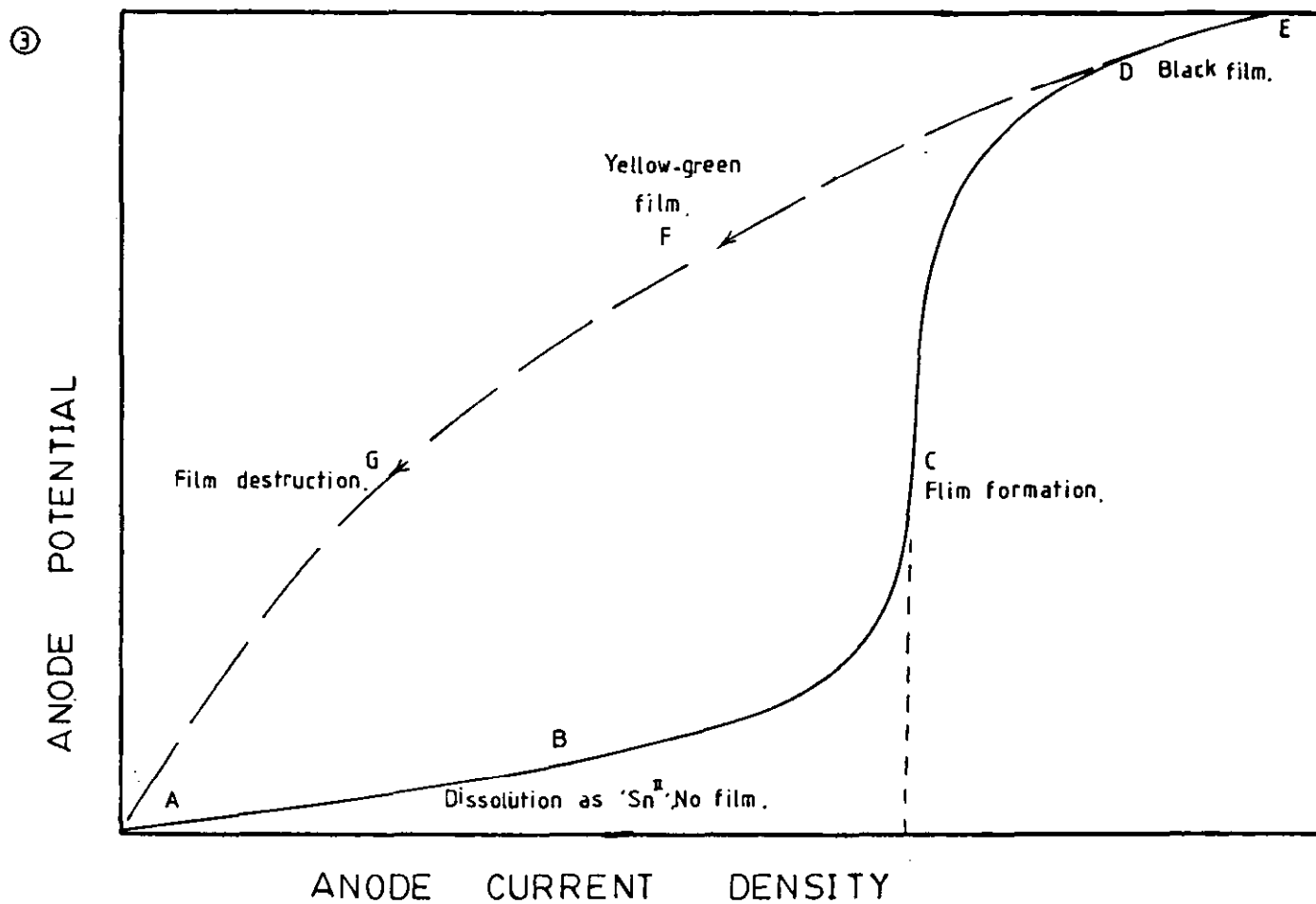


FIGURE 3: A SCHEMATIC CURVE SHOWING THE ANODIC BEHAVIOUR OF TIN IN STANNATE SOLUTIONS

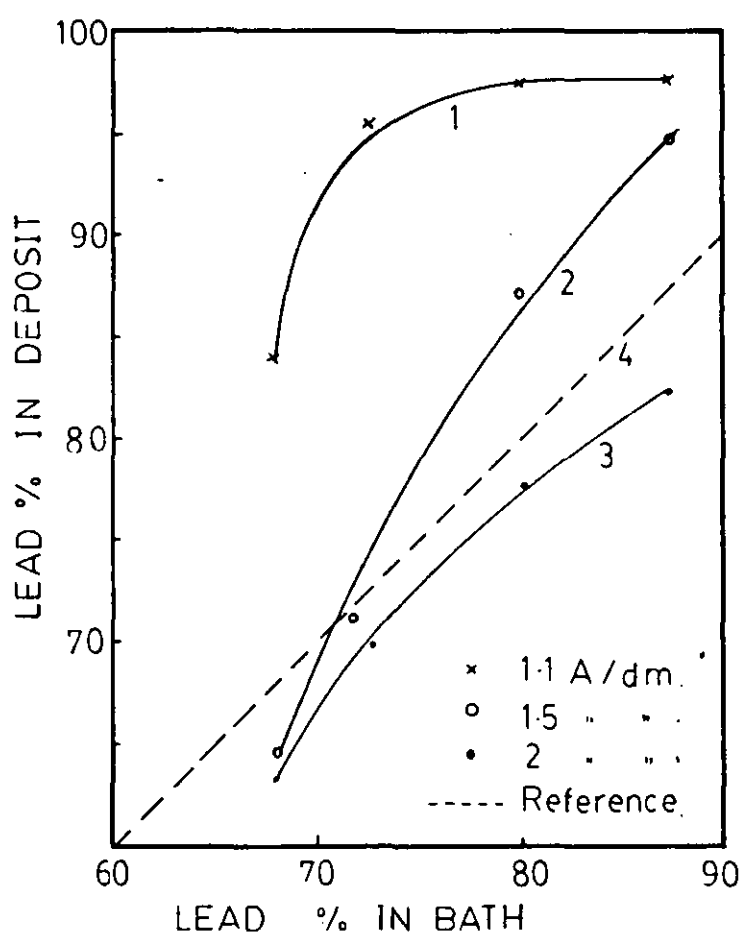


FIGURE 4: EFFECT OF INCREASING CD ON THE PERCENTAGE OF MORE NOBLE METAL IN DEPOSIT(32)

⑤

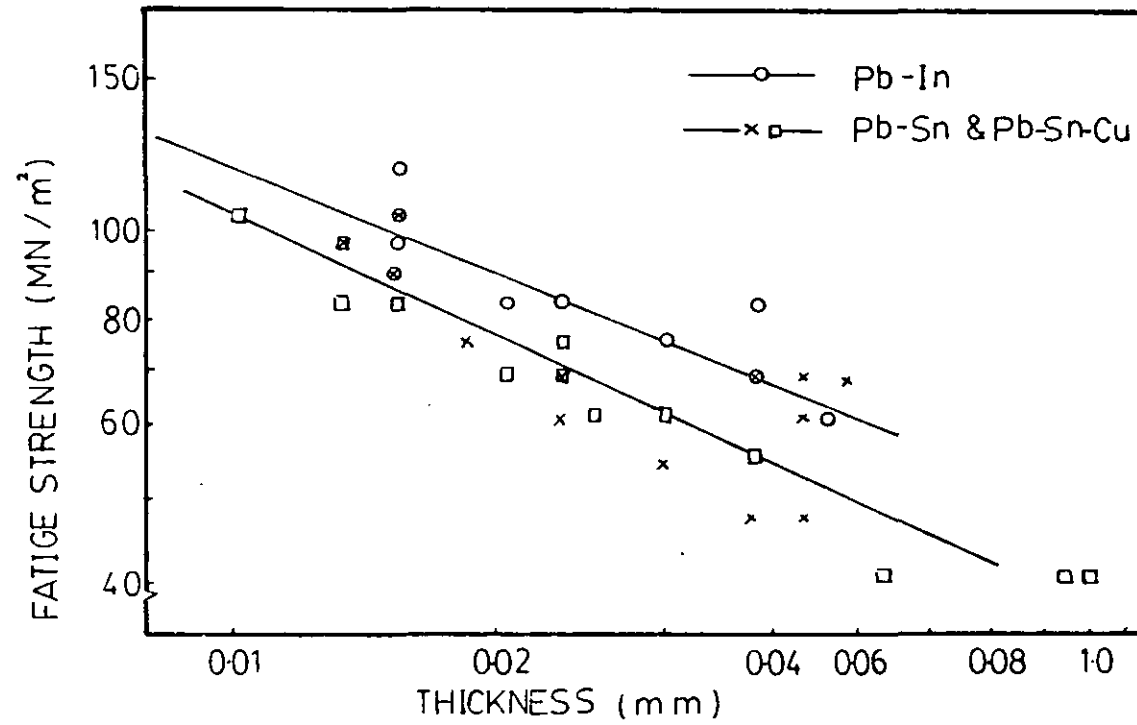


FIGURE 5: EFFECT OF OVERLAY THICKNESS ON FATIGUE STRENGTH

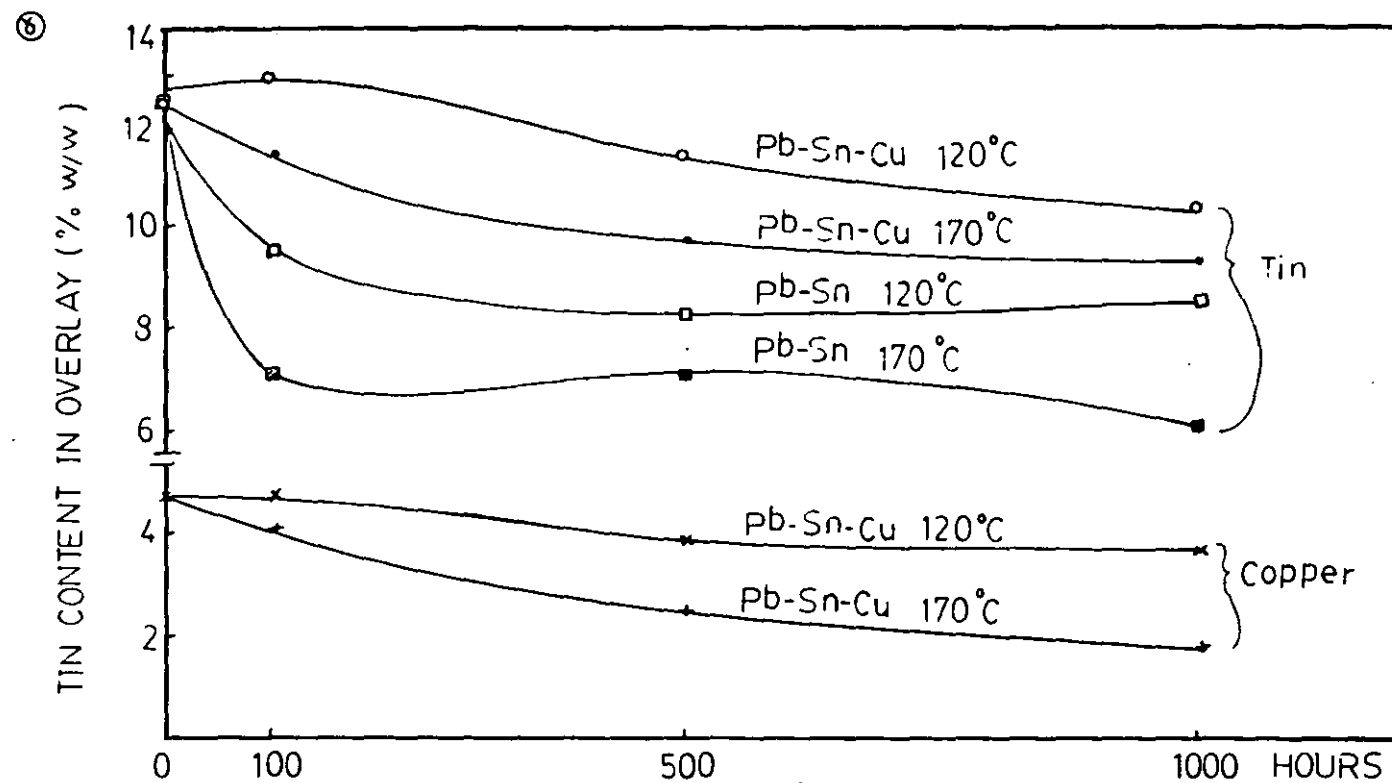
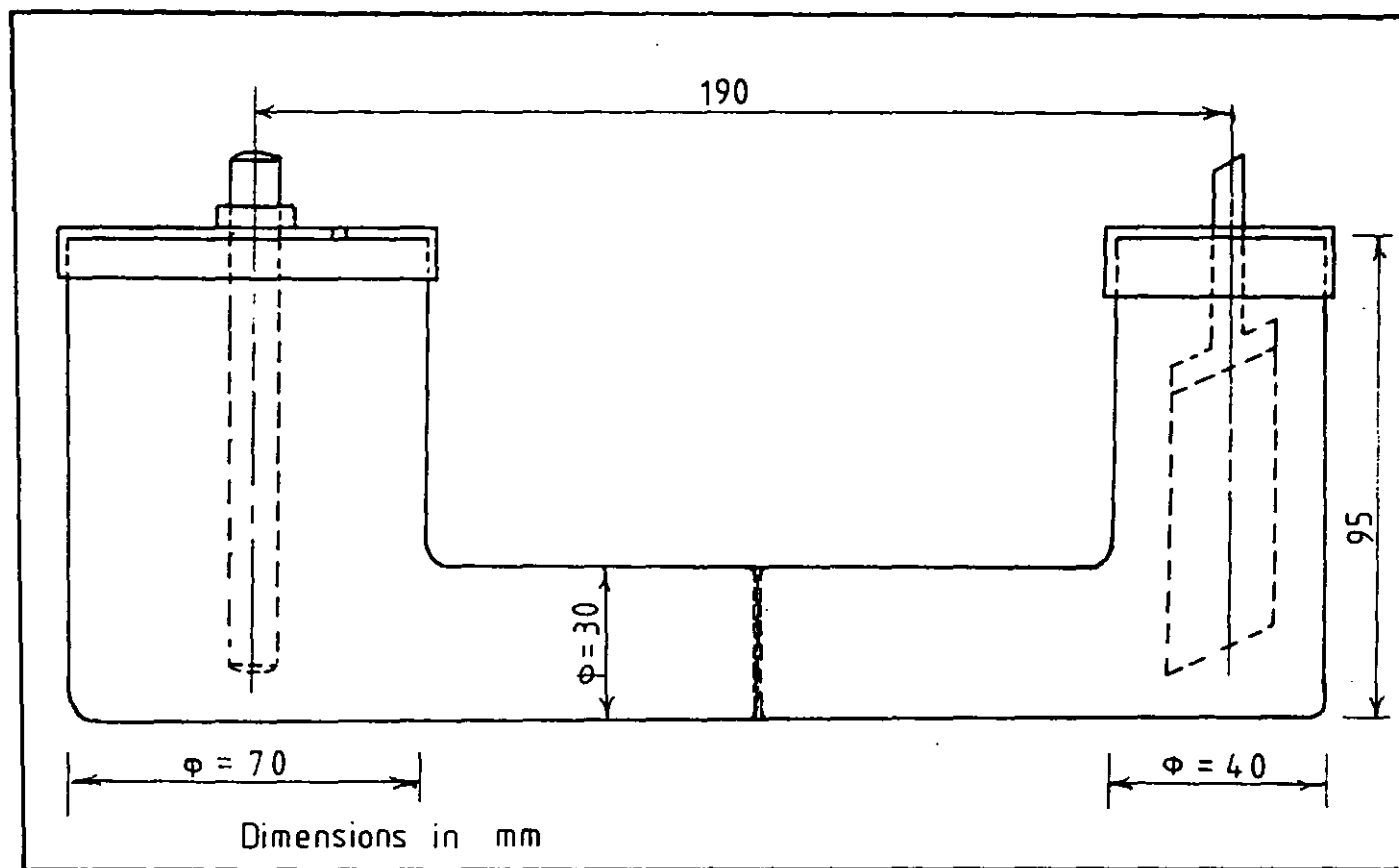


FIGURE 6: TIN DIFFUSION IN LEAD-TIN AND LEAD-TIN-COPPER OVERLAYS

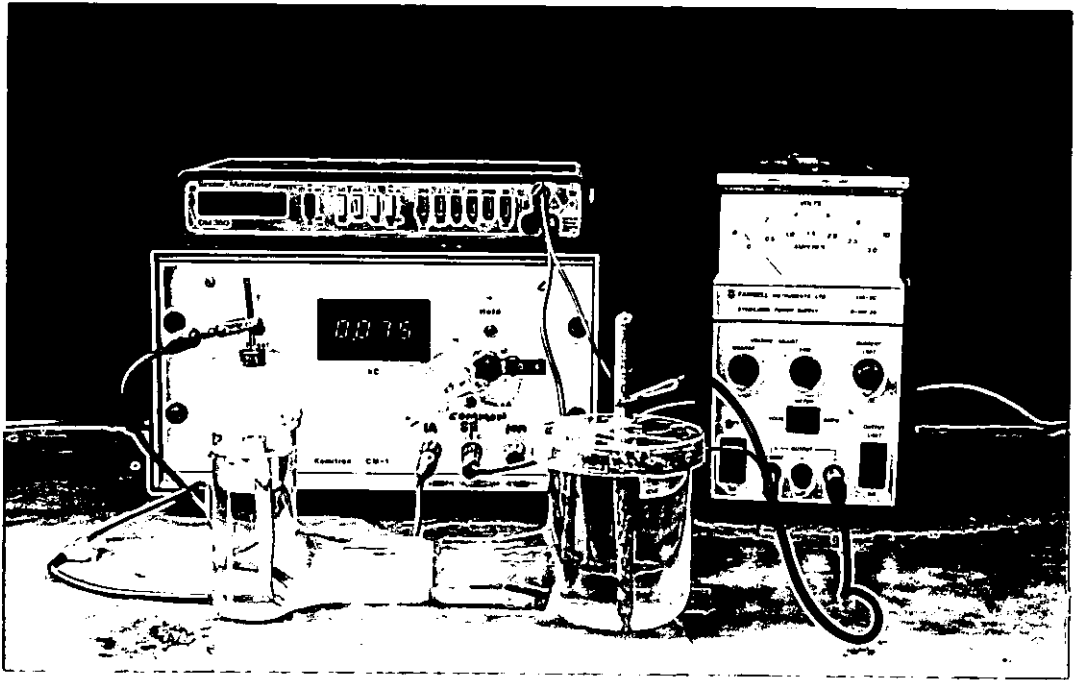
⑦



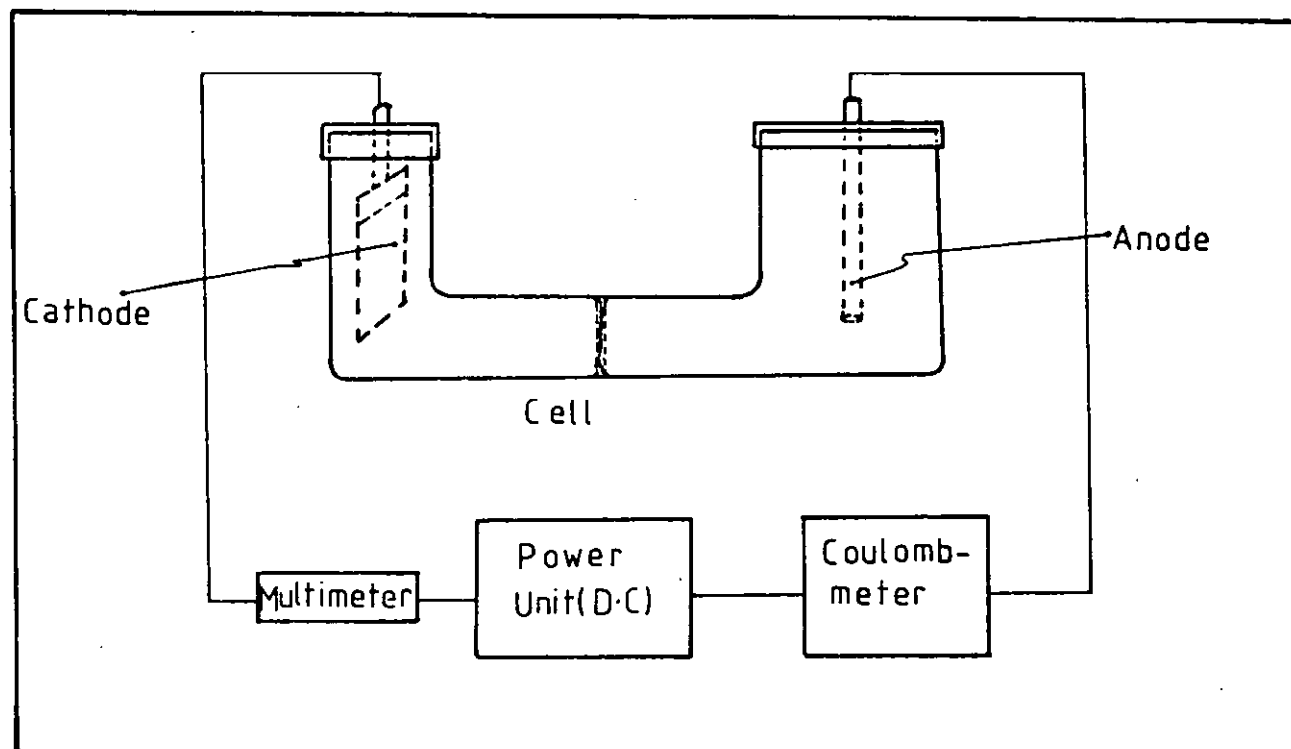
SCHEMATIC DIAGRAM OF THE CELL (Full Scale).

FIGURE 7: TWO COMPARTMENT CELL FOR PREPARING TIN SULPHAMATE SOLUTION BY FARADAIC METHOD

CELL  
FIGURE 7a: THE TWO COMPARTMENT<sup>^</sup> AT WORK  
(Photograph)



⑧



## ELECTRODE ASSEMBLY

FIGURE 8: THE ELECTRODE ASSEMBLY OF THE CELL.

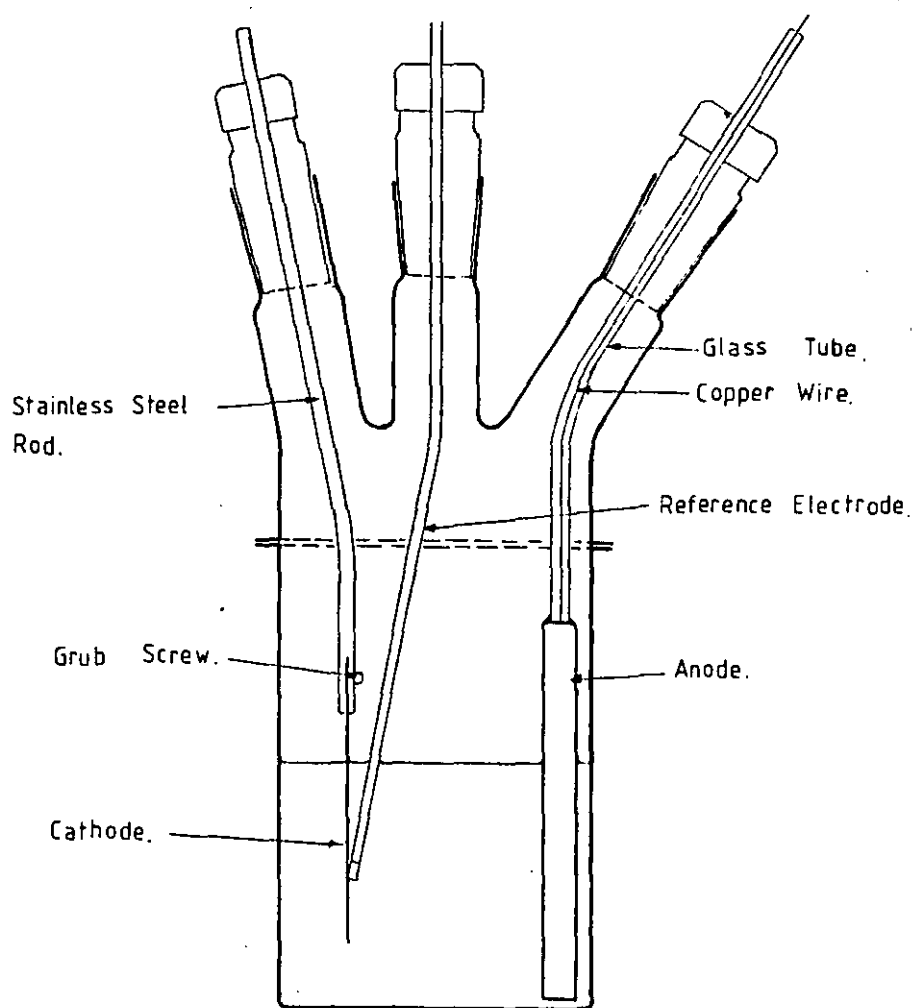
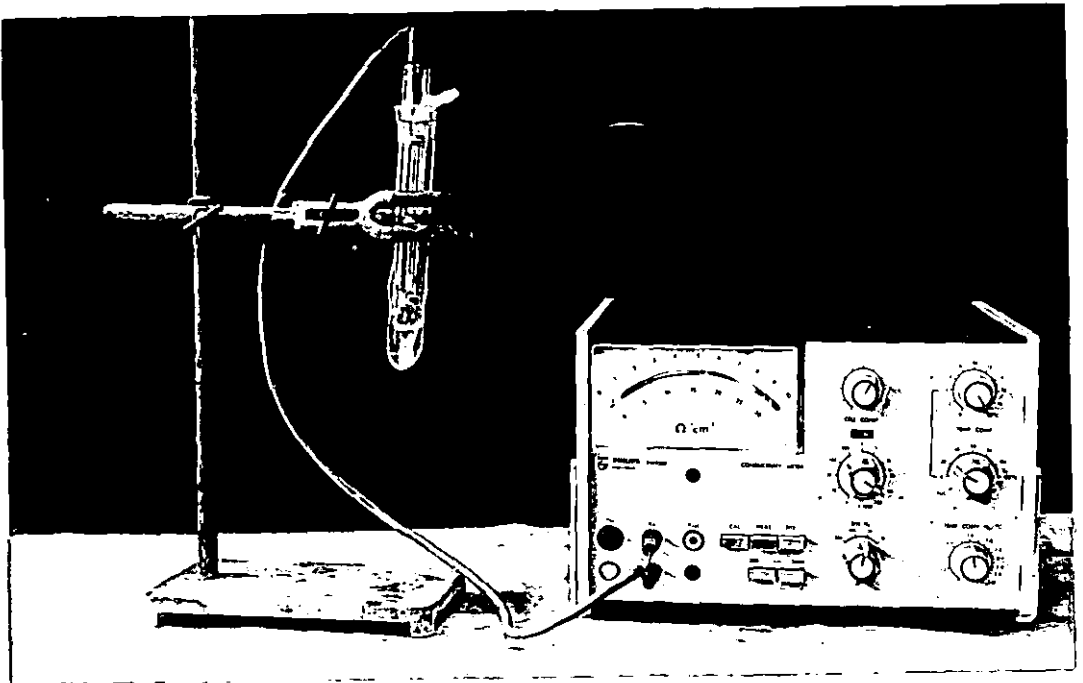
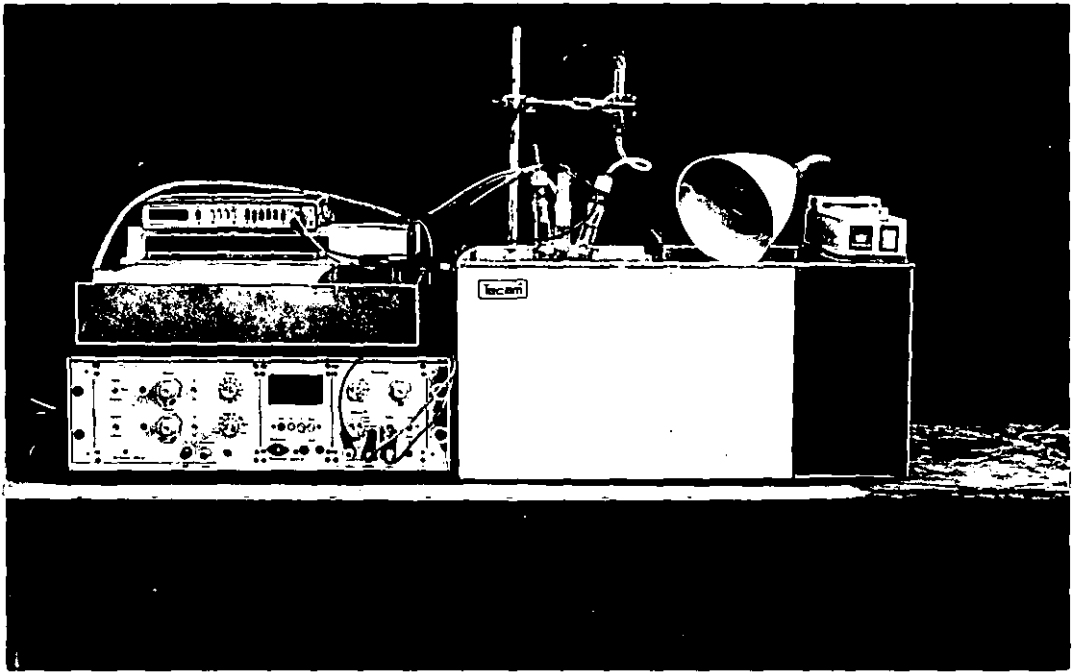


FIGURE 9: THE SMALL CELL ELECTRODE ASSEMBLY

FIGURE 10: THE EQUIPMENT USED FOR PLATING TRIALS AND PLOTTING  
THE POLARIZATION DATA

FIGURE 11: THE CONDUCTIVITY METER AND CONDUCTIVITY CELL FOR  
MEASURING THE CONDUCTIVITY OF THE SOLUTION



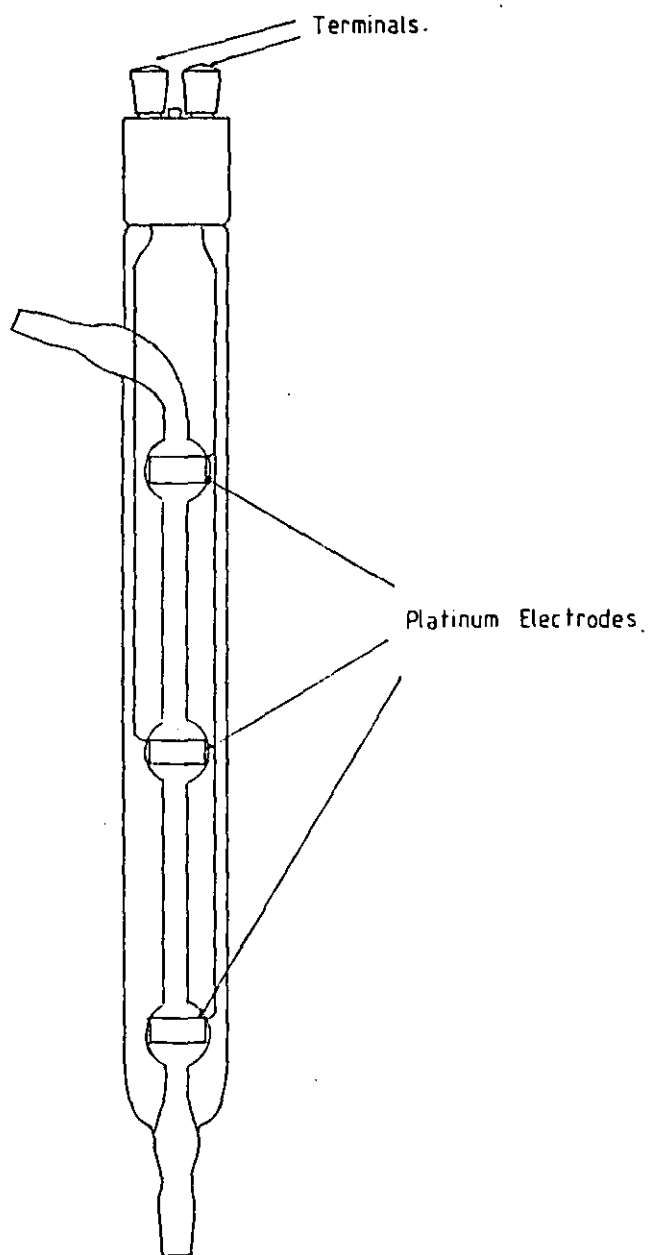


FIGURE 12: THE PRE-CALIBRATED CELL FOR CONDUCTIVITY METER  
(SCHEMATIC DIAGRAM)

⑬

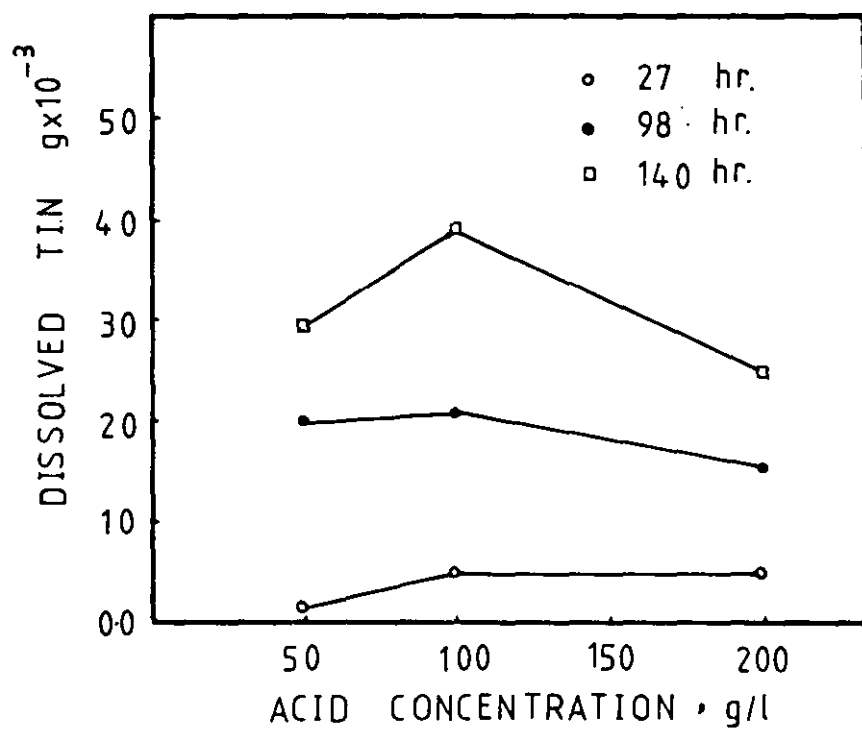


FIGURE 13: THE EFFECT OF SULPHAMIC ACID CONCENTRATION ON DISSOLUTION OF TIN BY CHEMICAL REACTION

14

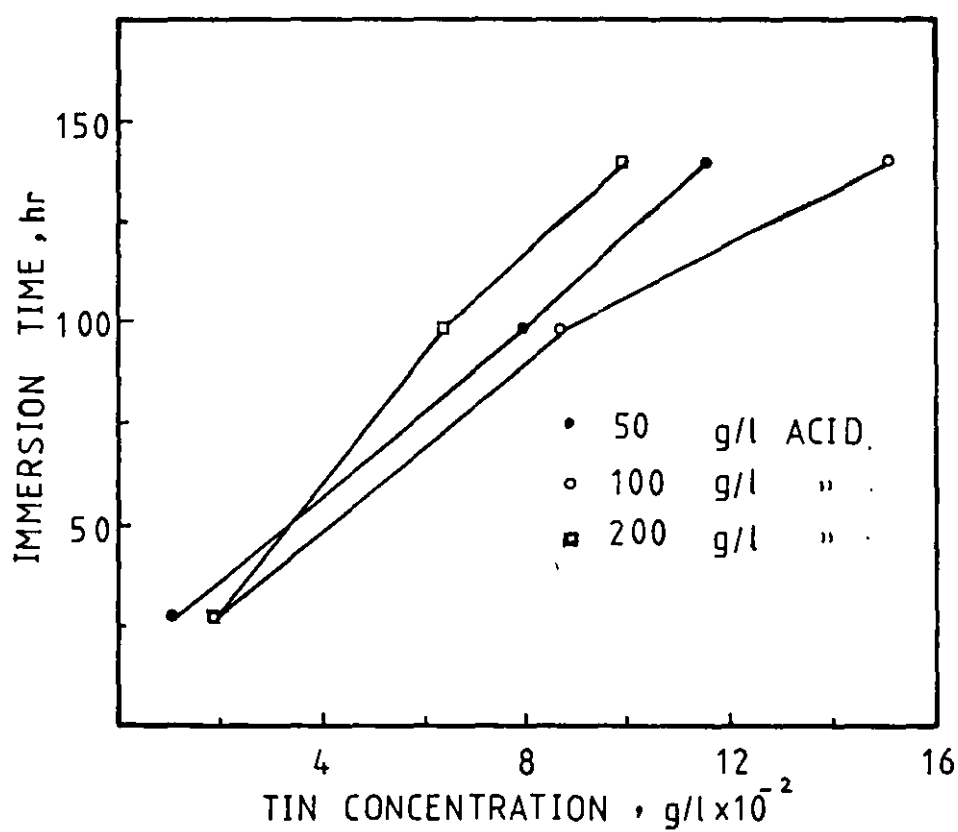


FIGURE 14: THE EFFECT OF TIME IMMERSION ON TIN DISSOLUTION BY CHEMICAL REACTION

⑮

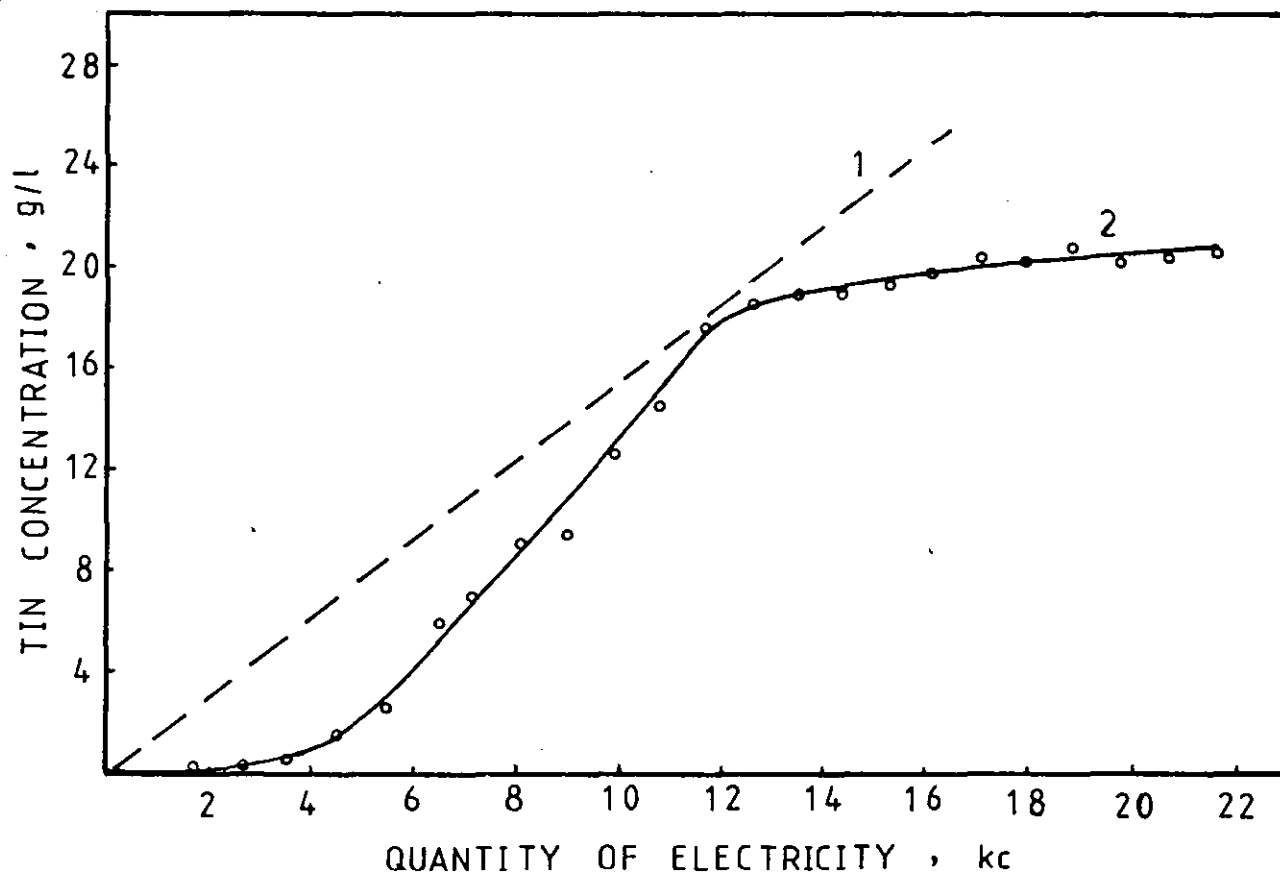


FIGURE 15: TIN CONCENTRATION OF SOLUTION PRODUCED BY THE FARADAIC METHOD WITH RESPECT TO THE QUANTITY OF COULOMB PASSED THROUGH THE CELL

- 1) FARADAIC DISSOLUTION AT 100% EFFICIENCY
- 2) EXPERIMENTAL DATA

16

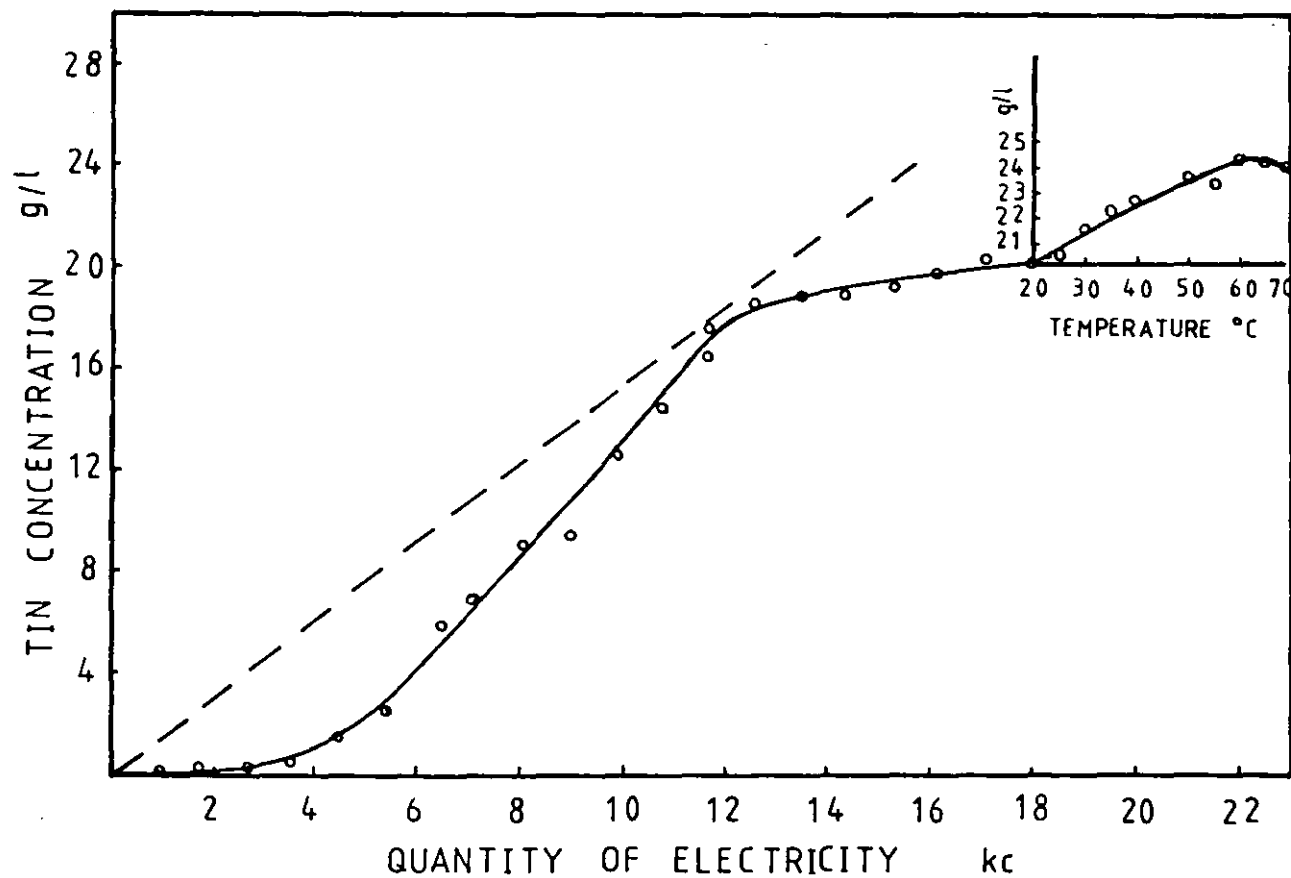


FIGURE 16: THE EFFECT OF TEMPERATURE ON THE SOLUBILITY LIMIT OF TIN IN SULPHAMIC ACID

⑪

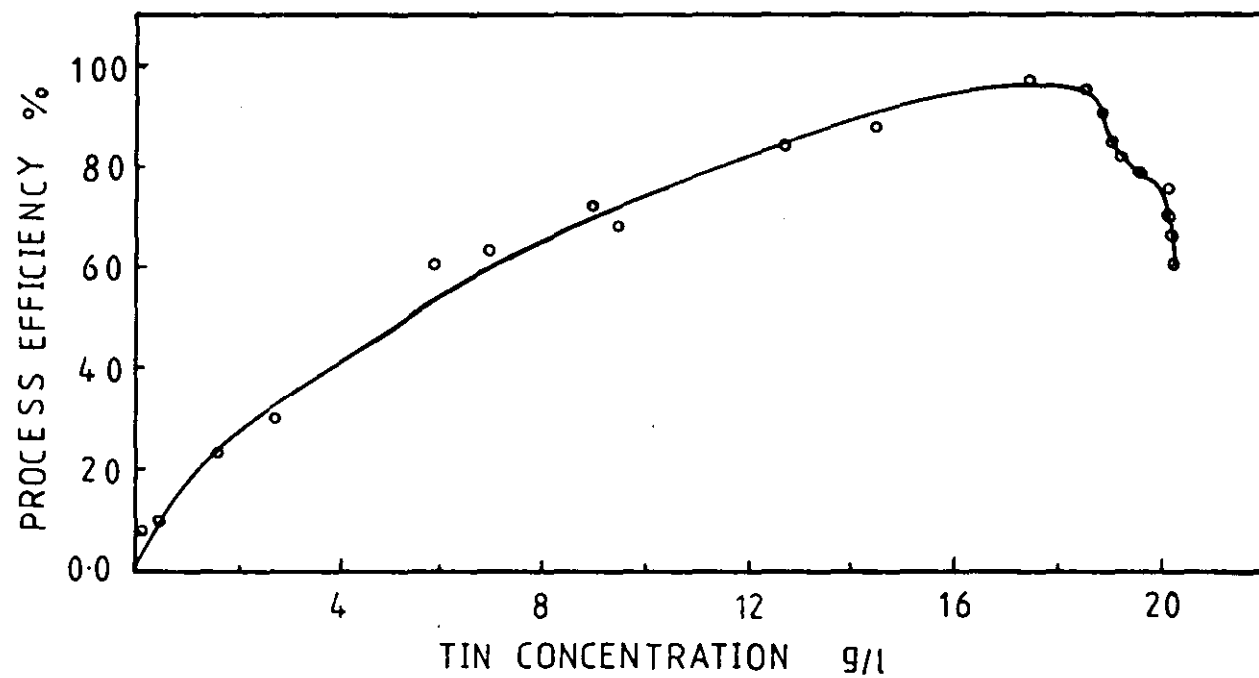


FIGURE 17: THE EFFICIENCY OF THE PROCESS OF TIN DISSOLUTION WITH RESPECT TO THE CONCENTRATION OF TIN IN SOLUTION PRODUCED BY FARADAIC METHOD

(18)

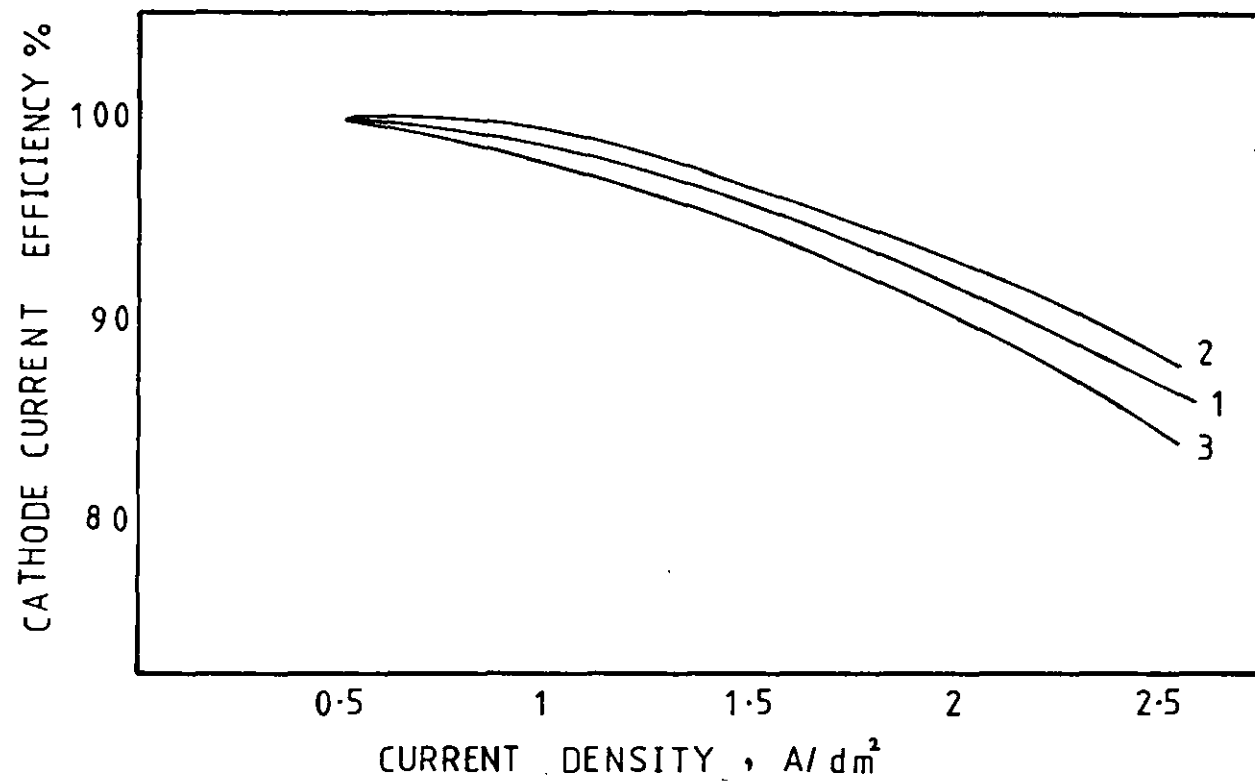


FIGURE 18: THE EFFECT OF CURRENT DENSITY ON THE CATHODE CURRENT EFFICIENCY CURVE.  
 CURVE 1: FOR SOLUTIONS CONTAINING 2.5 g/l OF PHENOLSULPHONIC ACID, PEPTONE AND GELATIN  
 CURVE 2: FOR SOLUTIONS CONTAINING 2.5 g/l OF PHENOLSULPHONIC ACID, PEPTONE AND PYROGALLOL  
 CURVE 3: FOR SOLUTIONS CONTAINING 2.5 g/l OF PHENOLSULPHONIC ACID, PEPTONE AND POLYETHYLENE OXIDE

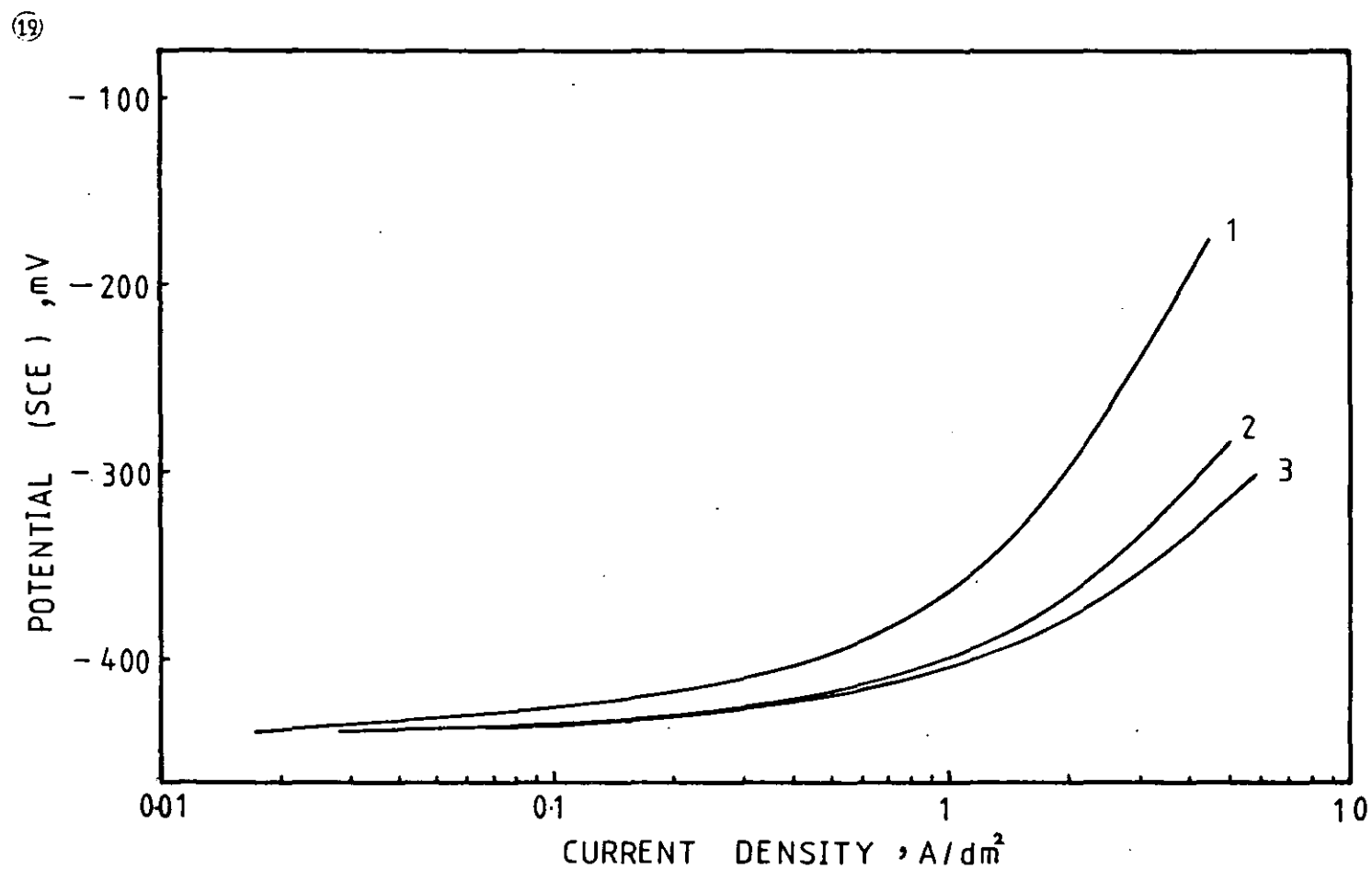


FIGURE 19: EFFECT OF PHENOLSULPHONIC ACID ON THE ANODIC POLARIZATION OF TIN SULPHAMATE SOLUTION.  
CURVE 1: FOR SOLUTION CONTAINING 2.5 g/l  
CURVE 2: FOR SOLUTION CONTAINING 5 g/l  
CURVE 3: FOR SOLUTION CONTAINING 10 g/l

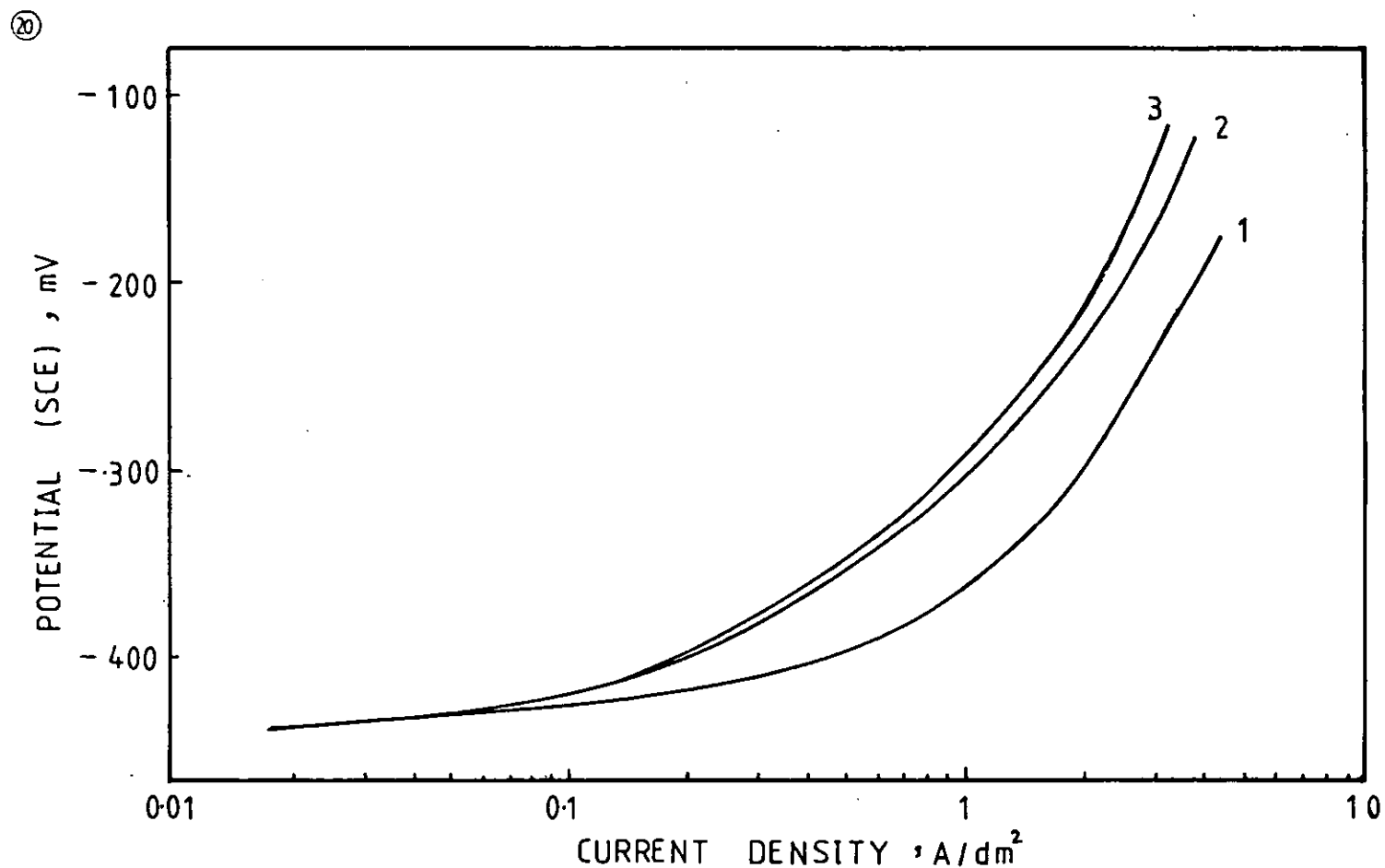


FIGURE 20: ANODIC POLARIZATION FOR TIN SULPHAMATE SOLUTION CONTAINING DIFFERENT AMOUNTS OF PYROGALLOL.

CURVE 1: NO ADDITIVES; CURVE 2: FOR SOLUTION CONTAINING 2.5 g/l, and  
CURVE 3: FOR SOLUTION CONTAINING 10 g/l

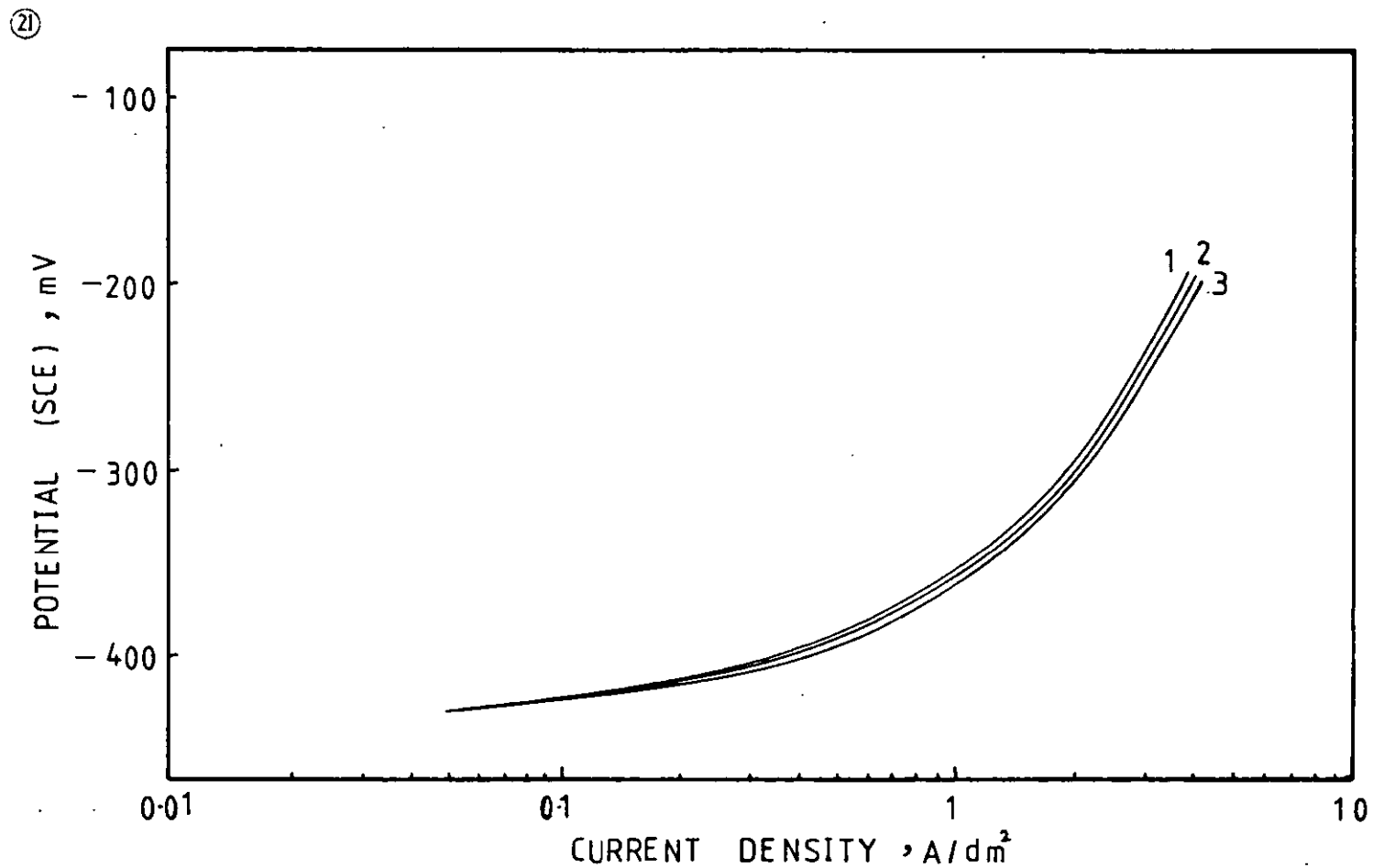


FIGURE 21: ANODIC POLARIZATION CURVES FOR TIN SULPHAMATE SOLUTIONS CONTAINING GELATIN.

CURVE 1: FOR SOLUTION CONTAINING 2.5 g/l  
CURVE 2: FOR SOLUTION CONTAINING 5 g/l, AND  
CURVE 3: FOR SOLUTION CONTAINING 10 g/l

②

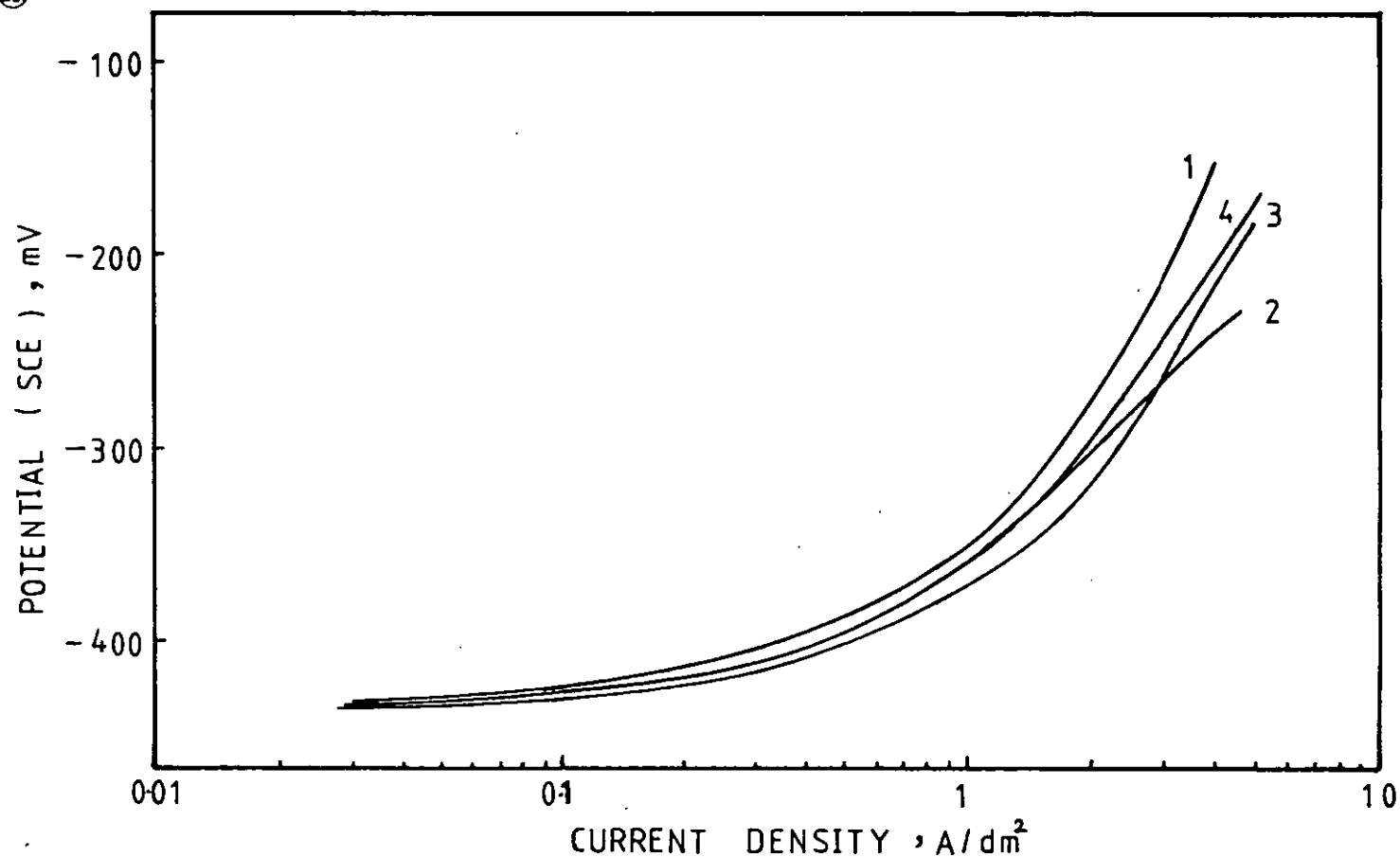


FIGURE 22: ANODIC POLARIZATION CURVES FOR TIN SULPHAMATE SOLUTION.

- CURVE 1: FOR SOLUTION CONTAINING 2.5 g/l PHENOLSULPHONIC ACID, PEPTONE AND GELATIN  
 CURVE 2: FOR SOLUTION CONTAINING 2.5 g/l PHENOLSULPHONIC ACID, PEPTONE AND PYROGALLOL  
 CURVE 3: FOR SOLUTION CONTAINING 2.5 g/l PHENOLSULPHONIC ACID, PEPTONE AND POLYETHYLENE OXIDE  
 CURVE 4: FOR SOLUTION WITHOUT ADDITIVES

23

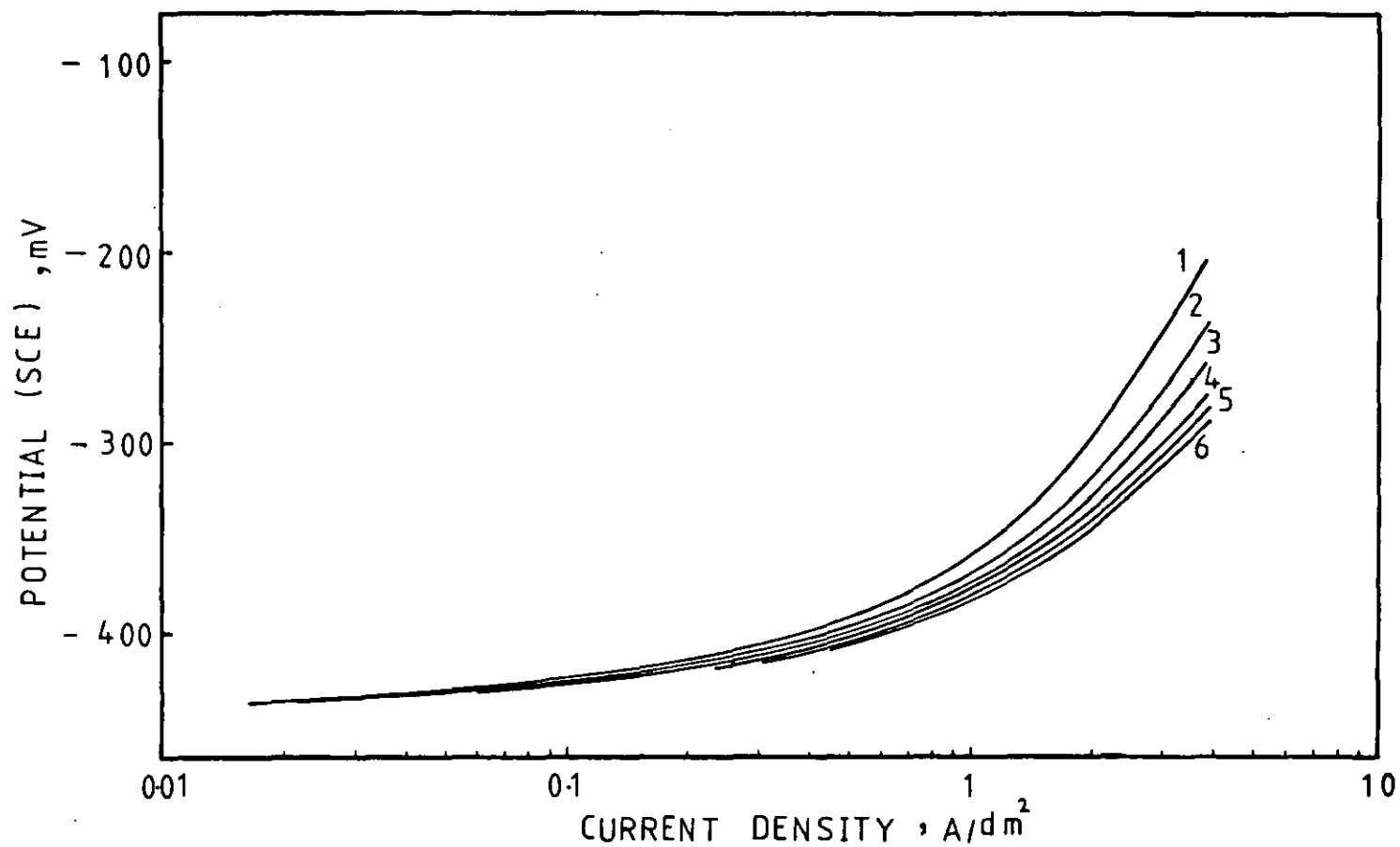


FIGURE 23: THE EFFECT OF TEMPERATURE ON THE ANODIC POLARIZATION CURVES OF TIN SULPHAMATE SOLUTIONS.  
 CURVE 1: At 20°C; CURVE 2: AT 30°C; CURVE 3: At 40°C; CURVE 4: At 50°C; CURVE 5: At 60°C  
 CURVE 6: At 70°C.

24

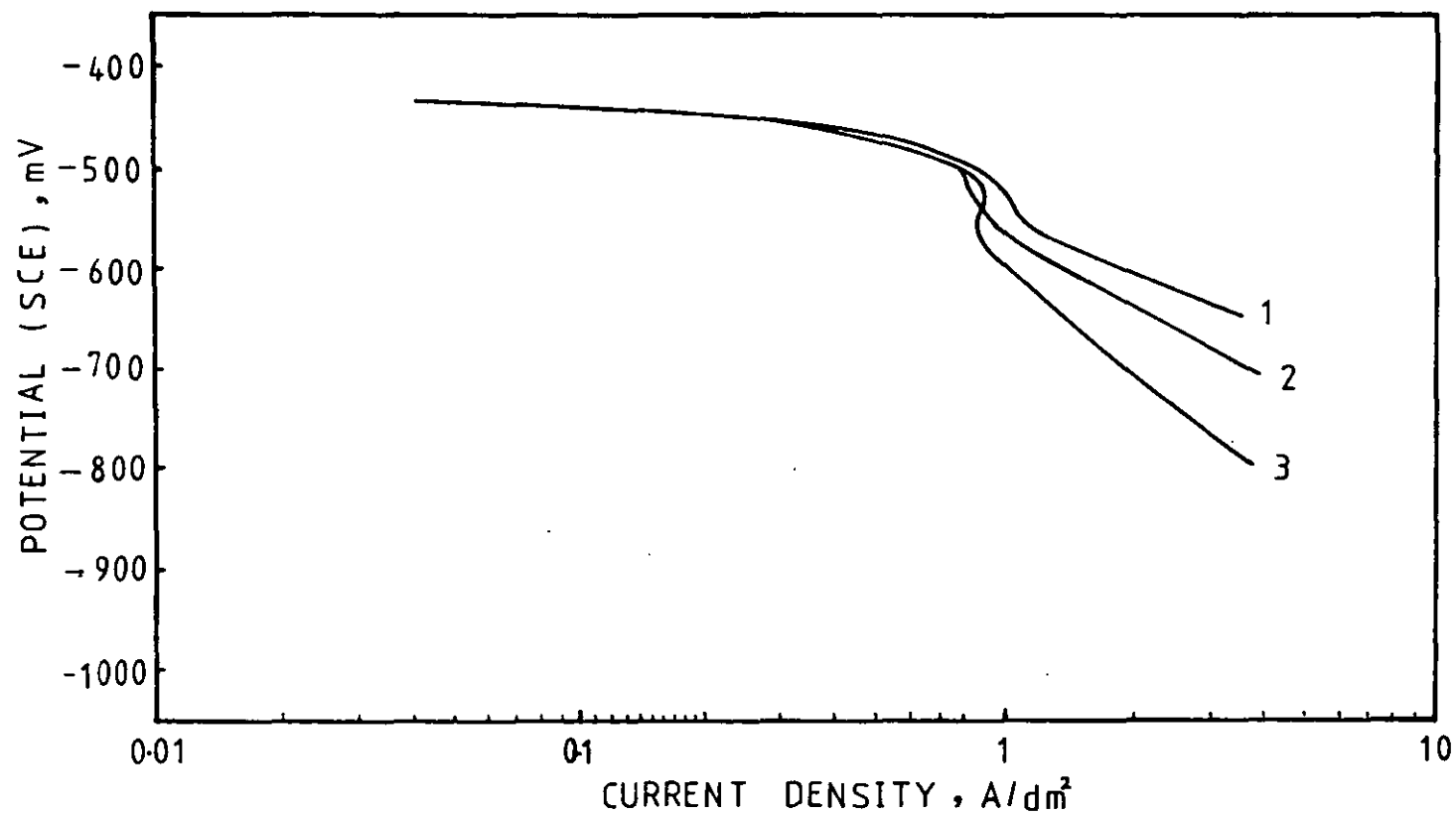


FIGURE 24: EFFECT OF SWEEP RATE ON CATHODIC BEHAVIOUR OF TIN SULPHAMATE SOLUTION.  
CURVE 1: FOR 30 mV/min; CURVE 2: FOR 60 mV/min; CURVE 3: FOR 120 mV/min

25

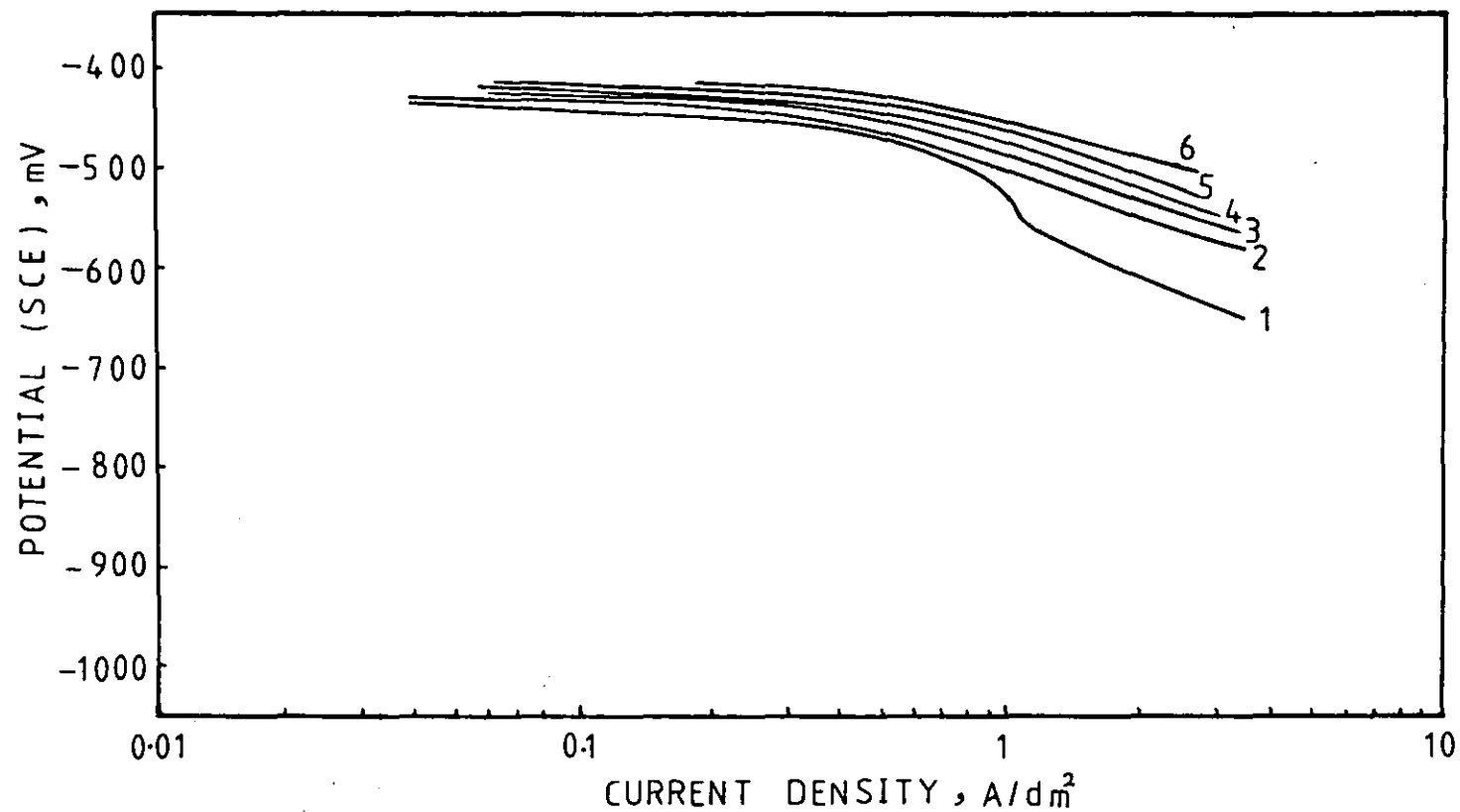


FIGURE 25: EFFECT OF TEMPERATURE ON CATHODIC BEHAVIOUR OF TIN SULPHAMATE SOLUTION.

CURVE 1: At 20°C; CURVE 2: At 30°C; CURVE 3: At 40°C; CURVE 4: At 50°C; CURVE 5: At 60°C  
CURVE 6: At 70°C.

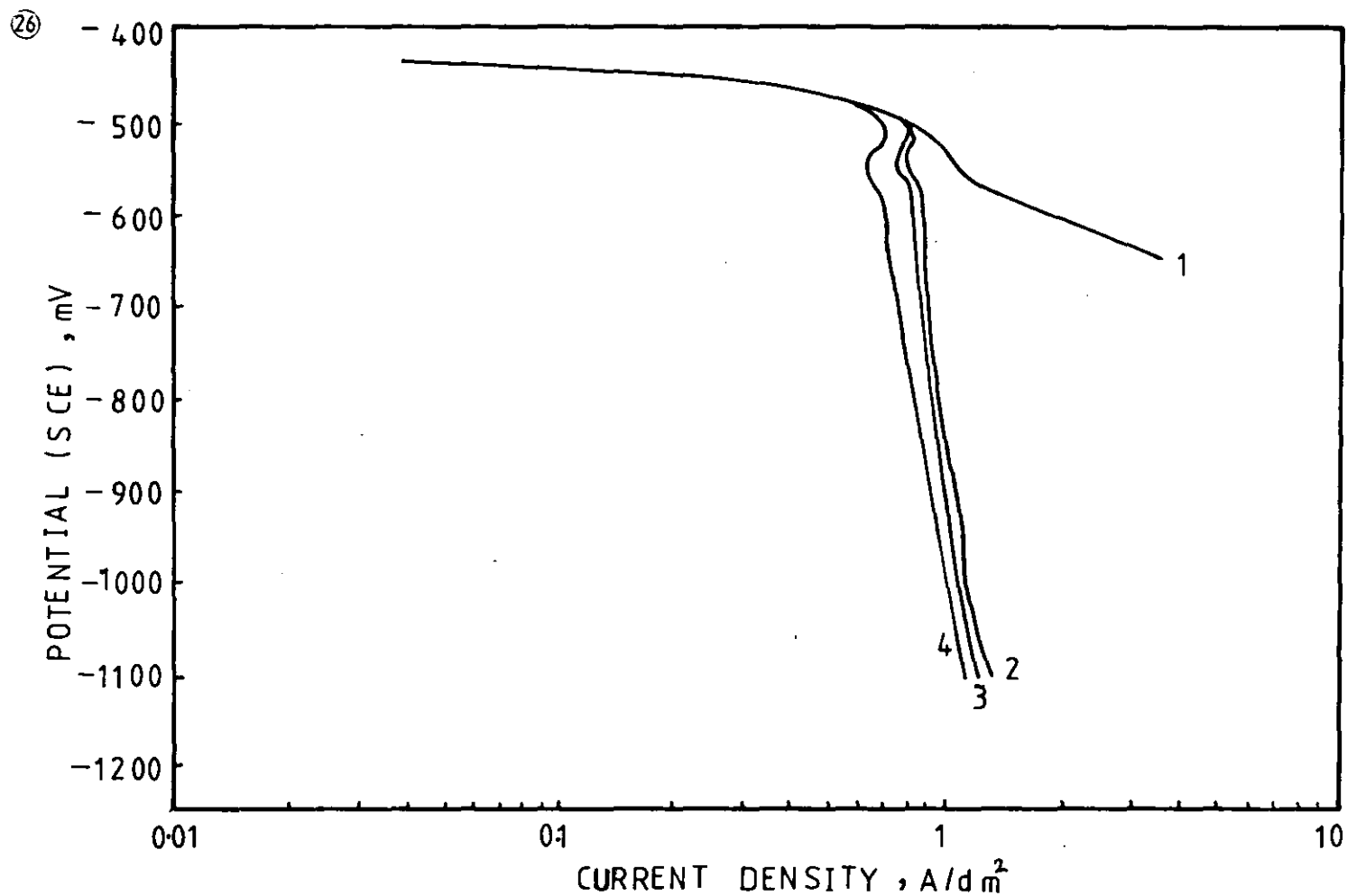


FIGURE 26: CATHODIC BEHAVIOUR OF TIN SULPHAMATE SOLUTION CONTAINING GELATIN,  
CURVE 1: NO ADDITIVES; CURVE 2: FOR 2.5 g/l; CURVE 3: FOR 5 g/l; and  
CURVE 4: FOR 10 g/l

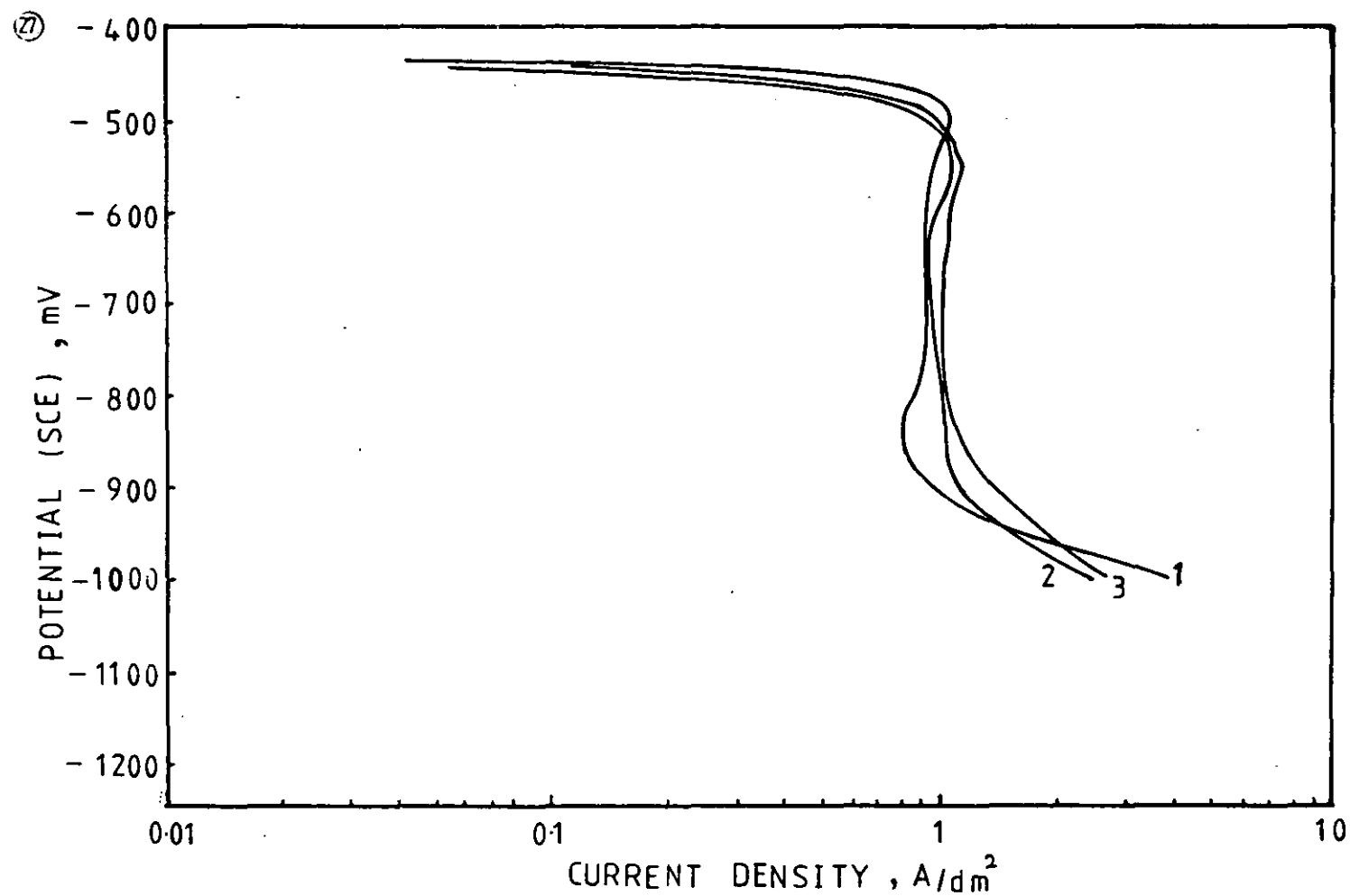


FIGURE 27: CATHODIC BEHAVIOUR OF TIN SULPHAMATE SOLUTION CONTAINING PEPTONE.

CURVE 1: FOR SOLUTION CONTAINING 2.5 g/l; CURVE 2: FOR SOLUTION CONTAINING 5 g/l;  
CURVE 3: FOR SOLUTION CONTAINING 10 g/l

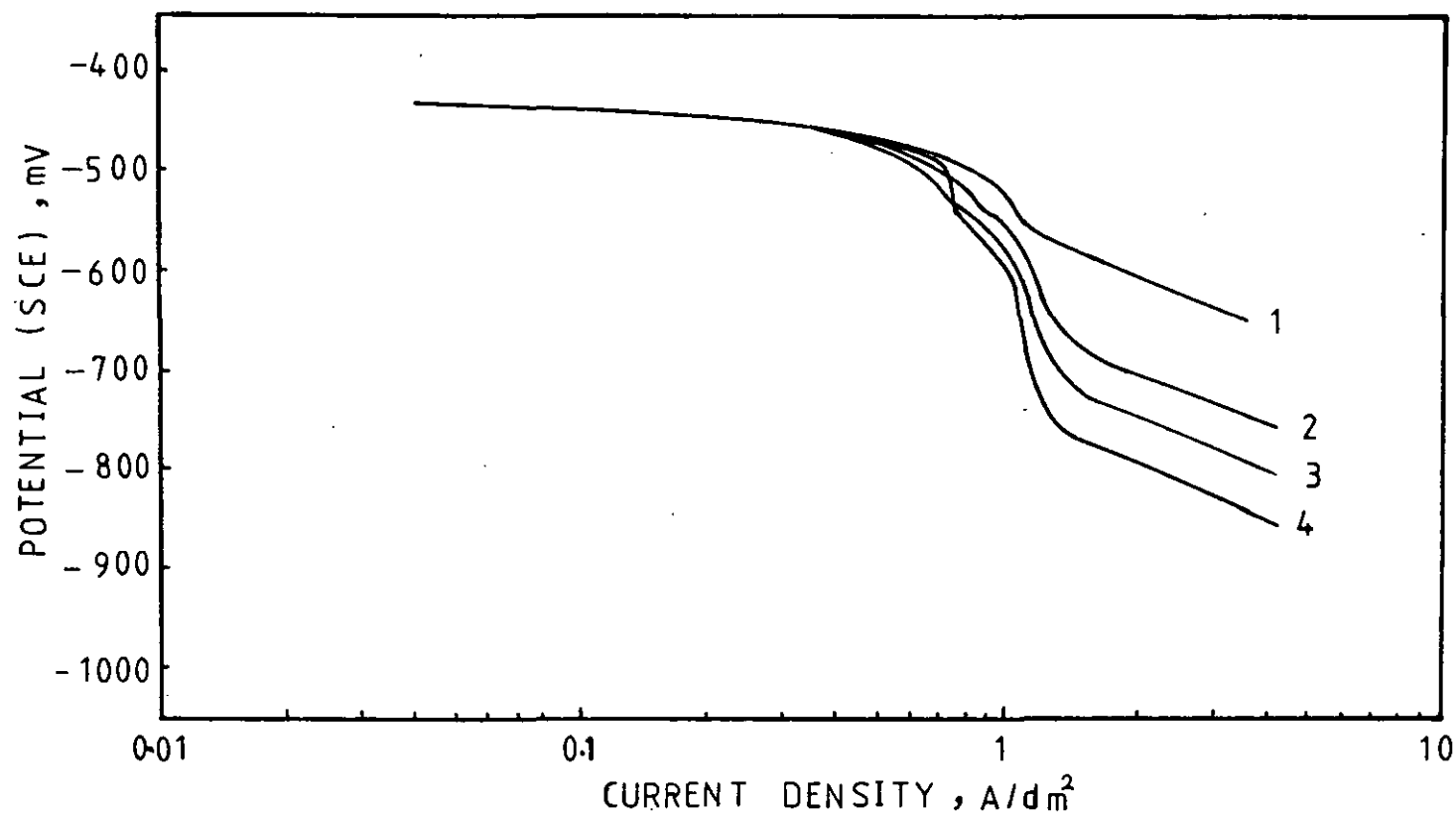


FIGURE 28: CATHODIC BEHAVIOUR FOR TIN SULPHAMATE SOLUTION CONTAINING RESORCINOL.

CURVE 1: FOR SOLUTION WITHOUT ADDITIVES; CURVE 2: SOLUTION CONTAINING 2.5 g/l;  
CURVE 3: SOLUTION CONTAINING 5 g/l, and CURVE 4: SOLUTION CONTAINING 10 g/l

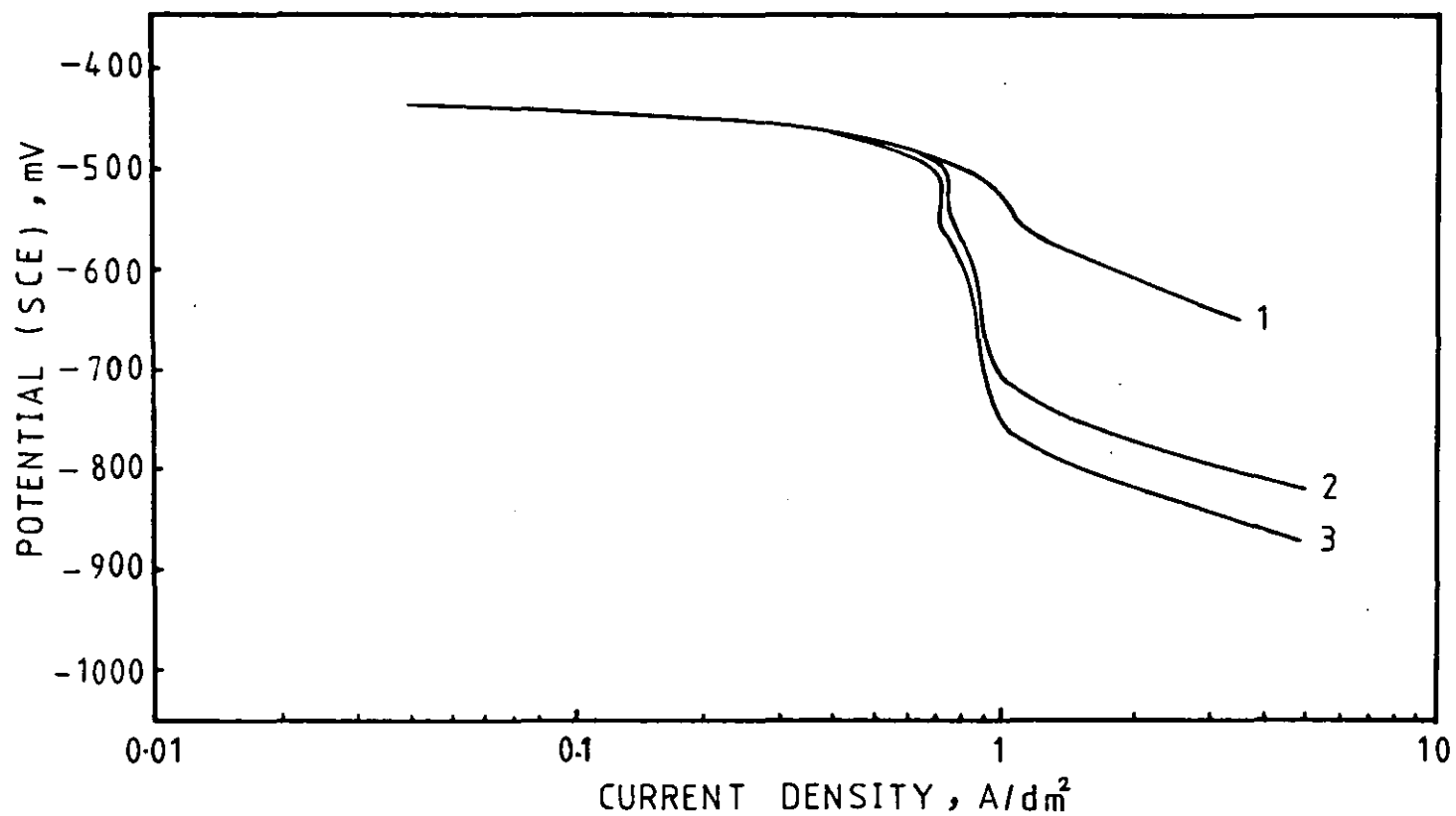


FIGURE 29: CATHODIC BEHAVIOUR OF TIN SULPHAMATE SOLUTION CONTAINING PYROGALLOL.

CURVE 1: FOR SOLUTION WITHOUT ADDITIVE; CURVE 2: FOR SOLUTION CONTAINING 2.5 g/l, and  
CURVE 3: FOR SOLUTION CONTAINING 10 g/l

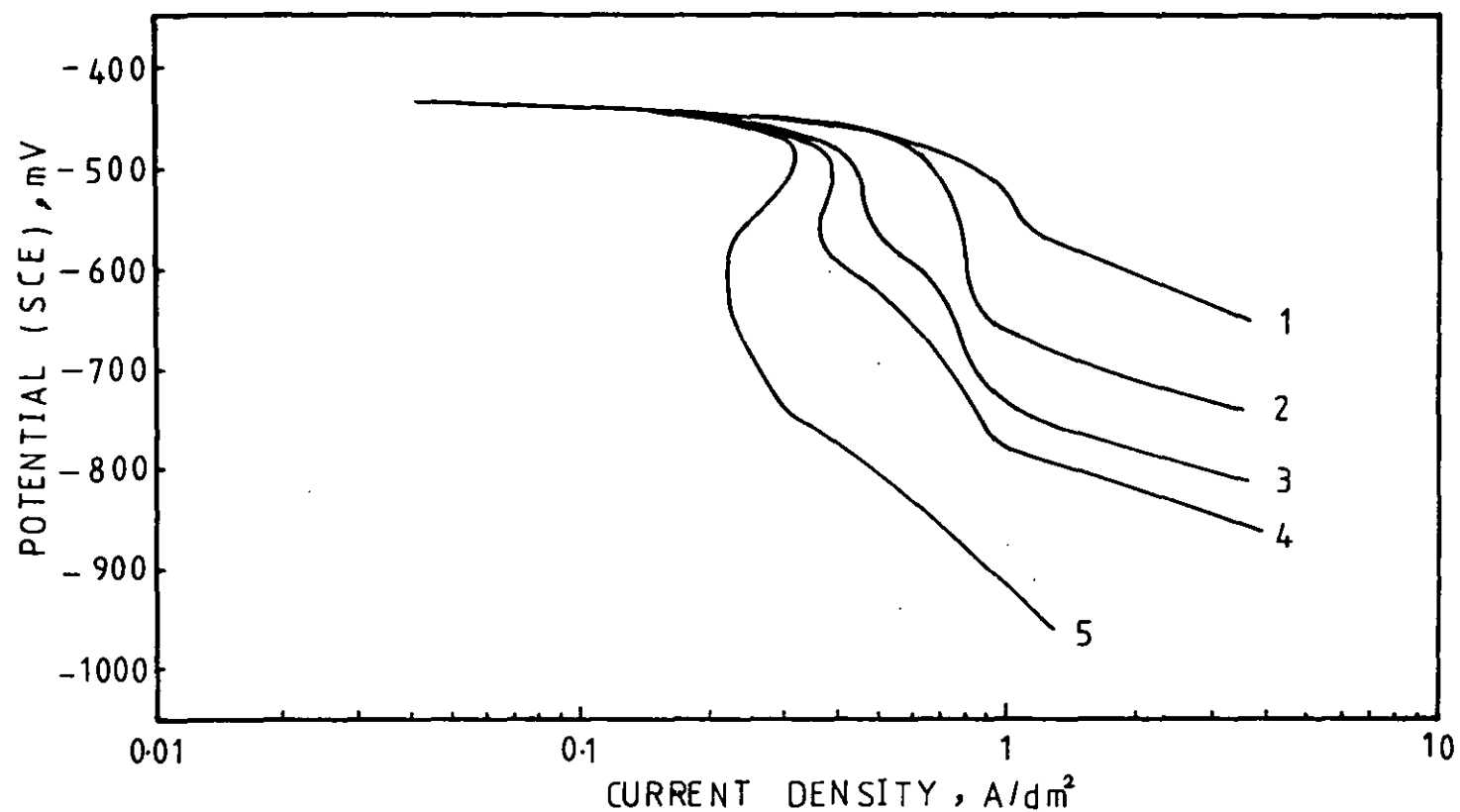


FIGURE 30: CATHODIC BEHAVIOUR FOR TIN SULPHAMATE SOLUTION CONTAINING PHENOLSULPHONIC ACID.

CURVE 1: NO ADDITIVE; CURVE 2: CONTAINS 2.5 g/l; CURVE 3: CONTAINS 5 g/l;  
CURVE 4: CONTAINS 10 g/l; and CURVE 5: CONTAINS 10 g/l PHENOLSULPHONIC ACID AND 5 g/l GELATIN

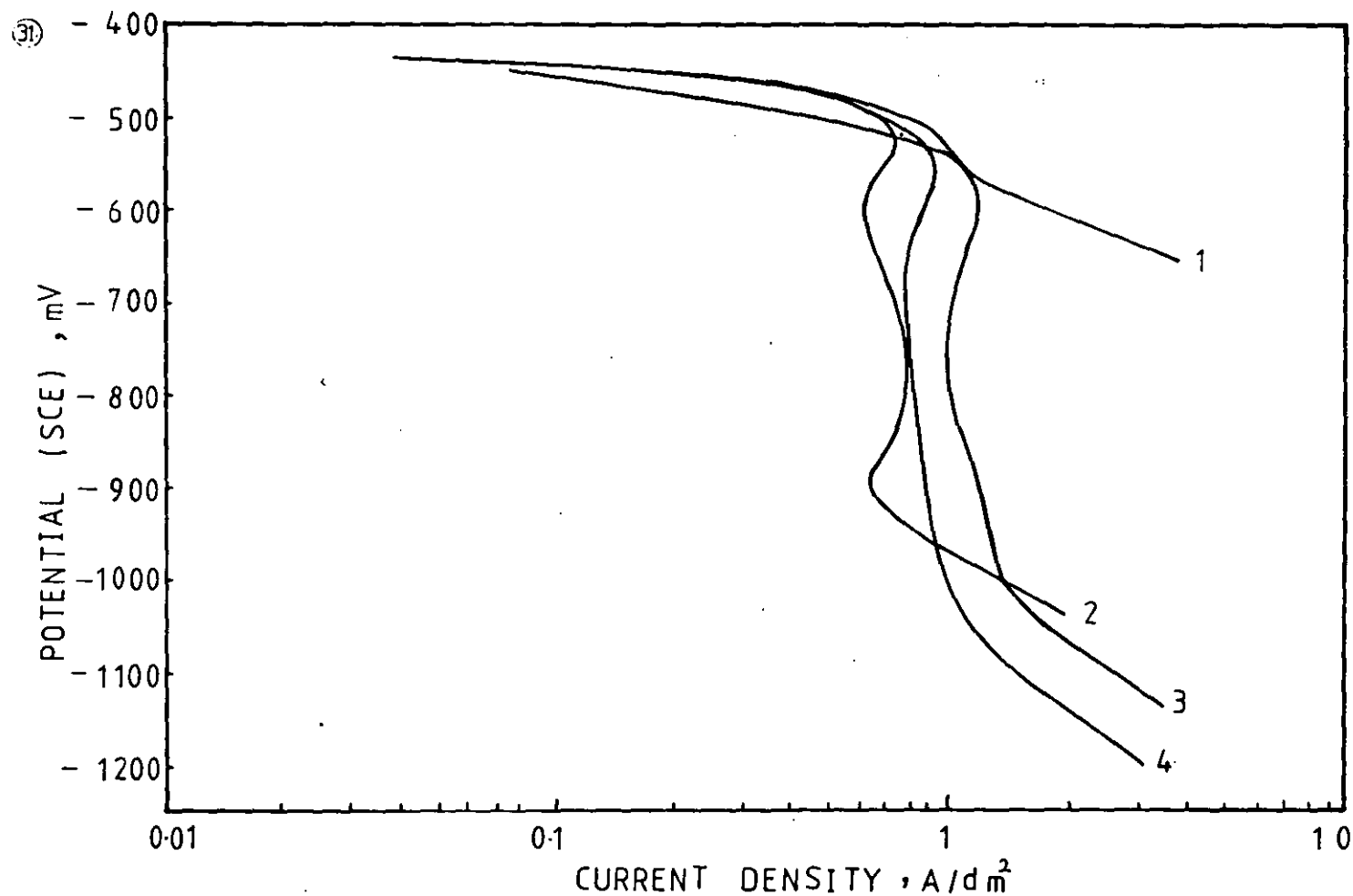


FIGURE 31: CATHODIC BEHAVIOUR FOR TIN SULPHAMATE SOLUTION CONTAINING GROUP OF ADDITIVES.

CURVE 1: NO ADDITIVE; CURVE 2: CONTAINS PHENOLSULPHONIC ACID, PEPTONE AND POLYETHYLENE OXIDE 2.5 g/l EACH; CURVE 3: SOLUTION CONTAINS PHENOLSULPHONIC ACID, PEPTONE AND PYROGALLOL 2.5 g/l EACH  
 CURVE 4: SOLUTION CONTAINS PHENOLSULPHONIC ACID, PEPTONE AND GELATIN 2.5 g/l EACH

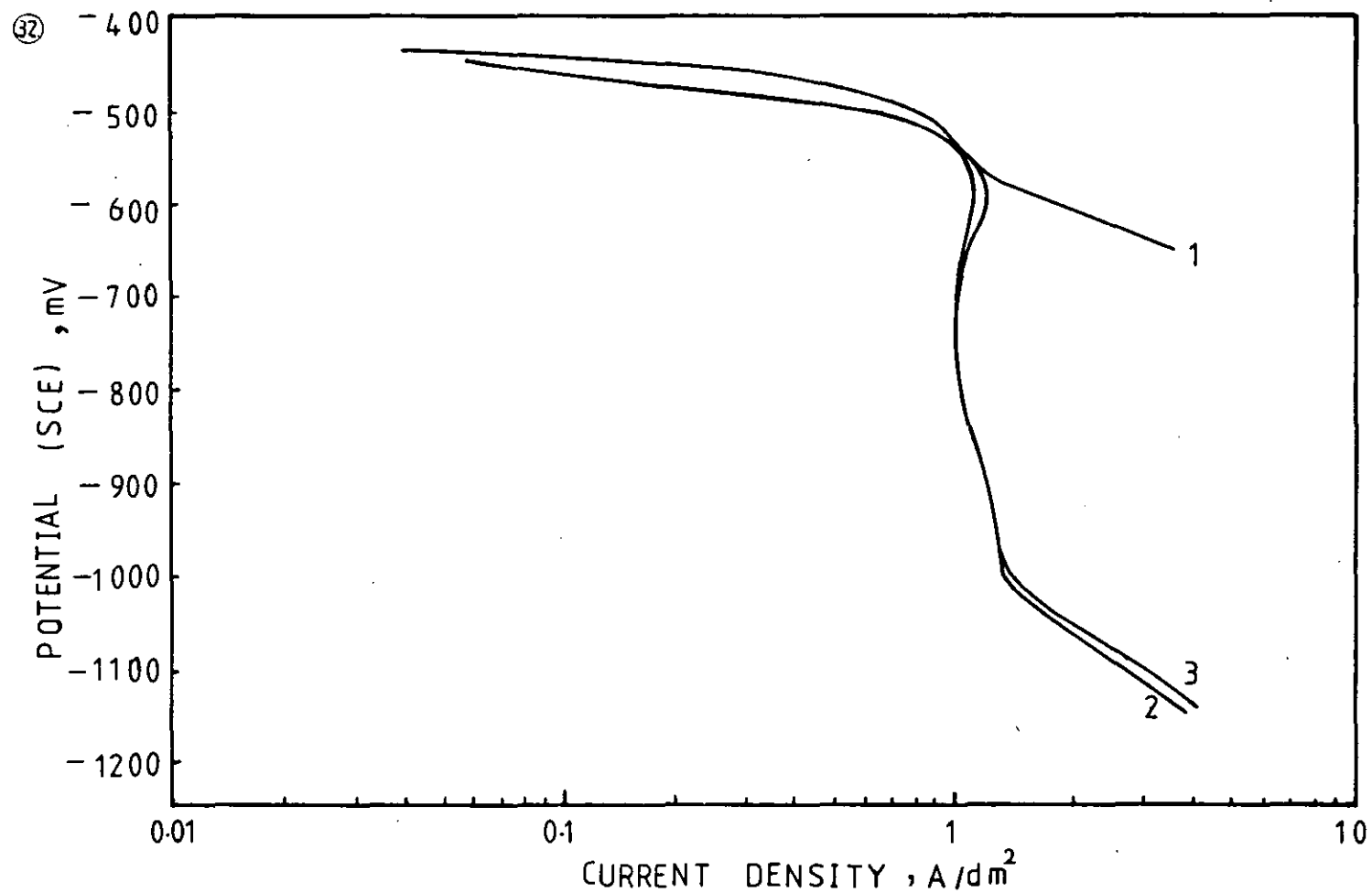


FIGURE 32: EFFECT OF TIME ON CATHODIC BEHAVIOUR OF TIN SULPHAMATE SOLUTION.

CURVE 1: FRESH SOLUTION WITHOUT ADDITIVES; CURVE 2: FRESH SOLUTION CONTAINS PHENOLSULPHONIC ACID, PEPTONE, AND PYROGALLOL 2.5 g/l EACH; and CURVE 3: THE SAME AS (2) BUT AFTER 30 HOURS

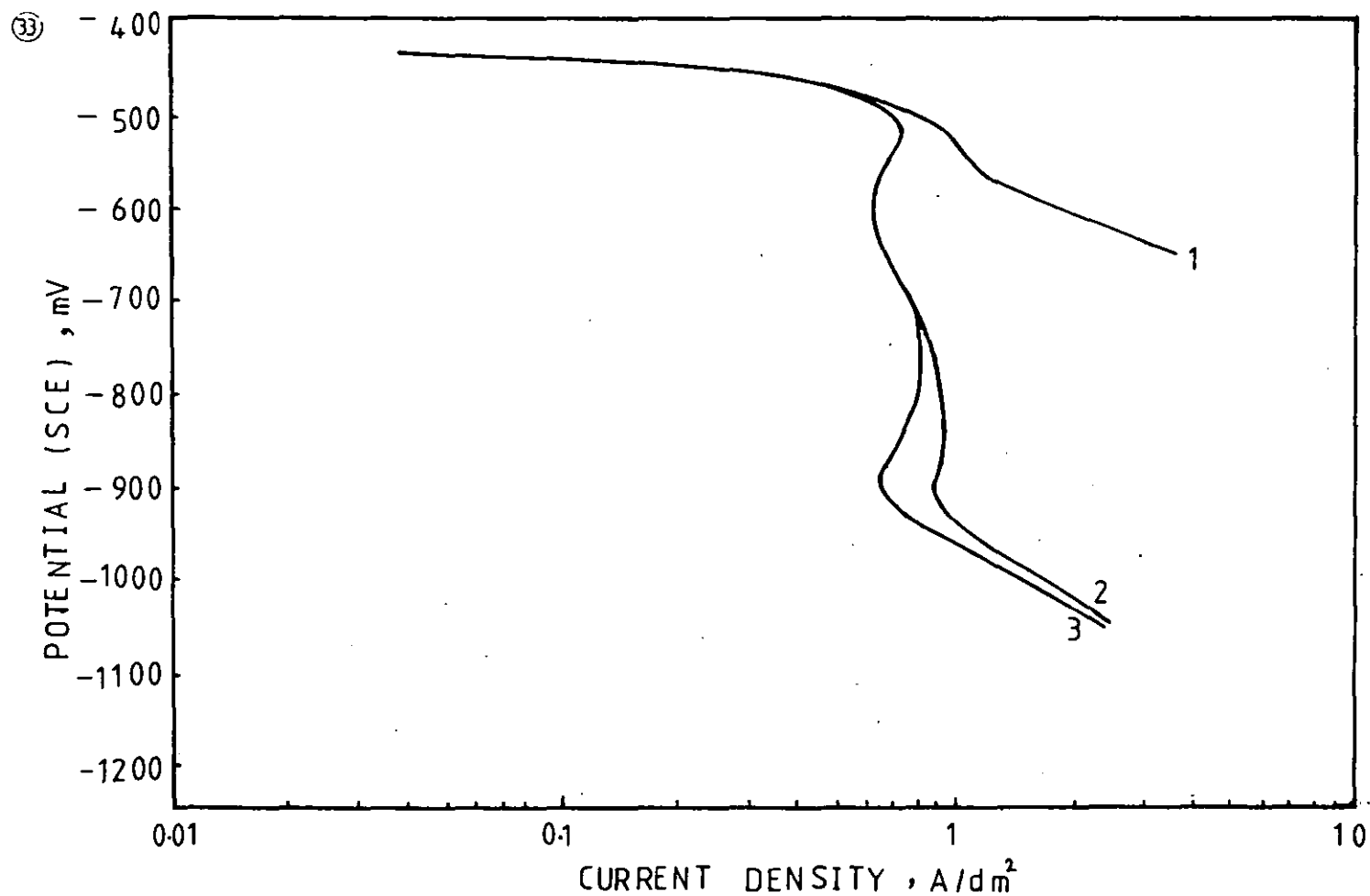


FIGURE 33: EFFECT OF TIME ON CATHODIC BEHAVIOUR OF TIN SULPHAMATE SOLUTION.

CURVE 1: FRESH SOLUTION WITHOUT ADDITIVES; CURVE 3: FRESH SOLUTION CONTAINING PHENOLSULPHONIC ACID, PEPTONE AND POLYETHYLENE OXIDE, 2.5 g/l EACH AND CURVE 2 THE SAME AS (3) BUT AFTER 30 HOURS

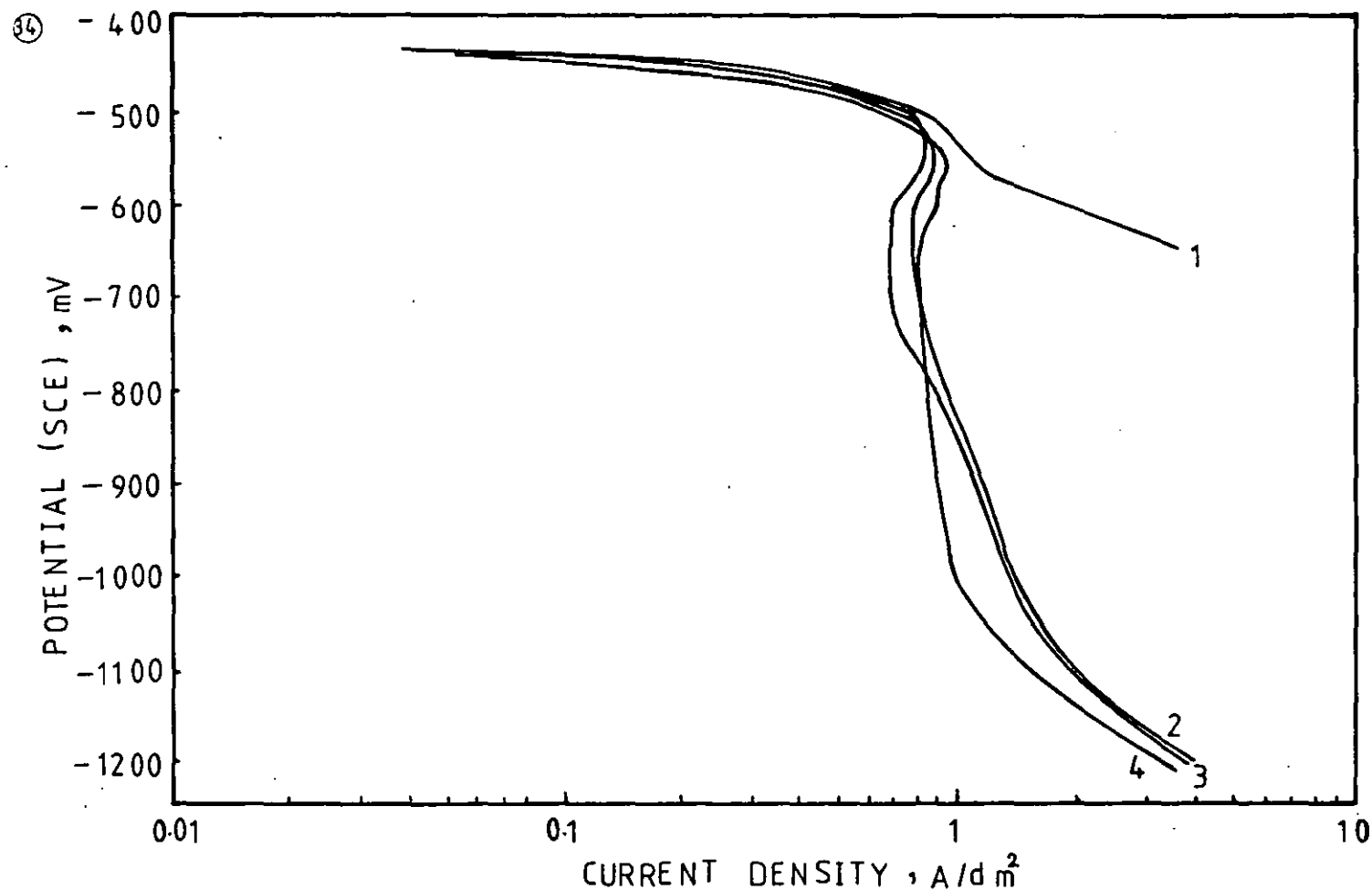


FIGURE 34: EFFECT OF TIME ON CATHODIC BEHAVIOUR OF TIN SULPHAMATE SOLUTION.

CURVE 1: FRESH SOLUTION WITHOUT ADDITIVES; CURVE 4: FOR FRESH SOLUTION CONTAINING PHENOL-SULPHONIC ACID, PEPTONE AND GELATIN 2.5 g/l EACH; CURVE 2 AS (4) BUT AFTER 30 HOURS AND CURVE 3 AS (4) BUT AFTER 78 HOURS

35

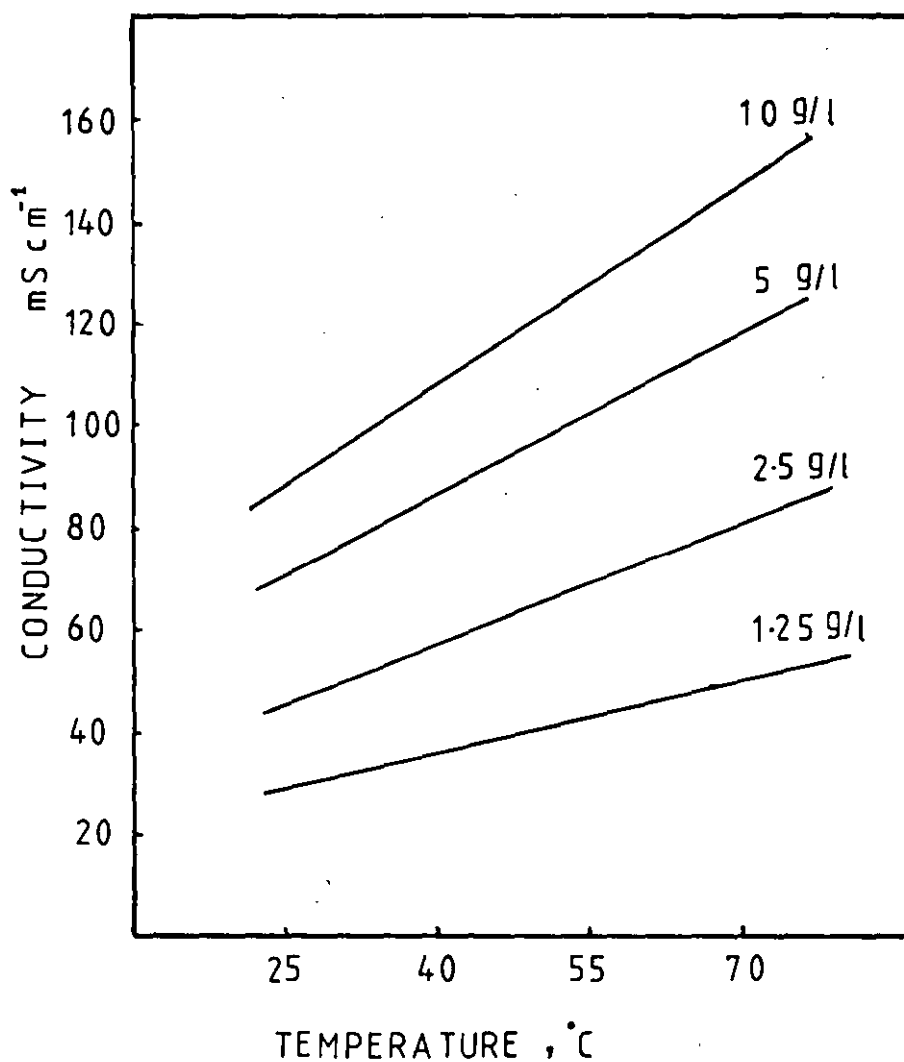


FIGURE 35: EFFECT OF TEMPERATURE ON THE CONDUCTIVITY OF TIN SULPHAMATE SOLUTIONS (DIFFERENT CONCENTRATIONS)



FIGURE 36: MICROGRAPHS FOR DEPOSITS ELECTROPLATED FROM  
SULPHAMATE SOLUTIONS, CURRENT DENSITY APPLIED  
1 A/dm<sup>2</sup>. (Mag. 2200X)

- a) Solution contains 2.5 g/l peptone
- b) Solution contains 2.5 g/l gelatin

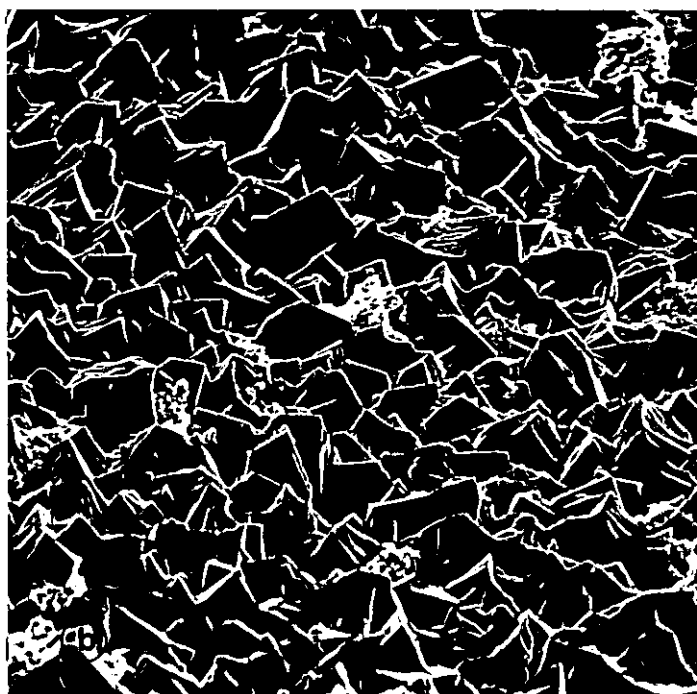
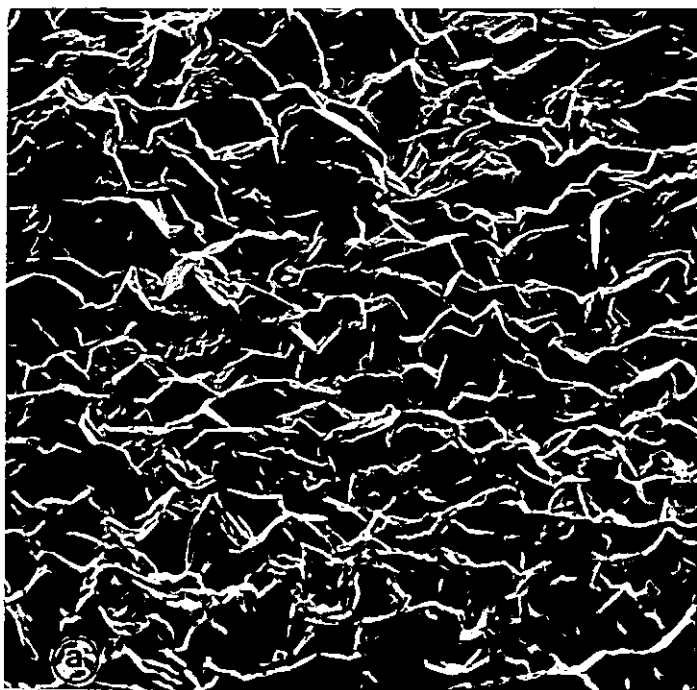


FIGURE 37: MICROGRAPH FOR DEPOSITS ELECTROPLATED FROM  
SULPHAMATE SOLUTION, CURRENT DENSITY  
APPLIED 1 A/dm<sup>2</sup>. (Mag. 2200X)

- a) Solution contains 2.5 g/l pyrogallol
- b) Solution contains 2.5 g/l resorcinol

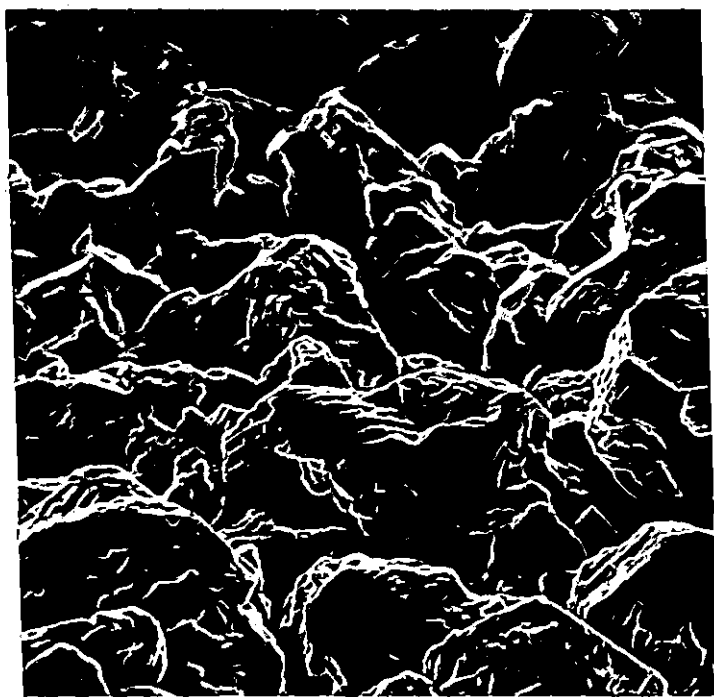
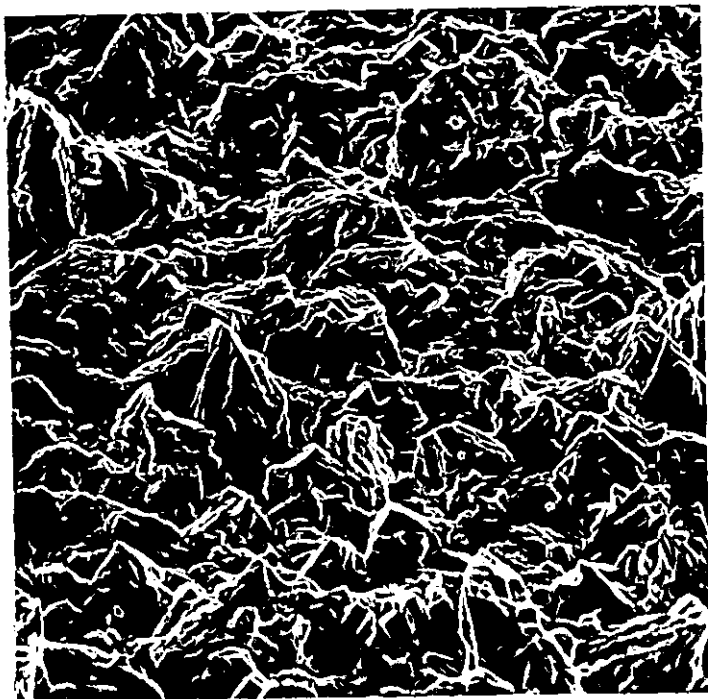


FIGURE 38: MICROGRAPH FOR DEPOSITS PLATED FROM  
SULPHAMATE SOLUTION CURRENT DENSITY  
APPLIED 1 A/dm<sup>2</sup>. (Mag. 2200X)

- a) Solution contains 2.5 g/l polyethylene  
oxide
- b) Solution contains 2.5 g/l polyethylene  
glycol

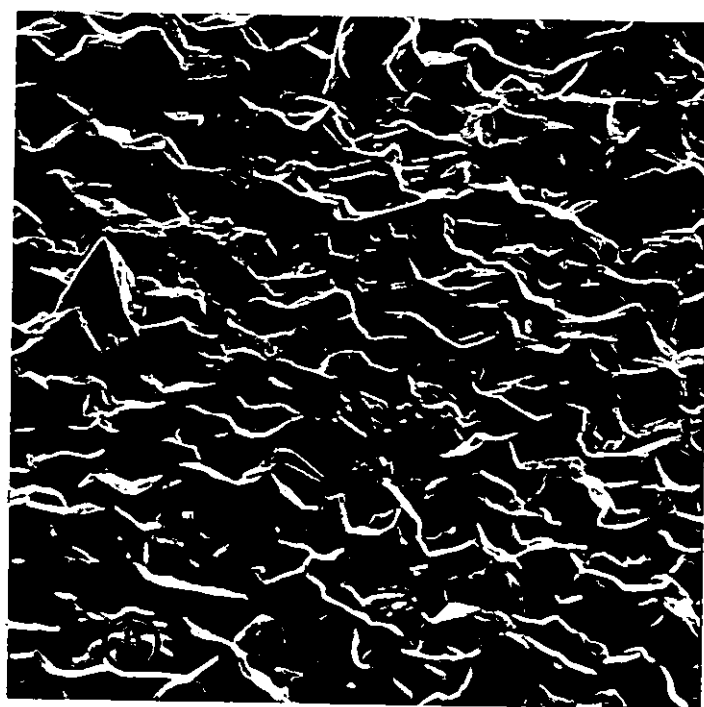


FIGURE 39: A BEARING HOLDER (a) AND DIFFERENT TYPES  
OF ANODES USED IN THE TRIALS (b)

FIGURE 40: A SPECIAL JIG FOR HOLDING THE BEARING FOR  
PLATING IN LARGE CELL (a) AND THE ANODE  
USED (b)

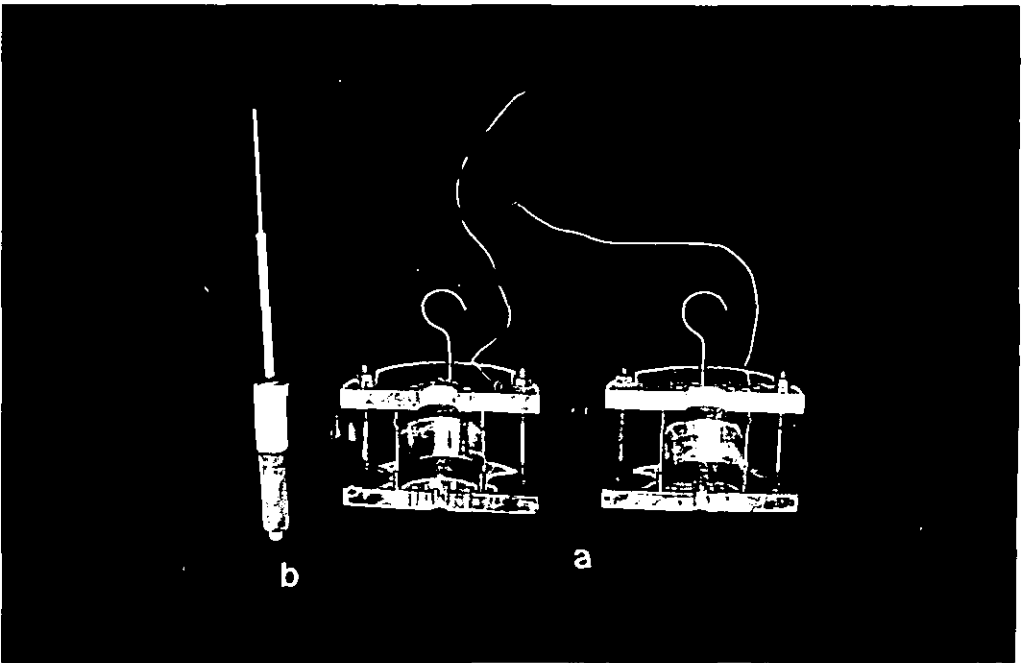
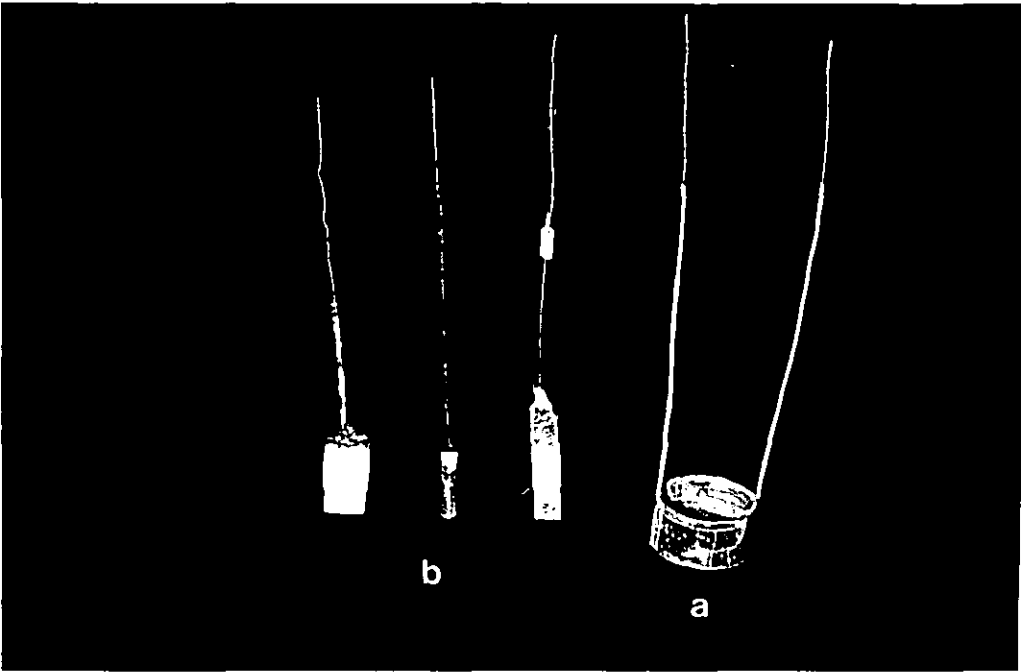
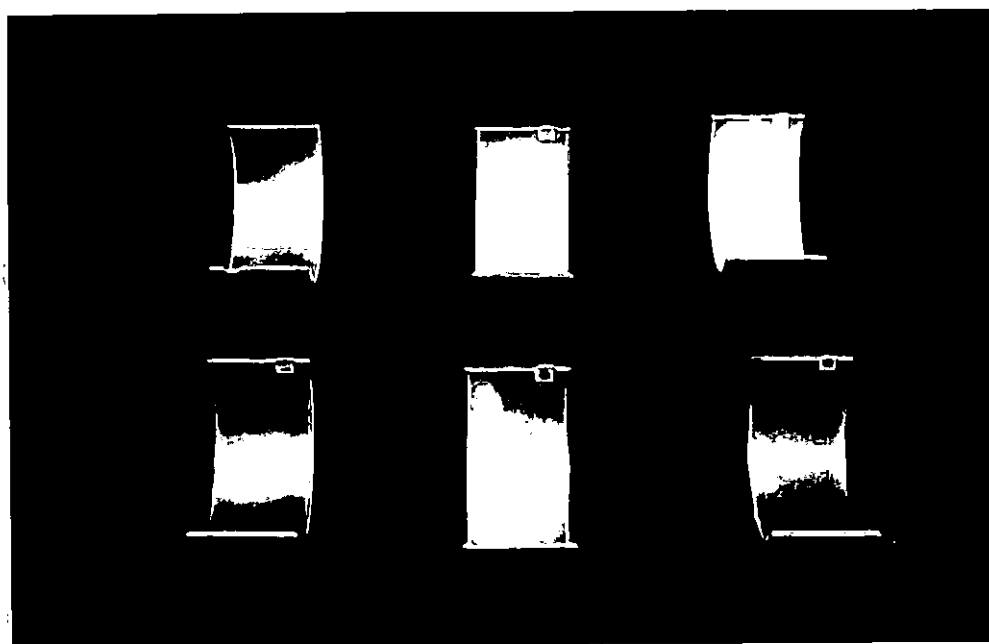


FIGURE 41: SOME PLATED BEARINGS USING THE LARGE CELL



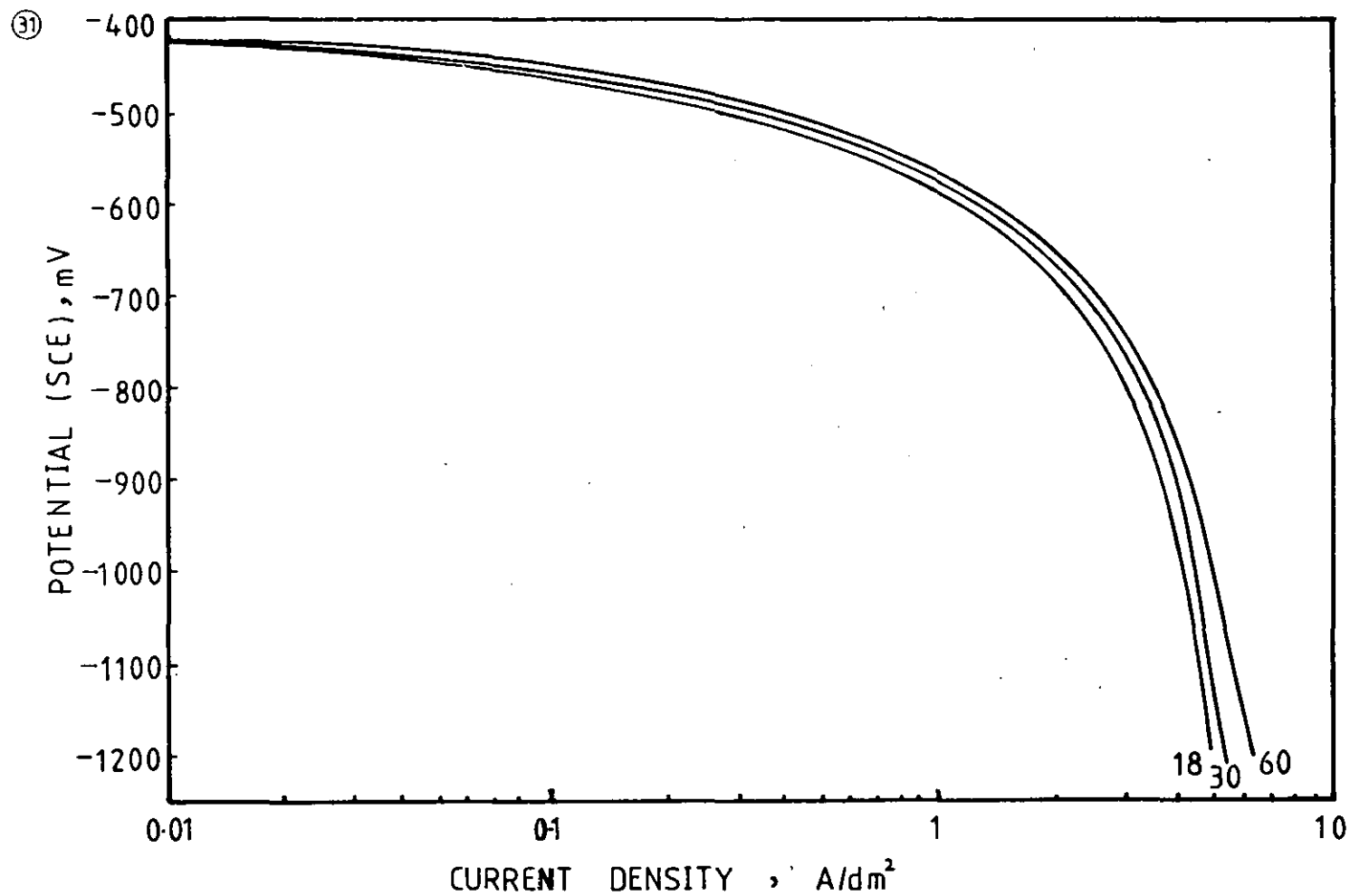


FIGURE 42: THE EFFECT OF SWEEP RATE ON THE CATHODIC BEHAVIOUR OF 90 Pb:10 Sn SOLUTION CONTAINING THE ADDITIVES; PEPTONE, GELATIN AND PYROGALLOL 2.5 g/l EACH

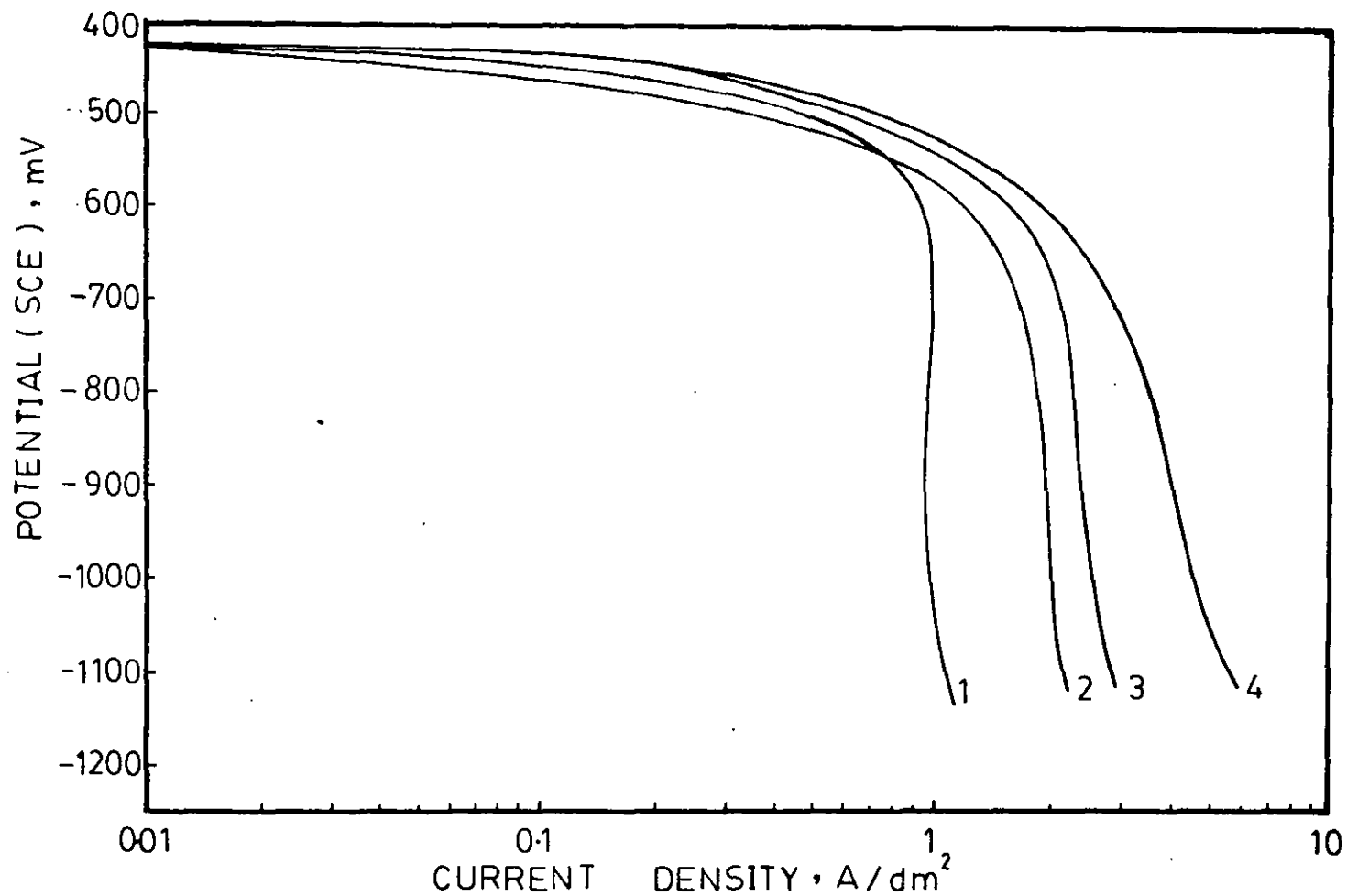


FIGURE 43: THE EFFECT OF TIN CONTENT IN THE SOLUTION ON LIMITING CURRENT DENSITY

- |                             |                             |
|-----------------------------|-----------------------------|
| 1. SOLUTION OF 40 Pb:60 Sn, | 2. SOLUTION OF 70 Pb:30 Sn, |
| 3. SOLUTION OF 80 Pb:20 Sn, | 4. SOLUTION OF 90 Pb:10 Sn  |

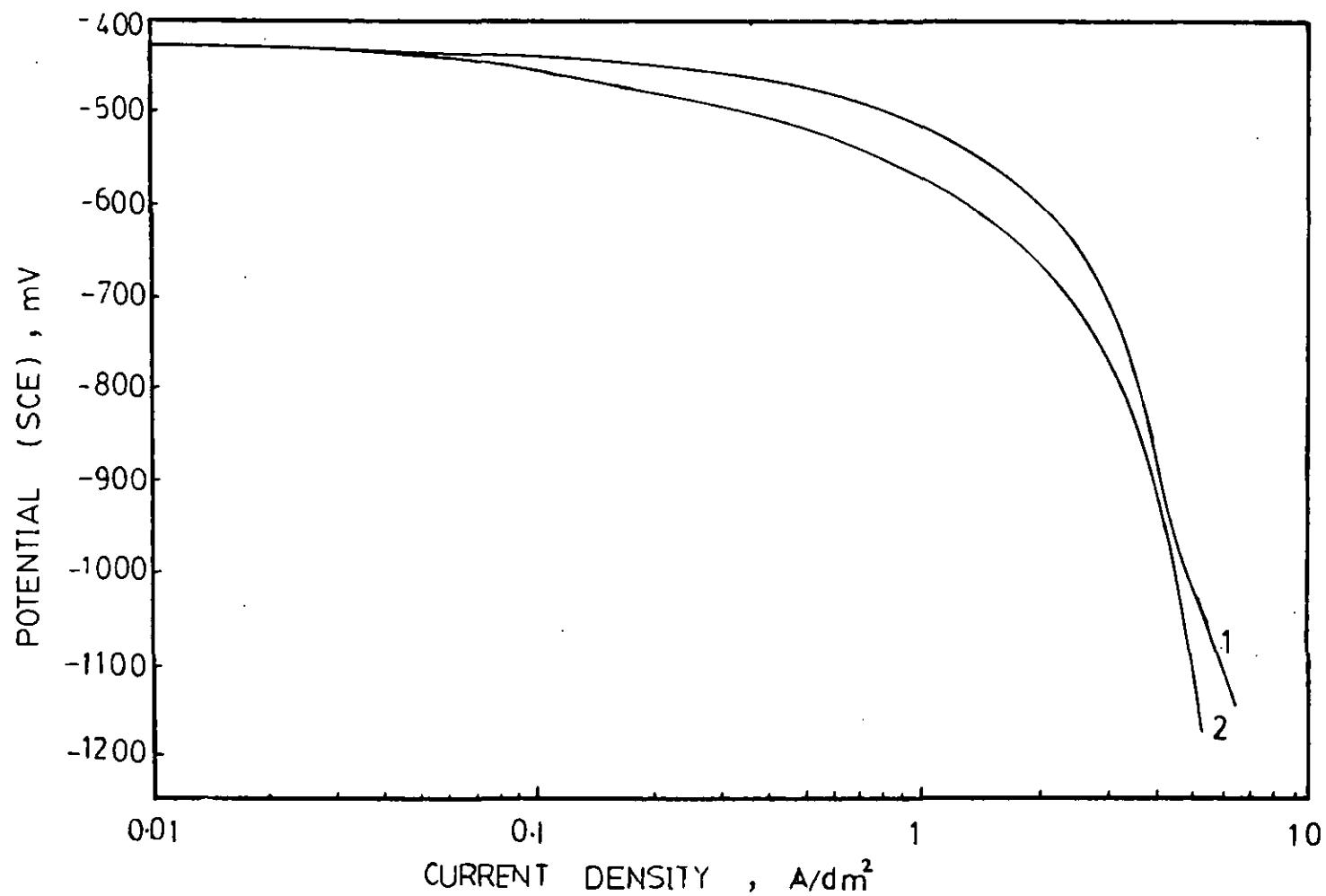


FIGURE 44: THE EFFECT OF FREE ACID ON THE CATHODIC BEHAVIOUR OF 90 Pb:10 Sn SOLUTION.

CURVE 1: SOLUTION CONTAINING 50 g/l FREE ACID

CURVE 2: SOLUTION WITHOUT FREE ACID

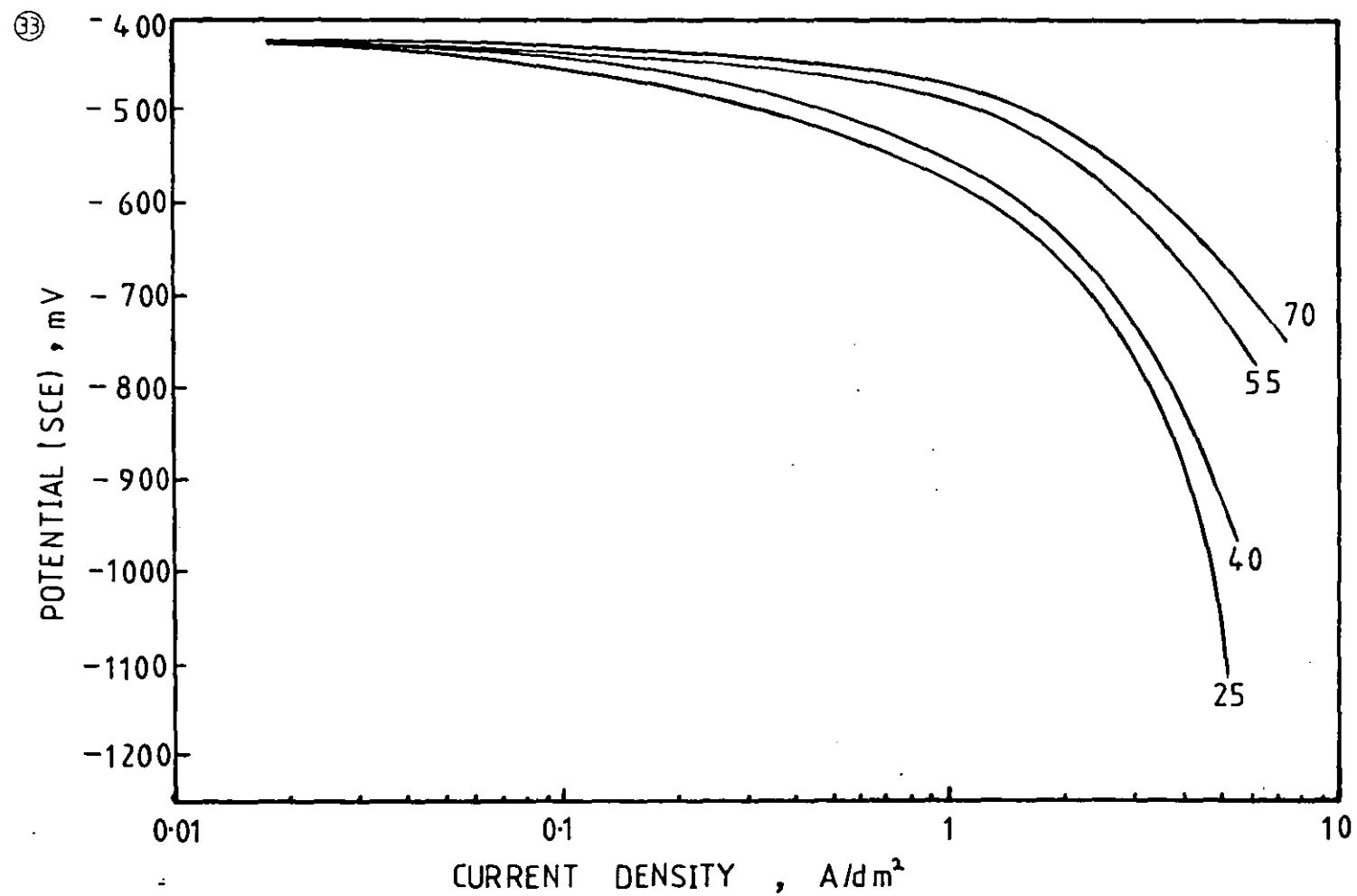


FIGURE 45: THE EFFECT OF TEMPERATURE ON THE CATHODIC BEHAVIOUR OF SOLUTION OF 90 Pb:10 Sn RATIO CONTAINING PEPTONE, GELATIN AND PYROGALLOL 2.5 g/l EACH.  
(Figures on curves temperature in °C)

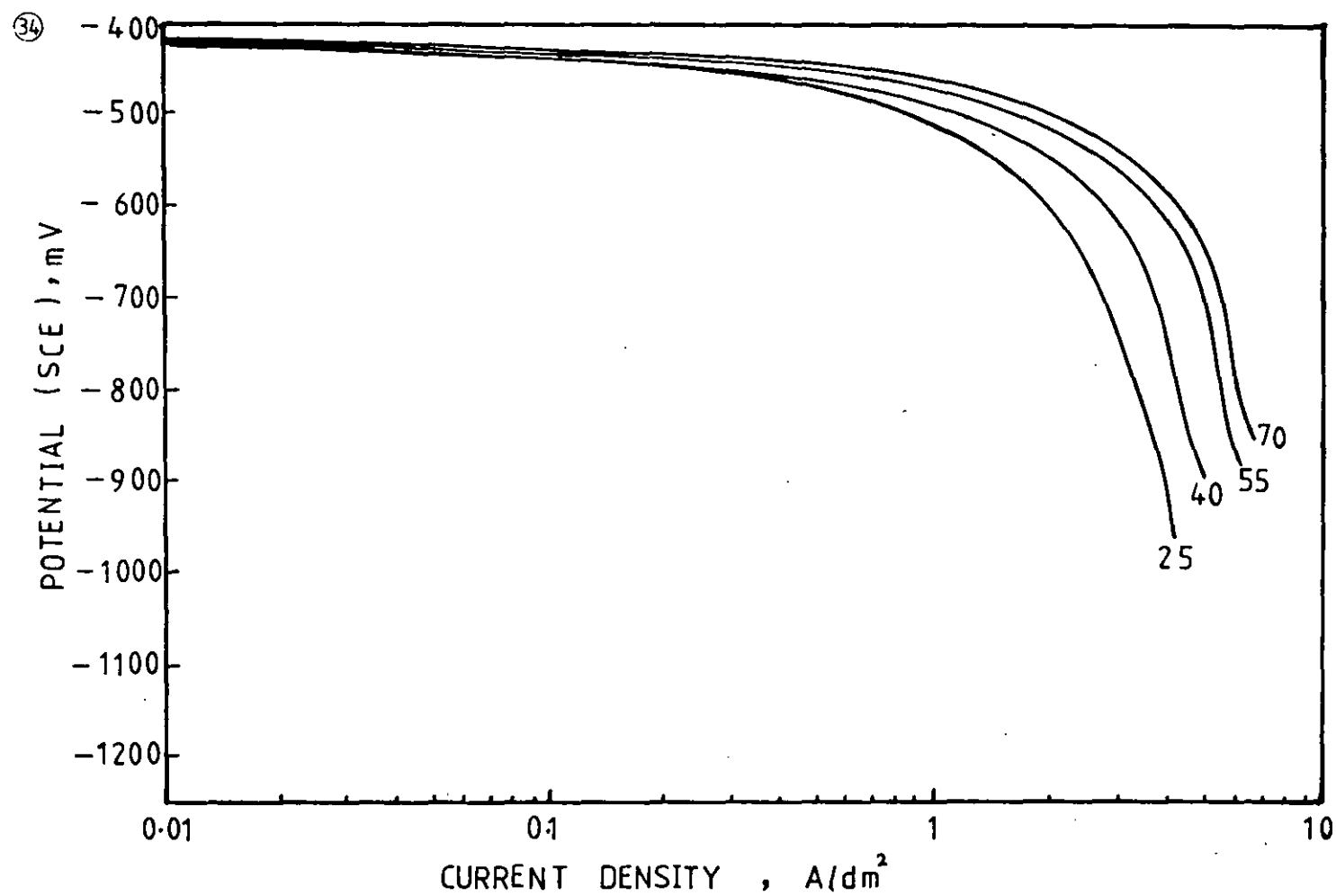


FIGURE 46: THE EFFECT OF TEMPERATURE ON THE CATHODIC BEHAVIOUR OF SOLUTION OF 90 Pb:10 Sn CONTAINING ADDITIVES AND 50 g/l FREE ACID.  
(Figures on curves temperature in °C)

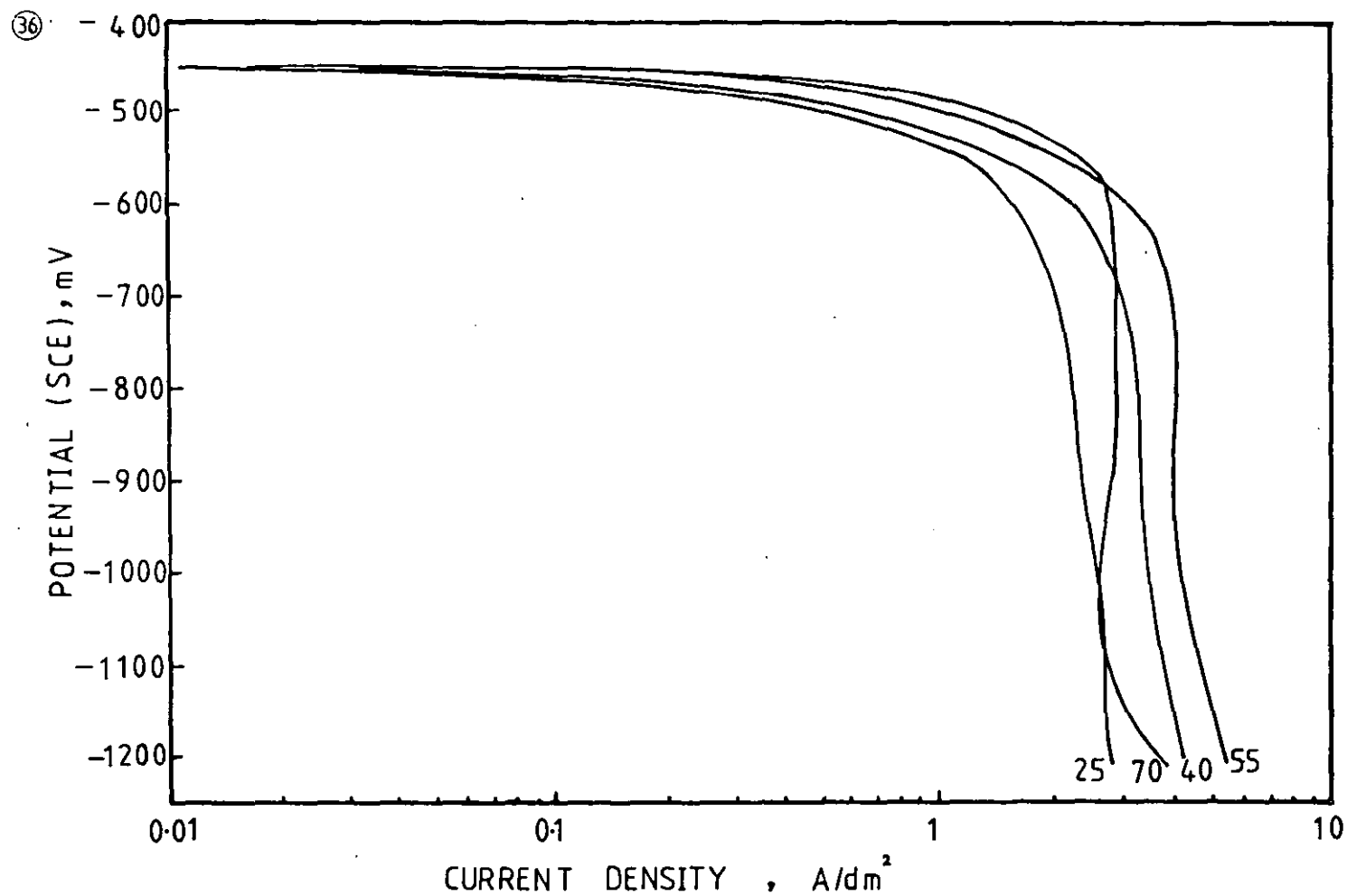


FIGURE 47: THE EFFECT OF TEMPERATURE ON CATHODIC BEHAVIOUR OF SOLUTION OF 80 Pb:2 Sn RATIO CONTAINING ADDITIVES.  
(Figures on curves, temperature in °C)

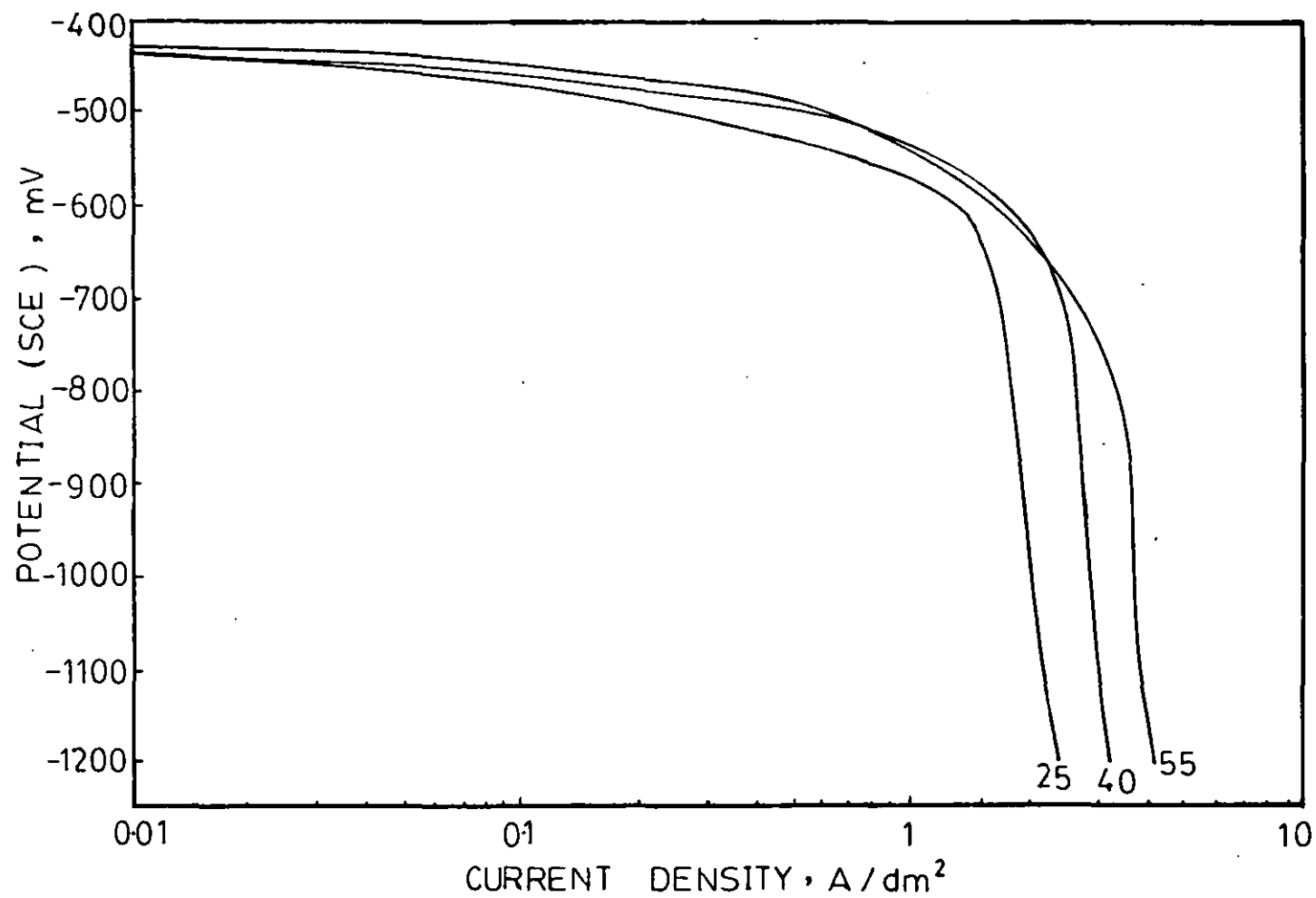


FIGURE 48: EFFECT OF TEMPERATURE ON CATHODIC BEHAVIOUR OF SOLUTION OF 70 Pb:30 Sn RATIO, CONTAINING ADDITIVES.  
(Figures on curves are temperature in °C)

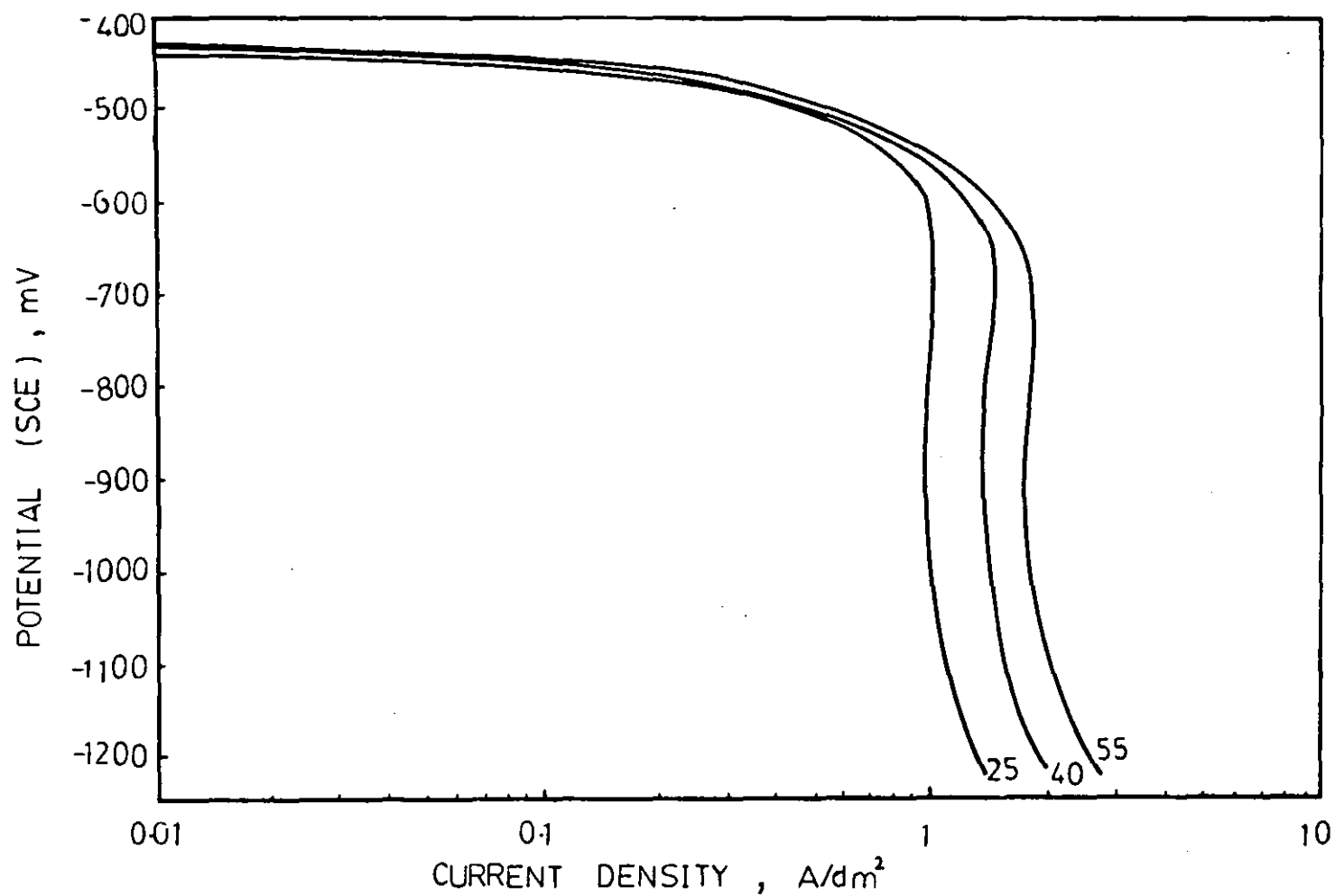


FIGURE 49: EFFECT OF TEMPERATURE ON CATHODIC BEHAVIOUR OF SOLUTION OF 40 Pb:60 Sn RATIO CONTAINING ADDITIVES..  
(Figures on curves are temperature in  $^{\circ}\text{C}$ )

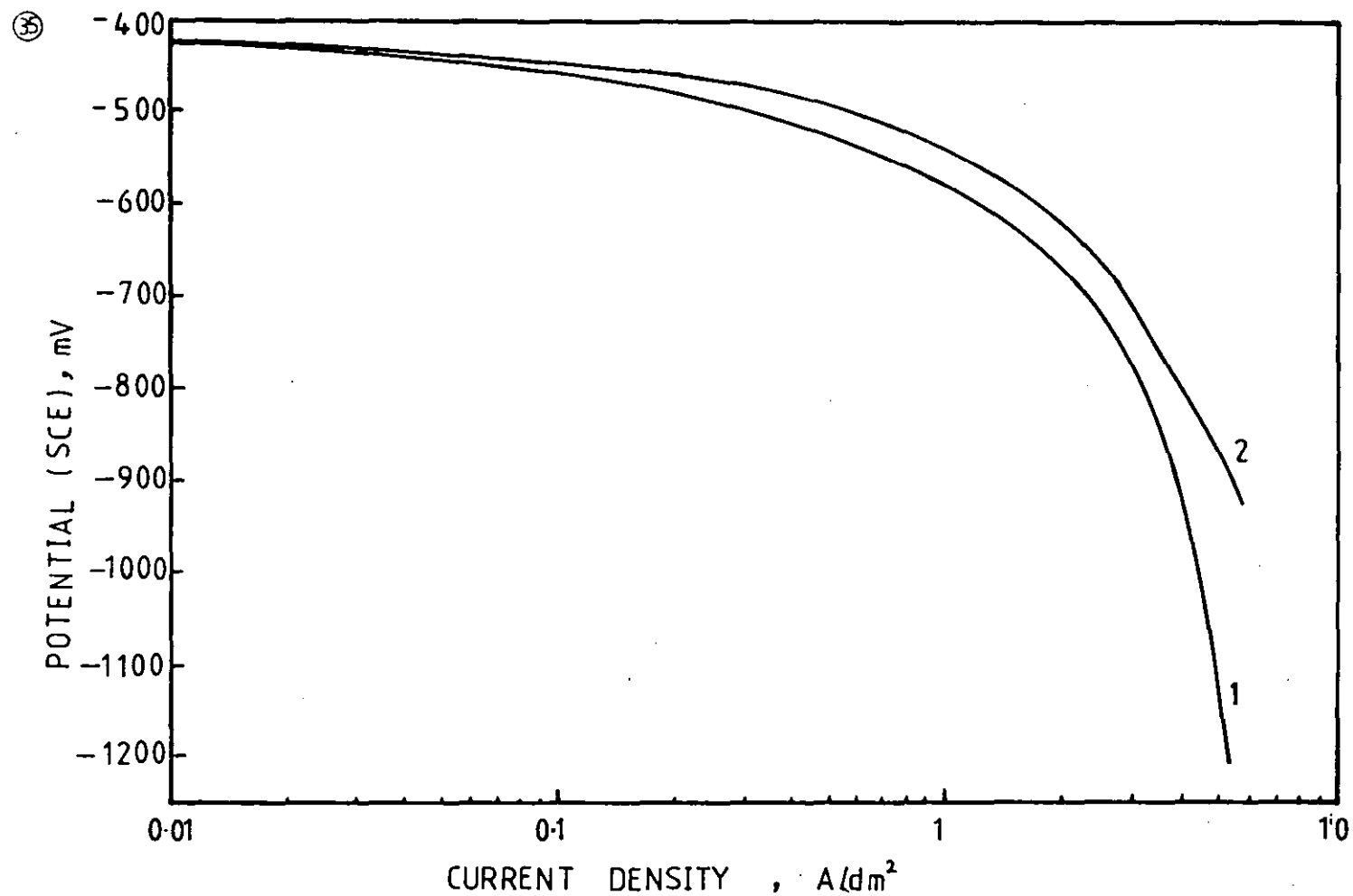


FIGURE 50: THE EFFECT OF MILD AGITATION ON SOLUTION OF 90 Pb:10 Sn RATIO CONTAINING ADDITIVES.

1. STILL SOLUTION.
2. AGITATED SOLUTION MILDLY, WITH NITROGEN

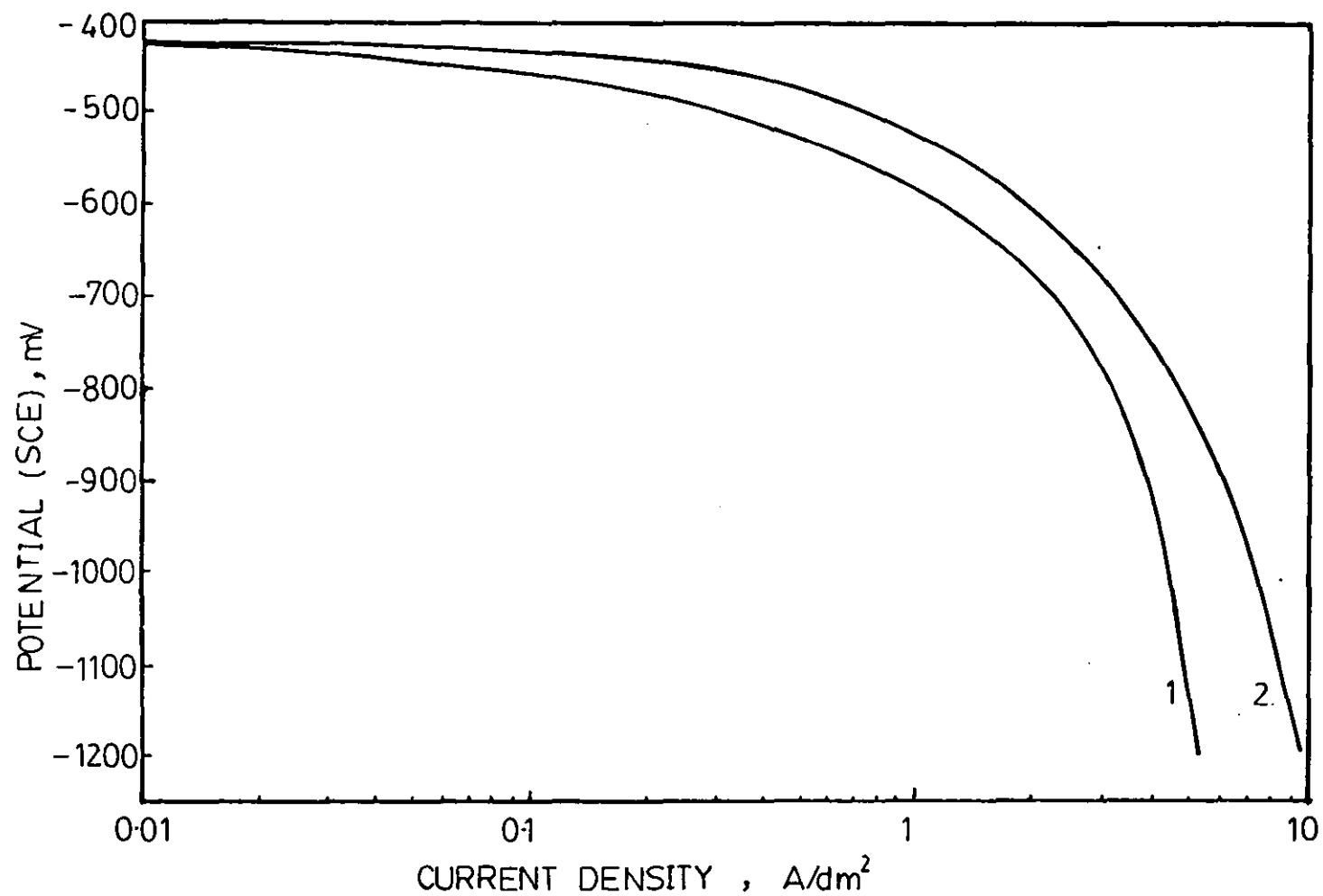


FIGURE 51: EFFECT OF CELL SIZE AND CATHODE ON CATHODIC DEPOSITION FROM SOLUTION OF 90 Pb:10 Sn CONTAINING ADDITIVES.

1. SMALL CELL
2. LARGE CELL (BEARING AS CATHODE)

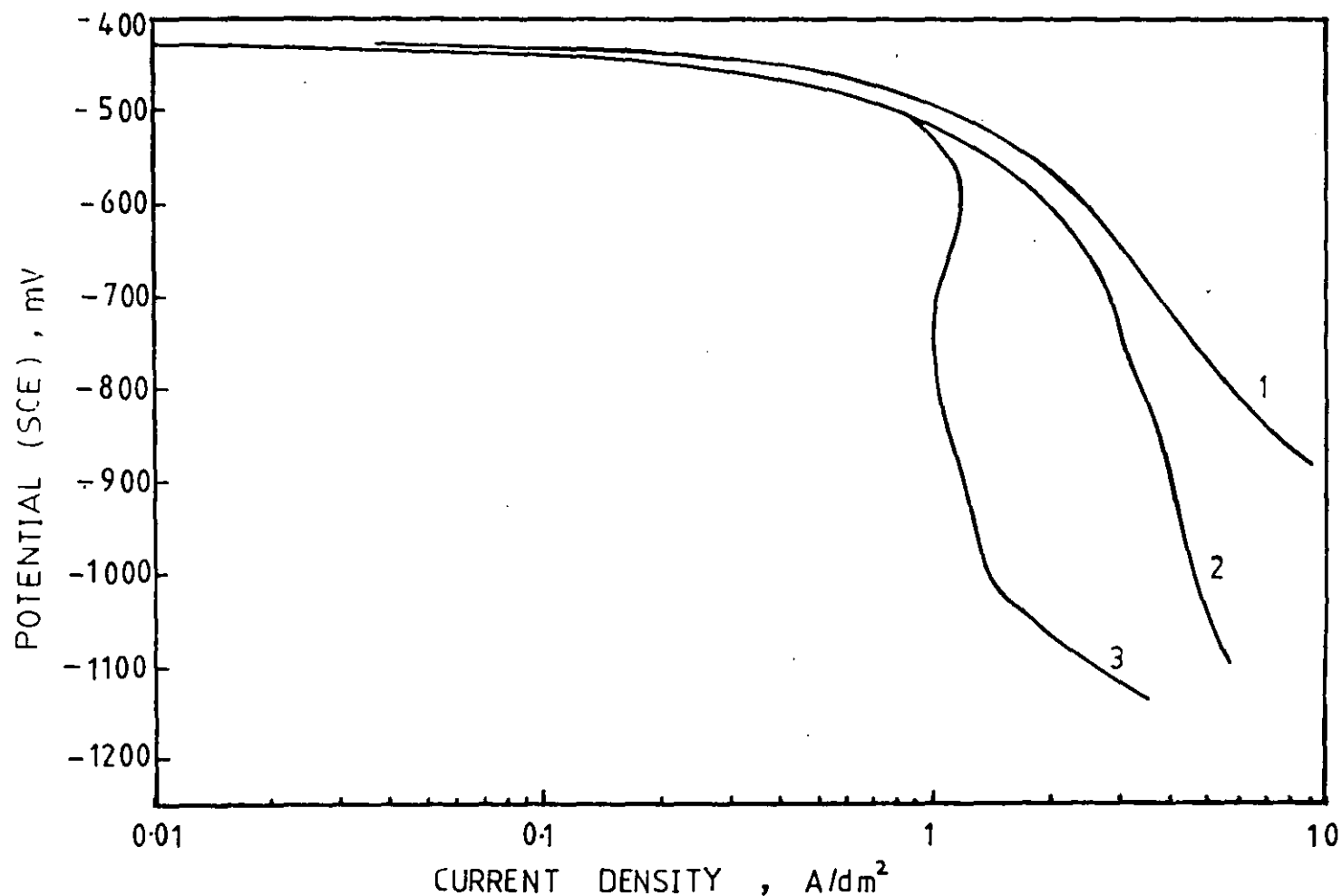


FIGURE 52: POLARIZATION CURVES FOR TIN, LEAD AND LEAD-TIN ALLOY FROM SULPHAMATE SOLUTION

1. LEAD SOLUTION CONTAINING 54 g/l LEAD, 3 g/l GELATIN AND 50 g/l FREE ACID.
2. LEAD-TIN SOLUTION CONTAINING 49 g/l LEAD, 5.5 g/l TIN AND PEPTONE, GELATIN AND PYROGALLOL 2.5 g/l EACH
3. TIN SOLUTION CONTAINING 10 g/l TIN AND PEPTONE, PYROGALLOL AND PHENOLSULPHONIC ACID 2.5 g/l EACH, ALSO 50 g/l FREE ACID

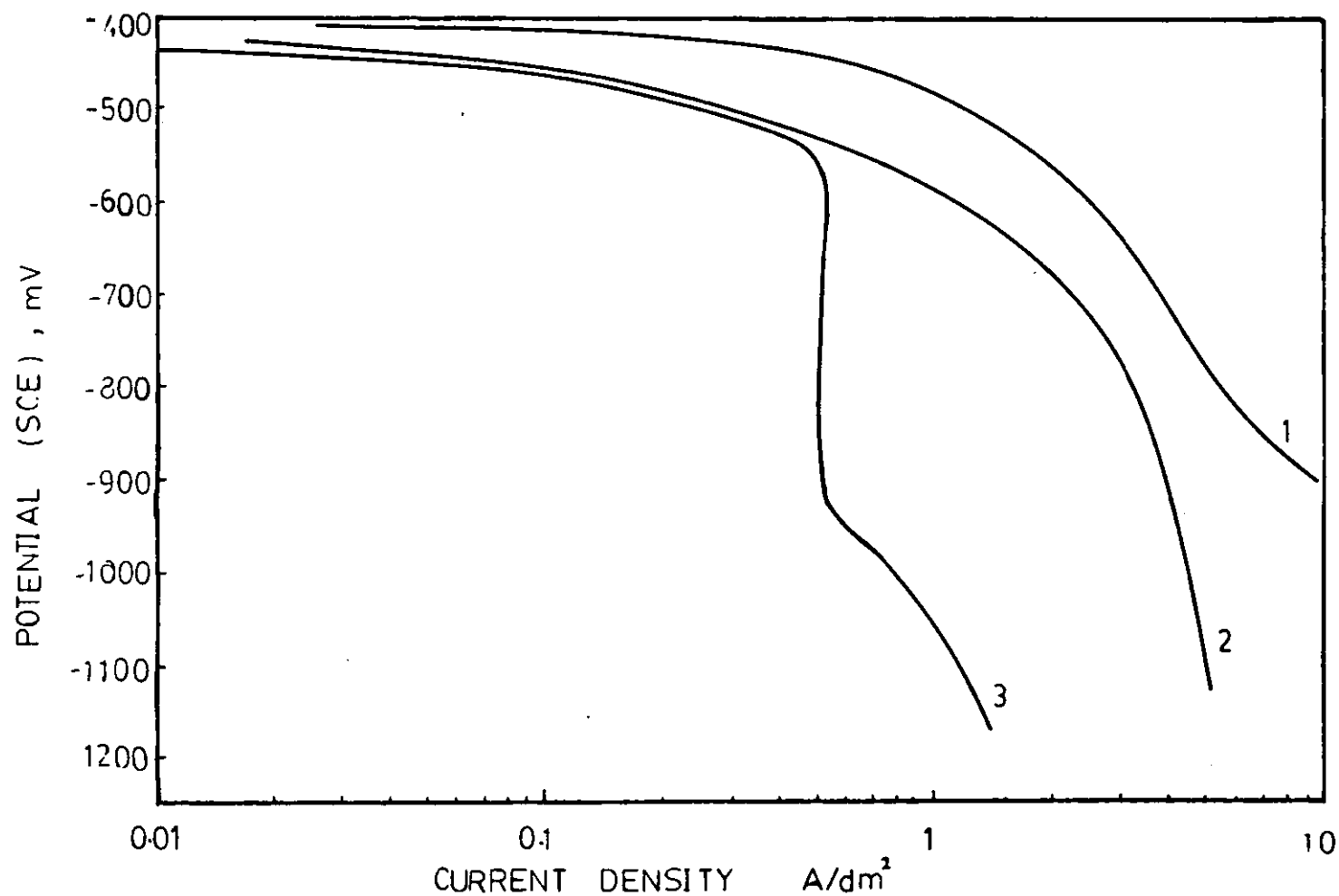


FIGURE 53: POLARIZATION CURVES FOR LEAD, TIN AND LEAD-TIN ALLOY.  
 CURVE 1: SOLUTION CONTAINS 49 g/l LEAD AND 2.5 g/l GELATIN  
 CURVE 2: SOLUTION CONTAINS 49 g/l LEAD, 5.5 g/l TIN AND THE ADDITIVES OF (1) and (2)  
 CURVE 3: SOLUTION CONTAINS 5.5 g/l TIN AND PEPTONE, AND PYROGALLOL 2.5 g/l EACH

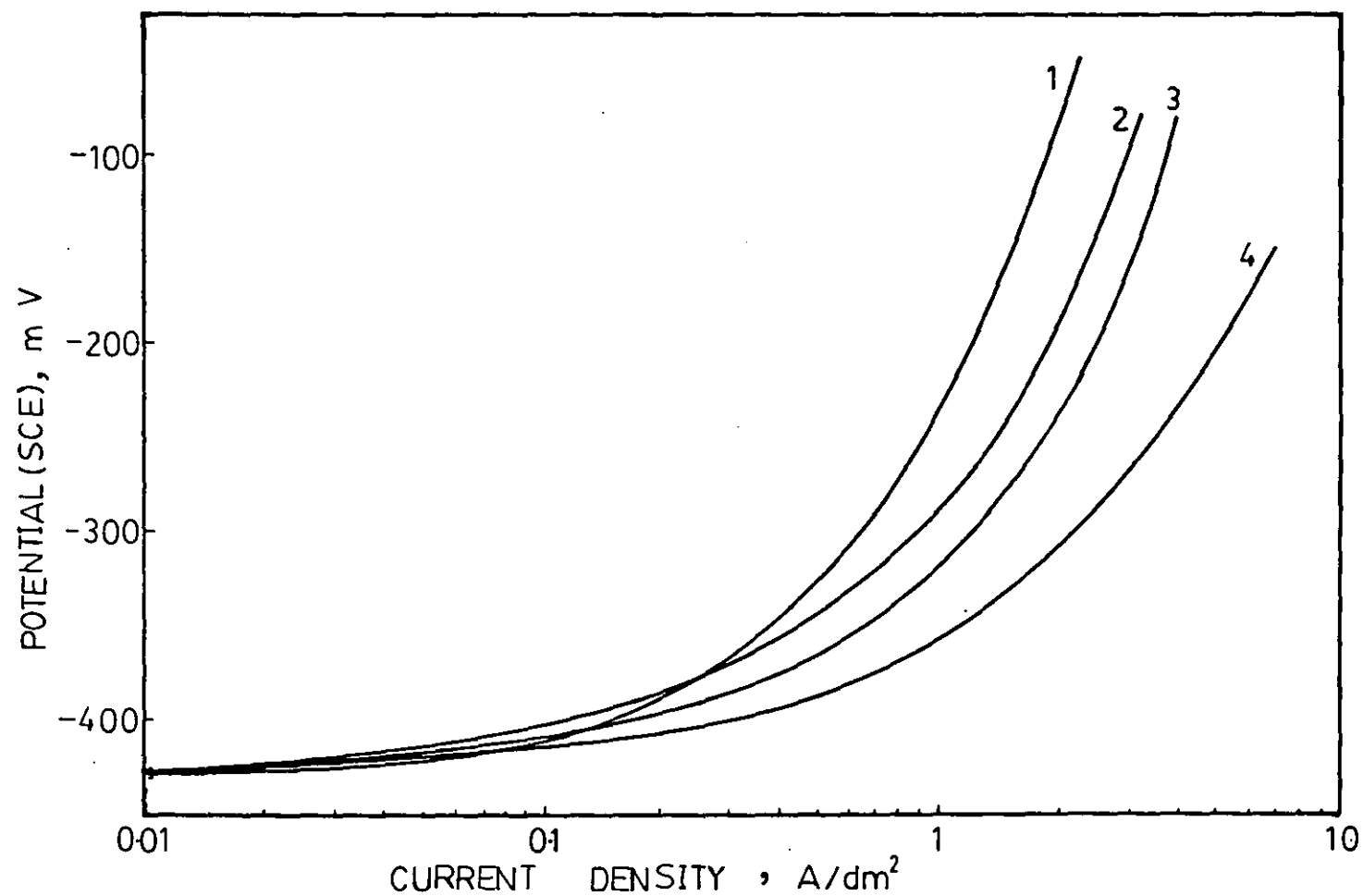


FIGURE 54: THE EFFECT OF INCREASING THE TIN CONTENT IN SOLUTION ON THE ANODIC DISSOLUTION

CURVE 1: SOLUTION OF 40 Pb:6 Sn;      CURVE 2: SOLUTION OF 70 Pb: 30 Sn;  
 CURVE 3: SOLUTION OF 80 Pb:20 Sn;      CURVE 4: SOLUTION OF 90 Pb:10 Sn.

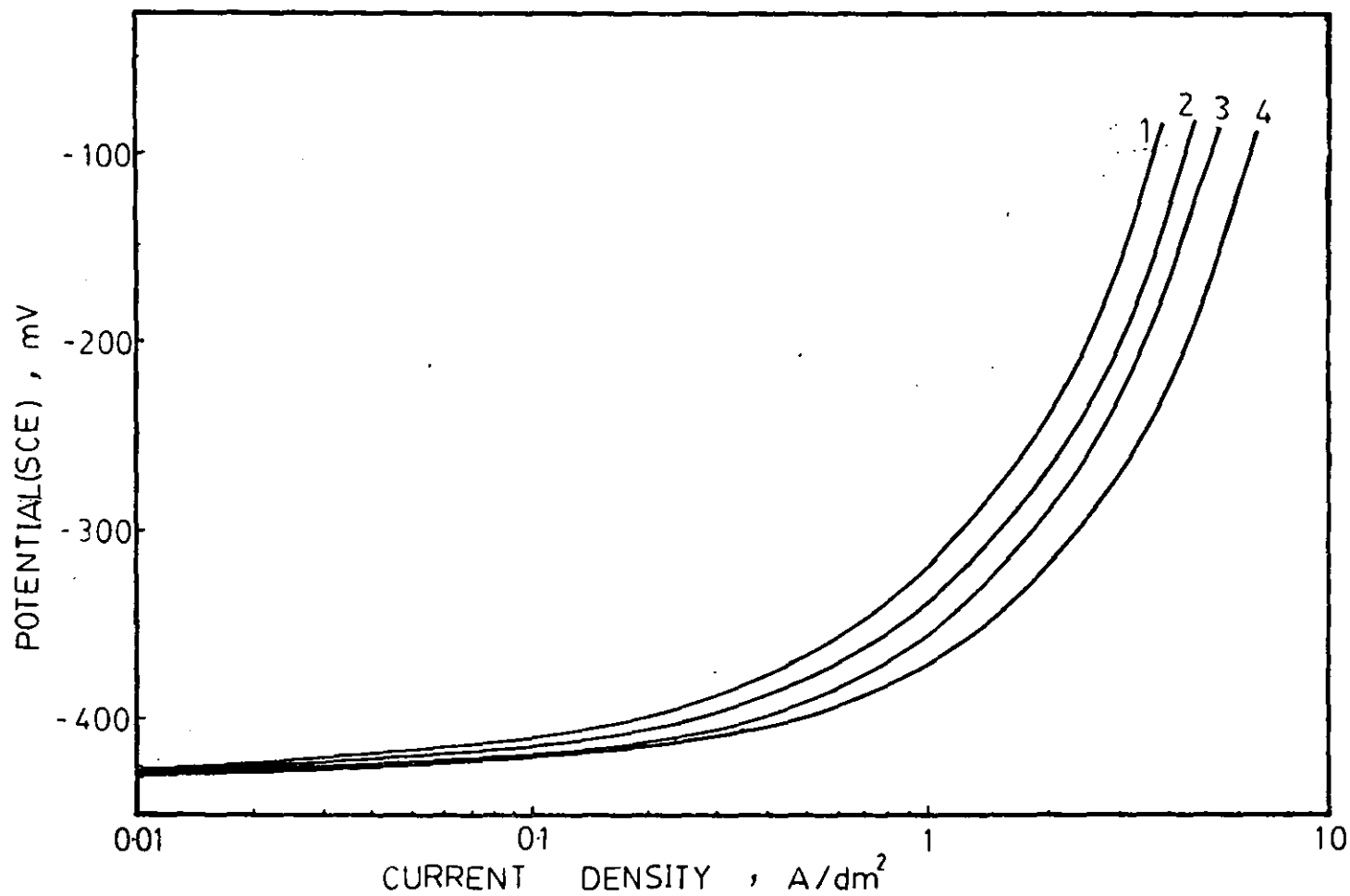


FIGURE 55: EFFECT OF TEMPERATURE ON THE ANODIC BEHAVIOUR OF SOLUTION OF 90 Pb:10 Sn RATIO CONTAINING ADDITIVES. CURVE 1: AT 25°C; (2) AT 40°C; (3) AT 55°C; AND (4) AT 70°C.

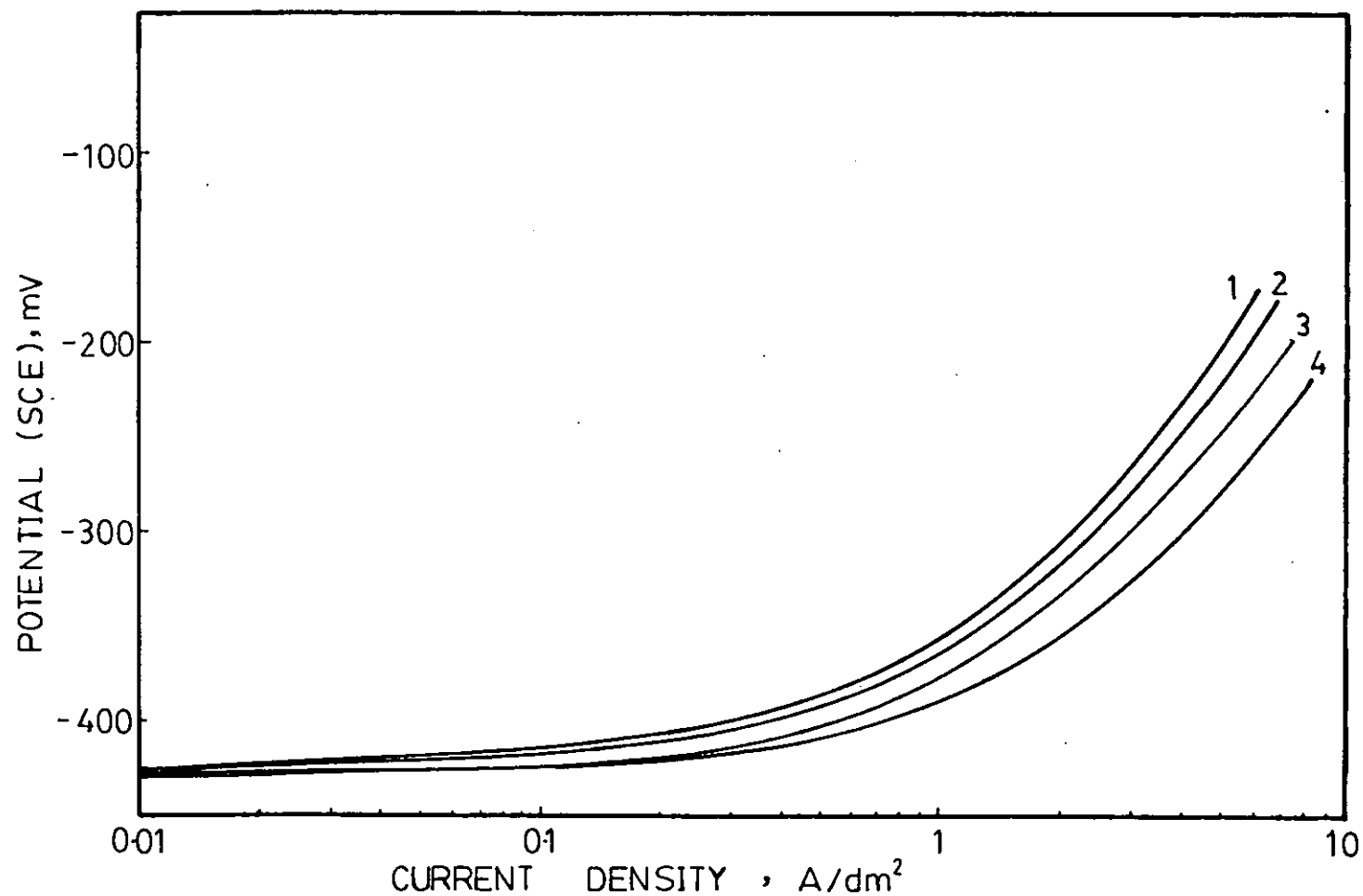


FIGURE 56: EFFECT OF TEMPERATURE ON ANODIC BEHAVIOUR OF SOLUTION OF 80 Pb:20 Sn RATIO CONTAINING ADDITIVES AND 50 g/l FREE ACID.

CURVE (1) AT 25°C; (2) AT 40°C; (3) AT 55°C, AND (4) AT 70°C.

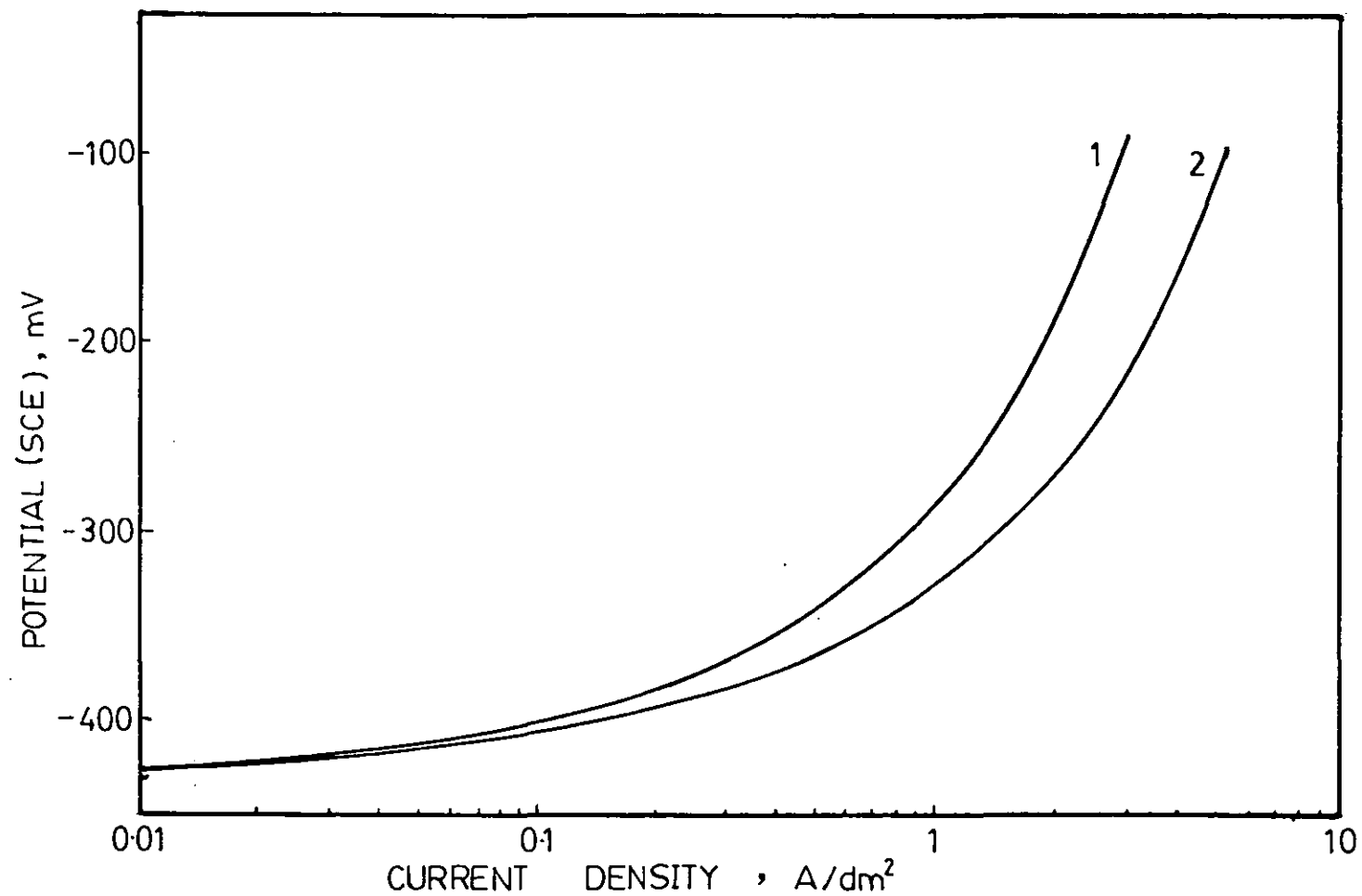


FIGURE 57: EFFECT OF TEMPERATURE ON THE ANODIC BEHAVIOUR OF SOLUTION OF 70 Pb:30 Sn CONTAINING ADDITIVES.  
CURVE (1) AT 25°C AND CURVE (2) AT 40°C.

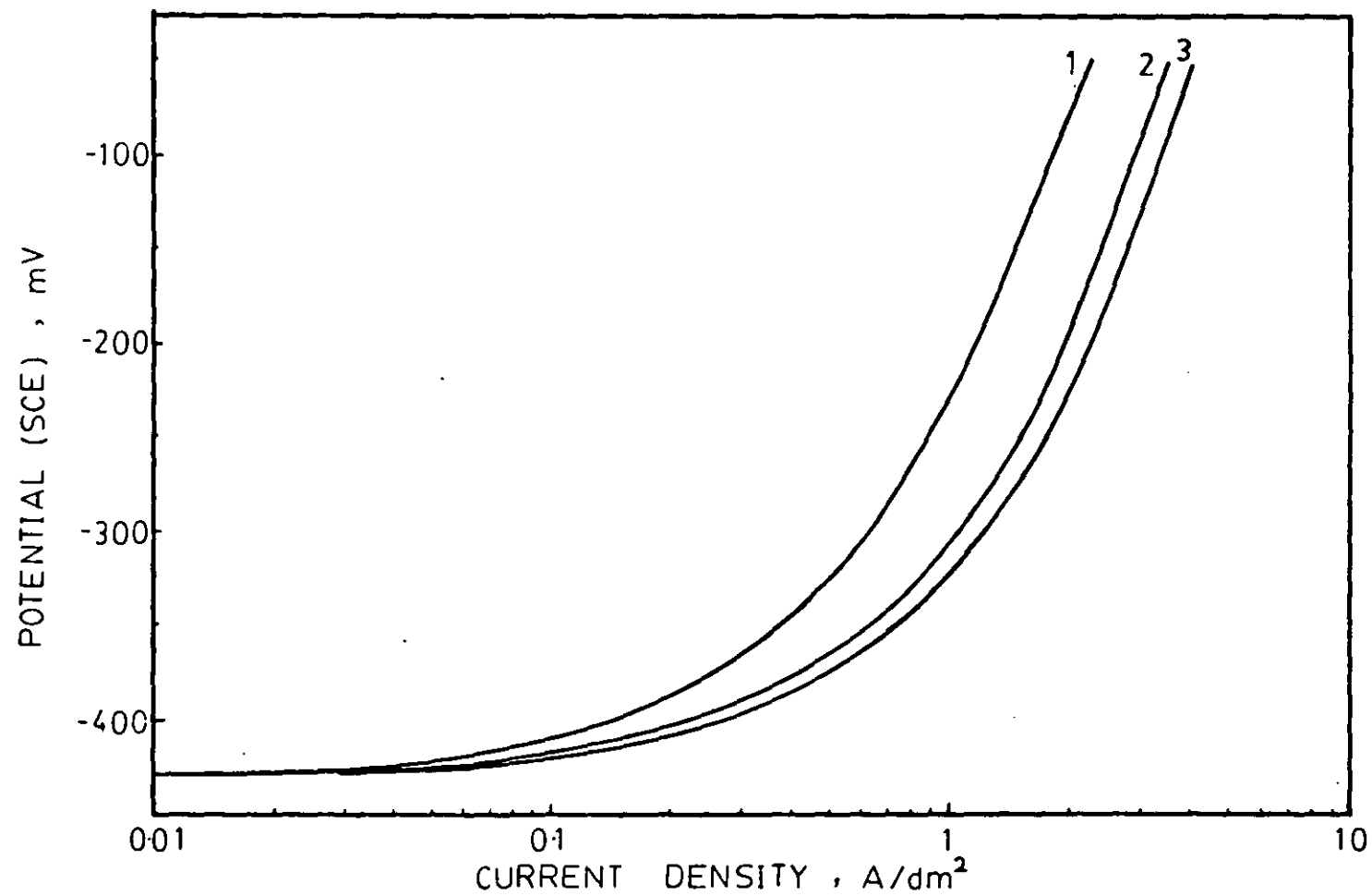


FIGURE 58: EFFECT OF TEMPERATURE ON THE ANODIC BEHAVIOUR OF SOLUTION OF 40 Pb:60 Sn CONTAINING ADDITIVES: CURVE (1) AT 25°C; CURVE (2) AT 40°C, AND CURVE (3) AT 55°C.

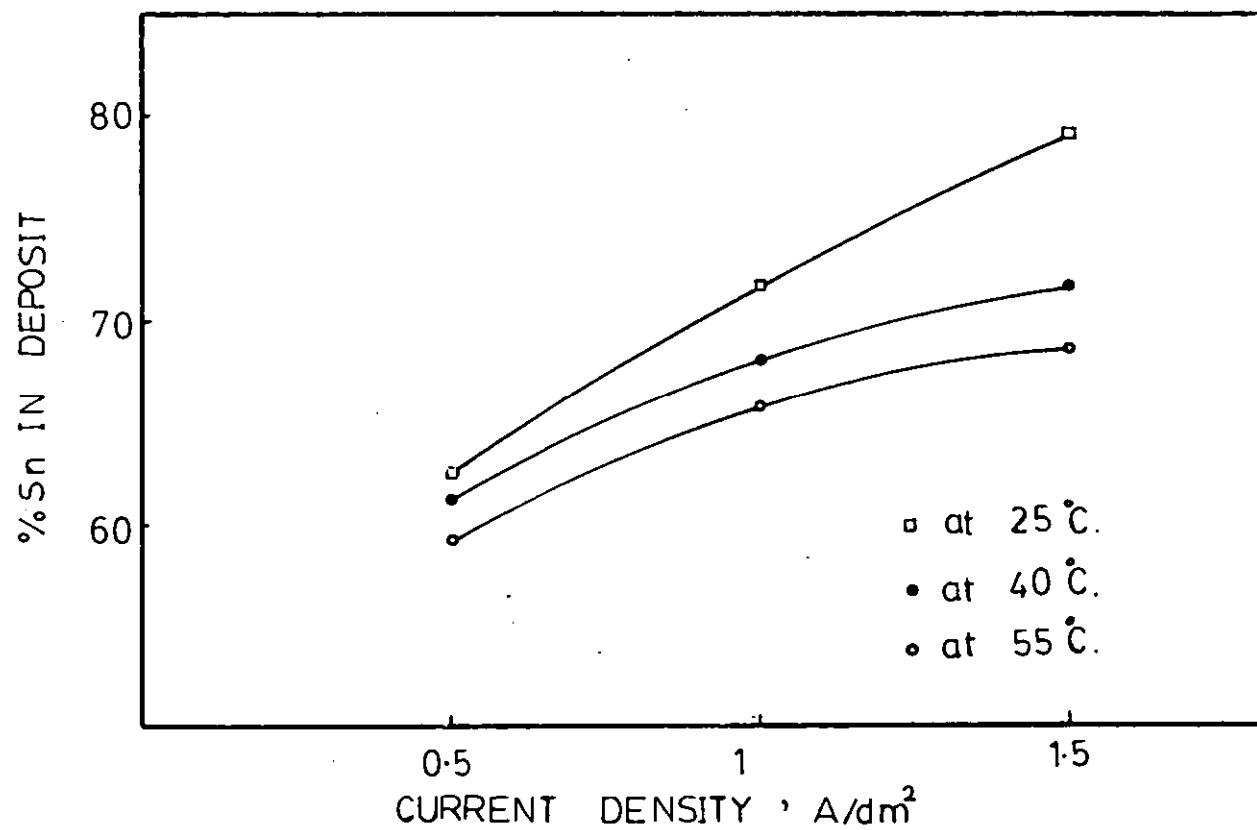


FIGURE 59: EFFECT OF CURRENT DENSITY AND TEMPERATURE ON TIN PERCENTAGE IN DEPOSIT FOR SOLUTION OF 40 Pb: 60 Sn.

(38)

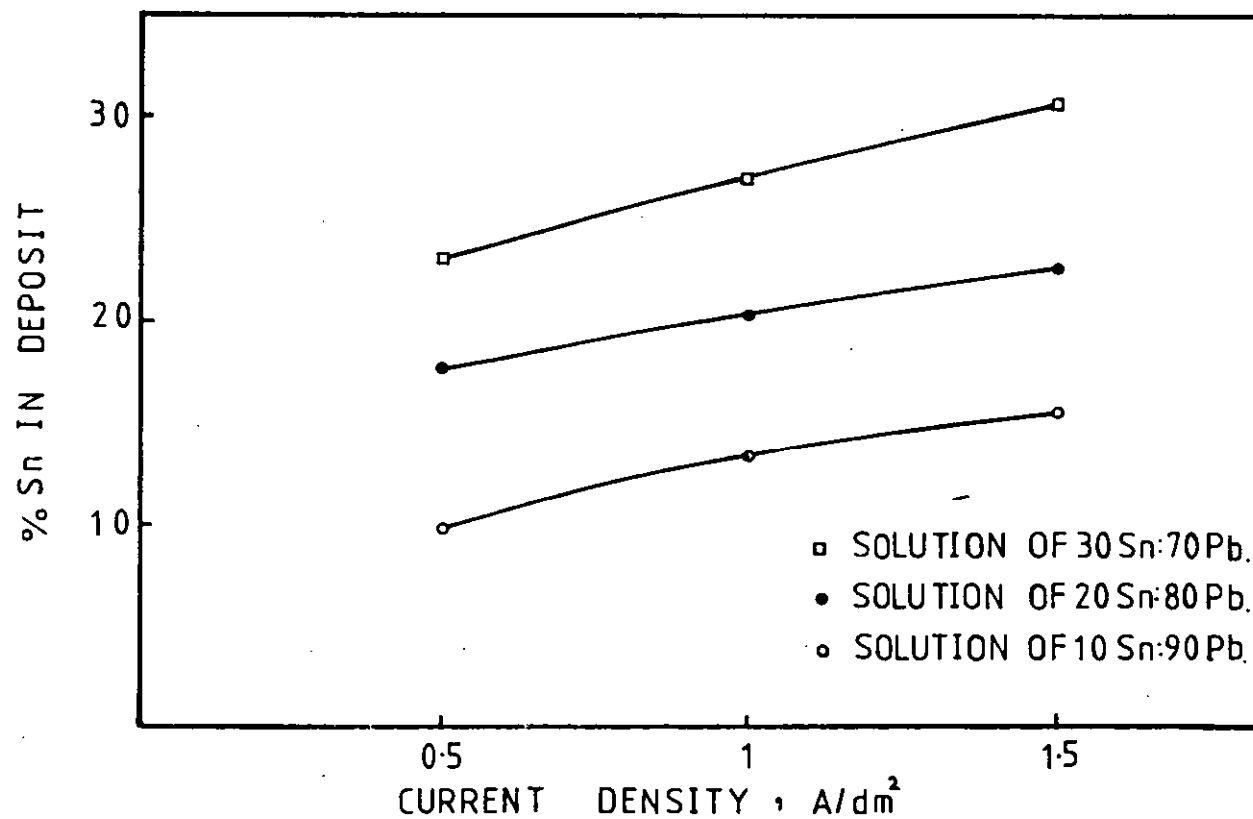


FIGURE 60: EFFECT OF CURRENT DENSITY ON TIN PERCENTAGE IN DEPOSIT

(39)

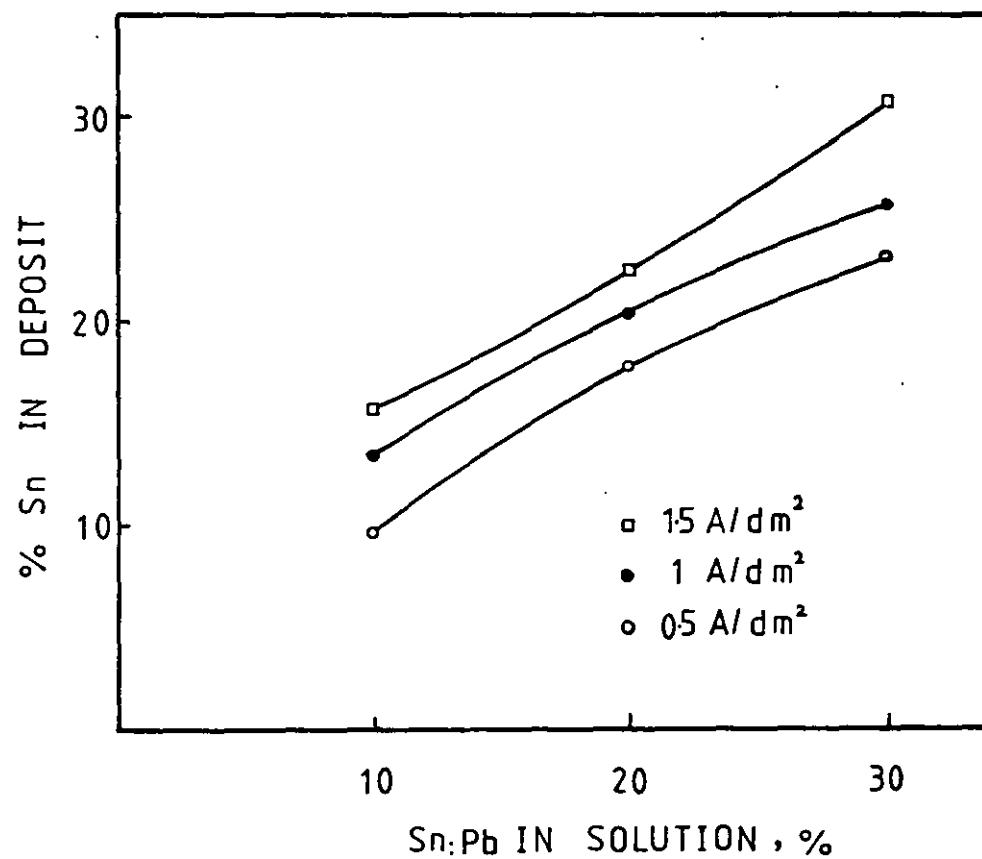


FIGURE 61: EFFECT OF TIN:LEAD RATIO IN THE SOLUTION ON THE PERCENTAGE OF TIN IN DEPOSIT

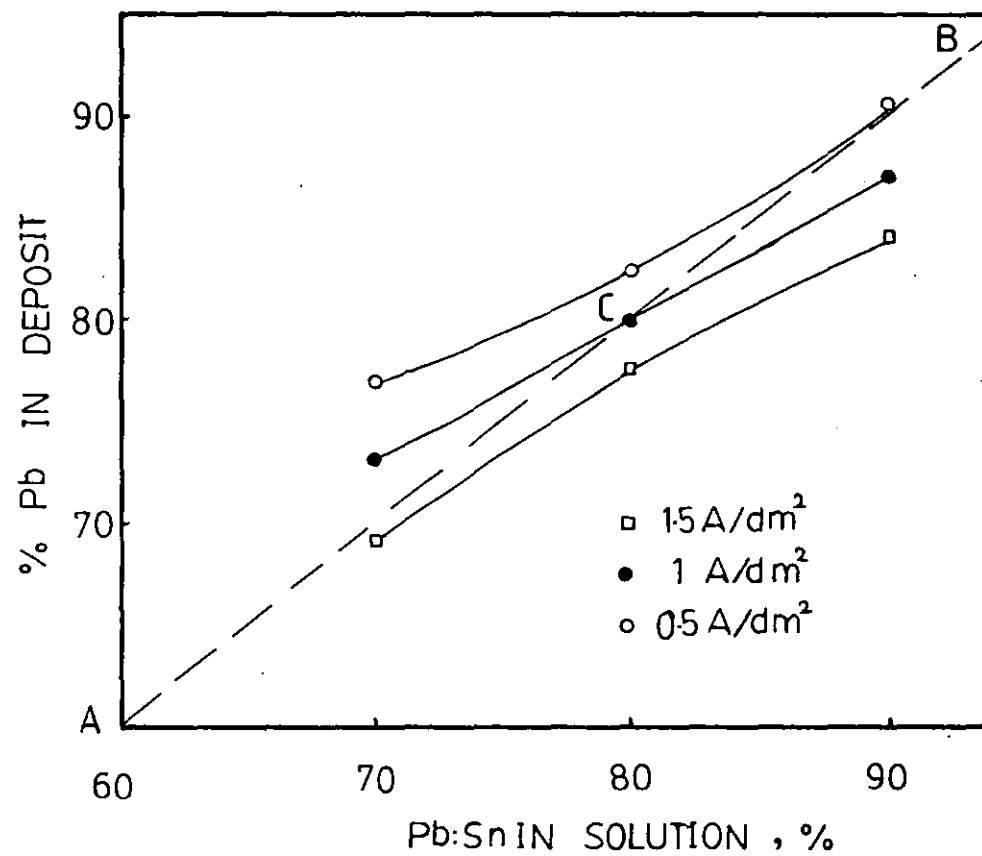


FIGURE 62: EFFECT OF LEAD:TIN RATIO IN SOLUTION ON LEAD PERCENTAGE IN DEPOSIT



FIGURE 63: ELECTRON MICROGRAPH FOR DEPOSITS FROM  
SOLUTION OF 90 Pb:10 Sn (Mag 2200X)

a) Current density  $0.5 \text{ A/dm}^2$

b) Current density  $1.5 \text{ A/dm}^2$

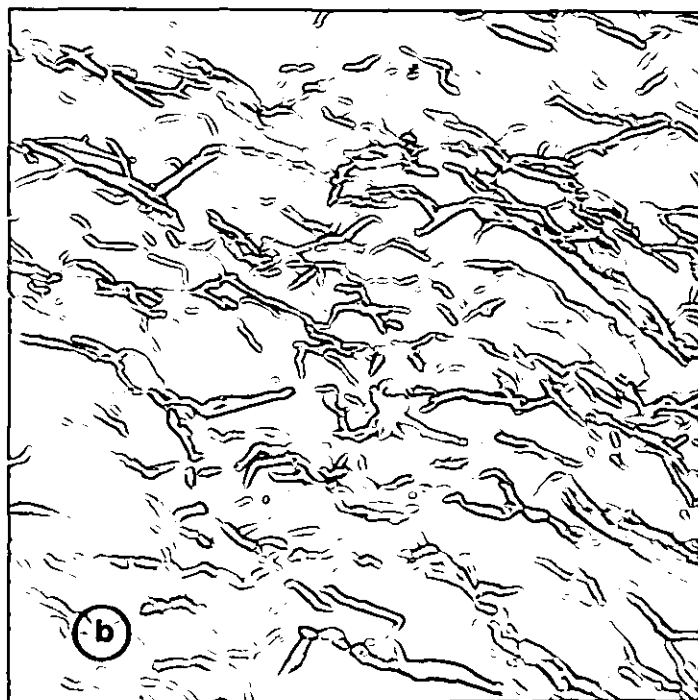
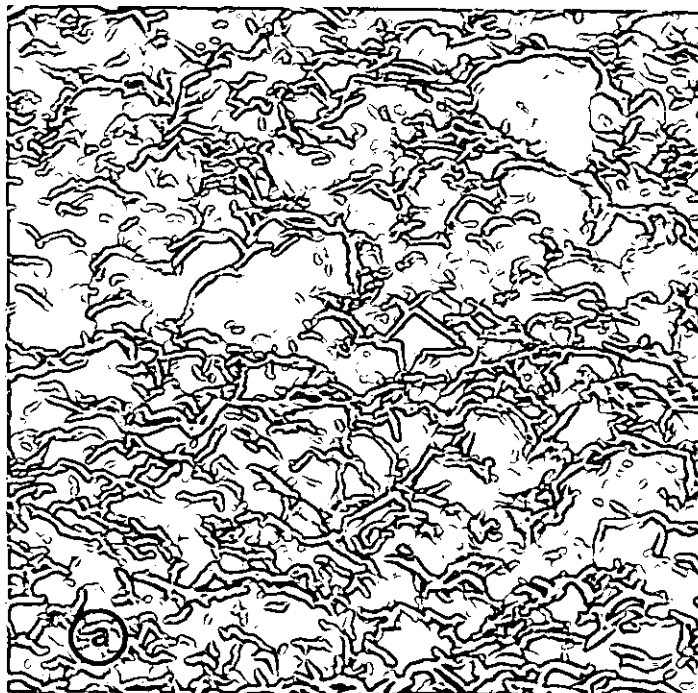


FIGURE 64: ELECTRON MICROGRAPH FOR DEPOSITS FROM  
SOLUTION OF 80 Pb:20 Sn (Mag. 2200X)

c) Current density  $0.5 \text{ A/dm}^2$

d) Current density  $1.5 \text{ A/dm}^2$

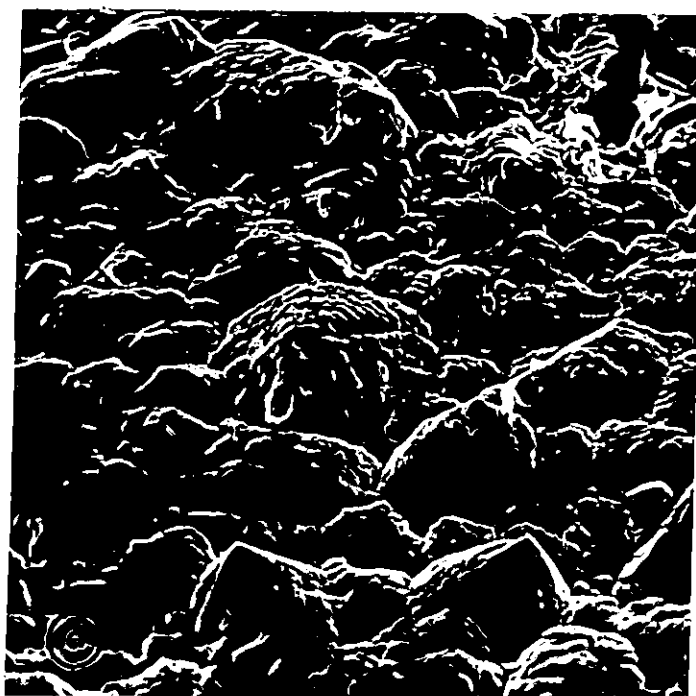
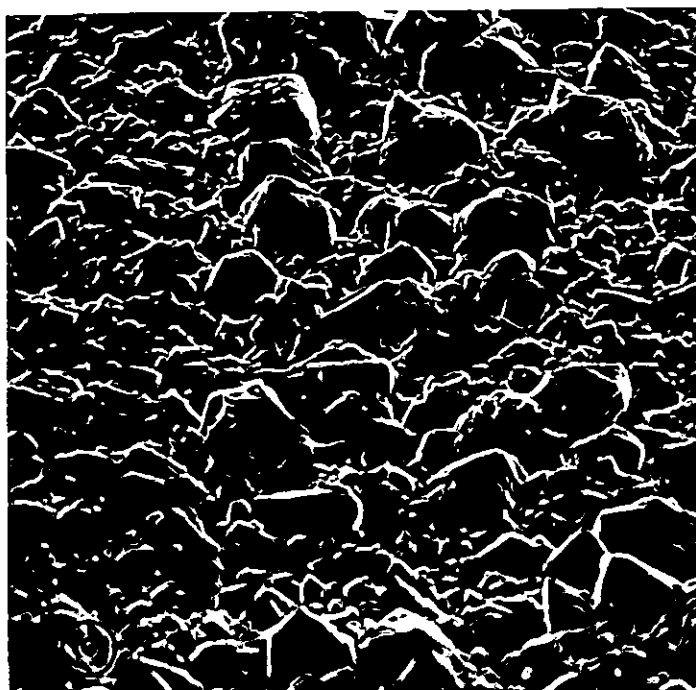
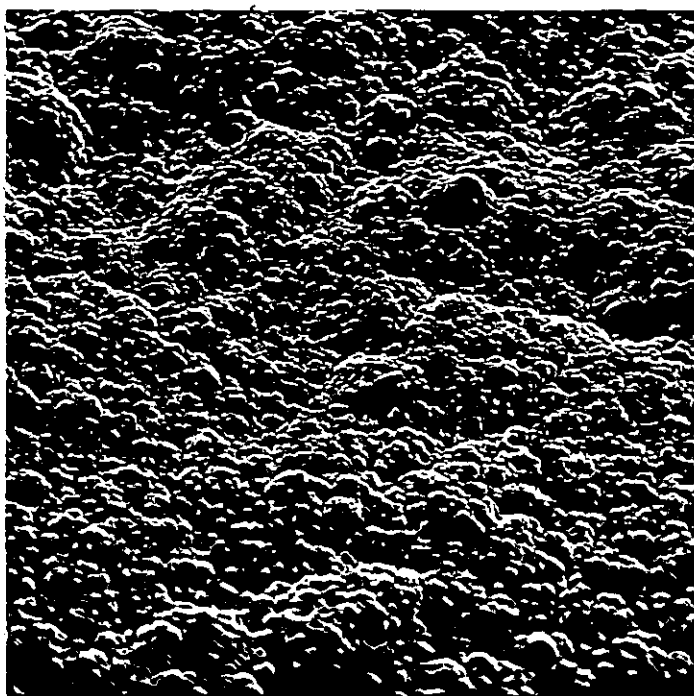


FIGURE 65: ELECTRON MICROGRAPH FOR DEPOSITS FROM  
SOLUTION OF 70 Pb:30 Sn  
(Mag. 2200X)



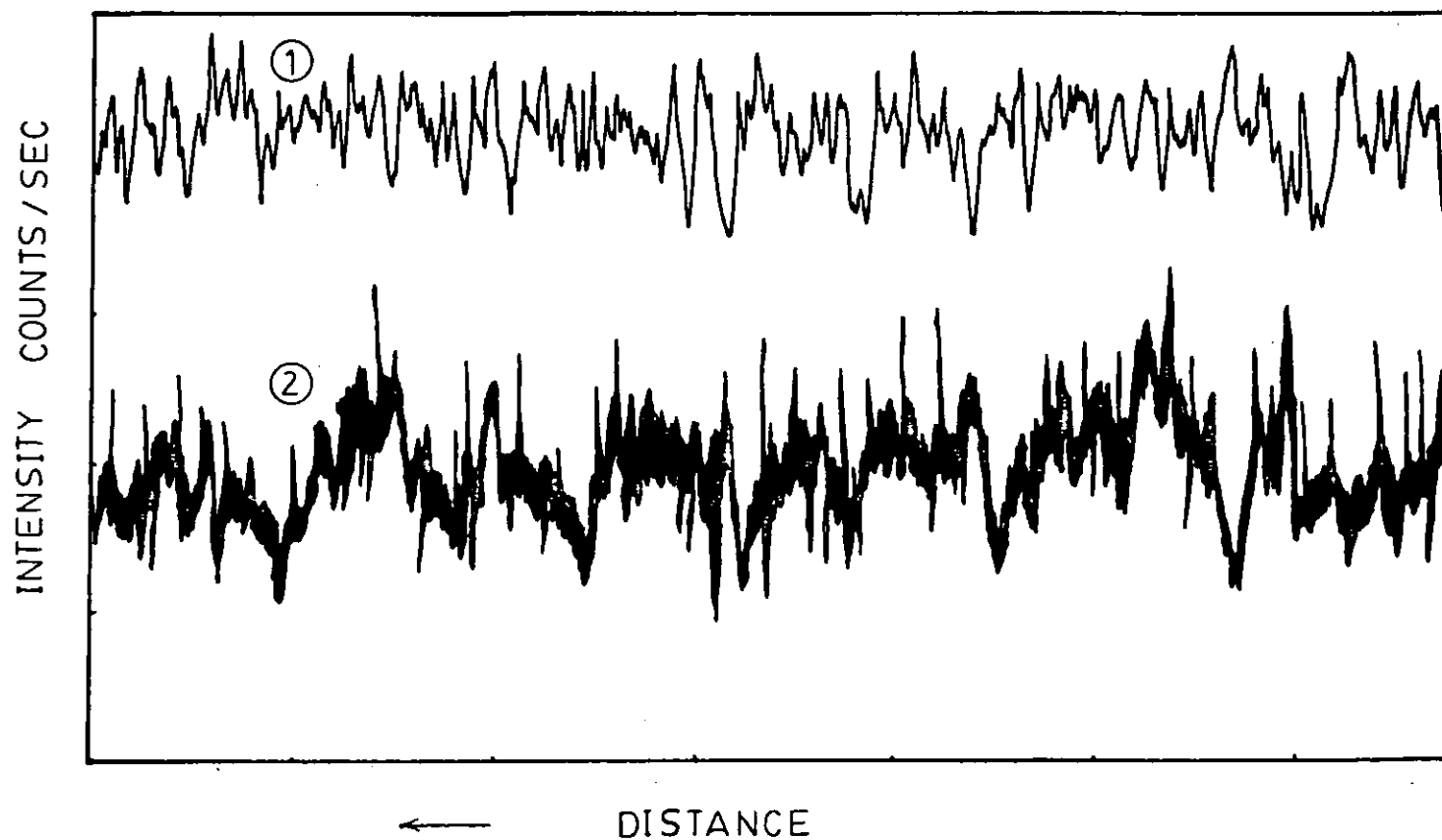


FIGURE 66: PART OF AN X-RAY SPECTRUM FOR LEAD-TIN ALLOY OF 90.2 Pb:9.8 Sn COMPOSITION

1. Lead

2. Tin

