Electroplated Lead Alloys for Plain Bearing Overlays

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SYNOPSIS

A review has been prepared of the history of bearings, the different types of bearing in use and their main characteristics and properties. Plain bearings have been reviewed in some detail with emphasis on the overlay and its design, application and performance characteristics. A brief summary of alloy plating in general introduces a detailed review of lead-tin, cadmium-tin and lead-cadmium alloy electroplating.

The electrodeposition of lead-cadmium alloys has been investigated using three different electrolytes. The electrolytes, based on sulphamates, fluorosilicates and fluoroborates were investigated using a small cell. Various plating parameters were altered in order to find the optimum conditions for plating a lead-cadmium alloy of known composition. The fluoroborate electrolyte was studied further using a large cell in which several half shell bearings were plated for mechanical and corrosion testing.

The electrolytes based on sulphamates and fluorosilicates showed some potential as a solution for plating lead-cadmium alloys but only the fluoroborate showed sufficient potential to warrant further investigation to the extent where a possible viable commercial process could be developed.

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1. INTRODUCTION

Bearings are of great antiquity and the Egyptian tombs contain pictures of chariots from which it is obvious that the artists were familiar with wheeled vehicles, which of necessity had bearings even though of a primitive kind [1]. The invention of the wheel gave rise to a necessity for bearings and today there is scarcely a aspect of life into which they do not enter in some form.

The first bearings were probably made of wood. It is a well known fact that ancient man moved large blocks of stone on rows of logs, the earliest form of roller bearing and before that sledges were used, a form of plain bearing.

With the invention of the wheel, selection of materials for bearings become important. The main function of a bearing is to transmit a force between two components of a machine with a minimum of power loss while allowing relative motion and providing some type of location between them. To meet these requirements, the bearing material has to be carefully chosen. Long ago it was found that one of the best woods for bearing was Lignum vitae [2] because of its high density and resin content. In later bearings, the wood was lined with iron, brass or bronze, leather or a fibre of some kind. It was not until the end of the eighteenth century that special alloys were introduced for bearing surfaces. Babbitt [3] patented the first use of an alloy containing 89% tin, 8.9% antimony and 1.8% copper as a lining alloy. According to Cherpy [4], the best alloy of this type was that containing 83% tin, 11% antimony and 6% copper, this has since been modified considerably.

The main impetus for the development of bearing technology was the introduction of the engine, in its earliest form as the steam engine and later the petrol and diesel engines. At the present day, there are many types of bearings. The form of bearing which can be used in any situation is determined by the relative movement required in the situation, the load and the type of constraints which have to be applied to it [5]. Some examples of relative motion between components and the constraints applied are shown in Table 1. To meet these differing demands, three main technological approaches have been developed, i.e. soft metal bearings, hard metals hydrodynamically lubricated, and ball or roller type bearings. The first named have particular virtues of wear, corrosion resistance and seizure resistance combined with plasticity which can tolerate misalignment and absorb particles which would otherwise wear.

Traditionally the tin-based white metals, (Babbitt metal) have been the basic soft meterials, but although these are excellent in terms of seizure resistance and softness, they do possess serious limitations, the most serious of which is the rapid fall in fatigue resistance with temperature rise. As a result of this and the continued uprating of engines, it has been necessary to produce metals with improved fatigue and wear properties. At the present time, these metals are principally alloys of copper-lead, aluminium-tin or aluminium-silicon and although many of them are suitable for direct use in engines, it is necessary in many instances to overlay them with a softer alloy which has properties more akin to the white metals. Such alloys of thickness normally about 25 um consist usually of lead-tin, lead-tin-copper or lead indium and are conventionally applied by electrodeposition.

The demands of high performance have shown that the corrosion resistance of the overlay to standard lubricants can become a limiting factor in the life of the bearing. The engine bearing environment is oil at a temperature in the range of 70 - 170°C. At the upper end of this range, a typical engine oil will suffer breakdown of the antioxidant additives. Oxidation of the oil occurs in consequence and the overlay will become subject to corrosion attack by the acid and peroxide content created [6]. Furthermore, in recent years, because of fuel shortage and cost, attempts have been made to use heavier fuel oils and to run standard lubricants for longer periods in engines; these oils are often highly contaminated and corrosion can become a serious problem.

The development of a more corrosion resistant overlay is essential if existing fuel supplies are to be used more effectively. Preliminary work at Glacier Metal Company Limited suggested that a lead-cadmium alloy may provide such an answer.

This thesis reviews the types of bearing in use and their main characteristics and properties. Plain bearings have been reviewed in some detail with emphasis on the overlay. A brief summary of alloy plating in general introduces a detailed review of lead-tin and lead-cadmium alloy electroplating.

The practical work reported consists of an investigation of lead-cadmium alloy plating using three different electrolytes. The electrolytes, based on sulphamates and fluorosilicates were investigated using a small cell. Polarisation data was obtained under the influence of various plating parameters. Conductivity measurements were taken and the optimum conditions for plating a lead-cadmium alloy of known composition were found. The fluoroborate electrolyte was studied using both the small cell and a large cell in which several half shell bearings were plated for mechanical and corrosion testing. Electronmicrographs of the electrodeposited alloy were prepared and some electron diffraction and electron microprobe analysis of the lead-cadmium electrodeposit has been reported.

The results are discussed in detail with a view to developing an industrial process by which plain bearings can be overlay plated with a lead-cadmium alloy.

2. BEARING TYPES

A bearing is a mechanism which allows loads to be transmitted across surfaces which move relatively to each other. Such mechanisms fall into the following categories [7].

2.1 Rolling Mechanisms

Roller bearings are used for very high speed operation or where frequent stopping and starting is usual. High strength steels are used to produce the balls which carry the load by point contact or line contact for rollers. A 1% carbon, 1% chromium steel EN31 hardened and tempered at temperatures upto 120°C to give a hardness of 600 to 650 V.P.N. is used almost exclusively.

In certain applications, other steels with a high surface fatigue resistance are also used such as case hardened steels. For high corrosion resistance, the chromium content may be increased to 18% and with the addition of cobalt or the use of high speed tool steel, the dimensional stability and high temperature hardness is increased.

The balls are produced by closed die forging of blanks and the races, manufactured from similar materials, are machined from rod or tube. Needle bearings fall into this category and are usually manufactured of similar materials. A typical selection of roller bearings are shown in Fig 1.

2.2 Sliding/Rubbing Mechanisms

Self-lubricating or inherently low friction materials generally fall into this category, such as carbon and P.T.F.E. Metals in the absence of lubrication are restricted to very low loads and speeds. Lubrication extends the use of rubbing mechanisms, the lubricants normally consisting of long chain molecules which are absorbed onto the bearing surface. The applications of sliding/rubbing mechanisms cover a very wide spectrum. Bearings may range in size from miniature instrument bearings, supporting a few grammes to bridge supports carrying thousands of tonnes. Other applications include gears, machine tool slideways, piston rings, seals and sliding electrical contacts [8]. Several types of plain bearings are included in this category (Fig. 2).

2.3 Fluid Films

These types of bearings can be divided into several categories depending on the type of lubrication employed - oil, grease, water, gas, etc. or mode of operation - hydrodynamic, hydrostatic, mixed or boundary.

The most common bearing is the hydrodynamic type in which the fluid film is self generated. There is some incompatability of bearing material property requirements and a compromise must be reached. During start-up when the fluid film has been generated, boundary lubricating properties are required and the strength of the bearing material imposes load limitations.

As the surfaces move relative to one another, a hydrodynamic wedge is generated and a pumping action may be generated within the bearing itself [9]. During running, when the fluid film is fully developed, the film thickness imposes limitations and conformability and embedability are amongst the necessary material properties. Others are strength, fatigue strength and high melting point.

The first choice materials for this application are the white metals, alloys of lead and tin. Limitations on the use of white metal bearings are their load - bearing capacity, an upper temperature limit of approximately 140°C and in some applications a lack of chemical resistance. Alternative materials are silver for resistance to chemical attack and copper alloys, such as phosphor-bronze and copper-lead for higher temperature and higher strength applications.

In a hydrostatic bearing, the surfaces are separated by a film of lubricant supplied (externally) under pressure to one or more recesses in the bearing surface. If the two bearing surfaces are made to approach each other under the influence of an applied load, the flow is forced through a smaller gap. This causes an increase in the recess pressure. The sum of the recess pressure and the pressures across the area surrounding the recess, build up to balance the applied load. The ability of a bearing film to resist variations in gap with load, depend on the type of flow controller. A typical hydrostatic journal bearing is shown in Fig. 3. The other main type of hydrostatic bearing is the plane thrust pad.

Hydrostatic lubrication enables extremely low coefficient of friction values to be obtained and is particularly suitable for heavy loads and slow speeds. However, the need to provide the necessary ancillary equipment and the high power requirements force this type of lubrication to be adopted only when there is no satisfactory substitute [10].

Externally pressurised gas bearings have the same principle of operation as hydrostatic liquid lubricated bearings.

Gas bearings are used mainly in the form of smooth surface cylindrical journal bearings, pivoted pad journal and thrust bearings and spiral grooved surface bearings in the form of flat thrust bearings cylindrical journal bearings and spherical and conical bearings.

2.4 Other Bearings

Other bearings are more specialised in their application, design and manufacture and include such mechanisms as electrical and magnetic fields. These bearings are of a complex nature and will not be discussed any further.

A further type of more simple bearing in the flexure pivot (Fig. 4). These types of bearings are used for oscillatory movement only.

3. PLAIN BEARINGS

Plain bearings are designed to allow free movement between two surfaces in sliding contact. The reduction of friction caused by this sliding contact is usually achieved by the use of a fluid lubricant film. The bearing material must be chosen so as to minimise the consequences of a breakdown of this lubricating film. The major properties of the material as listed by Petty [11] are:-

i) Compressive strength coupled with fatigue and shock resistance.

ii) Wear resistance (but the bearing must not be so hard that the shaft is worn).

iii) Plasticity, to tolerate misalignment and to embed any grit particles.

iv) High thermal conductivity to remove frictional heat.

v) Good corrosion resistance to the acid products of oil decomposition.

vi) Low melting point (but well above operating temperatures) so that melting out would occur in preference to complete seizure which would cause much damage.

vii) Ability to retain an oil film to reduce the effective friction.

As most of these properties are conflicting in nature, the eventual choice of material is inevitably a compromise. Combinations of materials are used to optimise various of these properties and so a variety of bearings are produced to meet a wide range of uses and conditions. Pratt[12] lists the four main types of plain bearing applications as :-

i) Reciprocating engine bearings operating with hydrodynamic lubrication, the dynamic load being applied through the oil film, eg. the big end and main bearings of the automotive (internal combustion) engine.

ii) Rotating plant bearings operating with hydrodynamic lubrication, the load applied to the bearing surface through the oil film being steady, eg. turbine journal bearings, rolling mill bearings, marine stern tubes and tilting pad thrust bearings.

iii) Lubricated bearing applications operating under conditions that do not create full hydrodynamic lubrication. Included in this category are the common copper base alloys, grease lubricated in general engineering applications, as well as graphitized bronze, wick lubricated white metal and the important classes of oil impregnated porous bronze bearings and pre-lubricated plastic or plastic-lined bearings.

iv) Non-lubricated bearing applications, ie. bearings operating dry or in non-lubricating media. Most bearings of this type are based on P.T.F.E. or nylon.

To meet the demand of these differing applications, a variety of bearings have been developed.

3.1 White Metals

Babbitt metal was the first alloy to be widely used for bearings. The alloy is usually based on lead or tin with additions of antimony or copper.

On their own, white metals have a very low fatigue strength. The load carrying capacity is greatly increased by supporting the alloy on a steel or bronze backing shell and reducing the white metal thickness to 0.1 - 0.3mm. These bearings work perfectly satisfactorily at low loads (see Table 2) and can cope with misalignment, dirt and temporary lubrication failure. Because of the low loading, their use is restricted to one or two automobile engines and large conservatively rated diesel engines. A further drawback to the use of these alloys is the corrosive attack from the oils. If the engine oil breaks down, the acids and peroxides formed will attack the lead phase to form a "soap". The tin based alloy is more resistance to this type of attack.

Although the typical composition of the white metal alloy is shown in Table 2, over the years various compositions and additions have been tried.

Vanadium has been reported [1] to increase density as well as tensile and compressive strengths. An alloy of 78% tin, 9.4% antimony, 6.3% copper and 6.3% vanadium has been suggested.

Phosphorus has a hardening effect and has been used on a French railway in an alloy containing 80% tin, 12% antimony, 7.7% copper and a maximum of 0.3% phosphorus. It has also been found [13] that cadmium and tellurium increase the hardness and tensile and fatigue strengths of alloys.

An alloy containing 3% arsenic has been claimed [14] to have superior strength properties to tin-base alloys and an alloy with 1% arsenic is widely used in the U.S.A. for linings in internal combustion engine bearings.

The white metal bearings are usually manufactured by continuous strip casting although in the U.S.A. one lead based specification [12] (92.5Pb, 4Sn, 3.5Sb) is impregnated into a steel backed cupro-nickel sinter. Rotary lining is also used although this generally gives a lower fatigue strength.

3.2 Copper-Lead and Lead-Bronze Alloys

Copper-lead alloys with a high lead content (25 - 50%) were introduced in the 1930's. Compared with white metals, they offer a much wider range of strength and hardness although it is still too low for many automobile engines. The properties of the copper lead alloys depend on the lead content.

The lead is distributed in such a way in the copper matrix, that it does not harden the matrix. The lead content varies between 25% and 40% although a content of greater than 30% is not often used.

The higher the lead content, the lower the fatigue strength but the surface properties are improved. However, the lead phase of the alloy is particularly susceptable to corrosion from organic based acids in certain oils. This was overcome in the late 1930's by the introduction of the lead or tin based eletrodeposited overlay. The overlay was introduced primarily to improve the surface properties of the harder and stronger lead-bronzes although the overlays could be made more corrosion resistant with the addition of small amounts of tin or indium, thus protecting the lead phase in the underlaying alloy lining.

A wide variety of alloying elements have been used with copper-lead base alloys. Additions of tin, phosphorus, zinc, aluminium, nickel and other elements have been investigated and some are still used to improve particular properties.

An arsenic content of 0.4% to 0.5% has a slight hardening effect and an equally slight increase in the tensile strength has been observed [15].

Phosphorus additions harden the alloy, but its prime function is as a deoxidizer [1]. The tensile strength and fatigue range are increased, the increase in tensile strength at elevated temperatures is considerably more than that resulting from arsenic. Antimony up to 0.22% increases the tensile strength of oxygen-free copper without any decrease in ductility.

As with white metals, copper-lead and lead-bronze alloys can be manufactured by strip casting. The bimetal strip can also be prepared by sintering copper-lead powders on the steel strip in a reducing atmosphere. The lead-bronzes are used under conditions of high load.

3.3 Aluminium Base Alloys

Aluminium alloys were first used in the 1930's when a tin-aluminium alloy was used in aircraft engines [1]. In the 1940's, the U.S. used a 6% tin-aluminium alloy in solid form (ie. no steel back) in some automotive engines. However, due to a high expansion co-efficient which precludes their use in modern high speed engines, all aluminium based alloys are in the form of a thin lining on a steel backing (with the exception of Volkswagon

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engines which are alloy based and can handle solid aluminium bearings). The most widely used alloy is the 20% reticular tin-aluminium alloy [16] with a fatigue resistance close to that of 70-30 copper-lead but with a considerably higher fatigue resistance. The surface properties of this alloy are so good, that no overlay is required and corrosion does not arise unless the oil is contaminated with water. An alloy containing 30% tin is used in Japan and has even better seizure resistance although its fatigue strength is somewhat lower.

The 6% tin-aluminium alloy is still used widely in the U.S. although it has an overlay plate after a special pretreatment for compatibility with modern day thin oil film conditions. For high strength engine bearings, an alloy containing 11% silicon - 1% copper-aluminium has been developed, the fatigue strength is as high as the strongest copper based alloy and this is improved even more by the use of an overlay plate (necessary to improve embedability).

The main advantage of aluminium alloy bearings over tin based white metal is shown in Fig. 5 where the fatigue strength of the aluminium alloy is retained with increase in temperature compared to tin based white metal which drops off dramatically with temperature rise.

3.4 Plastics

Several plastics possess good surface properties, ie. good wear resistance, seizure resistance and a low coefficient of friction. Unfortunately, they have inherently low strength, high thermal expansion and low thermal conductivity [8]. These shortcomings are usually partially overcome by incorporating additives to modify the thermal characteristics and using the plastic as a thin lining on a steel backing.

There are two main types of plastic bearings, those that operate with lubrication and those that do not. Those that operate with lubrication are either thermoplastic or thermosetting plastics.

Solid thermoplastic bearings can be used in a variety of non-arduous applications [12]. The most common polymers used are nylon and polyacetal. Bearings based on these polymers can run unlubricated in very mild conditions, but they are usually run with oil or grease lubrication and in some cases a solid lubricant in the form of P.T.F.E. powder or fibre is used. Higher bearing loads can be carried by using a steel-backed thermoplastic lined bearing. The most important type of this bearing is one consisting of a thin polyacetal lining bonded to porous bronze on a steel backing. A fatigue rating approaching that of 20% tin-aluminium may be obtained with this type of bearing. However, the polymer degrades under acid attack and it can only be run up to 120°C.

Thermosetting resins such as phenolic and epoxy resins, reinforced with cotton fabric or asbestos fibre have good strength and creep resistance compared with thermoplastics and can be used in highly loaded applications. Bearings of this type can be run at temperatures upto 175°C and as water works as a lubricant, these bearings are used to a large extent in marine applications.

Plastic bearings which do not require any lubrication are generally based on a P.T.F.E. composite. These composites include a woven P.T.F.E. fibre on a glass-reinforced phenolic backing, a steel-backed, P.T.F.E. filled epoxy resin and glass fibre in a matrix of P.T.F.E. Solid P.T.F.E. bearings can only operate effectively upto 200°C. The high temperature polymer, polyimide can operate upto 250°C and offers superior characteristics to P.T.F.E., especially with a graphite filling.

3.5 Other Plain Bearings

Other plain bearings include oil-impregnated porous bronze or iron, steel-backed P.T.F.E. - impregnated bronze and for high temperature dry bearing applications, carbon bearings can be used.

4. OVERLAYS

Overlay plating was introduced in the late 1930's as a means of overcoming the seizure problem posed by hard and rather incompatible bronze bearing alloys. The overlay also protected the lead phase in the lining from corrosive attack by the oil. At present with the use of higher performance engines, bearings with higher fatigue ratings are being developed. High strength alloys such as aluminium-silicon with consequent high hardness (50 - 100 HV) and low conformability are used. Thus, the use of overlays has become essential to improve the bearing properties of many bearing alloys. They are not intended as a sacrificial layer but are intended to last the life of the bearing.

4.1 Design and Required Properties

In practice, a number of conflicting properties are required of a bearing material [17] :

i) It must be able to withstand fatigue loads in the order of 100 MN/m^2;

ii) To withstand these loads at temperatures in the order of 100°C;

iii) To operate during starting and stopping with a limited oil supply without damaging the journal;

iv) To embed particles of dirt from the lubricant;

v) To withstand the possibly corrosive attack of the lubricant.

In order to carry these heavy fatigue loads, an engine bearing consists of a relatively thin lining of bearing alloy on a steel backing and it is the support given by the steel backing that enables the lining to carry the load. However, the remaining four properties have more to do with the overlay than anything else. Most overlays will withstand temperatures in the order of 100°C but if metal to metal contact should occur as in starting or stopping or misalignment, then the melting point of the alloy may be reached. Under normal conditions, this would not cause any damage as the temperature rise would only be momentary. Under a sustained temperature rise, the low melting point of the overlay is beneficial in that melting out would probably occur as opposed to complete seizure which would cause much damage.

In order to cope with the possibility of metal to metal contact, misalignment and embedding of foreign particles, the overlay alloy must process good compatibility, conformability and embeddability. The alloy must have the ability to conform to imperfections of shaft geometry with a minimum tendency for local welding to occur between the alloy and asperities on the shaft. Therefore, the overlay must be soft with a relatively low melting point. The overlay must be able to resist corrosive attack from the acid and peroxide content of the oil and to some extent, resist cavitation erosion, although cavitation erosion is usually overcome by a change in the geometry of the bearing.

4.2 Types of Overlay

There are three types of overlay in common use, lead - 10% tin, lead - 10% tin - 2% copper and lead - 8% indium. The first two are plated from an alloy plating bath in the latter, the metals are plated separately followed by a heat treatment to diffuse the two layers together.

The bearing characteristics of the differing overlays vary quite considerably. The fatigue strength of the lead-indium overlay is approximately 20% better than lead-tin or lead-tin-copper of an equivalent thickness (Fig. 6).

The wear of the lead-indium overlay under simulated engine bearing conditions is considerably more than an equivalent bearing with a lead-tin overlay [12, 18] (Fig. 7).

Corrosion attack of the overlays does not usually occur unless the content of the corrosion inhibiting phase, ie. tin or indium, drops below a critical value (3% in the case of tin, 5% in the case of indium). This can occur if the engine temperature is high (Fig. 8). Attempts to overcome this by putting a nickel barrier down between the copper-lead and the overlay is reported not to work (although the Glacier Metal Co. has found it beneficial) as nickel-tin compounds formed [6]. Increasing the content of tin or indium in the overlay partially overcomes the problem although the rate of diffusion is increased [19, 20].

A further problem encountered with the overlay is bond deterioration. This usually only occurs on steel-backed bearings with a cast lead-bronze lining. It manifests itself in a loss of adhesion between the coper-lead and the overlay and is believed to be due to the formation of a ternary copper-tin-iron compound, the iron having being picked up by the molten metal and subsequently diffusing to the overlay. The problem is generally overcome by plating a nickel barrier before deposition of the overlay.

Cavitation erosion is rarely a problem although it is becoming increasingly common, particularly in high speed diesel engines. It has been shown that lead-tin-copper overlays are 2-3 times more resistant to this form of damage than the other overlays [21]. This can be related to the relative hardness of the differing overlays. The as-plated hardness for the three overlays are :-

Lead - 80% tin	8 - 10 VHN	)
Lead - 10% tin - 2% copper	13 - 15 VHN	) using 0.5g wt.
Lead - 8% indium	8 - 10 VHN	)

4.3 Quality Control and Production

The cost of producing the overlay is not a great problem in itself, although the increasing cost of indium is becoming a problem to most manufacturers. The cost of automotive bearings is increased by 10 - 30% due to the overlay plating process. Much of this increase in cost is due to the necessity for the overlay to be applied within very close, prescribed limits and the fact that the overlay plating process is usually the last process in the production of the bearing. Thus, any mistake in the process at the final stages of production is bound to be more costly than a mistake at the start.

Quality control of the overlay is maintained chiefly by measuring the thickness and composition [17]. It is on these two properties that the other more important properties of fatigue strength and wear and corrosion resistance are dependent. Most overlay thicknesses on bearings smaller than 120 mm are specified in the range 12 - 25 μm and have to be plated within 2 μm of the specified thickness.

5. ALLOY ELECTRODEPOSITION

The electrodeposition of alloys probably took place at about the same time that cyanides were introduced to electroplating. The first alloy plating process to be patented, produced a coating of zinc and copper. It was patented in 1838 by Elkington and Barratt[23]. Since then, a large number of alloys have been plated for decorative, protective and engineering applications (See Fig. 9). At this stage, a short description of the principles of alloy deposition, electrolyte selection and process control will be of value. For a more comprehensive study, Brenner[24] should be consulted.

The most important consideration for codeposition of two metals to occur, is that their deposition potentials be fairly close together. This condition may occur in several different ways.

i) Metals with similar static potentials plated from a single salt solution. In this case, the polarisation curves for the individual metals are very similar (Fig 10a) and close together. The classic example of this type is the lead-tin plating system from a fluoroborate electrolyte where the static potentials are only 10mV apart.

The conditions for simultaneous discharge of two different metal ions at the cathode may be written as:

$$E_0 + \frac{RT}{ZF} \ln a + n = E_0' + \frac{RT}{ZF} \ln a' + n' \quad - (1)$$

where: E_0 and E_0' are the standard metal potentials, a and a' are the activities of the discharging ions n and n' are the cathodic overvoltages, R is the gas constant, F is Faradays constant, Z is the valence of the ions and T is the absolute temperature.

When the static potentials of the metals are far apart, the deposition potentials may be brought together in several differing ways.

ii) According to equation 1 by adding a complexing agent the activity of the discharging ions will be altered. By selectively complexing the more noble metal its static potential is shifted closer to that of the more base metal. Common complexing agents include cyanide, tartrate, pyrophosphate, hydroxide, etc. The action of these complexing agents varies for each metal but a powerful complexant can shift the static potential of a metal by as much as 1.5V. An example of this form of control is the silver-lead alloy. The standard electrode potential of silver is 0.789V and for lead -0.13V, a difference of 0.802V. Complexing the silver ions with cyanide lowers the standard potential of the silver to that of lead so that codeposition can take place.

iii) Complexing agents not only affect the standard electrode potential, they can also polarise the metal deposition reaction. By selectively polarising the more noble metal reaction a dynamic deposition potential of a similar value for both metals can be achieved. (Fig. 10b). The introduction of suitable surfactants can also have this effect. With the polarisation curves intersecting a wide range of composition is possible in the resulting alloys. Metals having 'parallel' polarisation curves have a deposit composition varying systematically with deposition potential but the noble metal always predominates.

iv) In some cases, the potentials are brought closer together as a result of the shift in the dynamic potential of the more noble metal due to lowering of its concentration in the vicinity of the cathode during electrolysis owing to concentration polarisation. (Fig. 10c). In particular, a considerable shift of the deposition of the more noble metal may be obtained at the limiting diffusion current as given by:

$$i\,(L) = \frac{Z\,F\,D\,(C_b - C_o)}{\delta} \qquad - \quad (2)$$

under diffusion control C_o tends to zero and $(C_b - C_o)$ approximates to C_b, the bulk concentration. However, in practice the use of limiting currents is not usually employed as rough and course deposits are generally formed. Similarly, attempting to bring the static potential closer together by lowering the concentration of the more noble metal is of little practical importance because of the difficulty of controlling such low concentrations in an industrial process.

From the Nernst equation :-

$$E = E^{0} \quad \frac{-0.059}{Z} \; \mathrm{Log} \; C_{m+} \qquad - \; (3)$$

it can be seen that a tenfold decrease in concentration for a monovalent noble metal the resulting shift in static potential would only be 0.059V (for an ideal solution only). Any significant shift in static potential would involve a much greater decrease in concentration which is generally impracticable for adequate process control, except in the case of a highly soluble base metal and a sparingly soluble noble metal.

5.1 Bath Types

Brenner has listed five types of alloy plating processes. The effect of plating variables on the composition of the alloy deposit varies with the type of bath. The normal solutions are those which behave according to simple theory of potential and current density prediction.

i) Regular solutions having simple ions and diffusion control. The static potentials may be far apart. The percentage of the more noble metal in the deposit is increased by increasing the total metal ion content of the bath, decreasing the current density, elevating the bath temperature and increasing the agitation. The pH of the solution has very little or no effect on most regular plating solutions.

ii) Irregular solutions under cathode potential control having one or both metals present as complex ions.

iii) Equilibrium solutions where at low current densities the bath metal ratio gives the deposit metal ratio.

The abnormal solutions are those where the noble metal does not deposit preferentially.

iv) Anomalous solution where the less noble metal may deposit preferentially. This may be caused by selective complexing or polarisation.

v) Induced systems where elements which do not deposit individually may deposit as alloys.

5.2 Effect of Plating Variables

The effect of variables on the composition of electrodeposited alloys is a vast and complex subject. It is not intended to treat the subject in any great detail but a short summary of some of the main effects is attempted.

Metal ratio in bath :

For regular, irregular and equilibrium deposition increasing the ratio of the more noble metal increases the percentage of the more noble metal in the deposit. By altering the metal ratio in the bath a full range of alloy compositions is usually possible although a limiting bath composition is usually reached where a further increase in the ratio of the more noble metal results in deposition of 100% noble metal.

The behaviour of metals in anomalous deposition varies depending on the polarisation curves of the metals. In some cases, the metals may codeposit in a normal fashion, in others the metals may codeposit in an anomalous fashion.

For induced codeposition, increasing the ratio of the reluctant metal, increases its concentration in the deposit. Usually, an indefinite percentage is reached above which the amount of reluctant metal in the deposit cannot be increased by increasing the ratio of the reluctant metal in the bath.

Variation of the total metal concentration, at a fixed metal ratio, affects the composition of alloys in regular codeposition but has either slight effect or no uniform trend in irregular, anomalous and induced codeposition.

Complexing Agent :

The general effect of increasing the concentration of a complexing agent is to shift the deposition potential of a metal to a more negative value.

In an alloy bath if the deposition potential of one metal is shifted to a more negative value than the other, then the resulting deposit will contain less of the former metal than before the addition of the complexing agent. Generally speaking, large changes in the composition of the alloy deposit only occur with a mixed type of plating bath.

Addition Agents :

Addition agents are usually most effective in baths containing the metals as simple ions. The effect of addition agents is specific in nature. Only certain addition agents affect particular metals. Certain addition agents can alter the composition of the alloy deposit (e.g. glue in the lead-tin system [26] and aloin in the zinc-cadmium system [25] see Fig. 11) by changing the dynamic potential of the more noble metal. The amount of addition agent required to do this is very much smaller than with complexing agents and the composition of the deposit rapidly approaches a limiting value above which any further increase in the addition agent content of the bath has not effect.

Current Density :

With regular alloy plating systems increasing the current density increases the amount of base metal in the deposit. With other alloy systems, the content of the more noble metal may either increase, decrease or remain virtually constant depending on the solution composition.

Temperature :

Altering the temperature of an alloy plating bath may alter the equilibrium potentials of the individual metals but this effect is only very small. Increasing the temperature depolarises the cathode deposition reaction. Whether the more noble or less noble metal is favoured depends on which deposition undergoes the greatest depolarisation. An increase in temperature also increases the concentration of metal in the diffusion layer. Any increase in metal concentration in the diffusion layer favours the deposition of the metal which is already plating preferentially[24].

The cathodic current efficiency may also be affected by a change in temperature. This may indirectly affect the composition of the alloy deposit particularly from complex solutions. (i.e. if the efficiency of one metal were affected and the other remained unaffected, then the composition of the alloy deposit would change).

Agitation :

Agitation of an alloy plating bath results in an increase in the metal concentration in the diffusion layer. As already stated, this favours the deposition of the metal which is already depositing preferentially. With baths of simple salts, the effect on the composition of the alloy deposit is predictable. With complexed baths, the effect is more difficult to predict because not only does the metal concentration increase in the diffusion layer, the free complexing agent does also thereby creating the possibility of an opposing trend in the composition of the alloy, resulting from a change in the metal concentration.

pH :

The effect of pH on the composition of the electrodeposited alloy depends very much on the chemical nature of the metals in solution. pH has very little effect on a solution where the metal is present as simple ions. On the other hand, if the metal is present in a complexed form, then the stability of the complex is almost certainly dependent on the pH of the solution and so the composition of the electrodeposited alloy may vary widely with pH.

5.3 Lead-Tin Alloy Electrodeposition

Lead-tin alloy plating is one of the simplest of alloy plating processes. The standard electrode potentials of the two metals differ by only 10mV and since the potentials of tin and lead are only slightly less noble than hydrogen and because the metals have a high hydrogen overvoltage, the alloys deposit from acid solutions with a cathode current effeciency of 100%.

The lead-tin alloys were first plated as long ago as 1920 when Groff [27] patented the process using a fluoroborate solution. Although the fluoroborate solution is still the most widely used, the alloys can be plated from several other solutions.

A process based on fluorosilicates was patented by Speichart [28] in 1927. A sulphamate bath was studied by Piontelli and Canonica [29] but this bath is believed to be of very little practical value as the tin sulphamate hydrolyses very easily. Rama Char [30] published work on a pyrophosphate bath and a bath based on phenolsuphonates has been studied by Kudryavtsev. None of these baths have any commercial importance as the fluoroborate bath offers a far easier process to control.

Using a fluoroborate electrolyte, the tin and lead can be plated in any desired proportion, depending on the metal ratios in the bath. Table 3 shows the percentage composition of some commonly required tin-lead alloy deposits with the approximate solution requirements for each [32].

The operating conditions are usually.:

Cathodic current density 3 A/dm ^{2}

Temperature 25 - 30°C

Mild agitation is recommended but is not essential. Air agitation must not be used as this will oxidise the stannous tin. Anodes should be of lead-tin alloy of the same composition as that required in the deposit.

Although the tin-lead alloy plating system is of the regular type, with lead acting as the more noble metal, it does not show a large variation in the composition of the deposit with variation in the plating conditions as with other regular systems. This is because the potentials of lead and tin are so close together and the presence of addition agents affects the polarisation curves of the metals, bringing them close together. The effects of agitation and acid content of the bath are negligible and the effect of temperature is small (changing the temperature by 4°C can alter the content of the deposit by as much as 1%). Any increase in the content of addition agent and an increase in current density increases the content of tin in the deposit.

5.4 Cadmium-Tin Alloy Electrodeposition

The standard electrode potentials of cadmium and tin are 267 mV apart. This is close enough to permit alloy deposition from an acid bath and it is from such solutions that is plated commercially. The interest in the electrodeposition of cadmium-tin alloy is of recent origin. Zinc or cadmium coatings were found to deteriorate rapidly as protective coating on aircraft parts, especially jet aircraft. The protection offered by tin-cadmium alloys was found to be superior to both zinc and cadmium. For this reason, much of the published data dates from the 1950's.

The alloy can be deposited from a variety of acid baths. With sulphate baths, the cadmium-tin deposit tends to be coarsely crystalline unless a number of addition agents are used. Bennett [33] used a combination of four addition agents : Saponine, Dreft, 2 naphthol-6, sulphonic acid and di-hydroxymethane, a bath formulation obviously too complicated for commercial use. Scott and Gray [34] reported on an acid fluoroborate bath utilising three addition agents. Davies et al [35], [36] have studied solutions of fluoroborate and fluorosilicate and also a fluorosilicate bath containing fluoride ions with polyethylene glycol and MalgofenO* as addition agents. A chloride-fluoride bath has been looked at in some detail by Kudryavtsev [37], [38], [39].

The only non-acid bath of any importance is the stannate-cyanide bath investigated in detail by Davies [40].

* Proprietary non-ionic water-soluble compound.

A typical bath composition for the fluoroborate process would be (in grammes per litre) [41].

Cadmium fluoroborate	230
Cadmium as metal	80
Tin fluoroborate	49
Tin as metal	20
Fluoroboric acid	60
Ammonium fluoroborate	50
Boric acid	20
Sodium phenol sulphonate	2
Gelatin	2

The operating conditions are :

pH 3
Temperature 27°C
Cathode current density 3 A/dm^2

This type of bath operated under these conditions would give an alloy with 73% cadmium.

All the acid cadmium-tin alloy plating baths are of the regular type. Thus, the plating variables affect the composition of the deposit to a large degree. An increase in temperature, pH, agitation and total metal content of the bath will increase the amount of tin in the deposit and an increase in current density and addition agents will decrease the amount of tin in the deposit. Hence, the process is far more difficult to control than the lead-tin alloy plating system.

The stannate-cyanide bath behaves as an irregular system. The plating variables affect the composition of the deposit indirectly by changing the relative cathodic efficiencies of the metal deposition reactions.

5.5 Lead-Cadmium Alloy Electrodeposition

There is very little in the literature on lead-cadmium alloy plating. The standard electrode potentials are only 277 mV apart so that in theory, alloy plating from acid solutions is feasible. Brenner [24] reported that he had successfully plated a lead-cadmium alloy from a perchlorate solution but gave no details of the process. Gusev et al [42] developed a process based on a citrate-polyethylenepolyamine solution. They reported that alloys containing 30 - 85% cadmium could be obtained from an electrolyte of the following composition (grammes per litre):

Cadmium acetate	50 - 90
Lead acetate	10 - 50
Sodium citrate	120 - 150
Polyethylenepolyamine	30 - 50
Joiners glue	0.2 - 1.0

and the conditions were:

Temperature 30 - 60°C
pH 8 - 9
Cathode current density 0.5 - 1.5 A/dm ^{2}

They used separate lead and cadmium anodes, the current density at the cadmium anode was up to 0.6 A/dm^2 and at the lead anode up to 0.5 A/dm^2. Under these conditions, they found the cathode and anode current efficiencies to be 100%. Increases in temperature and pH were found to decrease the cadmium content whilst increases in polyethylenepolyamine and/or citrate ion concentration and current density were found to increase the cadmium content in the deposit. They did report that above pH 9.5 the solution becomes unstable with time. A considerable part of the report is devoted to the corrosion resistance and antifrictional properties of the deposited alloys, although very few details are given, and they found from X-ray diffraction data that lead-cadmium alloys containing 35, 51, 63 and 85% Cd were present as two-phase systems.

Research carried out for Glacier Metal Co. [43] reported on a possible process using a fluoroborate solution and the data was later included in a patent [44]. It was found that it was difficult to obtain reproducible results using a solution containing 25 to 50 gl^{-1} lead and 280 gl^{-1} cadmium as metal, at a current density 3 - 10 A/dm^2. It was found necessary to use three addition agents: resorcinol 10 gl^{-1}, peptone 1 gl^{-1} and polyethylene glycol 1 gl^{-1}. Several after addition agents were studied, (identity not specified), but they found that these three addition agents gave the best results. Deposits from this bath were found to have cadmium contents in the range 2% - 16%.

A process for plating a ternary alloy of tin, lead and cadmium containing 48 - 50% tin, 32 - 36% lead and the rest cadmium has been patented in both the United States [45] and Russia [46]. Both use essentially the same solution composition (in gl^{-1})

Tin fluoroborate	91
Lead fluoroborate	25
Cadmium fluoroborate	40
Fluoroboric acid	30
Boric acid	12
Gelatin	5

The Russian patent also used 1 gl^{-1} hydroquinone. The current density used was 10 A/dm^2 and the process was carried out at room temperature. Again, as with the Glacier Co. research, the process appeared to be difficult to control.

A bath for plating a ternary alloy of lead, tin and cadmium has also been developed using a fluorosilicate electrolyte [47]. The bath composition (in gl^{-1}) is:

Tin fluorosilicate	78 - 85
Lead fluorosilicate	20 - 34
Cadmium fluorosilicate	30 - 38
Fluorosilicic acid	40 - 60
Peptone	3 - 5

The ternary alloy appears to have been developed for use in the electronics industry because of its ease of soldering and its corrosion resistance as compared to the ordinary lead-tin solder plate.

6. EXPERIMENTAL

The purpose of the experimental work was to develop a process in which a lead-cadmium alloy of a known composition could be plated as an overlay, the main criteria being consistent quality and ease of control of the process.

Most of the experimental work centres around polarisation studies of three different electrolytes based on sulphamates, fluorosilicates and fluoroborates. Further work includes some conductivity and efficiency measurements. Addition agent behaviour was studied using a Hull cell, anodic polarisation measurements and some use was made of IR and UV spectrophotometry.

The structure of the deposit was studied using electron diffraction and the physical properties of the deposit in relation to its bearing characteristics were investigated at Glacier Metal Co. Ltd. using specialised test equipment.

6.1 Solution Make Up

All the solutions used, except the fluoroborates were made up using standard laboratory reagents. The fluoroborates were technical grade solutions obtained from M and T Chemicals Limited. The cadmium fluoroborate, as supplied, contained 347 gl^{-1} cadmium and 20 gl^{-1} free acid. The lead fluoroborate contained 520 gl^{-1} lead and 45.3 gl^{-1} free acid. These solutions were diluted to make up electrolytes with the required metal content.

The fluoroborate electrolytes were made up by dissolving a known weight of lead carbonate or cadmium carbonate in 32% fluorosilicic acid. These solutions were also diluted to obtain an electrolyte with the required metal content.

The sulphamate electrolytes were made up in a similar fashion to the fluorosilicates although the sulphamic acid was supplied in solid form and so had to be dissolved first.

Where possible, the electrolytes were made up in bulk quantities up to 2 litres from which 250 ml quantities of a known metal content could be diluted.

All liquid measurements were done using measuring cylinders and all solids were weighed using an 'Oertling' three figure balance.

6.2 Small Cell

The cell used for the polarisation studies consisted of a 500 ml flat bottomed culture vessel with a five socket lid. The cell is shown in diagrammatic form in Fig. 12. The cathode was originally a 1 cm^2 block of copper 5mm thick, mounted in epoxy resin. This kept the area of the cathode constant for various polarisation experiments. After each experiment, the face of the cathode was rubbed down on varying sizes of emery paper down to 1200 size. This arrangment worked well for several experiments until the epoxy detached itself from the side of the copper, creating a crevice. This altered the surface area of the cathode as well as making it very difficult to clean. It was decided to abandon this form of cathode in favour of the more simple copper foil. This was 99.99% copper foil, 0.5 thick, cut into strips 15.0mm wide and approximately 70mm long. The strip was masked using 'Lacomit' (a proprietary stopping off medium obtained from Canning Ltd) so that 3 cm^2 of one side at the lower end and 5mm of the top end were unmasked. The upper end was held in a slot on a steel rod by a grub screw and the steel rod was located in the central socket of the cell lid (as in Fig. 12). This type of cathode has a reproducible surface area provided care was taken in the masking.

The reference electrode used was a saturated calomel electrode with a remote junction obtained from E.I.L. Electrodes Ltd. The calomel electrode was situated at the side of the water bath at the same height as the tip of the remote junction when inserted in the cell. This reduced the head of saturated potassium chloride to a minimum thus alleviating the problem of potassium chloride leaking through the ceramic tip of the remote junction. As a further precaution, a ground glass top was inerted in the tube between the remote junction and the reference electrode with the stopper in the off position. This ensured electrical continuity whilst preventing a head of potassium chloride forming.

Some consideration was given to the IR drop caused by using the remote junction as the ceramic tip was over 1mm distant from the cathode. This was unavoidable because of the thickness of the glass tube used to make the remote junction. This IR drop would have been quite considerable if low conductivity solutions or high current densities were used. Under these conditions, a luggin capillary would have been employed. However, as high conductivity solutions and relatively low current densities were used, the remote junction was found to be very convenient and quite adequate. A further consideration was that the polarisation data obtained using the small cell, was used for comparison purposes only and so any source of error was consistant throughout.

Agitation was provided by bubbling nitrogen through a gas bubbler into the electrolyte. The gas flow was monitored using gas flow meters rated 0 - 700 cm^3/min and 0 - 250 cm^3/min. The flow could be switched from one flow meter to the other using a two-way ground glass tap. This provided accurate monitoring of the flow rate at a low level of agitation.

6.3 Anodes

The anodes used throughout were made from 99.9% pure lead. Cadmium anodes were tried but these were immersion plated with lead when used in an alloy solution. Cadmium anodes were only used in cadmium plating solutions.

The anodes were made from rolled metal approximately 3mm thick cut into strips 13mm wide by 100mm long. Copper wire was soldered to the top of the anode and covered by a glass tube which was then glued to the anode using epoxy resin. The glass tube was held in position in the cell by a ground glass adapter. Using this arrangement, the anode could be held in the same position in the cell each time it was used. Furthermore, it could be removed from the cell quickly and easily.

For anodic polarisation studies, the anode was totally masked off using 'Lacomit' except for 1 cm^2 on one face. After each potential sweep, a fresh area on the anode was selected as the dissolution of the anode altered the surface area exposed.

6.4 Potentiodynamic Studies

Most of the polarisation data were obtained using the small cell. The equipment used is shown in Fig. 13. The cell was contained in a "Techne" temperature controlled water bath. The temperature was controlled to ± 0.05°C.

The potentiostat used was a 6A Kemitron' with a built-in digital sweep generator (Kemitron SG2) and voltmeter (Kemitron LCV-2). The sweep generator had a maximum output of 2 volts and could sweep at rates from 0.1 mV/second to 10 V/second in decades, with a multiplication factor from 1 to 10. The output from the potentiostat was recorded on a 'Bryans' 27000 series chart recorder.

The following procedure was used to obtain all polarisation data using the small cell.

The cathode after having been degreased in "Genklene" and the relevant areas having been masked, was degreased again using industrial alcohol in an ultrasonic bath. The cathode was degreased for a minimum of 5 minutes. It was then dried under a hot air blower and electropolished using an electrolyte of 66% orthophosphoric acid placed in a beaker with a copper sheet as a cathode and a copper wire as a reference electrode. The working electrode potential was held at +1000 mV with respect to the copper wire. The electropolishing was carried out for 3 minutes. The working electrode was then rinsed using distilled water and placed into the small cell containing the electrolyte under study.

250 ml of electrolyte was used for each polarisation run. The electrolyte was placed in the previously cleaned cell and placed in the water bath. The electrolyte was agitated using nitrogen until it reached the temperature at which the water bath was set. The nitrogen agitation also served to de-airate the electrolyte.

When the electrolyte had reached the required temperature, the anode, cathode and reference electrode were placed in the cell. The cathode was then preplated at a nominal constant current density of 0.2 A/dm^2 for a period of 5 minutes.

After preplating, the static potential was measured, recorded on the chart recorder paper and then the cell was reconnected and potentiostat was adjusted to the static potential so that zero current flow was established. The potential was then swept cathodically or anodically until dendritic growth occured.

Initially, several sweep rates were tried and these are recorded in the results. However, for most of the polarisation data, a sweep rate of 30 mV/min was used.

It was accepted that agitation provided by gas bubbling was an inherently imprecise form of agitation. However, it was used so that polarisation data could be obtained from a quiessant solution, a gently agitated solution and a vigorously agitated solution.

A more precise form of agitation would have been to use a rotating cylinder electrode. This method was not used because:

a) The effect of agitation was to increase the lead content of the alloy deposit. It was realised at an early stage that the major problem in the project would be to increase the cadmium content of the deposit whilst decreasing the cadmium content of the electrolyte.

b) The object of the project was to develop an industrial process for plating a lead cadmium alloy. A rotating cylinder would be difficult to use in an industrial situation related to plating of shell bearings.

c) Again, because the project had to be related to an industrial context, the accuracy of agitation was not considered to be important. It was decided that a quiessant solution, a gently agitated solution and a vigorously agitation solution would be enough to indicate the effect of agitation on the composition of the alloy deposit.

6.5 Sulphamate Solutions

A 0.5M cadmium sulphamate solution was made up by dissolving 100 gl^{-1} sulphamic acid in distilled water. 86 gl^{-1} cadmium carbonate was dissolved in the sulphamic acid solution. 250 ml of this solution was used as an electrolyte.

Using a cadmium anode and copper foil as a cathode, polarisation data was obtained at temperatures from 30°C - 60°C following the procedure outlined in Section 6.4. The results were checked for reproducibility by repeating the experiment. Where the results were not reproduced, the electrolyte was replaced and the experiment repeated.

The effect of resorcinol as an addition agent was studied by adding various quantities of resorcinol to the above solution and carrying out cathodic potential sweeps on the resultant solution. Data was obtained for the solution containing 2, 4 and 6 gl^{-1} resorcinol at 30°C.

A 0.5M lead sulphamate solution was made up by dissolving 100 gl^{-1} sulphamic acid in distilled water. 133 gl^{-1} lead carbonate was dissolved in the resultant sulphamic acid solution. 250 ml of this solution was used as an electrolyte.

Using a lead anode and copper foil as a cathode, cathodic polarisation data was obtained at temperatures from 30°C - 50°C, following the procedure outlined in Section 6.4. The results were checked for reproducibility by repeating the experiment. If the results were not reproduced, the electrolyte was replaced and the experiment repeated.

The effect of resorcinol as an addition agent was studied in the same way as for 0.5M cadmium sulphamate.

Four sulphamate alloy solutions were made up by dissolving 129, 96, 64.5 and 32 gl^{-1} lead carbonate into solutions containing 400 gl^{-1} sulphamic acid and 344 gl^{-1} cadmium carbonate. This gave solutions with the following metal contents:

220 gl^{-1} Cd) 1
100 gl^{-1} Pb)

220 gl^{-1} Cd) 2
75 gl^{-1} Pb)

220 gl^{-1} Cd) 3
50 gl^{-1} Pb)

220 gl^{-1} Cd) 4
25 gl^{-1} Pb)

To each solution, 6 gl^{-1} resorcinol was added. The cathodic polarisation characteristics of each solution was determined at 30°C and the effect of agitation on the cathodic polarisation was found. In addition to the effect agitation had on the cathodic polarisation its effect on the deposit composition was also studied. Copper foil samples were plated at constant potential with varying degrees of agitation and the resultant deposit was analysed using the procedure outlined in Section 6.11. The potentials used were -550, -575, -600. -625, -650 and -700 mV (SCE).

6.6 Fluorosilicate Solutions

A 0.5M cadmium fluorosilicate solution was made up by dissolving 86 gl^{-1} cadmium carbonate in 230 ml/l fluorosilicic acid, the rest was distilled water. 250 ml of this solution was used as an electrolyte.

Using a cadmium anode and copper foil as a cathode, cathodic polarisation data was obtained at temperatures from 30°C - 60°C following the procedure outlined in Section 6.4.

Reproducibility was checked using the same technique as for the sulphamate solutions. The effect of resorcinol as an addition agent was studied in the same way.

A 0.5M lead fluorosilicate solution was made up by dissolving 133 gl^{-1} lead carbonate in 230 ml/l fluorosilicic acid. 250 ml of this solution was used as an electrolyte. Using a lead anode and a copper foil cathode, cathodic polarisation data was obtained at temperatures from 30°C - 60°C. Reproducibility was checked and the effect of resorcinol as an addition agent was studied in the same way as for cadmium sulphamate.

Four fluorosilicate alloy solutions were made up by dissolving 129, 96, 64.5 and 32 gl^{-1} lead carbonate into solutions containing 344 gl^{-1} cadmium fluorosilicate in 32% fluorosilicic acid. This gave solutions with the following metal ion contents:

220 gl^{-1} Cd) 1
100 gl^{-1} Pb)

220 gl^{-1} Cd) 2
75 gl^{-1} Pb)

220 gl^{-1} Cd) 3
50 gl^{-1} Pb)

220 gl^{-1} Cd) 4
25 gl^{-1} Pb)

To each solution 6 gl^{-1} resorcinol was added. The cathodic polarisation chacteristics of each solution were determined at 30°C. The effect of agitation of the electrolyte on the cathodic polarisation was studied as well as its effect on the composition of the alloy deposit Copper foil samples were plated at constant potential and varying degrees of agitation and then the deposit was analysed using the method in Section 6.11 to determine the alloy composition. The potentials used were -550, -575. -600, -625, -650 and -700 mV (SCE).

6.7 Fluoroborate Solutions

0.1M and 1M cadmium fluoroborate solutions were made by diluting the technical grade cadmium fluoroborate to the required level. (32 and 322 ml/l for 0.1M and 1M, solutions respectively). 250 ml of each solution was used as an electrolyte.

Using a cadmium anode and copper foil cathode, cathodic polarisation data was obtained at temperatures varying from 30°C - 60°C following the same procedure as the sulphamate and fluorosilicate electrolytes. The same procedures were followed to gain information on the effect of resorcinol as an addition agent.

A 0.1M and 1M lead fluoroborate solution was prepared by diluting technical grade lead fluoroborate to the required level. (40 and 398 ml/l for 0.1M and 1M solutions respectively). 250 ml of each solutions was used as an electrolyte. The same procedures as for cadmium fluoroborate were used to obtain similar data.

Five fluoroborate alloy solutions were made up by using 230, 192, 144, 96 and 48 ml/l lead fluoroborate with 634 ml/l cadmium fluoroborate. This gave solutions with the following metal contents:

220 gl^{-1} Cd) 1
125 gl^{-1} Pb)

220 gl^{-1} Cd) 2
100 gl^{-1} Pb)

220 gl^{-1} Cd) 3
75 gl^{-1} Pb)

220 gl^{-1} Cd) 4
50 gl^{-1} Pb)

220 gl^{-1} Cd) 5
25 gl^{-1} Pb)

To each solution 6 gl^{-1} resorcinol was added. The cathodic polarisation characterisitc of each solution was determined at 30°C and the effect of agitation on the cathodic polarisation was found. Copper foil samples were plated at constant potential and varying degrees of agitation and the deposits were subsequently analysed. The potentials used were -350, -400, -450, -500, -550 and -600 mV (SCE).

6.8 Acetate - Citrate Electrolytes

A solution containing:

50 gl^{-1} Cadmium acetate
50 gl^{-1} Lead acetate
150 gl^{-1} Citric acid

was made up using the following procedure:

The solution had to be made up by separate dissolution of thethree constituents. The citric acid was dissolved at as high a concentration as possible. The lead and cadmium acetates were dissolved up at as low a concentration as possible. The acetate solutions were then slowly and carefully added to the citric acid solution at a temperature of 60°C. Care was taken to avoid local pH changes where possible. The resultant solution was found to be very susceptable to pH change forming insoluble precipitates at too low or too high a pH. pH 7 ± 0.5 was the only pH at which the solution remained stable for any length of time. The pH was adjusted by small additions of dilute sodium hydroxide. Several solutions were made up to different pH's but only the solution at pH 7 remained stable for more than 2 hours. It was found that this solution would only remain stable for more than 24 hours if the temperature was maintained above 50°C. 250 ml of this solution was used as an electrolyte.

The cathodic polarisation characteristics of this solution was obtained at a temperature of 60°C with no agitation.

Several attempts were made to make up an electrolyte containing cadmium acetate and citric acid. An insoluble precipitate formed on each occasion.

More success was found with lead acetate and citric acid. A solution containing 38 gl^{-1} lead acetate and 50 gl^{-1} citric acid was found to be reasonably stable. Solutions containing either more lead acetate or more citric acid were found to be very unstable with insoluble precipitates forming within a short period of time after mixing the solutions. As with the alloy solution, the lead solution was found to be susceptable to pH change and temperature. The solution was made up to pH 7 and maintained at 60°C to prevent formation of an insoluble precipitate.

6.9 Addition Agents

Several addition agents for the fluoroborate alloy electrolyte were investigated and their effect on the quality of the deposit was recorded using a Hull cell. The addition agents investigated were:

resorcinol
polyethyleneglycol
peptone
diastase
gelatin

These addition agents were tried in different combinations and quantities in a fluoroborate plating solution with the following metal ion composition :

220 gl^{-1} cadmium
50 gl^{-1} lead
+ addition agent

The choice of addition agents was governed by their availability in the laboratory and whether or not they had been used as a lead plating addition agent in the literature.

In all ten combinations of addition agents were investigated using the Hull cell. Of these, four were considered to give a fairly wide range of current density where the deposit was fairly good. A strip 1cm wide was cut horizontally across the centre of the Hull cell panel after plating. This strip was then cut into three portions corresponding to the three current density regions : 0-1, 1-2 and 2-3 A/dm^2. These portions were then analysed using the method outlined in Section 6.11 to ascertain the percentage cadmium content of the deposit.

Potentiodynamic Studies (Anodic)

From the work on the Hull cell, it became apparent that a combination of three addition agents (resorcinol, polyethyleneglycol and peptone) would give a good quality deposit containing more cadmium than any of the other addition agents that were studied. It was noted, however, that their effect on the quality of the deposit changed with time and use of the plating solution. Anodic polarisation studies were carried out on the three addition agents in an attempt to determine whether they were breaking down at the anode.

250 ml of fluoroborate electrolyte was used with the following metal ion concentrations:

220 gl^{-1} cadmium
50 gl^{-1} lead
+ addition agent

The addition agents were studied individually in the following concentrations in the above electrolyte:

6 gl^{-1} resorcinol
1 gl^{-1} polyethyleneglycol
1 gl^{-1} peptone

In addition, anodic polarisation data was obtained for a solution containing all three addition agents in the same concentrations. After carrying out anodic potential sweeps using the fresh solutions, all four electrolytes were used for plating on scrap copper until 7000 coulombs had passed through each one. The anodic sweeps were then repeated using the procedure outlined in Section 6.4. Subsequently, activated carbon was added to each plating solution and shaken. The solutions were then left overnight. After the solutions were filtered to remove the carbon, the anodic sweeps were repeated.

IR Spectrophotometry

Some attempt was made to identify the breakdown product of resorcinol in a fluoroborate plating solution using infa-red spectrophotometry. A fluoroborate electrolyte with the following composition:

220 gl^{-1} cadmium
50 gl^{-1} lead
6 gl^{-1} resorcinol

was used to plate scrap copper until 7000 coulombs had passed. The organic constituent in the electrolyte was then extracted into methylisobutylketone (M.I.B.K.).

The IR spectrum of this extract was then recorded using a Unicam SP200G IR spectrophotometer. In addition, two other spectra were produced, one from extracted organics from a fresh fluoroborate plating solution of the following composition:

220 gl^{-1} cadmium
50 gl^{-1} lead
6 gl^{-1} resorcinol

and the other from M.I.B.K.

6.10 Conductivity Measurements

All conductivity measurements were carried out using a Philips PW 9501 conductivity meter. The plating solutions under test were made up as described in Section 6.1 or they were taken from a commercial type plating bath. The electrolytes were held in a series of boiling tubes enclosed in a water bath. The platinised electrode cell was soaked in distilled water for several hours before use. It was then calibrated. The experimental arrangement of the conductivity cell is shown in Fig. 14. The conductivity cell itself, is shown in Fig. 15. The conductivity meter consists essentially of an oscillator, a measuring bridge with a bridge amplifier, a temperature compensation stage and an output amplifier. The measuring bridge is fed by the oscillator whose frequency can be adjusted to 200 Hz or 2000 Hz. The choice of frequency depends on the quotient.

$$\frac{\text{Cell constant}}{\text{Conductivity}} = \text{cell resistance}$$

When this value is high, a low frequency should be selected and vice versa. As relatively high conductivity electrolytes were being used, a frequency of 2000 Hz was used.

6.11 Analysis and Thickness Measurement of Deposit

The analysis of the electrodeposit and the metal content of the electrolytes was performed by atomic absorption spectrophotometry. The model used was an Instrument Laboratories aa/ae spectrophotometer.

After plating the cathodes in the small cell, the lacomit was removed using a solvent (acetone). The area that was plated was then cut from the rest of the cathode and dissolved in 10 ml aqua regia. (80% HCl, 20% HNO_3). The resulting solution was then made up to 100 ml in a grade 'A' volumetric flask using distilled water. This solution was then analysed for its lead and cadmium content using the method of standard additions. This method allows for any background interference although it was not considered likely that there would be any background interference with lead and cadmium. Both metals are considered to be very easy to detect using aa spectrophotometry.

From the analysis, the ratio of lead to cadmium in the solution could be determined and hence the alloy composition. The presence of the copper substrate dissolved in solution was ignored.

The thickness of the deposit was measured by sectioning the deposit, mounting in araldite resin, polishing, then viewing the cross section of the deposit using a Quantimet. Using a calibration chart, the thickness of the deposit could be measured directly from the television screen on the Quantimet. Some difficulty was experienced with bevelling of the deposit. This made focusing difficult. This problem was partially overcome by plating a thin layer of nickel on top of the deposit using a Watts type nickel plating bath. This provided a comparatively hard supporting surface to polish and the bevelling was reduced to a minimum.

A coulometric plating gauge manufactured by Evershed and Vignolles was used to measure the thickness of the deposit. However, this proved to be unsatisfactory as the curvature of the bearing distorted the shape of the plating gauge cell giving erronous reading.

6.12 Efficiency Measurements

The efficiency of a particular plating solution was measured when it was considered to be of importance. The cell used for efficiency measurement is shown in Fig. 16. The cell was enclosed in a 500 ml beaker contained in a 'Techni' water bath. The temperature was maintained at 30°C. A current density of 2 A/dm^2 was used for all efficiency measurements. The plating solutions were not agitated. The anodes used depended on the electrolyte. Where the electrolyte was a cadmium plating solution, cadmium anodes were used. When the electrolyte was a lead or a lead/cadmium alloy plating solution, lead anodes were used. Copper foil was used as the cathode in all cases. The procedure adopted was as follows:

a) The anodes and cathode were degreased for 5 minutes in an ultrasonic bath containing 'Genklene'.

b) The anodes were then pickled for 10 seconds in dilute nitric acid.

c) After washing and drying the weight of the cathode and anode was measured and recorded using a Stanton four figure balance.

d) The anodes and cathodes were then fitted into the cell and the wires were connected. The cell was then lowered into the electrolyte contained in the 500 ml beaker and the power was switched on immediately.

e) After 5000 coulombs had passed, the cell was removed from the beaker. The anodes and cathodes were washed, dried and reweighed.

f) The anodic and cathodic current efficiencies were calculated from the weight of anodic dissolution and cathodic deposition and the coulombs passed using Faradays law:

$$W = \frac{ita}{ZF}$$

where W = weight (g)
i = current
t = time (s)
Z = valancy
F = Faradays constant
a = atomic weight

6.13 Large Cell

The cell used for plating bearings is shown in Fig. 17.

It was made from perspex. The two half shell bearings were each clamped between two semi circular pieces of perspex. The four semi circular shaped pieces of perspex were then clamped together around a lead anode so that the half shell bearings completely surrounded the anode. Care was taken to position the bearings so that their distance from the anode remained constant around their full circumference.

The perspex plates contained several holes to allow circulation of solutions between the anode and cathode. A small hole was drilled through the top plate of perspex close to the inner surface of the bearings, in order to position the ceramic tip of the remote junction reference electrode as close as possible to the cathode surface.

The preplating process started with a vapour degrease followed by an alkaline clean, rinse, anodic etch, rinse, acid soak, rinse and when necessary, a nickel barrier was plated prior to a final rinse and application of the overlay plate. The process is shown in detail in Table 4. All the solutions were contained in 5 litre polypropylene beakers.

A fluoroborate plating solution was used for plating all bearings. Its metal ion composition was :

$220\ gl^{-1}$ cadmium
$50\ gl^{-1}$ lead
$6\ gl^{-1}$ resorcinol
$1\ gl^{-1}$ peptone
$1\ gl^{-1}$ polyethyleneglycol

The solution was made up by diluting and mixing the technical grade fluoroborate solutions to the correct amount. The addition agents were then dissolved or diluted in small amounts of distilled water then added to the electrolyte. 4 l of electrolyte was used at any one occasion and it was maintained at room temperature without agitation.

All bearings plated were steel backed Cu Pb 30 of a special size used for the 'Sapphire' fatigue test machine at the Glacier Metal Company Ltd.

For the acquisition of polarisation data, the bearings were preplated for 2 minutes at -450 mV (SCE) after the preparation process and prior to the cathodic potential sweep. The sweep rate used was the same as for the small cell (30 mV/min). The potentiostat and coulombmeter were also the same.

Cathodic polarisation data was obtained using this method for the fluoroborate electrolyte containing three combinations of addition agent: resorcinol; resorcinol and peptone; resorcinol peptone and polyethylene glycol. At this stage, it was noticed that the polarisation characteristics of the large cell were markedly different from those of the small cell.

Several bearings were plated at constant potential, at potentials varying from -700 - -760 mV (SCE), and the alloy deposit was analysed using the method in Section 6.11. When an attempt was made to repeat the experiment 7 days later using the same electrolyte the quality of the deposits was found to be very poor and the percentage of cadmium in the alloys was found to be considerably higher. Furthermore, the colour of the electrolyte had changed from clear to pink. It was assumed that the addition agents were breaking down with time and/or use. Repeating the cathodic potential sweep confirmed that some change was taking place. After standing unused for 7 days, the electrolyte had changed such that the cathodic reaction had polarised considerably. Additions of 1 gl^{-1} peptone and 1 gl^{-1} polyethyleneglycol were made and the cathodic potential sweep was repeated. This partially depolarised the reaction, but the static potential was altered.

At this stage, it was noted that metal was being plated on the reverse side of the bearings. At first, it was thought to be due to some sort of electrolytic action caused by the unmasked clamping bolts on the plating jig. However, the problem still arose after these were effectively masked using 'Durlac'. It was eventually found that the masking of the top and bottom part of the anode which protruded from the jig, had not been effective using 'Lacomit'. This masking was then replaced with P.T.F.E. tape.

Repeating the cathodic polarisation sweep, it was found that the polarisation characteristics of the cell had been altered. It was assumed that this indicated the reaction to be under partial anodic control due to the proximity of the anode to the cathode and the smaller size of the auxiliary electrode to the working electrode.

Several bearings were again plated at constant potential, this time at potentials varying from -600 - -660 mV (SCE). The alloy composition of the deposits showed a marked change from the bearing plated initially. In view of the problems encountered with the anodic control and the addition agent break down it was decided to plate all the bearings for fatigue, wear and corrosion resistant test at Glacier Co. laboratories using a P.T.F.E. masked anode and an electrolyte with a maximum age of 24 hours. Furthermore, the electrolyte was discarded after 10,000 coulombs had passed through it. All three addition agents were used in the electrolyte.

Initially, 6 pairs of bearings were plated for test at Glacier Co. laboratories. These were as follows:

3 pairs	Pb Cd 10
3 pairs	Pb Cd 20

As a result of the tests at Glacier's laboratories on these bearings, a further nine pairs of bearings were plated as follows:

3 pairs Pb Cd 5
3 pairs Pb Cd 10
3 pairs Pb Cd 10 + 2 um Ni Barrier

All the bearings were plated with an 18 um overlay ± 2 um. It was calculated that approximately 1800 coulombs would give an overlay of approximately 18 um. This was confirmed by measurement using the technique described in Section 6.11.

6.14 Drag-Out Measurements

Attempts were made to measure the amount of drag-out from the plating bath into the rinse tank on the production plant at Glacier Co. For convenience, the bath used was the nickel barrier plating bath. A jig containing 10 six inch bearings was used.
The jig was immersed in the plating bath and agitated for two minutes. It was then removed, allowed to drain, then rinsed in the counterflow rinse tank. During these measurements, the water circulation was turned off. The process was repeated several times. Samples of the rinse water were taken before and after the process and after each rinse. These samples were later analysed at the university using AA spectrophotometry. The rinsing process mirrored as closely as possible that of the actual industrial process carried out by workers at Glacier Co.

6.15 Fatigue, Wear and Corrosion Resistance

These tests were carried out by the research and the development department at Glacier Metal Company Limited in the absence of the writer. It is understood that the fatigue and wear machine used was the 'Sapphire' test rig. This rig was developed by Glacier specifically for testing bearings. A diagram of the loading system is shown in Fig. 18.

A unidirectional load is applied hydraulically and the test bearing is carried on the eccentric journal of a very stiffly supported shaft. There is no edge loading on the bearing and a comparatively high rating is obtained, relative to the loads that materials might be expected to survive in actual engine conditions.

The corrosion resistance testing was also carried out at Glacier. Initially, the test involved weighing the bearing and placing it in medicinal white oil at 120°C. The bearing was periodically removed, wiped, cleaned and reweighed. The first set of bearings was tested in this way. The following set was tested using the same method but with a different oil, SA30 engine oil.

6.16 Electron Optics, Probe and Diffraction Work

The electron micrographs were taken using a Jeol JEM - 100 cx series scanning transmission electron microscope fitted with a

'Link' energy dispersive analysis attachment. The electron diffraction data was obtained using the same instrument.

Samples for the SEM part of the machine were prepared by plating onto copper foil and the punching out a 2mm diameter disc from the foil. The disc was mounted in the machine using a special clamping arrangement.

In preparing samples for electron diffraction, several methods were tried. Initially, 2mm diameter copper grids were plated by sticking the grids onto different areas of a Hull cell panel using silver loaded glue. Diffraction patterns were then taken of the crystals formed on the edge of the grid cross pieces. It was considered that using a Hull cell panel was the quickest and easiest way of obtaining deposits with various alloy compositions. However, the crystals on the copper grids were considered to be dendrites and so were not comparable with the bulk of the deposit.

Another method tried used the Hull cell panels again only with 2mm carbon film discs supported by a circumferential copper surround. The carbon disc was formed by evaporation and contained minute holes. By plating on the carbon, it was possible to obtain diffraction patterns from around the edge of a hole. However, again the deposit around an edge was not considered to be comparable with the bulk of the deposit.

The third method and the one used, was to plate onto a Hull cell panel made from titanium sheet. Then the deposit was peeled off the titanium in small pieces and mounted in a 2mm folding copper grid. Diffraction patterns were then obtained from around the edge of the sample. A Hull cell panel made from titanium sheet was plated using a fluoroborate electrolyte of the following composition:

220 gl^{-1}	cadmium
50 gl^{-1}	lead
6 gl^{-1}	resorcinol
1 gl^{-1}	peptone
1 gl^{-1}	polyethyleneglycol

Small samples were peeled off from different current density regions and mounted in folding copper grids. Ten diffraction patterns were photographed in each region looked at on the sample. A gold standard was used for calibration purposes and diffraction rings were photographed before and after each sample.

After photographing the diffraction patterns on a sample, the deposit on the region was analysed using energy dispersive analysis (using the 'Link' attachment on the STEM). From the diffraction patterns photographed of both the alloy deposit and the gold standard, it was possible to work out the lattice parameter of the alloy at various compositions.

The electron microprobe analyser was used to look at an alloy deposit with a rough appearance obtained from a fluoroborate electrolyte in which the addition agents (6 gl^{-1} resorcinol, $1 gl^{-1}$ peptone and 1 gl^{-1} P.E.G.) had broken down. A curious feature of the rough deposit was an oval shaped bump. This was qualitatively analysed using the probe.

7. RESULTS

7.1 Sulphamate Solutions

The rest potentials of the 0.5M cadmium sulphamate solutions and the 0.5M lead sulphamate solutions were -650 and -405 mV respectively at 30°C. (Fig. 19,20). This gives a potential separation of 245 mV which remains effectively the same at all temperatures. Depolarisation of the cathodic reaction occurred in both solutions on increasing the temperature, slightly more so with the lead electrolyte. The current density/potential graphs for the lead sulphamate were only produced for three temperature values, 30, 40 and 50°C, because lead sulphamate becomes increasingly unstable with a rise in temperature. It is understood that the lead sulphamate hydrolyses to form ammonium bisulphate with the subsequent precipitation of lead sulphate.

Dendritic growths occurred in the higher current density regions with both electrolytes.

The effect of the addition agent was approximately the same on both electrolytes. (Fig. 21,22). The reaction was polarised 50 - 60 mV at a current density of 10 A/dm^2. No change in the rest potentials was detected.

Both electrolytes were found to have cathodic current efficiencies of 100% and the addition of more sulphamic acid to the solutions depolarised the reaction slightly and in the case of lead sulphamate an excess of sulphamic acid precipitated an insoluble white precipitate. This was probably lead sulphate.

The current density/potential graphs for the alloy solutions (Fig. 23), indicate that at a maximum current density of 10 A/dm^2 an alloy was only likely to be plated using a quiescent electrolyte containing 75 gl^{-1} of lead or less.

The polarisation data for the three concentrations of lead in the sulphamate alloy electrolytes (75 gl^{-1} Pb, Fig. 24; 50 gl^{-1} Pb Fig. 25, 25 gl^{-1} Pb, Fig. 26) show that they were very sensitive to any form of agitation. Both mild and vigorous agitation depolarised the reaction to a similar degree for all three concentrations.

This depolarisation was also reflected in the cadmium content of the alloy deposit. (Fig. 27). Agitation decreased the cadmium content of the alloy to such a degree that with 75 gl^{-1} Pb in the solution (Fig. 27a), no cadmium was plated out at potentials more positive than -700 mV (SCE).

It was noted that the quality of the alloy deposits from the sulphamate solutions was not very good. The deposits tended to be rough and of a dendritic nature.

7.2 Fluorosilicate Solutions

The rest potentials for the cadmium fluorosilicate and the lead fluorosilicate electrolytes were -606 mV and -362 mV respectively at 30°C (Fig. 28, 29). This gave a potential separation of 244mV.

Depolarisation occurred in both solutions on increasing the temperature, more so with the lead electrolyte.

An increase of temperature from 30 - 60°C depolarised the reaction by some 50 mV at 10 A/dm^2 as compared with 25 mV for the cadmium electrolyte.

In both cases, the polarisation was not as great as for the sulphamate electrolyte indicating that the fluorosilicates were only weakly complexed compared with the sulphamates or fluoroborates.

The addition of various amounts of resorcinol had very little effect on the cadmium cathodic polarisation (Fig. 31). The addition of 6 gl^{-1} resorcinol to the electrolyte polarised the reaction by only 50 mV at 10 A/dm^2. However, with the lead fluorosilicate (Fig. 30) 6 gl^{-1} resorcinol polarised the reaction by 90 - 100 mV at 10 A/dm^2.

Both the lead and cadmium electrolytes had cathodic current efficiencies of 100% and the addition of more fluorosilicic acid had a similar effect on both electrolytes, the reactions were shifted to a more noble potential and were slightly depolarised.

When the alloy solutions were made up, the solution containing Pb and 220 gl^{-1} Cd precipitated a lead salt and 100 gl^{-1}subsequent analysis showed that the solution had a new lead content of only 77 gl^{-1}. This suggested that the solution was unstable and that with 220 gl^{-} Cd in 32% fluorosilicic acid the maximum amount of lead that could be held in solution was only 77 gl^{-1}.

The current density/potential graphs for the alloy solutions (Fig 32), indicate that a solution containing 75 gl^{-1} lead or less could deposit an alloy containing some cadmium. Depolarisation occurred below a current density of 10 A/dm^2 and this suggested that cadmium deposition had occurred simultaneously with the lead deposition.

The current density/potential graphs for the fluorosilicate alloy electrolytes subjected to varying degrees of agitation (Fig. 33,34,35), indicated that the deposition reaction was less sensitive to agitation than the sulphamate electrolyte. Agitation of the solution containing 25 gl^{-1} Pb had a similar effect on polarisation as for the sulphamate electrolyte. Both mild and vigorous agitation depolarise the deposition reaction to a similar degree. However, with the electrolytes containing 50 and 75 gl^{-1} Pb vigorous agitation depolarised the deposition reaction by approximately twice as much as mild agitation.

The graphs of the percentage cadmium in the deposit versus potential show some curious trends (Fig. 36). For the electrolyte containing 25 gl^{-1} Pb, the alloys containing the most cadmium were obtained from a vigorously agitated solution rather than from a quiescent solution at low negative potentials. At high negative potentials, the alloys containing the most cadmium were obtained from the solutions which were quiescent followed by the vigorously agitated solution and then the mildly agitated solution.

For the electrolyte containing 50 gl^{-1} Pb, the alloys containing the most cadmium were obtained from a vigorously agitated solution followed by a mildly agitated solution and the quiescent solution. The electrolyte containing 75 gl^{-1} Pb produced an alloy containing a greater amount of cadmium from a mildly agitated solution. A vigorously agitated solution came next, followed by a quiescent solution.

It was noted during the experiment that the electrolyte changed colour from a clear liquid to a rose coloured liquid. The colouring was not due to any precipitation.

All the deposits obtained were rough in texture although they were considerably better quality than those obtained from the sulphamate electrolyte. Better quality deposits were obtained from a quiescent solution.

7.3 Fluoroborate Solutions

Several sweep rates were initially used for the cathodic potential sweeps using a 0.1M lead fluoroborate solution. These were 3 mV/min, 30 mV/min, 60 mV/min. Fig 37 graphically illustrates the effect of varying the sweep rate on the cathodic polarisation 30 mV/min was chosen for most of the work.

Very little change in the polarisation occurred with the 0.1M cadmium fluoroborate solution when the temperature was increased (Fig. 38). The change in polarisation is more noticeable with 1M cadmium fluoroborate (Fig. 39). Initially, there was an increase in polarisation upto a temperature of 40°C but then it followed the expected trend with depolarisation occurring on each successive increase in temperature. Furthermore, the more concentrated solution appeared to be approaching a limiting current at a lower current density than the lower concentration solution. This effect was not apparent for the lead fluoroborate polarisation curves (Fig. 40 and 41).

The effect of temperature on the 1M lead fluoroborate solution was to initially polarise the reaction. This reached a maximum at 50°C and then depolarisation occurred upon further increases in temperature. The 0.1M lead fluoroborate solution followed the expected trend with depolarisation occurring upon each successive increase in temperature. The temperature did not appreciably effect the discharge potentials of either the cadmium or lead fluoroborate. (The discharge potentials for cadmium and lead were -531 mV and -363 mV for the 1M solutions and -643 mV and -390 mV for the 0.1M solutions respectively).

The polarisation curves for the mixed solutions are shown in Fig. 42. As the concentration of lead ions in the solution decreased the polarisation of the initial part of the curve increases and the discharge potentials became more positive. The polarisation in the lower part of the curve was governed by the deposition of cadmium.

The polarisation curve for the solution containing 125 gl^{-1} of lead showed very little depolarisation at the more negative potentials which indicated that no deposition of cadmium was taking place. This was found to be the case when the deposits plated at various potentials were analysed (Fig 43). With the 100

gl^{-1} Pb solution depolarisation occurred at the lower potentials indicating that the cadmium ions were beginning to have some effect on the polarisation. However, analysis of the deposits showed that little or no deposition took place. Not until the lead content of the solution reached 75 gl^{-1} or less, when the depolarisation of the reaction at the lower potentials became obvious, did any significant deposition of cadmium take place.

The effect of agitation on the polarisation of the alloy deposition reaction from a fluoroborate electrolyte was considerably less than with a sulphamate electrolyte. Depolarisation of the deposition reaction occurred when the solution was mildly agitated. Vigorous agitation depolarised the reaction further. The effect was similar for solutions containing 25, 50 and 75 gl^{-1} Pb (Fig. 44, 45,46).

The depolarisation was reflected in the cadmium content of the alloys obtained under potentiostatic conditions at different potentials (Fig. 43) with various degrees of agitation. The alloy with the highest cadmium content was obtained from a quiescent electrolyte. The next highest cadmium content was obtained from a mildly agitated electrolyte. The lowest cadmium content was obtained from a vigorously agitated electrolyte. This trend was found for the three alloy solutions containing 25, 50 and 75 gl^{-1} Pb respectively.

The deposits tended to be dendritic and rough although a fairly good quality deposit was obtained from a quiescent solution. It was found that a useable alloy deposit could be obtained over a greater potential range from a fluoroborate electrolyte than from a sulphamate electrolyte.

Cathodic polarisation data was also obtained for a fluoroborate solution containing:

220 gl^{-1} cadmium
50 gl^{-1} lead
6 gl^{-1} resorcinol
1 gl^{-1} peptone
1 gl^{-1} polyethyleneglycol

This is shown in Fig. 56 but its significance will be discussed in a later section under the large cell work.

Some data was obtained by plating samples galvanostatically using a solution containing:

220 gl^{-1} cadmium
50 gl^{-1} lead
6 gl^{-1} resorcinol

The variation of cadmium content in the deposit with cathode current density (Fig. 47), was non-linear and there was considerable spread in the results.

7.4 Acetate - Citrate Electrolyte

The rest potential for the lead acetate-citrate solution was -550 mV (SCE) (Fig. 48). This is a fairly low potential for lead indicating the formation of a strong complex. However, the deposition reaction was not heavily polarised and the quality of the deposit was found to be very poor. The apparent depolarisation in the high current density region of the polarisation curve was probably caused by dendritic growth.

The rest potential for the acetate-citrate alloy solution was -595 mV (SCE) (Fig. 49). The polarisation curve for the acetate-citrate alloy solution gave no indication of cadmium being plated in the high current density region and subsequent analysis of deposits down to a potential of -780 mV (SCE) showed that no cadmium was deposited. During the electroplating, it was noted that a white gelatinous precipitate formed on the anode.

7.5 Addition Agents

The anodic polarisation curve for a fluoroborate alloy solution containing resorcinol as an addition agent had a rest potential of -334 mV (SCE) (Fig. 50). For a new electrolyte, a limiting current density of 9 A/dm^2 was reached at a potential just in excess of +1000 mV (SCE). After 7000 coulombs had passed through the electrolyte, the limiting current density was reached again in the region of +1000 mV (SCE), however, the value increased to 15 A/dm^2. In both cases, a white film formed on the anode. When the electrolyte had been treated with activated carbon to remove the organic content, no limiting current was apparent up to a potential of +1700 mV (SCE).

The anodic rest potential for a lead anode in a fluoroborate alloy solution containing peptone as an addition agent was -314 mV (SCE) (Fig. 51). For a new electrolyte, no limiting current was reached up to a potential of +1500 mV (SCE). After 7000 coulombs had passed through the solution, the anodic reaction became depolarised by some 150 mV at a current density of 10 A/dm^2. After carbon treating this electrolyte, the anodic reaction was again polarised approaching the curve for the fresh electrolyte.

The anodic polarisation curve for an alloy solution containing polyethyleneglycol as an addition agent (Fig. 52), had a rest potential of -314 mV (SCE) For a new electrolyte, no limiting current density was reached up to a potential of +1500 mV (SCE). However, after 7000 coulombs had been passed through the electrolyte, a limiting current density of 10.5 A/dm^2 was reached at a potential of +700 mV (SCE). After carbon treatment of this electrolyte, a limiting current density of 9.5 A/dm^2 was reached at a potential of +900 mV (SCE). It was noted that after some tome, a white film formed on the anode. This did not occur with a freshly made up solution but rather with one which had had several thousand coulombs passed through it. It also occurred after the solution had been carbon treated.

The anodic polarisation curve for an alloy electrolyte containing all three addition agents, resorcinol peptone and polyethyleneglycol, (Fig. 53) had a rest potential of -314 mV (SCE). With a freshly made up electrolyte, a limiting current density of 12 A/dm^2 formed at a potential of +1300 mV (SCE). After 7000 coulombs had passed through the electrolyte, a limiting current density of 15 A/dm^2 formed at a potential of +1300 mV. After carbon treatment of this electrolyte, no limiting current formed upto a potential of +1600 mV (SCE).

The anodic potential sweep on a 0.2M sodium sulphate solution containing 6 gl^{-1} resorcinol showed a peak in the current density at 1300 mV (SCE) (Fig. 54).

Hull Cell

The data obtained from the Hull cell work is contained in Table 5. It had been observed during the polarisation experiments that polyethyleneglycol and peptone did not give very good deposits by themselves and so it was decided to use resorcinol as the main addition agent as it seemed to give a reasonably good deposit. The Hull cell panel for an alloy solution containing just resorcinol as an addition agent did not show large bright areas. However, various combinations of peptone, polyethyleneglycol and diastase added in various quantities along with the resorcinol increased the current density range of the smooth deposit region.

The four Hull cell panels with the widest current density range for a smooth deposit were cut up and the deposits from three current density ranges were analysed. An alloy plated from a solution containing 6 gl^{-1} resorcinol, 1 gl^{-1} peptone and 1 gl^{-1} polyethyleneglycol has the largest percentage of cadmium at 9.7% for the current density range 2 - 3 A/dm^2.

IR and UV Spectrophotometry

Some attempt was made to identify the break down product of resorcinol in a fluoroborate solution using both IR and UV spectrophotometry.

Typical IR spectra are shown in Fig. 55 for M.I.B.K. methylisobutylketone), resorcinol extracted into M.I.B.K. from a lead fluoroborate plating solution after zero hours and resorcinol extracted into M.I.B.K. from a lead fluoroborate plating solution after 7000C had passed through it. No difference in the spectra was detected. No attempt was made to quantify the results of the IR spectrophotometry.

Similar solutions were used for UV spectrophotometry without the need for extraction (so the spectra for M.I.B.K. was not studied). The absorption spectra was looked at between 200 um and 700 um. The only significant absorption was detected at 278 um for both solutions (fresh and after 7000c). No difference in the size of the absorption could be detected. Absorption at 278 um is generally considered to be due to the benzene ring system.

7.6 Large Cell

The cathodic polarisation curve for the large cell showed considerably more polarisation than for the small cell (Fig. 56). The rest potential for the fluoroborate electrolyte containing:

220 gl^{-1} cadmium
50 gl^{-1} lead
6 gl^{-1} resorcinol
1 gl^{-1} polyethyleneglycol
1 gl^{-1} peptone

was -300 mV (SCE) in the small cell. In the large cell, the rest potential was -276 mV (SCE). Both polarisation curves were obtained at room temperature in a quiescent electrolyte.

The cathodic polarisation data for a fluoroborate electrolyte containing 220 gl^{-1} cadmium and 50 gl^{-1} lead with various addition agents is shown in Fig. 57. The electrolyte containing just resorcinol as an addition agent was the least polarised in the low current density regions, however, in the higher current density regions it was more polarised than either of the other two electrolytes. The electrolyte containing the resorcinol and peptone was polarised more in the lower current density regions than the electrolyte with resorcinol but was less polarised in the higher current density regions.

The electrolyte containing the resorcinol, peptone and polyethyleneglycol was polarised in both regions, i.e. the lower and higher current density regions.

Bearings were plated at constant potentials and the alloy deposit was analysed (Fig. 58). Initially, deposits containing from 7.6% to 21.4% cadmium were obtained from potentials varying from -700 to -750 mV (SCE). The electrolyte used was a fluoroborate one containing:

220 gl^{-1} cadmium
50 gl^{-1} lead
6 gl^{-1} resorcinol
1 gl^{-1} polyethyleneglycol
1 gl^{-1} peptone

After the electrolyte had stood unused for seven days in the laboratory, its colour changed from clear to a pinkish colour. Bearings plated in this electrolyte had deposits with cadmium contents varying from 14.2% to 33% from potentials ranging from -690 to -740 mV (SCE). Furthermore, the quality of the deposit on the bearing containing 33% cadmium was very poor. The surface was covered in small bumps as shown the electron micrograph (Fig. 59). Electron probe analysis of the bumps indicated that they may have been regions of high cadmium content (Fig. 60).

After the anode had been effectively masked (see below), the analysis of the deposits on bearings plated at potentials varying from -600 to -660 mV revealed cadmium contents in the alloys varying from 5.4% to 30.0%. (All these bearings were plated on the same day).

The change in colour of the electrolyte indicated that the addition agents were breaking down. Cathodic polarisation data confirmed that some change was taking place (Fig 61). After standing unused for seven days, the reaction had polarised by some 130 mV at 2 A/dm^2 (curve b). The addition of more peptone (curve c) and polyethyleneglycol (curve d) depolarised the reaction partially, although the rest potential remained at a new value of -332 and -375 mV (SCE) respectively compared with its original value of -276 mV (SCE).

During the acquisition of the above results, it was noted that deposition was occurring on the back of the shell bearings. It was assumed that the masking of the top half and underside of the anode was not effective and this was replaced with P.T.F.E. tape. Repeating the cathodic polarisation run on a freshly made up solution (Fig. 62) showed that the cathodic reaction was under partial anodic control. The rest potential was moved 74 mV (SCE) more negative from -276 mV (SCE) to -350 mV (SCE). The alteration in the polarisation characteristics dramatically altered the alloy composition of the deposits obtained at different potentials as described above.

All bearings plated for mechanical and corrosion testing at the Glacier Co. were plated using a masked anode and electrolytes with a maximum age of 24 hours. Furthermore, the electrolyte was discarded after 10,000 coulombs was passed through it.

7.7 Conductivity

The conductivity measurements on various plating solutions (Table 6), show that the alloy sulphamate solution had a low conductivity along with proprietary nickel plating solution 'Nisol 80'. Copper sulphate and copper 'Pyrobrite' (a proprietary type copper solution) have similar conductivities around 110 m-ohm^{-1} cm^{-1}. The alloy fluoroborate and fluorosilicate electrolytes have similar conductivities to the copper fluoroborate and lead and cadmium fluorosilicate. The proprietary zinc solution 'Zincalux' had the highest conductivity of the limited range of solutions which were tested.

Increasing the temperature of lead and cadmium fluoroborate plating solutions (Fig. 63) at several concentrations increased the conductivity of the electrolyte in a linear fashion. For an electrolyte containing 130 gl^{-1} Pb, the conductivity increased by 18 mohm^{-1} cm^{-1} for a 10°C rise in temperature. There was very little difference in the conductivites of the two electrolytes.

7.8 Efficiency

Cathodic efficiency measurements of some of the plating solutions were taken as a matter of course during the project. The efficiency of the sulphamate, fluoroborate and fluorosilicate alloy solutions was found to be almost 100% in each case.

7.9 Diffraction and Electronmicroscopy

Diffraction patterns were obtained using a S.T.E.M. for lead cadmium alloys of various compositions varying from 2 - 26% cadmium. The lattice parameter was calculated from the diffraction patterns and plotted against cadmium content (Fig. 64).

The lattice parameter reaches a maximum value of 5.04 with a cadmium content of 15.6%. It did not appear to vary linearly with cadmium content.

Electron Micrographs were taken of deposits plated from various electrolytes. The ones shown in Figs. 65 - 68 are all lead-cadmium alloys plated from fluorosilicate, sulphamate and two from fluroborate solutions. These illustrate the rough deposits obtained from the sulphamate electrolyte and the effect of the polyethyleneglycol and peptone on the grain size of the deposit plated from a fluoroborate bath.

7.10 Mechanical and Corrosion Tests

The corrosion test results are shown in Table 7 and compare lead cadmium of varying compositions with lead-tin overlays. The majority of tests were carried out in medicinal white oil (MWO) and these show that the lead-cadmium overlay was completely removed within 100 hours. At this point, it was decided at Glacier to carry out some testing in a standard automotive engine oil. The results show without a nickel barrier, there was a loss equivalent of between 4 and 9 microns of overlay, with a nickel barrier, the corrosion rate with a lead-cadmium overlay was approximately three times that of lead-tin without a nickel barrier.

The fatigue rating for overlays varying between 5 and 10% cadmium with and without a nickel interlayer, were found to be in excess of 69 Mpa. This figure is comparable with lead-tin and lead-tin-copper, although values less than 50 have been obtained with these types.

The wear resistance results (Fig. 69) show that the figures for lead-cadmium overlays lie essentially between lead-tin and lead-indium.

7.11 Drag-Out Measurements

Over the limited number of jig rinses carried out the amount of electrolyte carried over remained relatively constant for each rinse producing a linear increase in metal ion concentration in the rinse water (Fig. 70).

8. DISCUSSION

To simultaneously codeposit two metals, conditions must be such that the more negative potential of the less noble metal can be attained without employing an excessive current density. In effect, this means that the deposition potentials of the two metals must be fairly close together.

As a rough quide to whether two metals will codeposit the values of the standard electrode potentials can be compared. The standard reduction electrode potential for lead in an acid solution of simple salts is -0.126V and for cadmium it is -0.403V. The separation between the two is 277 mV. Generally speaking, satisfactory codeposition occurs if the static potentials are less than 200 mV apart. However, satisfactory alloys have been obtained from metals with potentials considerably further apart by employing baths containing complexing agents or addition agents. It was considered that the plating of a lead cadmium alloy from a simple acid bath was possible, provided the dynamic deposition potentials were close enough together.

8.1 Choice of Electrolyte

Because so many lead compounds are insoluble, the choice of electrolytes compatible with both lead and cadmium is somewhat limited. For example, sulphate and chloride solutions of lead are not possible unlike cadmium. The soluble salts which were considered for plating purposes were nitrate, fluorosilicate, sulphamate, fluoroborate, perchlorate, pyrophosphate, and complex solutions of cyanides, acetates, ethylenediamines and hydroxyquinoline. The formation constants of some of these solutions for lead and cadmium are shown in Table 8. Generally speaking, the greater the separation between the log K values for lead and cadmium, the more chance there is of one metal being selectively complexed in solution and therefore possibly bringing the deposition potentials closer together.

The log K values for cyanide have a separation of 2, larger than any of the others and was therefore considered as a possibility. However, because of the toxicity of the solution, it was ruled initially out as a possible industrial process. The perchlorates also were not seriously considered because of the potential handling problems. Both lead and cadmium have been plated from nitrates, however, the quality of the deposits has never been very good. Cadmium has been plated from an ethylenediamine solution although no data has been found for a possible lead solution. Similarly, no data has been found for electrolytes based on hydroxyquinoline.

Not enough time was available to undertaken any serious study of a pyrophosphate electrolyte. Both lead and cadmium have been deposited from pyrophosphate baths [30] [48] and interesting results have been obtained with a lead-tin bath based on pyrophosphate. It has been found that the tin content of the deposit can be varied from zero to almost 90% by adjusting the ratio of tin to lead in the solution, but there appears to be no direct relationship between the tin content in the solution and that in the deposit. Variations in the other plating parameters such as addition agents, total metal content current density, etc. also affect the tin contact of the alloy in an unpredictable way. This is contrary to the results obtained from a fluoroborate bath. A typical lead-tin pyrophosphate plating bath would contain less than 20 gl^{-1} lead with upto 260 gl^{-1} pyrophosphate. Studies of a cadmium pyrophosphate plating electrolyte [48] have shown that the solubility of a pyrophosphate complex of cadmium in a 192 gl^{-1} solution of potassium pyrophosphate is equivalent to 4.6 gl^{-1} cadmium sulphate at room temperature and almost double this value at 50°C. Freshly prepared solutions can contain more cadmium but they are unstable and, with time, the concentration drops to the limits indicated above. EDTA has been used as an addition agent with this electrolyte and is presumed to have a complexing action although no details are available.

In view of the low solubility of the cadmium complex, it seems unlikely that a usable lead-cadmium plating bath could be made from a pyrophosphate electrolyte.

The solutions studied in this project were electrolytes which have found wide use commercially or electrolytes which have been known to work in the laboratory. These were sulphamates, fluorosilicates, fluoroborates and acetate-citrates.

8.2 Experimental Techniques

The techniques chosen or developed for this project were governed by two overiding factors. The first and most obvious one which affects most projects was the limited amount of time available, and the second was the purpose of the project to develop a possible industrial process. In comparison to a laboratory situation, electroplating in industry, is carried out in a relatively imprecise way. The chemicals used are usually of low grade, the electrolytes are usually made up in a very ad-hoc fashion and are sometimes monitored on a regular but infrequent basis. The pre-treatment and plating procedure is usually in the hands of people with no sound theoretical knowledge and quality control at this stage is minimal.

The development of a process in a laboratory must consider the control problems in an industrial situation. The use of sophisticated techniques and equipment are usually inapplicable to an industrial situation. For this reason, and taking into account the time available, the techniques used during the project were designed to give quick reproducible results. The experimental work was designed not to provide highly accurate results, but when looked at as a whole and compared with one another, they do show the effect of altering the various plating parameters.

The equipment and method used to obtain the polarisation data, proved to be reliable and quick. The potentiostat was specifically designed for the project and apart from a few early difficulties, functioned well throughout the project. The small cell was found to have advantages over a beaker. The size was very convenient and, with the use of the culture vessel lid, the electrodes could be accurately positioned for each experiment.

The reference electrode arrangement proved to be very effective. The positioning of the remote junction cermaic tip could be carried out quickly and accurately without the problems associated with luggin capillaries.

In retrospect, more accurate results could have been obtained if concentric cylindrical electrodes had been used. Plane parallel electrodes in a cylindrical cell as used, produce current density variations across the surface of the electrode and the current density at the edge of the electrode was probably somewhat higher that at the centre.

The current density variations across the surface of the plane working electrodes was graphically illustrated during anodic polarisation studies. The edge of the plane anodes were dissolved to a greater degree that the centre of the anode. This resulted in an increasing anode surface during the polarisation experiment, For anodic polarisation studies, a constant surface area of working electrode exposed would have been desirable but difficult to achieve in practice. The error caused by the variation in surface area could have been minimised by an overall increase in surface area.

A uniform current distribution could have been obtained if an arrangement similar to the cell used for current efficiency measurements had been used. However, this arrangment would not have been suitable for potentiodynamic studies as the size of the working and auxiliary electrodes were similar. The use of concentric cylinders would have overcome this problem. Their use would not have overcome the surface area variation during anodic polarisation studies but they would have produced more accurate results for the cathodic polarisation studies. A further advantage of using concentric cylinders is that uniform agitation can be obtained by rotation of the working electrode. Uniform agitation was not always achieved using nitrogen bubbling.

The use of a Hull cell for studying the effect of addition agents on the morphology of a deposit is well documented. When a current is passed through the solution sample contained in the cell, the current density along the sloping cathodic varies in a known manner, so that the character of the plate at a range of current densities is determined in one experiment. It was realised that the use of the cell could be further extended by analysing the deposit from various current density ranges. This gave a rough guide to the most effect addition agents both in terms of deposit morphology and alloy composition.

The conductivity and efficiency measurements were not carried out to provide definitive data because they were considered to be of secondary importance related mainly to process control and cost. Although the addition of other salts would affect both the conductivity and probably the efficiency, the affect of such an addition on the polarisation characteristics was of primary importance. In most cases, it was recognised that it would only increase the lead content of the alloy deposits.

The large cell jig used for plating the bearings was supplied by the Glacier Metal Co. The jig was a standard design used by the research department at Glacier and its essential features were similar to those of the jigs used in the plant. The major difference between the two types of jig was the size, the plant type being considerably larger and designed to hold several bearings at any one time.

It was found that considerable skill was required to centralise the bearings on the jig to avoid, as far as possible, any variations in anode to cathode spacing. Care was also taken to match the two halves of the jig so that the half shells of the bearing formed a perfect cylinder, thus preventing "throw" onto the back of the bearing.

Problems were initially encountered with deposit build up on the back of the bearings caused by ineffective masking of the lead anode protruding above and below the jig. It was assumed that the lacomit used to mask off the anode degraded in the strongly acid solution. The problem was cured out by the use of P.T.F.E. tape.

The pre-treatment process for the bearings was developed by the Glacier Metal Co. for this type of bearing and no apparent difficulties arose during this stage of the process.

No quick method was found for coating thickness measurement. THe laboratory at the Glacier Metal Co. uses a coulombmetric plating gauge of a different manufacture to the one available in the University. The cell of the former meter was small enough to place on the inside of the bearing shell without the curvature deforming the cell. The cell from the University's model was found to be too large for a bearing of that size and so was not used.

In order to measure the deposit thickness, metallographic sections were prepared. Because this was destructive and time consuming, measurements were only carried out when it was felt necessary to check the deposit thickness. One shell bearing from each batch plated during a day was deemed to be sufficient.

8.3 Electrolytes

The application of solution diffusion theory to alloy deposition is difficult and is only applicable under certain conditions.

Metal deposition actually occurs at the cathode solution interface. Thus in the case of alloy deposition, the composition of the alloy deposit will be related to the concentrations and transport properties of the depositable metal ions at the cathode solution interface. The transport of metal ions is accomplished by diffusion, convection and electrical migration. At the cathode solution interface, the horizontal convective flow is zero and reaches a maximum at the outer boundary of the diffusion layer. Thus for a solution containing a single solute under steady state conditions, the concentration gradient at the cathode solution interface,

$$\frac{dc}{dx} = \frac{I\ (1-T)}{DF}$$

where I is the current density, T is the transference number of the depositable metal ions, D is the diffusion constant and F is Faradays constant. Assuming a 100% efficiency the concentration gradient will be at a maximum at the limiting current density and the deposition will be under diffusion control.

In alloy deposition, two or more metal ions are involved in the process. Each will have their own diffusion constant and transference number and the total current density will be the sum of the partial current densities required for deposition of the separate metal ions. As all these values can vary, the application of diffusion theory to general cases is not very useful.

However, special cases do occur where the alloy is deposited at the limiting current density of either both metal ions or the more noble metal ion. Other cases where the diffusion constant and ionic mobilities of the ions are the same may also be considered but as with limiting current densities they are not generally applicable.

In the absence of a limiting current and diffusion control, the primary factor controlling the relative concentrations of the depositable metal ions at the cathode solution interface is the deposition potentials of the two metals. By studying the effect of the plating variable upon the deposition potential, its effect on the deposit composition can be predicted.

The results of the polarisation studies show that the lead-cadmium alloy plating solutions used were all of the regular type. This was to be expected from electrolytes of simple salts where the potential separation of the individual metal is some 250 mV but the polarisation characteristics of the individual electrolytes are relatively similar. In view of the large separation between the two metals static potentials, it was realised at an early stage in the project that the major problem would be in increasing the amount of cadmium in the deposit whilst retaining deposit quality and control over the process. In order to plate a lead-cadmium alloy from the solutions studied, an electrolyte containing a high proportion of cadmium to lead was found to be necessary. With a cadmium concentration of some 220 gl^{-1}, the maximum lead concentration in the electrolytes from which an alloy could be plated, was found to be around 75 gl^{-1}.

The sulphamate electrolyte, although unstable at high temperatures, was considered to have possibilities as a lead-cadmium alloy plating bath. Both lead and cadmium sulphamate have high solubilities and the static potentials of the two metals in the electrolyte were found to be only 245 mV apart. The cathodic reaction was depolarised as the temperature increased for both the lead and cadmium sulphamates, considerably more so with the lead electrolyte. The addition of resorcinol did not markedly polarise one reaction more than the other, although its presence was found necessary to produce relatively smooth deposits. The alloy solutions were found to be very sensitive to agitation. This would make any process based on sulphamates be very difficult to control in an industrial situation. Under such conditions, mild agitation is usually employed to prevent preferential depletion of metal ions in the electrolyte held within the plating jig.

The addition of sulphamic acid did not markedly effect the polarisation, although a slight increase might have been expected. An electrolyte based on sulphamates would give deposits of varying compositions for minor variations in not only temperature but also agitation.

Better results may have been obtained by using a different addition agent or even a combination of addition agents, although it is unlikely that this would have overcome the problems which arose due to the sensitivity to agitation.

The fluorosilicate electrolyte proved to be more promising than the sulphamate electrolyte. The potential separation between the static potentials was similar at 244 mV and again the cathodic reaction was depolarised as the temperature increased for both the individual electrolytes. Again, the greatest depolarisation occurred with the lead electrolyte. As with the sulphamate electrolyte, this would suggest problems with control of the deposit composition.

The most interesting result obtained from the fluorosilicate electrolyte is the apparent preferential polarisation of the lead deposition reaction to the cadmium caused by the addition of resorcinol. This was reflected in the analysis of the deposits plated at constant potential. A greater range of compositions was obtained from the fluorosilicate electrolyte than either the sulphamate or the fluoroborate electolytes, although the most promising results were obtained with a relatively lower concentration of lead in the electrolyte.

The apparent anomaly in the results, whereby a greater concentration of cadmium was deposited from electrolytes which were vigorously agitated rather than mildly agitated, is probably explained by a breakdown of the addition agent. The electrolyte changed colour from pale straw colour to a rosy pink colour with time and use. In view of the problems experienced later with the fluorosilicate electrolyte, it would almost certainly indicate that the resorcinol was breaking down in some way.

Although the fluorosilicate electrolyte appeared to be as sensitive to temperature variations as the sulphamate electrolyte, the effect of agitation on the cathodic polarisation was found to be considerably less. Whether this was reflected in greater control of the alloy composition is difficult to say because of the breakdown of the addition agent.

The fluorosilicate electrolyte proved to be a viable alternative to the fluoroborate electrolyte although the deposit quality, as with the sulphamate electrolyte was not as good. It was considered that with a thorough investigation of other possible addition agents, the lead deposition reaction could have been polarised further, increasing the cadmium content of the deposit and possibly improving the quality of the deposit.

The separation between the static potentials for the fluoroborate electrolyte were 168 and 253 mV for the 1M and 0.1M electrolytes respectively. To compare this with the sulphamate and fluorosilicate electrolytes where the concentrations were 0.5M is difficult. However, the separation for a 0.5M fluoroborate electrolyte is almost sure to be less than the separation obtained for either of the other two electrolytes.

The effect of temperature on the fluoroborate electrolyte did not follow the expected trend. This could have been caused by two effects. It could have been related to the free acid content of the electrolytes, or the formation of dendrites on the cathode. The latter of the two is the most likely. The electrolyes were made up from industrial solutions and no attempt was made to check the free acid content but as the same electrolyte was used throughout the temperature variation polarisation runs, variations in the acid content would seem unlikely, although it may explain the difference in polarisation between the 0.1M solutions and the 1M solutions.

As with both the other types of electrolytes, alloy deposits containing cadmium were only obtained from solutions containing 220 gl^{-1} cadmium and 75 gl^{-1} or less lead. As with the other electrolytes, the cathodic reaction was depolarised as the electrolyte was agitated. The depolarisation was not as great as with the sulphamate electrolyte suggesting that the fluoroborate process may have been easier to control. A more detailed study of the alloy composition was carried out with the fluoroborate solution than with either the sulphamate or fluorosilicate electrolytes. This was done by plating samples galvanostatically at current densities varying from 2 - 8 A/dm^2. The resulting variation in cadmium content with cathode current density was non-linear and the points were considerably spread. This highlighted the problems in control and it was first thought that the spread was due to minor temperature fluctuations and agitation caused by convective flow. Later work, however, suggested that it may also have been due to breakdown of the resorcinol.

In view of the work carried out by Gusev et al [22], it was thought necessary to make some attempt to investigate the process they developed. Electrolytes based on acetate-citrate solutions have been receiving considerable attention because of their relatively high complexing power and their lack of toxicity. Their use with lead, however, was surprising as the pH of the solution was thought liable to cause insoluble precipitates to form.

Efforts to reproduce the work of the Russians were hindered by an inability to obtain any polyethylene polyamine. It is understood that this is not a specific polymer but the name of a 'family' of polymers. In the limited time available, no supplier of the chemical was found. Its use in the context of this electrolyte was difficult to determine, but it has been referred to in other papers as a complexing agent. Certainly, without it the acetate citrate electrolyte was found to be very unstable, so much so that an electrolyte based on cadmium acetate and citric acid was not produced due to insoluble precipitates forming each time attempts were made to dissolve the constituents in distilled water.

The rest potential for the lead acetate citrate solution was -530 mV. This was considerably lower than the simple acid solutions where the rest potentials were found to be around-400 mV. This would seem to indicate the complexed nature of the electrolyte. However, the reaction was not noticeably more polarised than the acid electrolytes.

The alloy electrolyte had a rest potential of -595 mV, 45 mV more negative than the lead electrolyte. This showed the effect of the cadmium complex on the rest potential. No alloy containing cadmium was plated from this electrolyte and it must be assumed that the lack of polyethylene polyamine was responsible. If the role of the polyethylene polyamine is to selectively complex the lead in the electrolyte, then the inability to produce an alloy containing cadmium would be explained. Further, during the electroplating, a gelatinous white precipitate formed on the anode. This was probably caused by a local pH change at the anode and would probably have lead to the passivation of the anode.

Without the polyethylene polyamine, it was therefore not possible to reproduce the Russians work. However, their report did suggest that problems with stability were encountered even with the polyethylene polamine and it would seem unlikely that such an electrolyte would give a viable industrial process.

8.4 Complexing and Addition Agents

Because of the large separation between the lead and cadmium deposition potentials in the simple acid solutions, some consideration was given to complexing the solution in the hope that the lead would be selectively complexed. The addition of E.D.T.A. (ethylenediaminetetra-acetic acid) to a lead fluoroborate electrolyte produced an insoluble precipitate. This may have been due to buffering action of the E.D.T.A. altering the pH and precipitating an insoluble lead salt. It was later found that E.D.T.A., and indeed most complexing agents, cannot be used in strongly acid solutions. The only complexing agent which was thought to have a reasonable chance of success was CDTA (trans 1, 2 - diaminocyclohexane - NNN'N' - tetra-acetic acid) which forms soluble complexes at lower pH values than almost all other commonly available complexing agents. However, it was found that CDTA was considerably more expensive and that even this was unlikely to work in pH's less than 2. The fluoroborate solutions could not be buffered to a pH greater than one without the formation of insoluble lead salts.

The effect of addition agents upon an alloy plating bath is similar to the effects of complexing agents. Unlike complexing agents, however, the concentration of addition agent necessary to produce an appreciable effect is much smaller.

The addition agent chosen for most of the work in this study was resorcinol. It is used for the lead-tin alloy plating process and is recognised as a good addition agent for lead plating. A further consideration was that it was a relatively simple chemical in comparison to other recognised addition agents for lead such as peptone and gelatin. As it was a relatively simple chemical, it could be obtained in a reasonably pure form cutting down the risk of using an addition agent where the impurities have more effect on the process than the supposed addition agent itself !

The resorcinol appeared to work satisfactorily with the small cell although it did not prevent dendritic growth in the high current density regions. It was only on changing to the large cell for plating bearings that it became apparent that the addition agent was breaking down. It also showed that resorcinol by itself did not give a very good quality deposit and so the Hull cell was used in order to find a combination of addition agents which would give a good quality deposit whilst promoting the deposition of cadmium.

It was found that resorcinol, peptone and polyethyleneglycol gave the best results from the small range of chemicals tested. This combination was used in the large cell in the following concentrations:

6 gl^{-1}	resorcinol
1 gl^{-1}	peptone
1 gl^{-1}	polyethyleneglycol

Resorcinol and peptone alone did not give a wide current density range in which smooth deposits could be obtained. The addition of polyethyleneglycol increased the range considerably. From the cathodic polarisation data obtained on these addition agents in the large cell, the peptone appeared to polarise the cathodic reaction in the lower current density regions where lead deposits, thereby enhancing the effect of the resorcinol. The addition of polyethyleneglycol did not increase this polarisation markedly and its effect appeared to be more related to deposit quality.

On comparing the cathodic polarisation data obtained from the large cell with that obtained from the small cell, it was clear that the change in cell geometry had a large effect on the poalrisation characteristics.

In the small cell, the cathode was a flat plate of 3 cm^2 held some 5 cm distant from a lead anode whose surface area was considerably greater. With the large cell, the cathode had a surface area which was considerably larger than the anode and the shapes were as concentric cylinders. For potentiodynamic studies, it is usual to have a small working electrode and a large auxiliary electrode so that the reference electrode is not affected by the reaction at the auxiliary electrode. This was not possible in the large cell and it was thought probable that the cathodic polarisation was under partial anodic control during the potentiodynamic sweep.

This idea was supported by the change in the polarisation curve when the anode was effectively masked. If the anode was not partially controlling the potential, changing the surface area of the anode should have had no affect on the cathode reaction.

This has far reaching consequences if an industrial process were to depend on potentiostatic control. It would mean that every jig of a different size would have to be 'characterised' in order to establish the correct potential at which to plate a given alloy.

It was whilst plating bearings at constant potentials, that it became apparent that the addition agent was breaking down. Several bearings were plated at constant potentials varying from -600 to -660 mV. The deposits were analysed and the solution was left to stand for seven days. Attempts to repeat the results after seven days resulted in very rough deposits. Polarisation data revealed that the cathodic reaction had become considerably more polarised and bearings with a similar cadmium content were obtained at more negative potentials of -700 to -760 mV.

Consultations with the Glacier Co. confirmed that resorcinol breaks down to a substantial extent and that in the industrial process for plating lead-tin alloys from a fluoroborate solution using resorcinol continuous carbon treatment of the electrolyte is necessary.

At the time this was considered to be a major handicap as bearings with a lead-cadmium overlay of a known composition were required for the mechanical testing programme. To overcome this, the test bearings were plated from fresh solutions. However, with hindsight the increased polarisation can be looked on as advantageous.A more thorough investigation would be necessary but if it could be established that the increase in polarisation reached definite limits after a period of time, and if the quality of the deposit could be retained, then it may be possible to increase the lead content of the alloy electrolyte above the limit of 75 gl^{-1}.

Attempts to find out how resorcinol was breaking down using IR and UV sprectrophotometry proved to be inconclusive. The use of MIBK (methylisobutylketone) as a solvent for the IR spectrophotometry was not helpful as the spectra for it was quite complex. To obtain meaningful results, a simpler solvent should have been used and the process should have been done quantitatively. Similarly, the UV spectrophotometry did not reveal anything of direct interest.

Anodic polarisation of a 0.2M sodium sulphate electrolyte containing resorcinol did reveal a change taking place at the anode at a potential of around 1.3V. This may have been associated with the oxidation of the resorcinol. A similar scan using the same electrolyte without resorcinol did not reveal any change. This result was obtained using platinum electrodes.

As the alloy plating solution had 3 addition agents and not one, the possibility of one or more addition agents changing with time was rather disturbing. The anodic polarisation data obtained for the alloy solutions with separate additions of the addition agents showed some interesting features.

The alloy solution containing resorcinol alone did not show the pronounced peak at 1.3V but did reveal a peak at 1.1V and then the current density decreased slightly. After some use, equivalent to 7000 coulombs, the anodic reaction was depolarised although a limiting current density appeared to be produced at 1.1V. This limiting current density corresponded with the potential of the peak induced using the fresh solution, although the current density wassome 5 A/dm^2 greater at 14 A/dm^2. The difference between the result obtained here and with the sodium sulphate was probably explained by the use of platinum foil as a working electrode in the sodium sulphate solution, whilst lead was used in the alloy solution.

After the solution had been carbon treated to remove all the organic constituents, no limiting current or potential peaks were found on the anodic sweep. This indicated that the limiting currents and peaks were features of the resorcinol and not the ions in the electrolyte.

The result for peptone, where no peaks or limiting currents were observed, would seem to indicate that this addition agent was relatively stable in the fluoroborate electrolyte. The variation in polarisation with use and carbon treatment could have been explained by the addition agent being used up. However, it would be expected that after carbon treating the anodic reaction would be further depolarised. It may be that this anomaly was due to the inability to retain an accurate surface area of the working electrode during the anodic polarisation experiment.

The anodic polarisation data obtained from the alloy solutions containing polyethyleneglycol would suggest that this also broke down with use and/or time. Initially, the anodic reaction was unaffected in a fresh solution, with no limiting current or peaks being induced upto a potential of +1600 mV. After the electrolyte had been used, equivalent to 7000 coulombs, a limiting current of 10A/dm^2 was found at around +600 mV, decreasing to 9 A/dm^2 at +1300 mV. This limiting current was retained after carbon treatment and therefore was most probably caused by the white film formed on the working electrode during the scan. What is surprising, is that it occurred after carbon treatment. No data has been found on the behaviour of polyethyleneglycol in acid electrolytes to support these results, but it may be assumed that the carbon treatment did not remove all the organic constituents of the bath.

A plating process which uses three addition agents has severe disadvantages and when two of the three addition agents are known to alter with time and use it imposes further limitations. The problems that would be encountered in trying to control such a process would be numerous in an industrial situation. However, it is considered that the increase in the cathodic polarisation caused by the breakdown of the resorcinol and/or polyethyleneglycol could be considered an advantage and would not therefore warrant the dismissal of these addition agents as part of an industrial process without extensive plant trials.

Further investigation into these addition agents and the wide range of others which were not looked at would be necessary to develop a process which could be controlled easily. The use of the Hull cell in conjunction with analysis and polarisation studies would suggest itself as a quick and relatively easy method for screening a wide range of addition agents.

8.5 Process and Control of a Fluoroborate Bath

As already discussed, the ability to control the plating process in an industrial context is of paramount importance if the process is to be taken further than the laboratory bench. The addition agents have been shown to be a major problem as far as controlling the deposit composition is concerned. Just as important is the control of the metal ion concentration in the electrolyte.

During the laboratory investigation, lead anodes were used almost exclusively. But the replenishment of the metal content of an alloy plating bath can be carried out in a number of ways. These can be summarised as follows:-

1) Soluble alloy anodes of the same composition as the deposit.

2) An insoluble anode with chemical replenishment.

3) Anodic replenishment of one metal, chemical replenishment of the other.

4) Separate anodes of the two metals either controlled together or separately.

5) Alternate use of the two metals as anodes.

For simple operation, the use of alloy anodes would seem to be the ideal method. However, problems can be encountered with this method. Alloys may be inhomogenous and the anodes may therefore not corrode satisfactorily in the bath. One phase may be more soluble than the other, causing sludging of solid particles into the bath. It was not possible to investigate the behaviour of a lead-cadmium alloy anode, although there is no evidence to suggest that it would behave in this manner.

The use of insoluble anodes was investigated. Several types of carbon were used as anodes. The types were:

CY9	Carbon graphite
CY11	Hard coke based carbon
CY9	Hard pantograph carbon
CY111	Fluorine cell carbon
Hard carbon bundling slate	

these were supplied by Morganite Special Carbons Ltd. In addition, platinum and platinised titanium were used. None of the carbon anodes worked satisfactorily. They all tended to spall and disintegrate at low current densities. This was associated with gas evolution on the anode. As the gas was evolved on sites in pores within the graphite, the anodes tended to spall. It was hoped that by using very hard graphite this problem would be overcome but without success. The other approach was to use a carbon with very large pores from which the gas could escape without spalling. The CY111 fluorine cell carbon was designed for that same situation: unfortunately, it too seemed to spall and disintergrate.

A type of carbon which was not used but which may have proved satisfactory, was a resin impregnated graphite. In this type, the pores are filled with resin preventing gas evolving. The type of resin used would depend on its ability to withstand the strongly acid conditions in a fluoroborate electrolyte. It is doubtful whether any such impregnated graphite at present commercially available would be able to do this.

The platinum performed satisfactorily but the platinised titanium tended to pit. The use of a platinum anode would not normally be possible owing to the cost, and no other types of insoluble anode were found which may have withstood the severe conditions in the fluoroborate electrolyte.

One of the problems associated with the use of insoluble anodes is the build up of extraneous ions in the electrolyte. In the case of the fluoroborate electrolyte, this would be the fluoroborate ion.

The anodic replenishment of one metal and the chemical replenishment of the other may work well in the lead-cadmium plating system. This technique is sometimes employed when the metal being replenished chemically is a relatively minor constituent of the deposited alloy. In tin-nickel plating, nickel anodes are used and the tin is replenished chemically by addition of stannous chloride. With the plating bath in its present state of development, the main constituent of the electrolyte, cadmium is a minor constituent of the deposit. In this situation, it may be possible to use lead anodes and replenish the cadmium metal chemically. This would lead to a gradual build up of lead in the solution (as a small percentage of the deposit is cadmium) but this may be offset for by drag out and other losses.

As an example we may consider a jig full of six inch bearings measuring say 15 inches in height, to be plated with a overlay 0.018 mm thick. (A jig of similar dimensions was used for making the drag out measurments from a nickel plating bath). If it is assumed that the bearings are to be plated from a fluoroborate bath containing 220 gl^{-1} cadmium and 50 gl^{-1} lead and the resulting deposit is to be 20% cadmium, 80% lead then:-

The total volume of the overlay $= 15 \times 6 \times 0.0018 \times \pi \times (2.54)^2 cm^3$

$= 3.28\pi cm^3$

for a 20% cadmium, 80%lead alloy

the total weight would be

$$= \frac{3.28\pi}{\left(\frac{1}{5 \times 8.65} + \frac{8}{10 \times 11.34} \right)}$$

$= 35.05\pi g$

Therefore the total wt of cadmium deposited

$= 7.00\pi g$

If 100% cathodic and anode efficiencies are assumed, then to plate 7.009 g of cadmium 13.59 g of lead is dissolved at the anode (from Faradays Law).

Thus, it can be seen that each time a jig full of bearings is plated, the quantity of lead in the electrolyte will be increased by approximately 13.5 g and the quantity of cadmium will decrease by 7g.

However, the drag-out measurements on the nickel bath have shown that a jig of this type can take approximately 0.29 l of electrolyte from a plating bath into the rinse tanks. If this were the lead-cadmium fluoroborate electrolyte described above, then the loss would be equivalent to 14.5 g of lead and 64 g cadmium from the electrolyte. Therefore, the lead concentration in the electrolyte would remain reasonably constant and the cadmium concentration could be maintained chemically.

This calculation obviously has its limitations, the drag out from a nickel plating bath will be different from a fluoroborate bath due to differences in viscosity, etc and the dimensions of the jig are only approximate and will obviously vary with the types of bearings being plating but the calculation does illustrate the type of control which can be achieved using a lead anode.

The use of separate anodes of the two metals connected together at a common potential can definitely not be used in this situation. This type of anode arrangement is very rarely used because if the metals are not close together in the emf series, then one will dissolve preferentially to the other. It is made further impractical by the centralised arrangement of the anode when plating bearings. Similarly, the separate control of the two metal anodes is impractical as the cadmium anode would be immersion plated. The alternate use of the two metals as anodes could not be used for the same reason.

The results have shown that all the electrolytes studied were very sensitive to agitation. Increasing the agitation increased the amount of lead in the alloy deposit. This was predictable and the deposits with the most cadmium in were obtained from quiescent solutions. The fluoroborate electrolyte used to plate the bearings in the large cell was not agitated for this reason.

If a plain vertical cathode held in a quiesscent electrolyte is considered then the diffusion boundary is normally accepted to be approximately 0.3 mm from the surface. As electrodeposition occurs, the electrolyte within this boundary becomes depleted of metal ions in comparison to the bulk electrolyte. The depleted electrolyte is less dense than the bulk electrolyte and will rise. This causes a variation in the concentration of the metal ions in the electrolyte in the vicinity of the cathode. In this situation, the cadmium content would vary across the surface of each bearing and from bearing to bearing held in the jig from top to bottom. The situation would be accentuated in a bearing jig where a relatively small volume of electrolyte is enclosed within the jig. When lead-tin is plated onto bearings, the jig is agitated by hand in an attempt to prevent depletion within the jig.

Evidently, this would require further investigation for a lead-cadmium plating bath based on the fluoroborate electrolyte. It may be that the variation in deposit composition would be within acceptable limits. If not, them some way of introducing mild agitation into the electrolyte in a controllable manner would have to be found.

The results have also shown that an increase in temperature merely increases the quantity of lead in the deposit. In some industrial plating processes, it is economically attractive to raise the temperature of the process, thereby increasing the conductivity and lowering the power consumption in the plating process itself. Raising the temperature would make an appreciable difference with the fluoroborate electrolyte as the conductivity measurements have shown. However, the electrolyte is already a highly conductive one at room temperature and anyway, as already stated, increasing the temperature would merely increase the lead content of the alloy.

The control of pH is not normally a major factor in alloy plating. Its effect is usually associated with the physical properties of the deposit or the stability of complexes if a complexed electrolyte is used. The pH of the fluoroborate electrolyte was less than 1 and control of the pH was not attempted as increasing the pH would have brought down an insoluble precipitate. It is not expected that small variations in pH would affect the polarisation in any great way.

The cathodic current efficiency of the sulphamate, fluorosilicate and fluoroborate electrolytes was found to be 100% (within the limitations of the measurement technique). This was to be expected at the low current densities which were being used. If higher current densities had been employed, then hydrogen evolution may have become a problem. This was evident when the addition agent broke down in the fluoroborate electrolyte in the large cell. This increased the polarisation of the lead deposition reaction, the lead ions were at a relatively low concentration and potentials were reached at which hydrigen was evolved. This caused poor quality deposits with 'streaking' and the curious 'bumpy' deposit shown in the electron micrograph. The high cadmium content of these deposits indicates the increased polarisation of the lead reaction and the drop in efficiency.

The question of whether to use constant current control or potential control is difficult to answer. Very little plating was carried out galvanostatically during the project. As the rest potentials of the lead and cadmium are relatively far apart and the plating variables have a large effect on the lead deposition reaction, constant potential control should give a more controllable deposit composition. Because of the problems with the addition agents, it was not possible to verify this. However, when plating bearings, the anode is considerably smaller than the cathode and as discussed in Section 8.4, this would cause problems for potential control. If the overlay were restricted to one or two types of bearing, then potential control would be viable and probably advantageous.

8.6 Structure of the Electrodeposited Alloy

The results of the electron diffraction were somewhat inconclusive. It was hoped that, by measuring the lattice parameter of single crystals in the deposited alloy, it would be possible to determine whether a solid solution was formed or whether separate phases were deposited. If the lead was considered to be the matrix metal and cadmium the substitutional solute metal then (if a solid solution were formed) as the percentage of cadmium in the deposit was increased from zero, it would be expected that the lattice parameter would change from that of pure lead (4.94^{0}A). According to Vegards Law this change would be linear for an ideal dilute solution. The results showed a non linear variation from 4.943 to 4.95^{0}A then down to 4.945^{0}A for alloys varying in cadmium content from 2 to 26%. Many deviations from Vegards Law have been reported in the literature, not least of all due to variations in the plating parameters for electrodeposited alloys. However, an increasing lattice parameter followed by a decrease, as in Fig. 64, is unlikely but could be explained by the formation of a second phase in the deposit.

Difficulty was experienced in obtaining good diffraction patterns from the deposited alloy because of the thickness of the deposit. Single crystals were difficult to find and in view of the small number of diffraction patterns analysed the overall accuracy of these results is questionable.

A more detailed investigation of the structure of the lead-cadmium deposits would be advantageous in view of the dissapointing results from the corrosion tests. The corrosion tests were carried out at the end of the project and so the failed samples were not specially examined to establish the reason for the failure. The possibility that second phases are present in alloys with 5 - 20% cadmium cannot be discounted.

A more detailed examination of the structure should involve X-ray diffraction and optical microscopy on thick deposits to determine the structure over a wide range of alloy compositions.

8.7 Properties of the Alloy Deposit

Of the wide range of properties which could have been investigated, only the corrosion resistance, fatigue and wear properties of the lead-cadmium plated bearings were studied. These three properties were considered to be the most important in relation to the possible bearing applications.

The corrosion test results were very dissapointing with complete removal of the lead-cadmium overlay within 100 hours in medicinal white oil. Medicinal white oil was used because it contains no inhibitors and degrades rapidly producing a very aggressive medium. The tests carried out in standard automotive engine oil did not produce results which were strikingly different. The corrosion rate with a nickel barrier was found to be approximately three times the rate without a nickel barrier.

Nickel barriers are used with lead-tin overlays to reduce the rate of loss of the tin due to diffusion at high operating temperatures, thus increasing the corrosion resistance of the bearing. It is clear that it does not have the same function with a lead-cadmium overlay. The corrosion rate of the lead-cadmium does not compare with the results obtained from previous experimental work at the Glacier Co. Unfortunately, the records of this work are rather sparse and cannot be compared in detail. It would seem that either the results obtained previously were misleading or that which was previously tested bore no relation to the overlays prepared in this project in terms of composition.

The overlays tested in this project contained 5, 10 and 20% cadmium. If the failure was due to diffusion of the cadmium from the overlay in a manner similar to the failure of the lead-tin overlay, then it is possible that an alloy with a high cadmium content may be more corrosion resistance. Alternatively, if two phases are present at these concentrations, then the premature failure may be due to preferential corrosion of a particular phase. The possibility then arises that high corrosion resistance may be obtained with a smaller amount of cadmium in the alloy. Without a detailed examination of the structure of the alloys, no clear understanding of the failure can be made.

The mechanical tests carried out on the overlay were more encouraging. These showed that the lead-cadmium overlay was well up to standard with respect to fatigue and wear resistance with fatigue ratings in excess of 69 MPa for overlays with 5 and 10% cadmium with and without nickel barriers. This figure is achievable with lead-tin and lead-tin-copper overlays but values of less than 50 MPa have often been obtained with these types.

The wear resistance results show the figures for lead-cadmium to lie essentially between lead-tin and lead-cadmium. This can be considered as acceptable but there is nothing particularly exceptional about the result.

The hardness of the lead-cadmium overlay was not measured. This would have given some indication of the embeddability and conformability of the overlay.

8.8 Possible Areas For Future Investigation

There is no reason to suggest that a lead-cadmium plating process would not be found useful for other applications. The most obvious one is for soldering purposes. Its possible uses as a solder are not known, although considerable data is available on a lead-cadmium-tin alloy which has a low melting point of 145°C for the ternary eutectic composition.

Apart from the other possible uses for the process, there are a considerable number of avenues which could be explored to further develop and understand the process. Some of these have been mentioned already and include:-

- testing of a wider range of addition agents using the Hull cell with analysis and some polarisation studies.

- Investigating further the breakdown of resorcinol and its apparent influence in increasing the cathodic polarisation.

- The fluorosilicate electrolyte showed promise and could be developed further in conjunction with an investigation of other addition agents with a view to finding one that selectively polarises the lead cathodic reaction.

- The microstructure of the alloy should be thoroughly investigated using X-ray diffraction and optical microscopy of thick deposits over a wider range of compositions.

In addition to these, there are several other points which could be looked at:-

- If the total metal ion content of the electrolyte was decreased considerably and inert salts added to increased the conductivity, then the ratio of cadmium to lead may be improved, both in the electrolyte and the deposit.

- The use of pulse plating has always attracted interest in alloy plating without many outstanding results. However, pulse plating using potential control may be advantageous in a case where the static potentials are far apart.

- The development of a ternary alloy process for lead-tin-cadmium would not be difficult and may produce a deposit with interesting properties including an increased corrosion resistance.

9. CONCLUSIONS

Lead-cadmium alloys can be electroplated from sulphamate, fluorosilicate and fluoroborate electrolytes.

It was found that if the cadmium concentration in the electrolyte was held at 220 gl^{-1}, then the maximum concentration of lead in the electrolyte from which a lead-cadmium alloy could be plated was around 75 gl^{-1}. This was true for all three electrolytes.

The electrolyte which was considered to produce the best deposits with compositions ranging from 0 - 30% cadmium was based on fluoroborates. The optimum composition of the electrolyte was found to be:

96 ml	lead fluoroborate
634 ml	cadmium fluroborate
6 g	resorcinol
1 g	peptone
1 g	polyethyleneglycol

made up to 1 l with distilled water.

This gave an electrolyte with the following metal ion concentrations:

220 gl^{-1}	cadmium
50 gl^{-1}	lead

Over a period of time and with use, the resorcinol and polyethyleneglycol was found to break down affecting both cathodic polarisation and deposit quality. The change in the cathodic polarisation directly effected the alloy deposit composition.

Using fresh electrolytes, several plain bearings were overlay plated with lead-cadmium alloys varying in composition from 5 to 20% cadmium.

Some bearings had an interlayer of nickel. All bearings were found to have excellent fatigue resistance with values in excess of 69 MPa from a Sapphire Test rig. The wear resistance was found to be comparable with overlays of lead-tin but was less than lead-tin-copper.

The corrosion resistance of the lead-cadmium overlay produced in this project was considered to be poor.

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TABLES

TABLE 1

RELATIVE MOVEMENT BETWEEN MACHINE COMPONENTS AND THE CONSTRAINTS APPLIED[5]

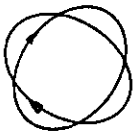
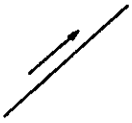
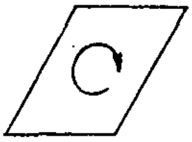
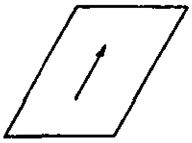
Constraint Applied to the Movement	Continuous Movement	Oscillating Movement
About a point 	The movement will be a rotation and the arrangement can therefore make repeated use of accurate surfaces	If only an oscillatory movement is required, some additional arrangements can be used in which the geometric layout prevents continuous rotation
About a line 	The movement will be a rotation and the arrnagement can therefore make repeated use of accurate surfaces	If only an oscillatory movement is required, some additional arrangements can be used in which the geometric layout prevents continuous rotation
Along a line 	The movement will be a translation. Therefore one surface must be long and continuous and to be economically attractive must be fairly cheap. The shorter, moving component must usually be supported on a fluid film or rolling contact for an acceptable wear rate	If the translational movement is a reciprocation, the arrangement can make repeated use of accurate surfaces and more mechanisms become economically attractive
In a plane 	If the movement is a rotation, the arrangement can make repeated use of accurate surfaces	If the movement is rotational and oscillatory, some additional arrangements can be used in which the geometric layout prevents continuous rotation
	If the movement is a translation one surface must be large and continuous and to be economically attractive must be fairly cheap. The smaller moving component must usually be supported on a fluid film or rolling contact for an acceptable wear rate	If the movement is translational and oscillatory, the arrangement can make repeated use of accurate surfaces and more mechanisms become economically attractive

TABLE 2

FATIGUE STRENGTH OF GLACIER MATERIALS DETERMINED ON THE GLACIER SAPPHIRE TEST MACHINE[43]

▨ Fatigue range of lining

☰ Fatigue range of overlay

Higher fatigue strength of overlay on aluminium materials is due to use of thinner overlays.

GLACIER CODE	COMMON NAME	NOM. % COMP
L2-GM 130	TIN BASE WHITEMETAL	Sn - 7½% Sb 3% Cu
GM 186	LEAD BASE WHITEMETAL	Pb - 15% Sb 1% sn 1% As
AS 15.	20% TIN ALUMINIUM	Al - 20% Sn 1% Cu
AS 11	6% TIN ALUMINIUM	Al - 6% Sn 1% Cu 1% Ni
AS 11 (P)	OVERLAY PLATED 6% TIN ALUMINIUM	Al - 6% SN 1% Cu 1% Ni
SL	COPPER LEAD	Cu - 30% Pb
SL (P)	OVERLAY PLATED COPPER LEAD	Cu - 30% Pb
SP (P)	OVERLAY PLATED LEAD BRONZE	Cu - 26% Pb 2% Sn
SX (P)	OVERLAY PLATED LEAD BRONZE	Cu - 22% Pb 4% Sn
AS 78	ALUMINIUM SILICON	Al - 11% Si 1% Cu
AS 78 (P)	OVERLAY PLATED ALUMINIUM SILICON	Al - 11% Si 1% Cu

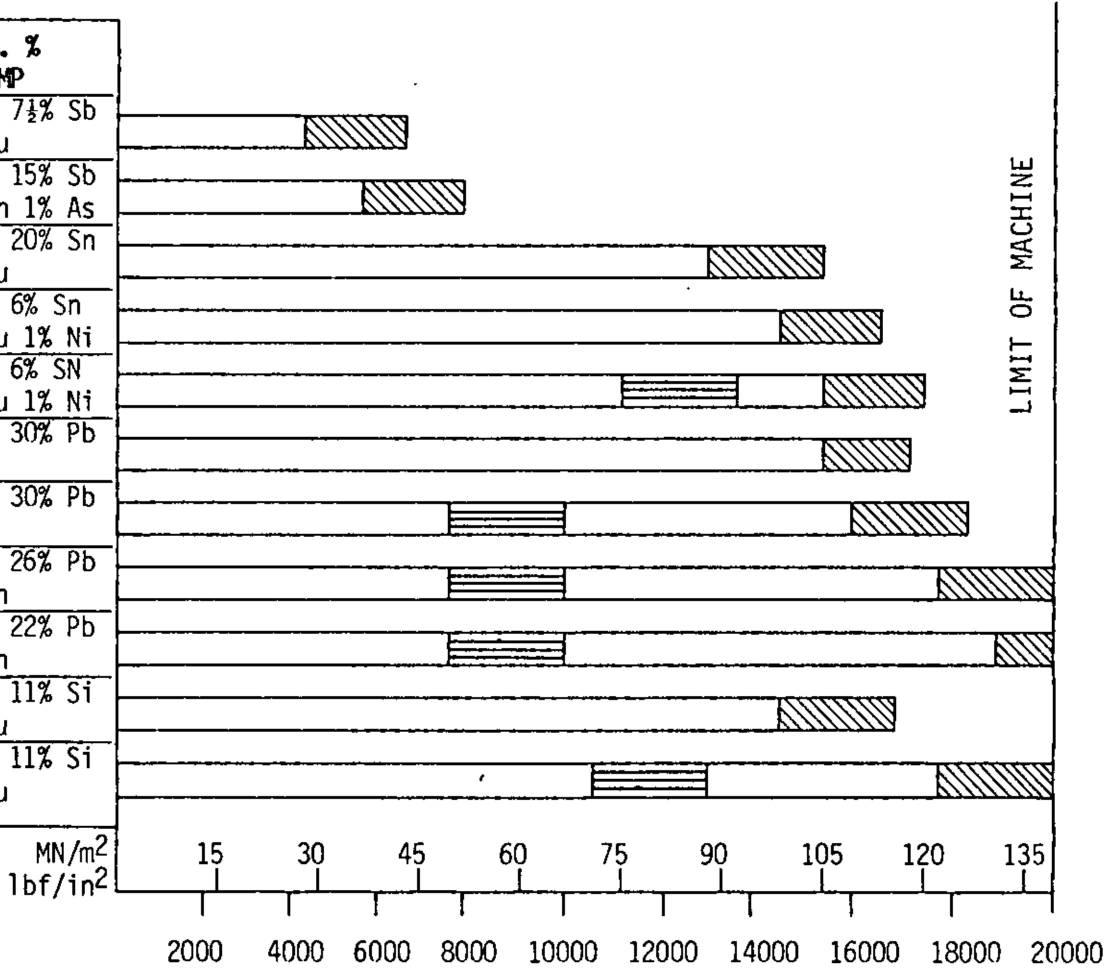


TABLE 3

COMPOSITION OF LEAD TIN ALLOY DEPOSIT
RELATED TO ELECTROLYTE COMPOSITION [32]

COMPOSITION OF DEPOSIT (Tin %	5	10	25	40	50	60
(Lead %	95	90	75	60	50	40
SOLUTION COMPOSITION	(Grams per litre or lb, per 100 Imp. gal.)					
Tin	5	10	25	40	50	60
Lead	85	90	65	45	35	25
Fluoboric acid (free)	100	100	100	100	100	100
Boric acid (free)	25	25	25	25	25	25
Glue	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 4

PRETREATMENT PROCESS FOR PLATING BEARINGS (COPPER LEAD)

Stage	Solution	Specific Gravity	Temp °C	Current Density A/dm^2	Immersion Time Seconds	Remarks
1	Trichlorethylene Vapour Degrease	-	-	-	120	Outside plating plant
2	Alkaline Cleaner Sodium Metasilicate 15 gl^{-1} Sodium Carbonate 5 gl^{-1}	-	85±5	2.5 Cathodic Switch on when bearings in bath	180	(i) When throughput reaches 0.25 m^2/litre add 10g/1 metasilicate. (ii) When throughput reaches 0.3 m^2/litre discard solution. (iii) Mild steel anode.
3	Rinse	2 tank counter current flow system, 30 sec each tank.				
4	Anodic etch Hydrochloric acid 60% $^{V}/v$	1.10-1.13 at 20°C	20 - 25	2.5 Anodic Switch on when bearings in bath	60	(i) Mode using concentrated acid of S.G. 1.18. (ii) Solution life approx. 10 working days. (iii) Test S.G. every 2 days. (iv) Test Cu content every 2 days and discard when reaches 1.25 gl^{-1}±0.1 gl^{-1}. (v) Mild steel cathode

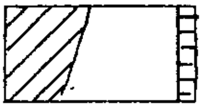
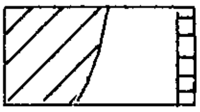
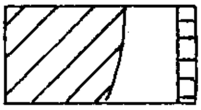
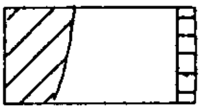
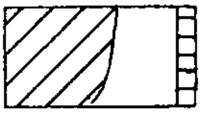
Cont'd.....

Table 4 (continued)

Stage	Solution	Specific Gravity	Temp °C	Current Density A/dm^2	Immersion Time Seconds	Remarks
5	Rinse	2 tank counter current flow system, 30 sec each tank.				
6	Acid Soak Hydrochloric acid 25% $^{V}/v$	1.10-1.13	20 - 25	-	150 - 180	(i) Vigorous air agitation (ii) Discard solution when anodic etch is replaced
7	2	2 tank counter current flow system, 30 sec each tank.				
8	Nickel Plate $NiSO_4.7H_2O$ 290 gl^{-1} ± 20 gl^{-1} $NiCl_2.6H_2O$ 45 gl^{-1} ± 5 gl^{-1} H_3BO_3 37 gl^{-1} ± 4 gl^{-1} pH 4.2 - 4.7	1.15-1.19 at 50°C	50+5	2 Cathodic	180 - 240	(i) Enter solution with current switched on. (ii) Air agitation necessary.
9	Rinse	2 tank counter current flow system, 30 sec each tank.				
10	Overlay plate as necessary					

TABLE 5

HULL CELL WORK

Addition Agent	% Cd in deposit in particular current density regions (A/dm^2)			Description
	0 - 1	1 - 2	2 - 3	
6 gl^{-1} Resorcinol 2 gl^{-1} PEG	0.9	2.7	6.0	
6 gl^{-1} Resorcinol 1 gl^{-1} Peptone 2 gl^{-1} PEG	0.6	3.6	9.24	
6 gl^{-1} Resorcinol 1 gl^{-1} Peptone 1 gl^{-1} PEG	0.75	5.0	9.7	
6 gl^{-1} Resorcinol 1 gl^{-1} Diastase	-	0.5	8.7	
6 gl^{-1} Resorcinol		No data		
6 gl^{-1} Resorcinol 1 gl^{-1} Peptone		No data		
6 gl^{-1} Resorcinol 1 gl^{-1} Gelatin		No data		
6 gl^{-1} Resorcinol 3 gl^{-1} PEG		No data		
6 gl^{-1} Resorcinol 1 gl^{-1} Gelatin 1 gl^{-1} PEG		No data		
1 gl^{-1} Gelatin		No data		

Legend:- ▨ Poor Quality □ Smooth, Bright ▤ No Plate

TABLE 6

CONDUCTIVITY OF VARIOUS PLATING ELECTROLYTES

PLATING SOLUTION	CONDUCTIVITY (milli-ohms^{-1} centimetres^{-1})
<u>Proprietary Solutions:</u>	
'Zincalux' Bright Zinc	260
'Nisol 80' Bright Nickel	67
Copper 'Pyrobrite'	115
<u>Laboratory Solutions:</u>	
Copper Fluoroborate	150
Copper Sulphate	107
Cadmium Fluoroborate	140
Lead Fluoroborate	137
<u>Lead/Cadmium Alloy Electrolyte:</u>	
Fluoroborate	156
Sulphamate	61
Fluorosilicate	150

TABLE 7

RESULTS OF CORROSION TEST

Nickel Barrier	Overlay Composition	Microns of Overlay Lost					Oil
		100 hrs	250	500	1000	2000	
No	PbCd10)	Completed overlay removal after 100 hours					MWO *
No	PbCd20)						
No	PbCd5	-	0.028	0.053	0.076	4.05)	Shell SAE 30
No	PbCd10	-	0.007	0.048	0.065	8.79)	
Yes	PbCd10	-	0.027	0.068	0.092	1.01)	
No	PbSn10	0.01	0.13	0.15	0.34	1.96	MWO
No	PbSn10	0.09	0.12	0.08	0.4	9.3	MWO
Yes	PbSn10	-	0.09	0.11	0.16	0.17	MWO
No	PbSn10	-	0.017	0.066	0.061	0.38	SAE 30

* MWO Medical White Oil

Bearings heat treated in oil at 120°C - examined for weight loss after 100, 250, 500, 1000 and 2000 hours

TABLE 8

FORMATION CONSTANTS OF SOME COMPLEXING AGENTS

Complexing Agents	Log K Values	
	Cd	Pb
Acetate (CH_3COO^-)	1.3 1.0 0.1	2.7 1.5
Citrate ($OOC\text{-}C(OH)\ (CH_2COO^-)_2$)	4.2	5.7
Cyanide (CN^-)	5.5 5.2 4.6 3.6	7.51
Pyrophosphate	5.6	5.3
Sulphamate	Probably low	Probably low
Perchlorate	Probably low	Probably low
Nitrate (NO_3^-)	0.4	1.19
Ethylenediamine ($HN\ CH_2\ CH_2\ NH_2$)	5.6 4.6 2.1	
Hydroxyquinoline	7.6 6.8	9.0 8.0
Diethylenetiaminepenacetic acid (D.T.P.A.)	19.1	18.6
1,2, dyaminocyclohexana NNN´N´- tetraacetic acid (DCy TA)	19.2	19.7
E.D.T.A.	16.5	17.9
Ethylene glycol-bis-(B-amimoethylether) -NN´- tetraacetic acid (E.G.T.A.)	16.7	14.6
Ethyletherdiaminetetraacetic acid (E.E.D.T.A)	16.3	14.4
N - hydroxyethylethylene diaminetriacetic acid (H.E.D.T.A.)	13.0	15.5
I - methylethyienediamine tetraacetic acid (M.E.D.T.A.)	16.0	17.3
Nitrilo triacetic acid (N.T.A.)	9.5 5.7	11.5
Tetraethylenepentamine (Tetren)	14.0	10.5
Triethylenetetramine (Trien)	10.8	10.4

FIGURES

60. Electron microprobe scan across raised lump in deposit shown in Fig. 59. Scan indicates cadmium rich areas.

61. Cathodic current density / potential graphs for fluorborate electrolyte in large cell. Electrolyte composition 220 gl^{-1} cadmium, 50 gl^{-1} lead and 6 gl^{-1} resorcinol, 1 gl^{-1} peptone and 1 gl^{-1} P.E.G.
a) freshly made up solution, b) after standing 7 days unused, c) solution (b) with the addition of 1 gl^{-1} peptone, d) solution (c) with the addition of 1 gl^{-1} P.E.G.

62. Typical cathode current density / potential curves for large cell.
a) before the anode was properly masked, b) after masking the anode with P.T.F.E. tape.

63. Conductivity plotted against temperature for various concentrations of lead and cadmium fluoroborate.

64. Lattice parameter v percentage cadmium in deposit plated from fluorborate electrolyte (220 gl^{-1} Cd, 50 gl^{-1} Pb, 6 gl^{-1} resorcinol, 1 gl^{-1} peptone, 1 gl^{-1} P.E.G.).

65. Electron micrograph of lead-cadmium alloy deposit plated from a fluorosilicate electrolyte. (Mag. 2000 x).

66. Electron micrograph of lead-cadmium alloy deposit plated from sulphamate electrolyte. (Mag. 2000 x).

67. Electron micrograph of lead-cadmium alloy plated from fluoroborate electrolyte containing resorcinol. (Mag. 2000 x).

68. Electron micrograph of lead-cadmium alloy plated from fluoroborate electrolyte containing resorcinol, peptone and polyethyleneglycol. (Mag. 2000 x)

69. Wear resistance for overlays of various compositions. Weight loss in mg plotted against test time in hours[43].

70. Drag-out in litres from a Watts type nickel plating bath. 6 inch bearing jig used, loaded with bearings.

FIG. 1 Photographs showing examples of typical ball and roller bearings

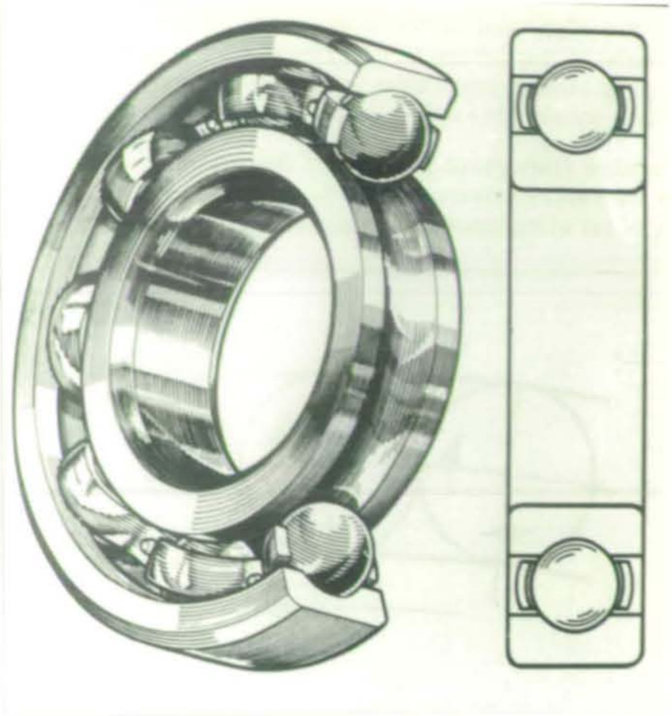



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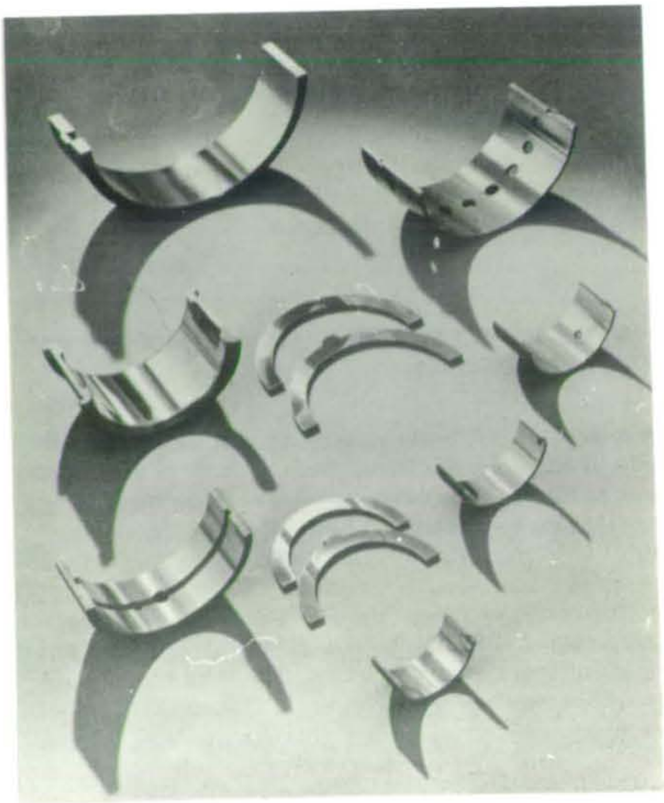
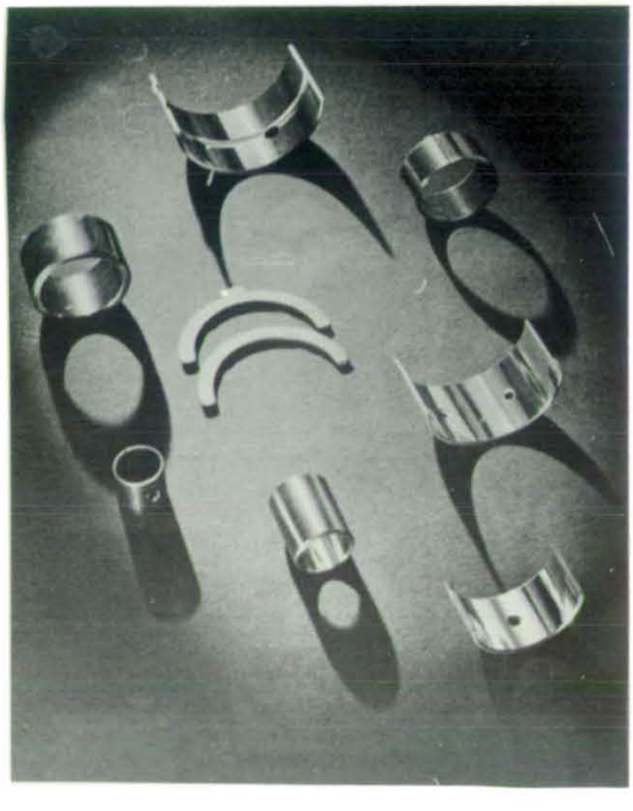
FIG. 2 Photographs showing examples of plain bearings





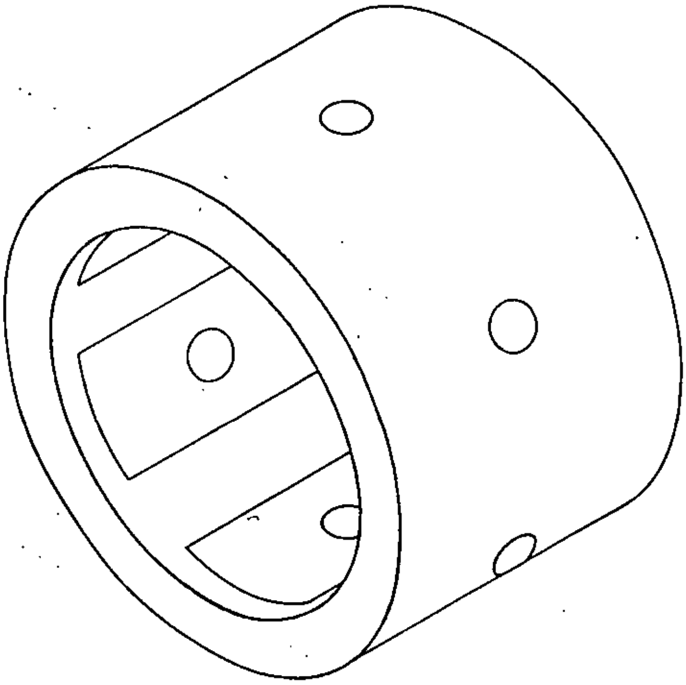


FIG. 3 Typical hydrostatic journal bearing.[5]

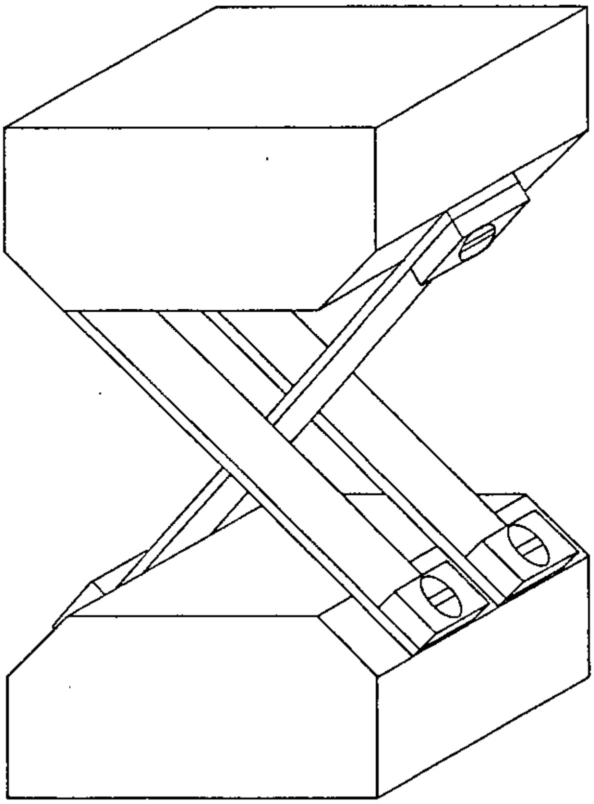


FIG. 4 Cross strip flexure pivot.[5]

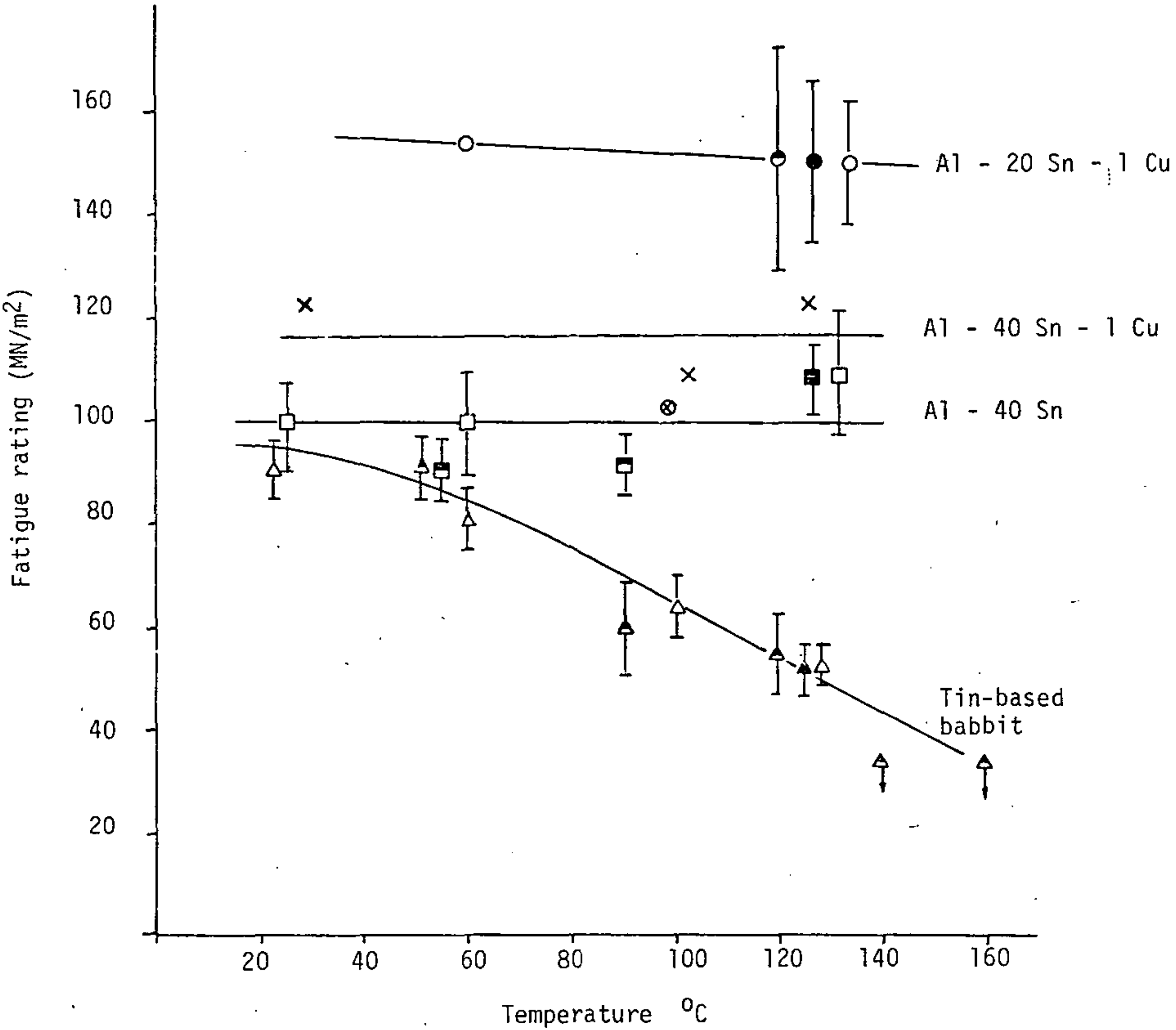


FIG. 5 Fatigue ratings against temperature taken from three test rigs. The values are rationalized relative to the rating given by the bending fatigue rig [16].

Rig	1	2	3
Alloy			
Al - 20 Sn - 1 Cu	○	○	○
Al - 40 Sn	□	□	□
Al - 40 Sn - 1 Cu	×	○	–
Tin-based babbit	△	△	△

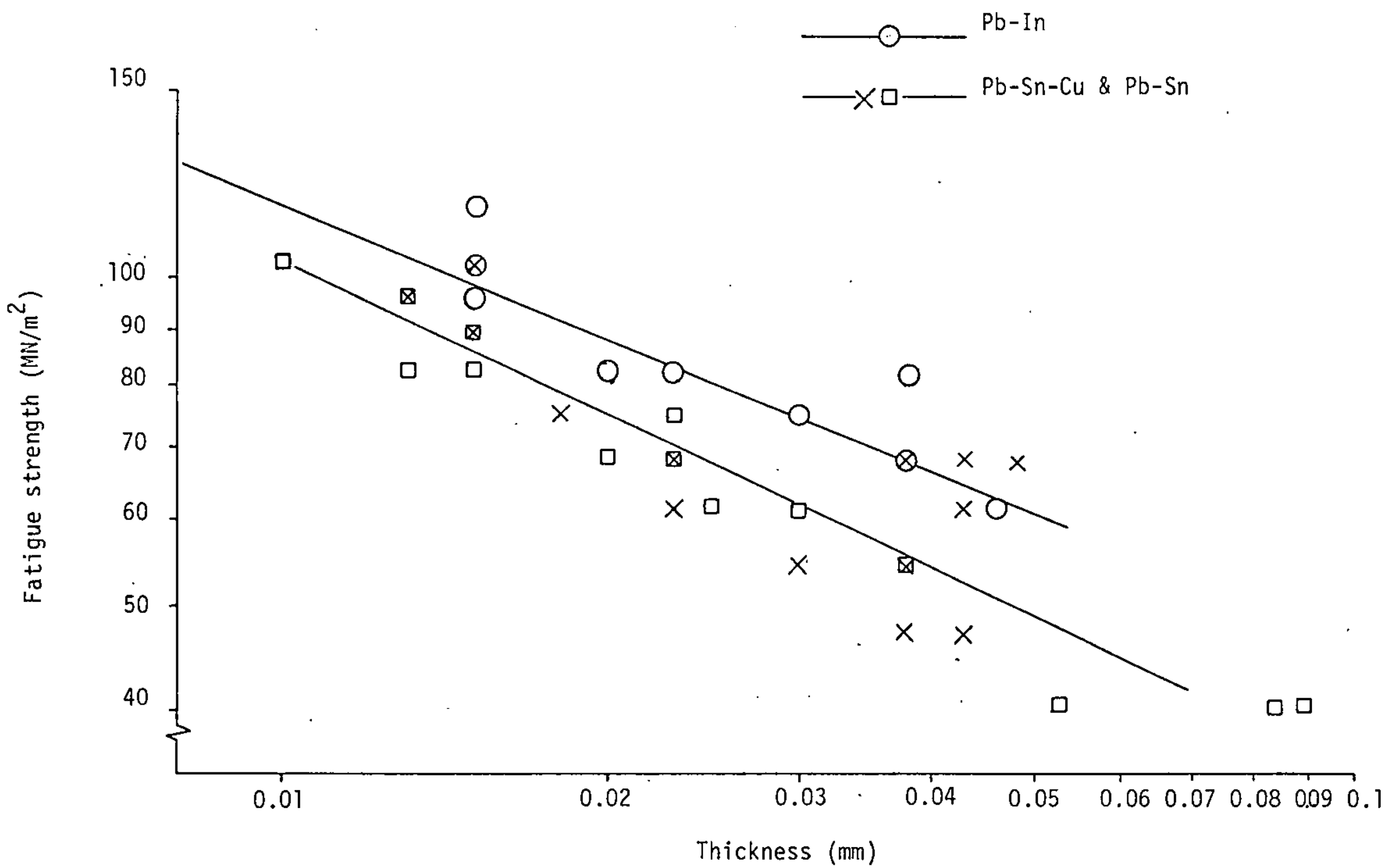


FIG. 6. Fatigue strength v Overlay thickness [43]

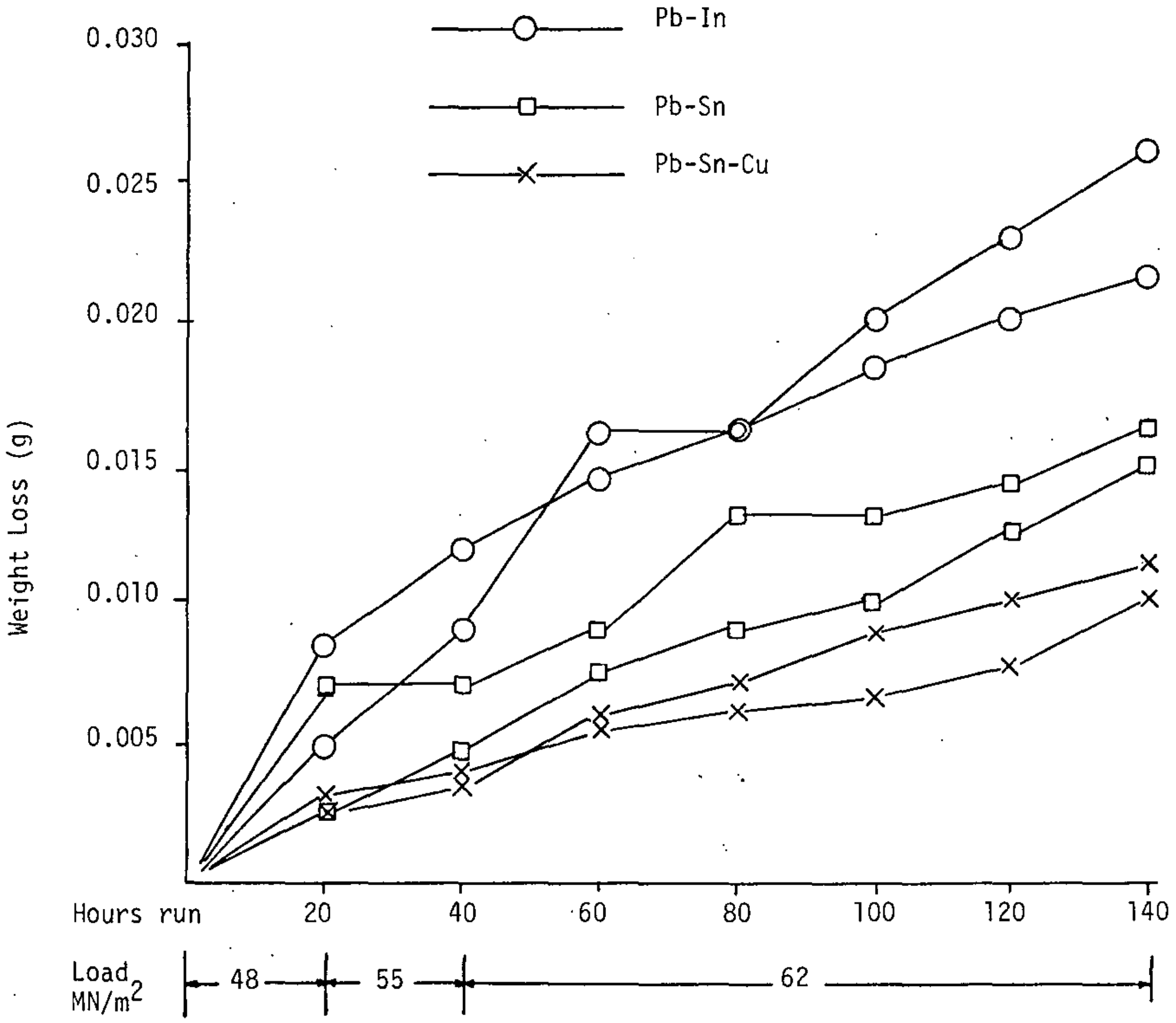


FIG. 7. Wear Comparisons for various overlay compositions

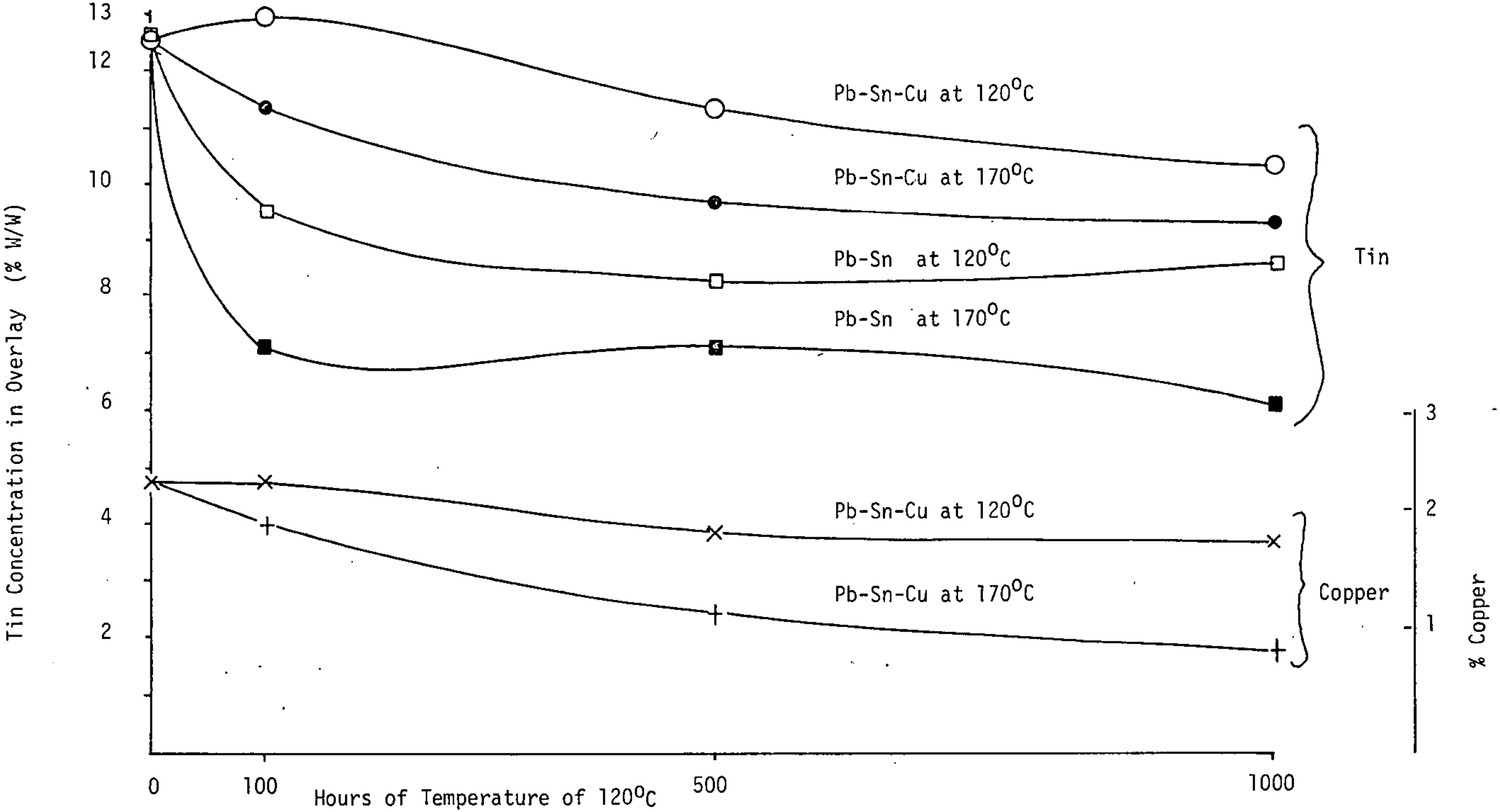
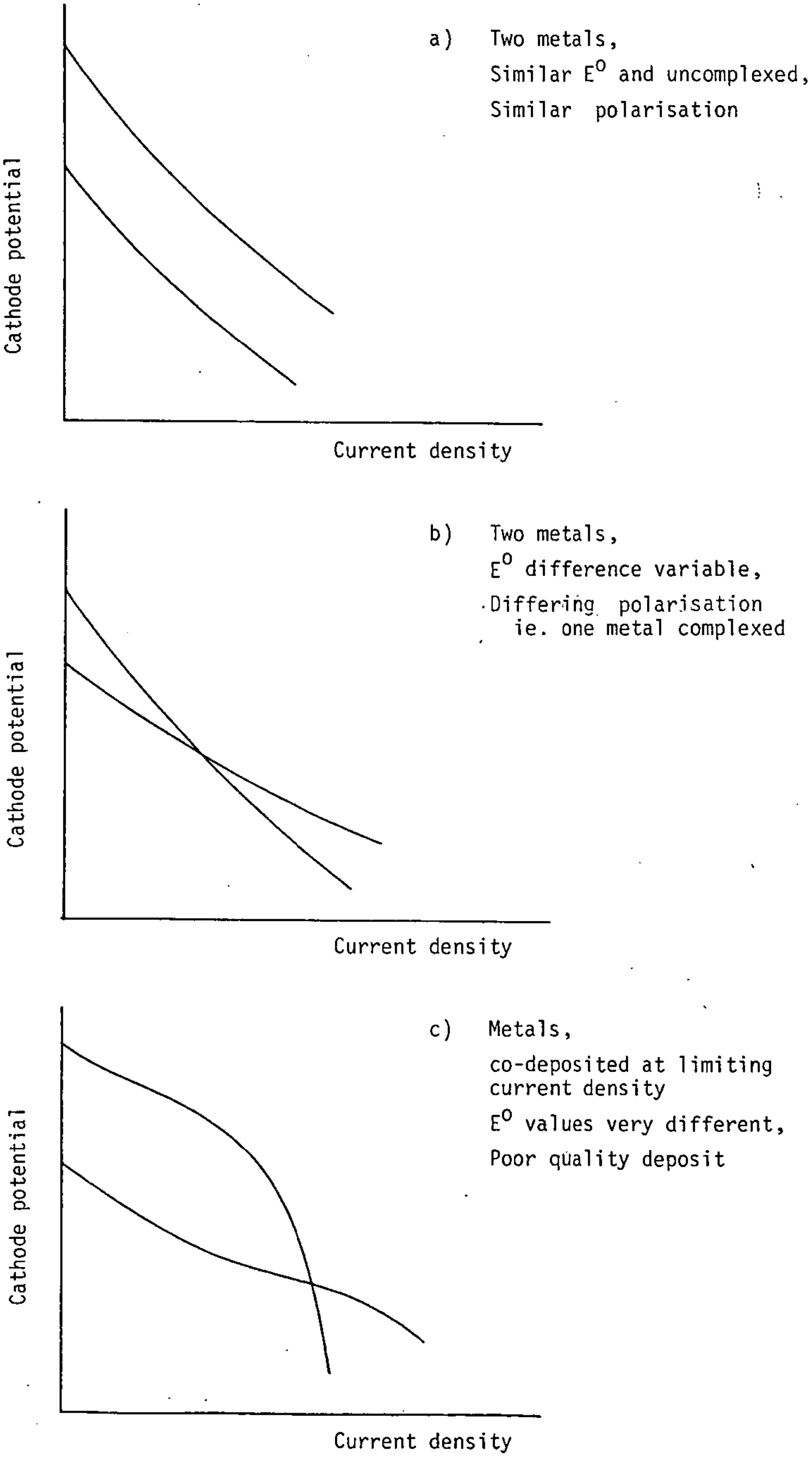


FIG. 8. Tin diffusion in lead-tin and lead-tin-copper overlays 43

	Ag	As	Au	Bi	Cd	Co	Cr	Cu	Ga	Ge	Fe	In	Mn	Mo	Ni	P	Pb	Pd	Pt	Rh	Re	Ru	S	Sb	Se	Sn	Te	Tl	W	Zn
Zn																														
W																														
Tl																														·
Te																														
Sn																														·
Se																														
Sb																										·				·
S																														
Ru																														
Re																														
Rh																														
Pt																				·		·								
Pd																			·	·										
Pb																								· Sn		· Zn		·		·
P																														
Ni																·	·		·	·	·		·			·		·	· Cu	·
Mo															· Fe														· Cu	
Mn														Fe Ni	·										·	·			·	·
In																	·									Pb				
Fe													·	·	· W	·	·				·					·			· Co	·
Ge											·				·											·				·
Ga										·																				
Cu										·	· Ni	Sn	·	·	Sn · Zn		· Sn		·				·	· Zn		· Zn		·	·	·
Cr											·				·														·	
Co							·	·		·	Ni		·	· W	· Sn	· Ni		·			·					· Cu			· Ni	·
Cd								· Zn				·			·		·						·	· Zn		· Zn				·
Bi								·									·													
Au					·	·		·				·			· Sn			·	·					·		·				
As			·					Zn				·			·		Sn													
Ag			· Cu	·	·	·		· Pt			·	·			·		·	· Pt	· Au	·				·	·	· Au		·		Pt Au

FIG. 9 Alloys which have been deposited from an aqueous solution. Ternary alloys are indicated by the third element positioned in the table. About 100 binary alloys and 15 ternary alloys are listed[24].



a) Two metals,
Similar E^0 and uncomplexed,
Similar polarisation

b) Two metals,
E^0 difference variable,
Differing polarisation
ie. one metal complexed

c) Metals,
co-deposited at limiting current density
E^0 values very different,
Poor quality deposit

FIG. 10. Typical cathodic polarisation curves for some alloy plating processes

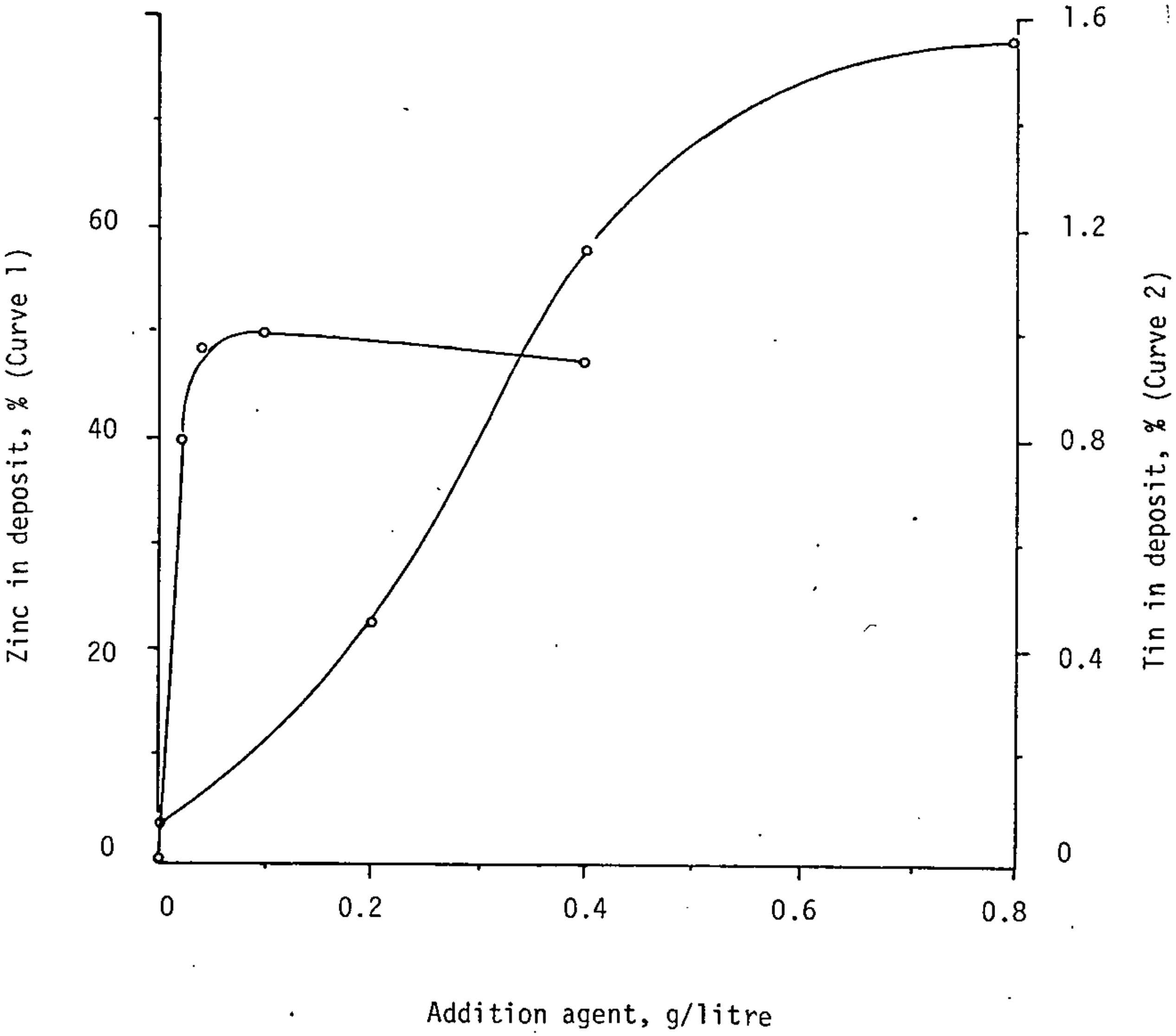


FIG. 11. Effect of addition agents on the composition of electrodeposited alloys. Curve 1, zinc-cadmium alloy deposited from a sulphate bath containing zinc, 70 g/l and cadmium, 5 g/l and aloin as addition agent. Curve 2, lead-tin alloy deposited from a fluoroborate bath containing lead, 218 g/l and tin, 11.6 g/l and glue as addition agent.[24]

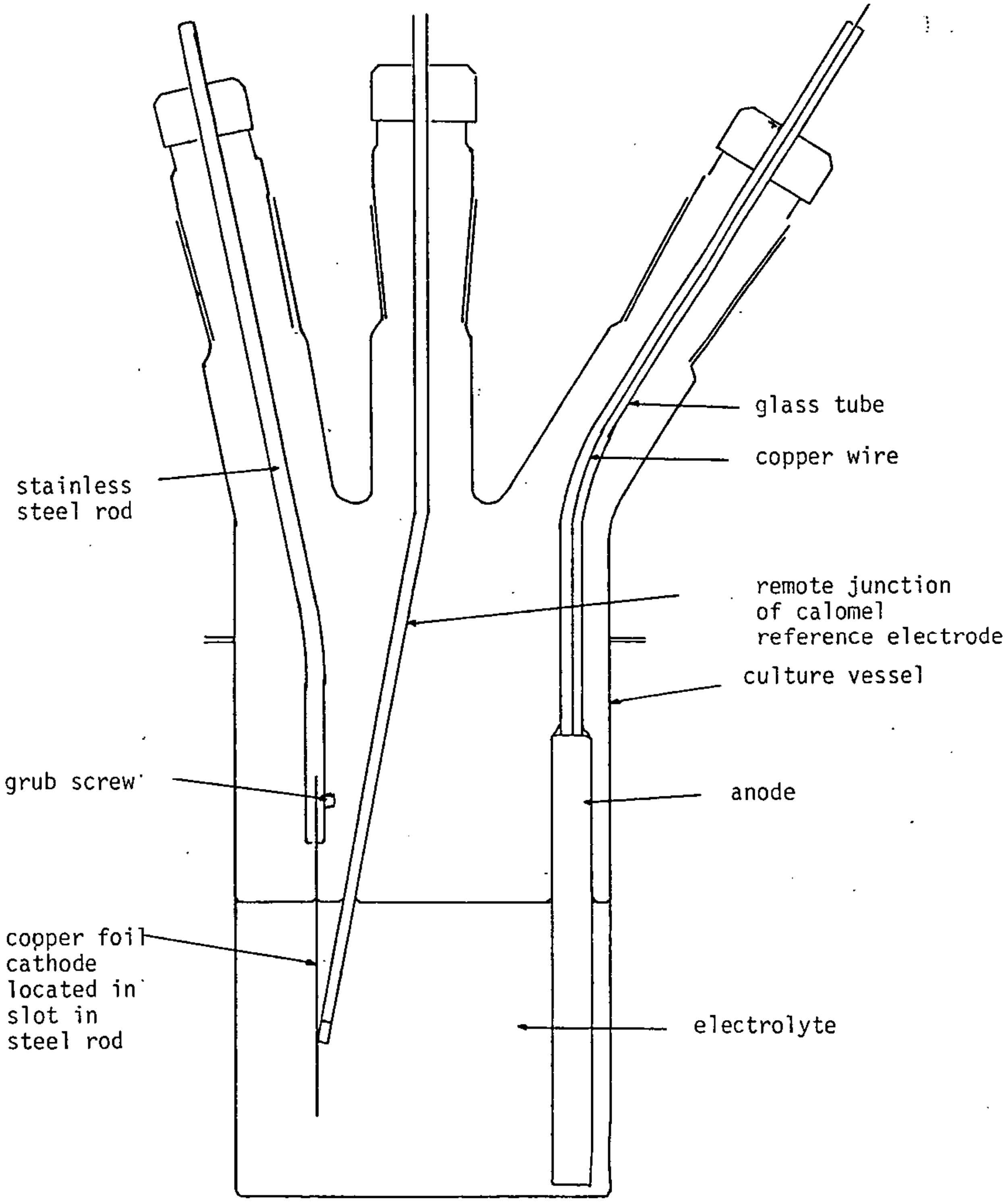
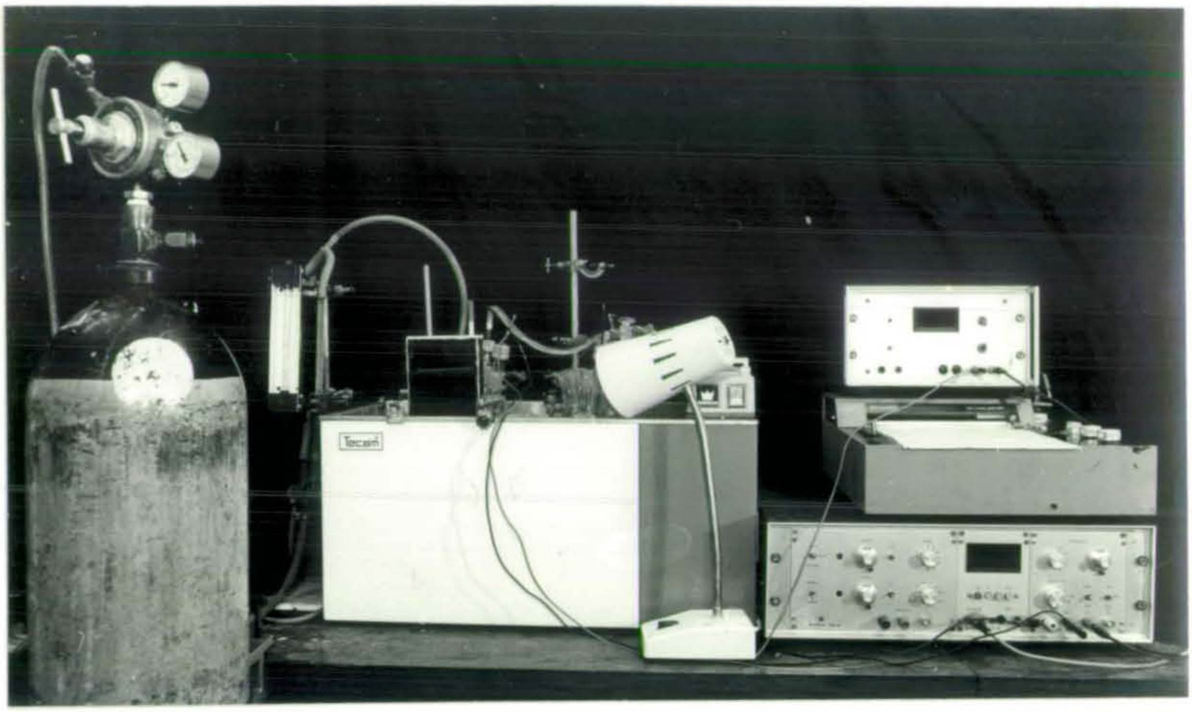
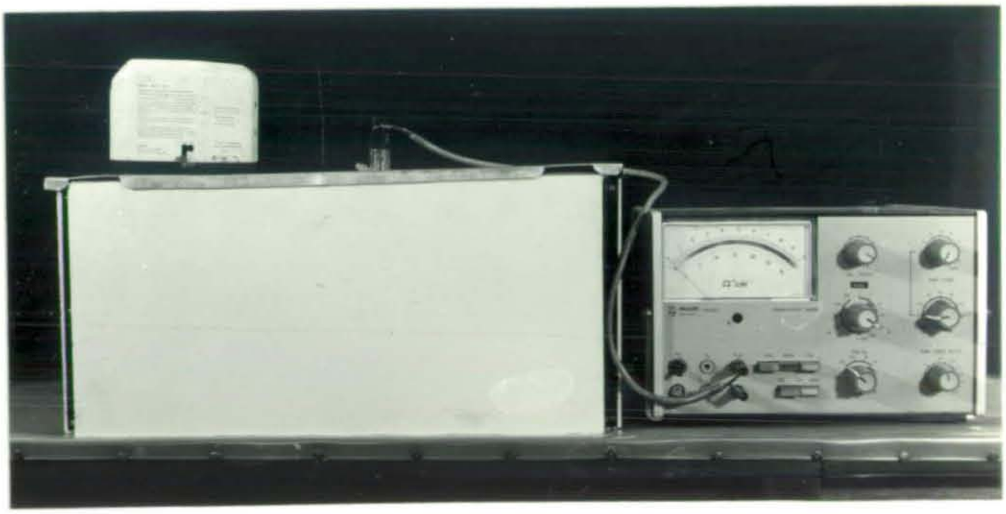


FIG. 12 Small cell, diagrammatic form.

FIG. 13 Arrangement of equipment used for obtaining polarisation data. Photograph shows nitrogen cylinder, water bath, potentiostat, chart recorder and coulombmeter

FIG. 14 Arrangement of equipment used for conductivity measurements. Photograph shows water bath with conductivity cell and conductivity meter


Tecam



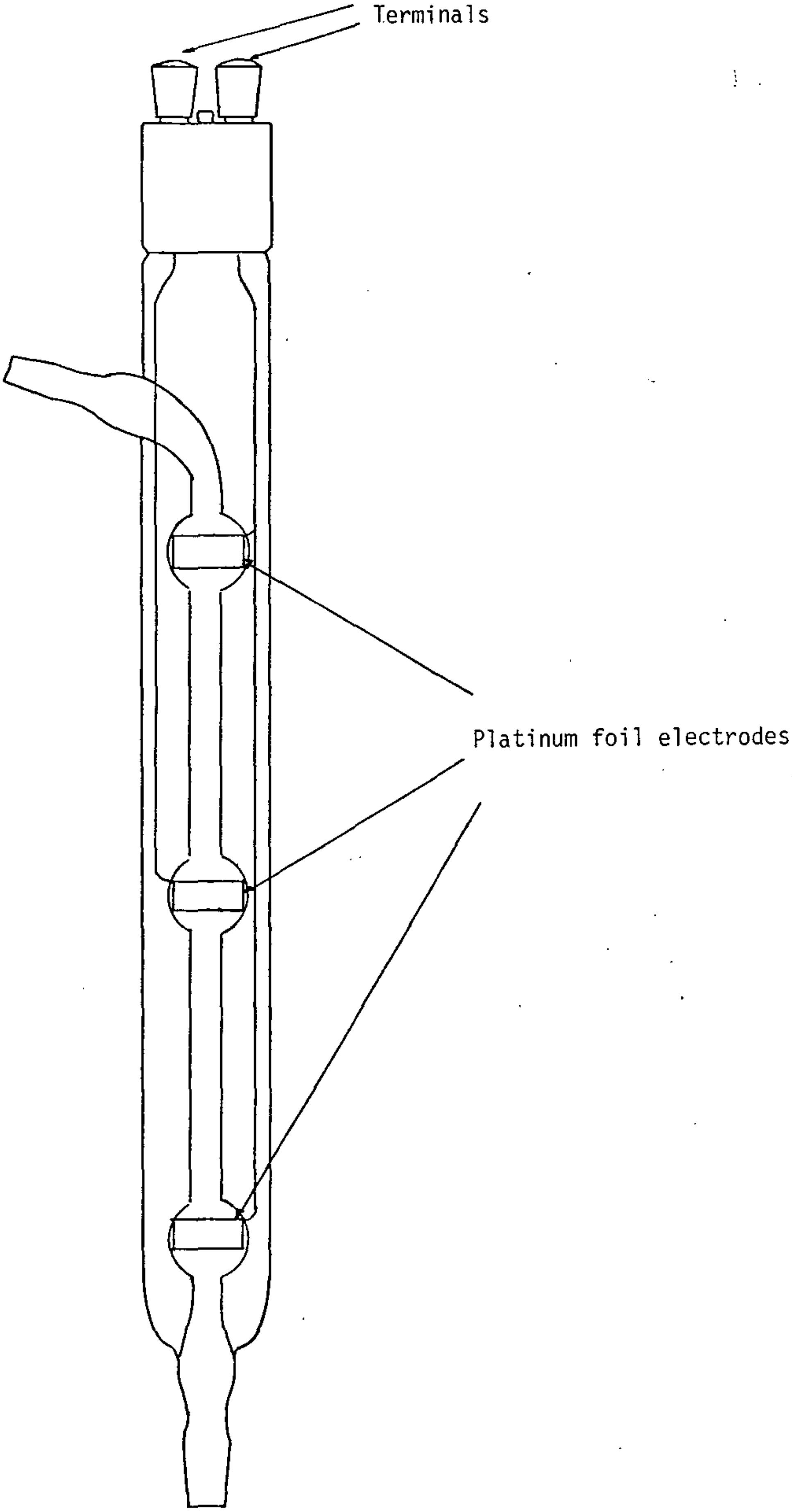


FIG. 15 Diagram of conductivity cell for Philips conductivity meter (actual size

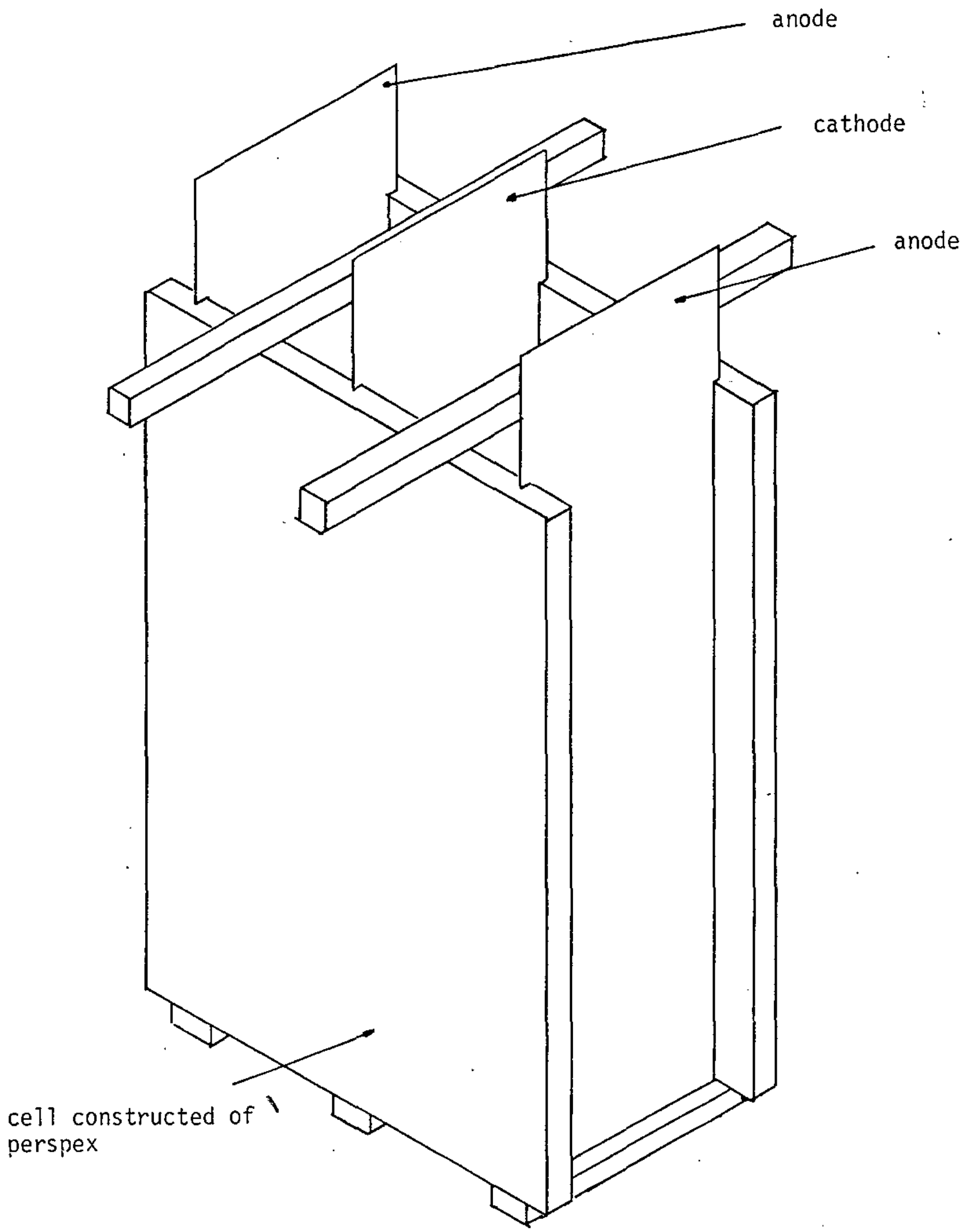
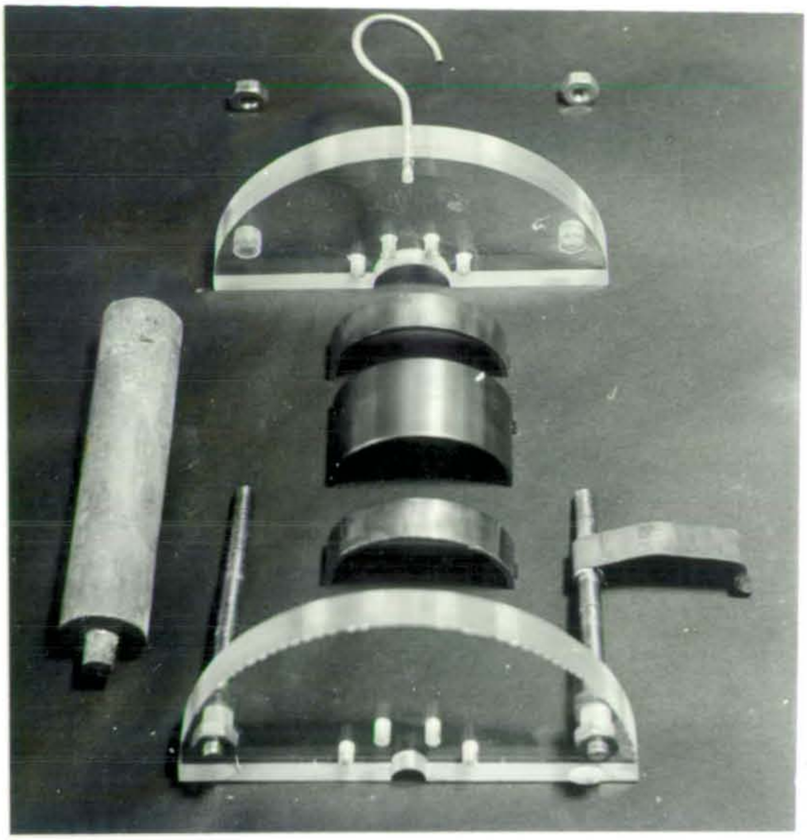
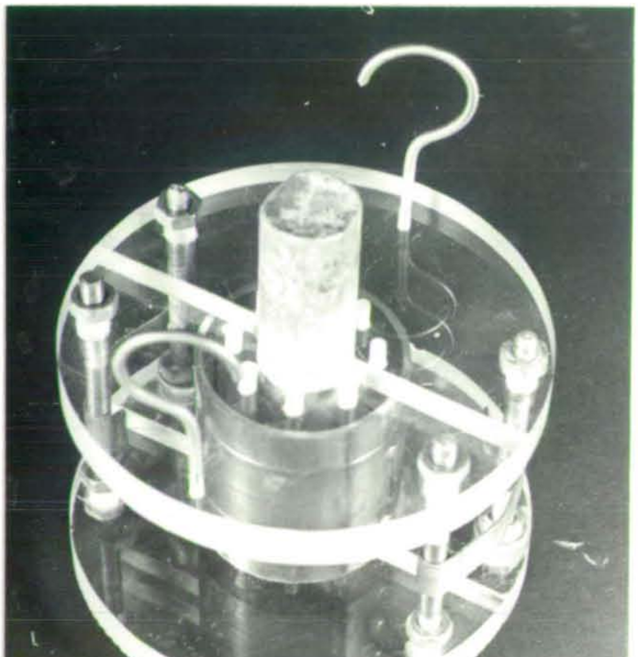


FIG. 16 Diagram of cell used for efficiency measurements.

FIG. 17 Large cell. Photographs showing large cell before and after assembly





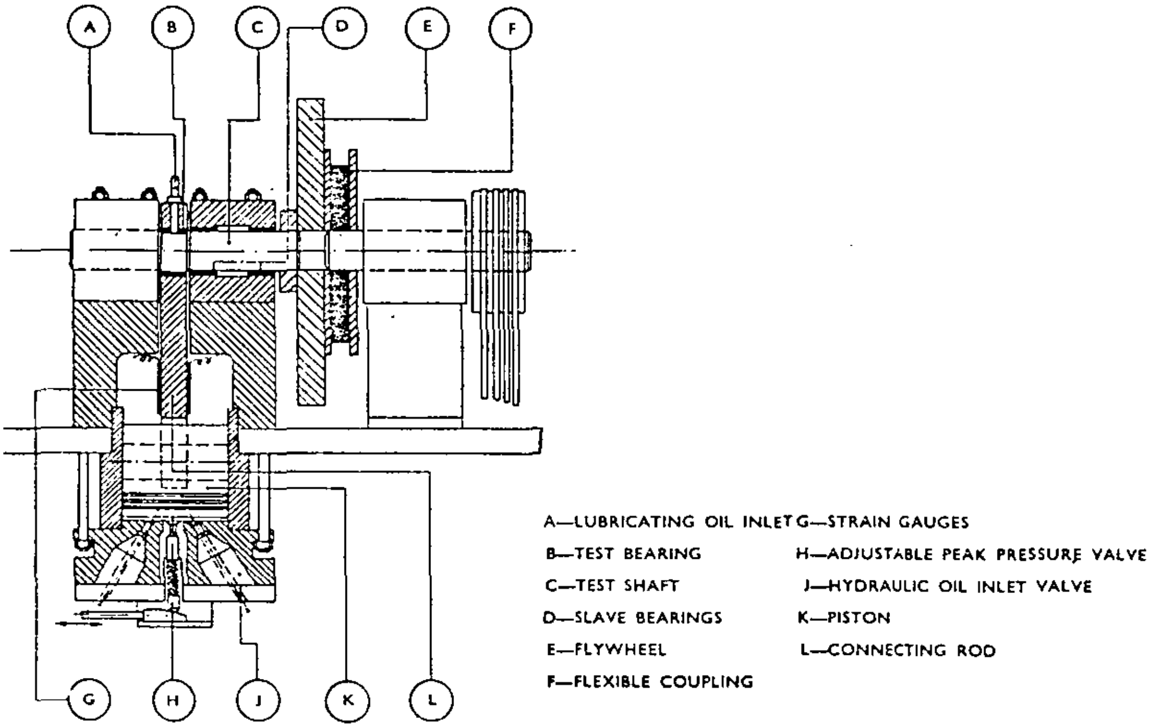


FIG. 18 Hydraulic loading arrangement for Sapphire Test Rig.[12]

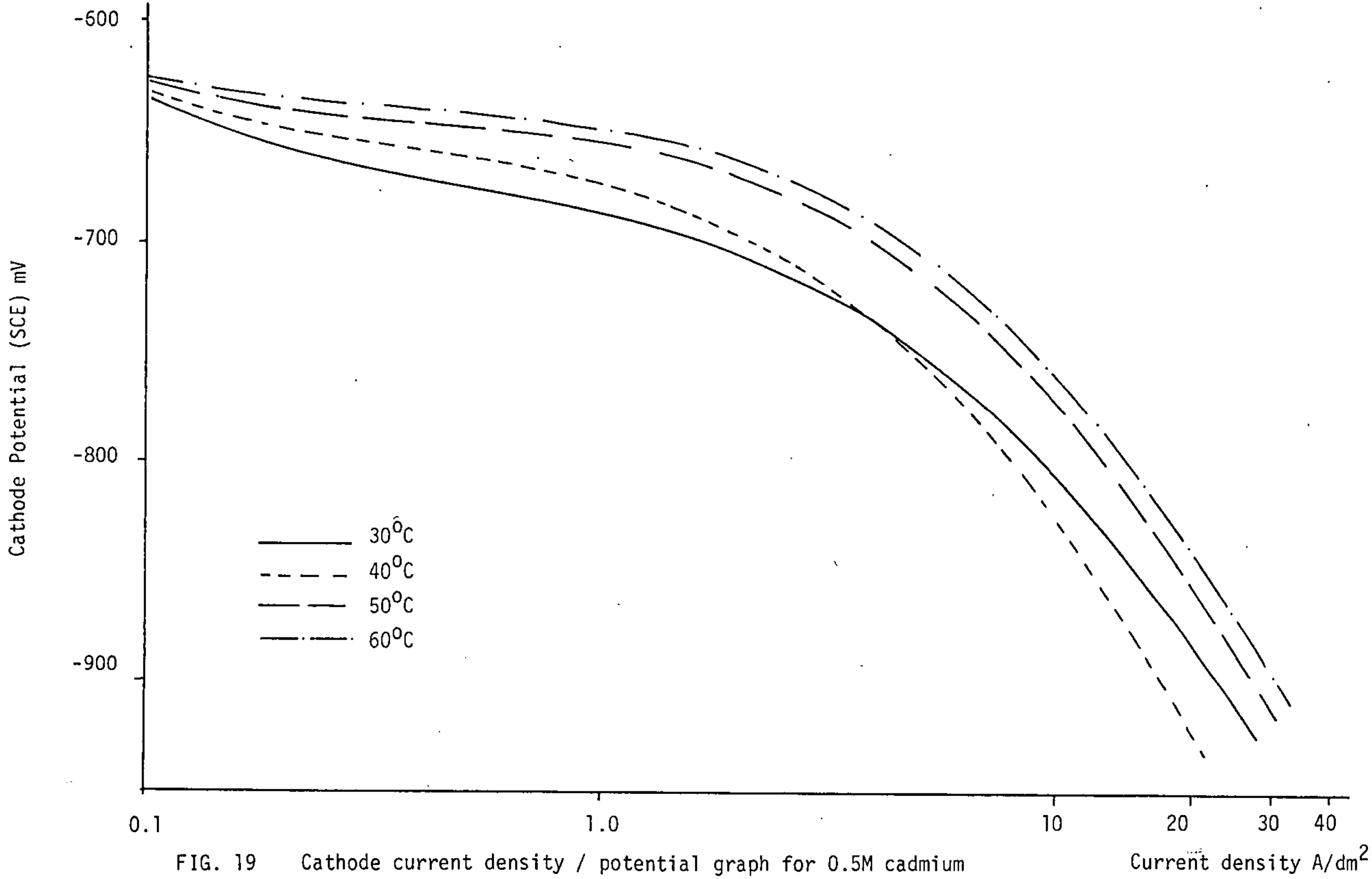


FIG. 19 Cathode current density / potential graph for 0.5M cadmium sulphamate at various temperatures.

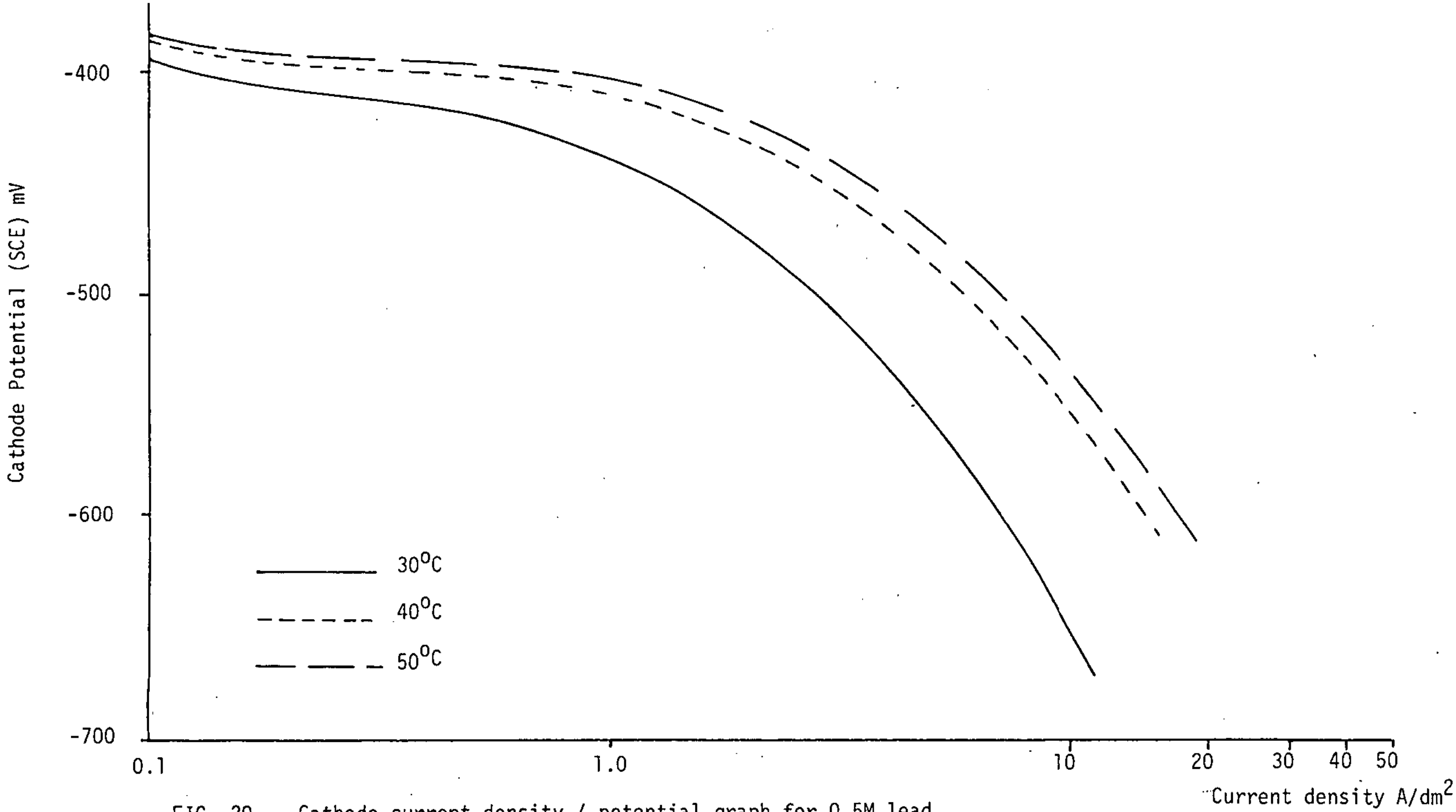


FIG. 20 Cathode current density / potential graph for 0.5M lead sulphamate at various temperatures.

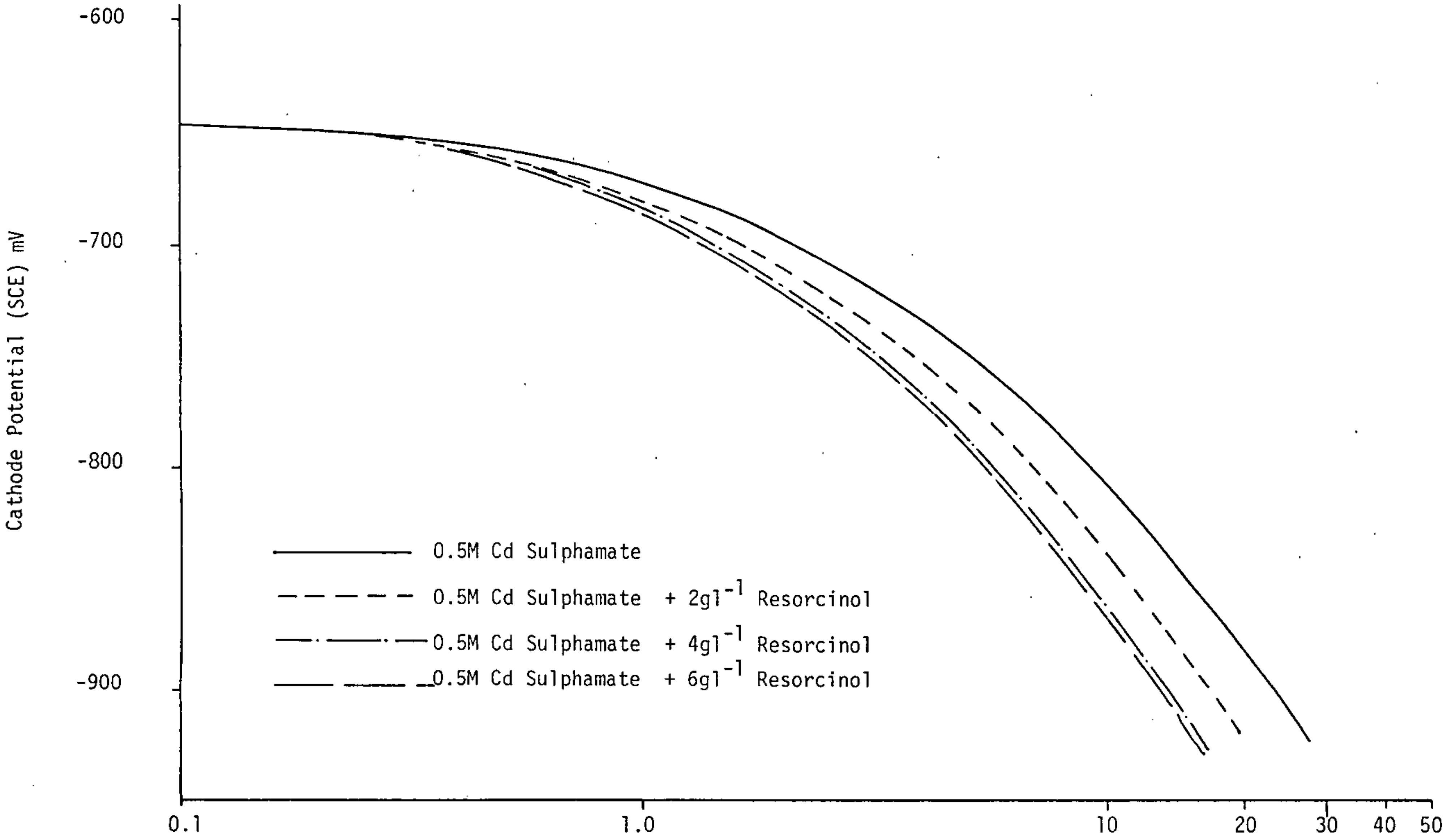


FIG. 21 Cathode current density / potential graph for 0.5M Cd sulphamate + addition agent at 30°C.

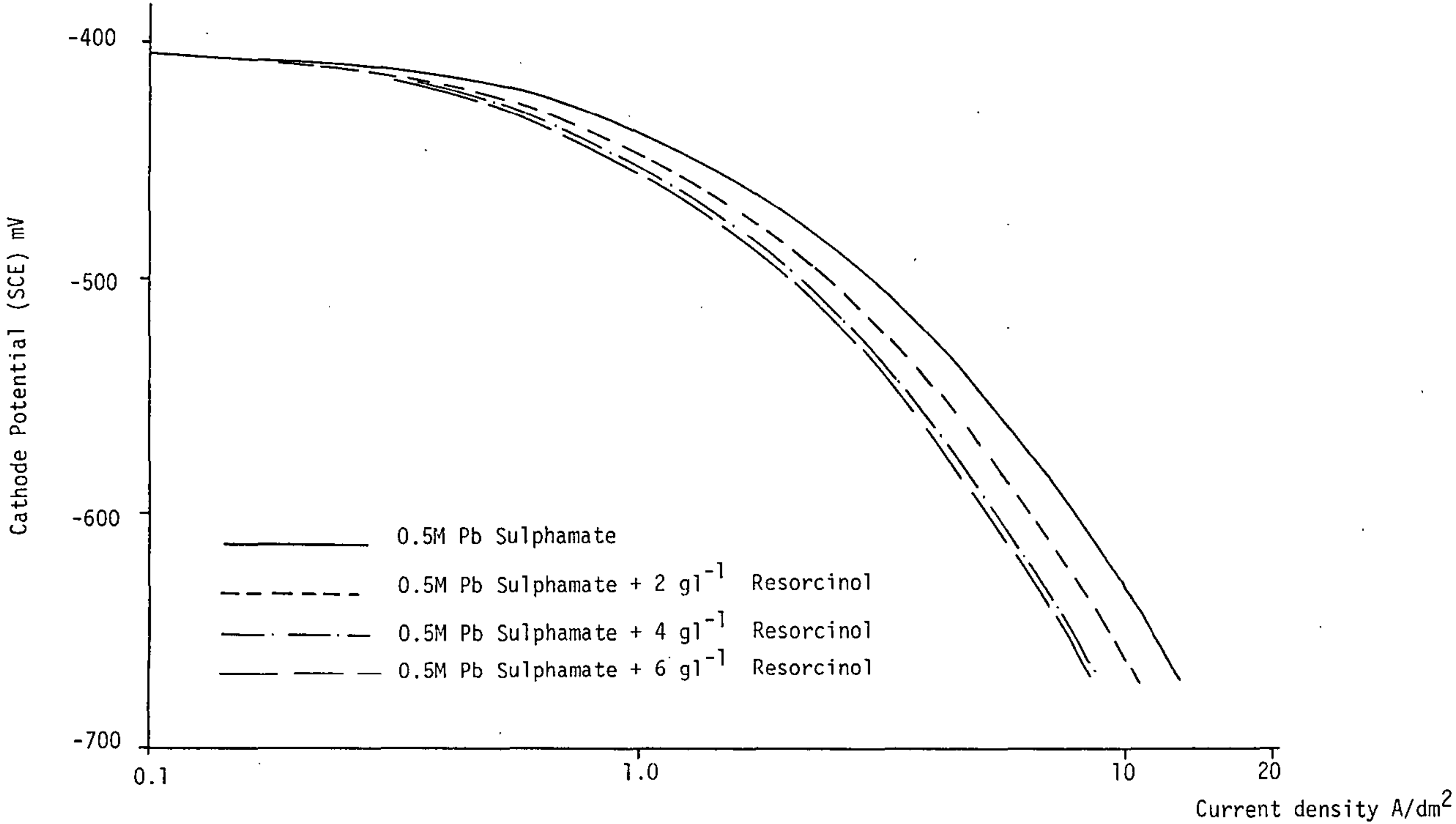


FIG. 22 Cathode current density / potential graph for 0.5M Pb sulphamate + addition agent at 30°C.

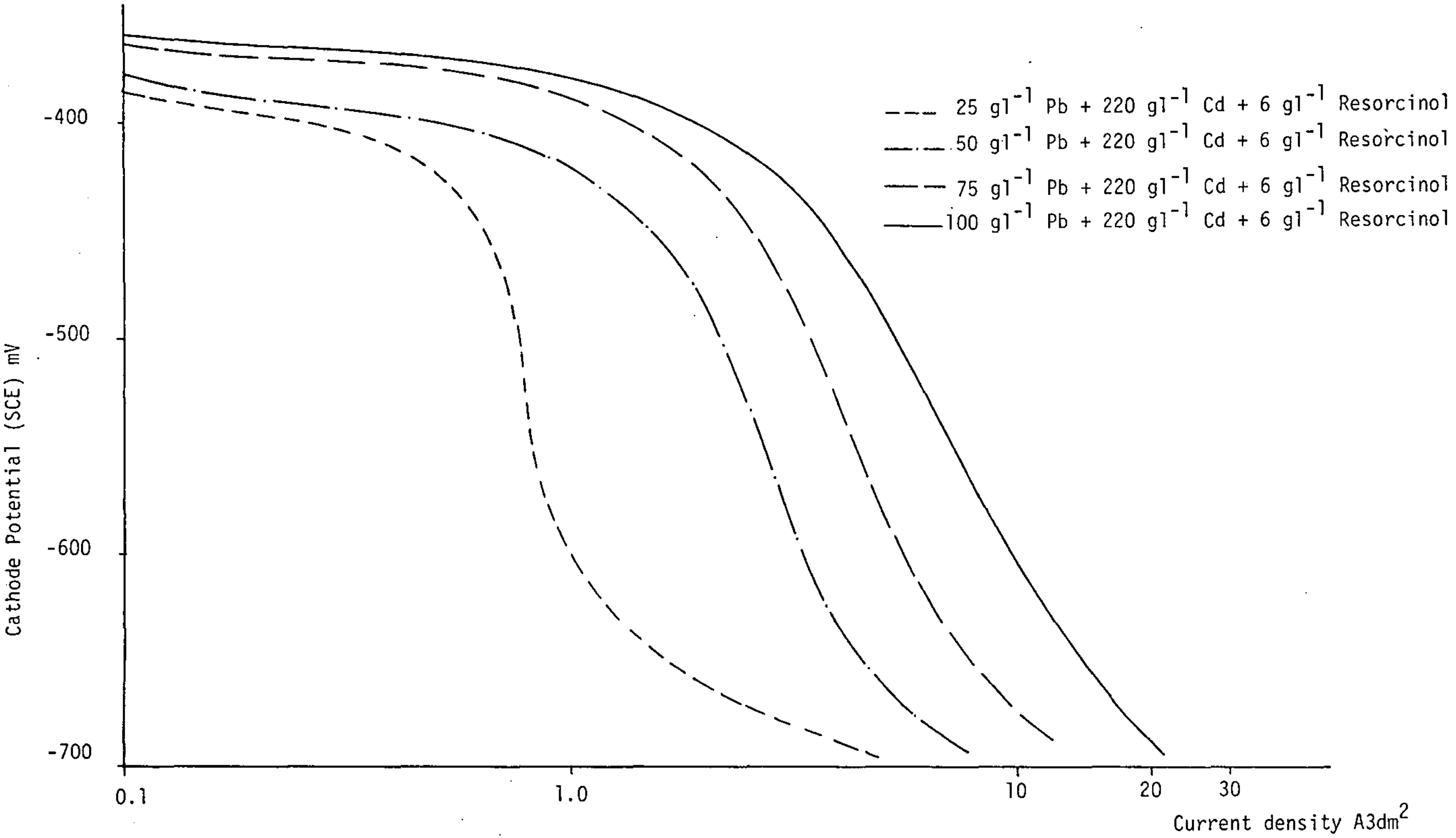


FIG. 23 Cathode current density / potential graph for sulphamate alloy solutions at 30°C with gentle agitation.

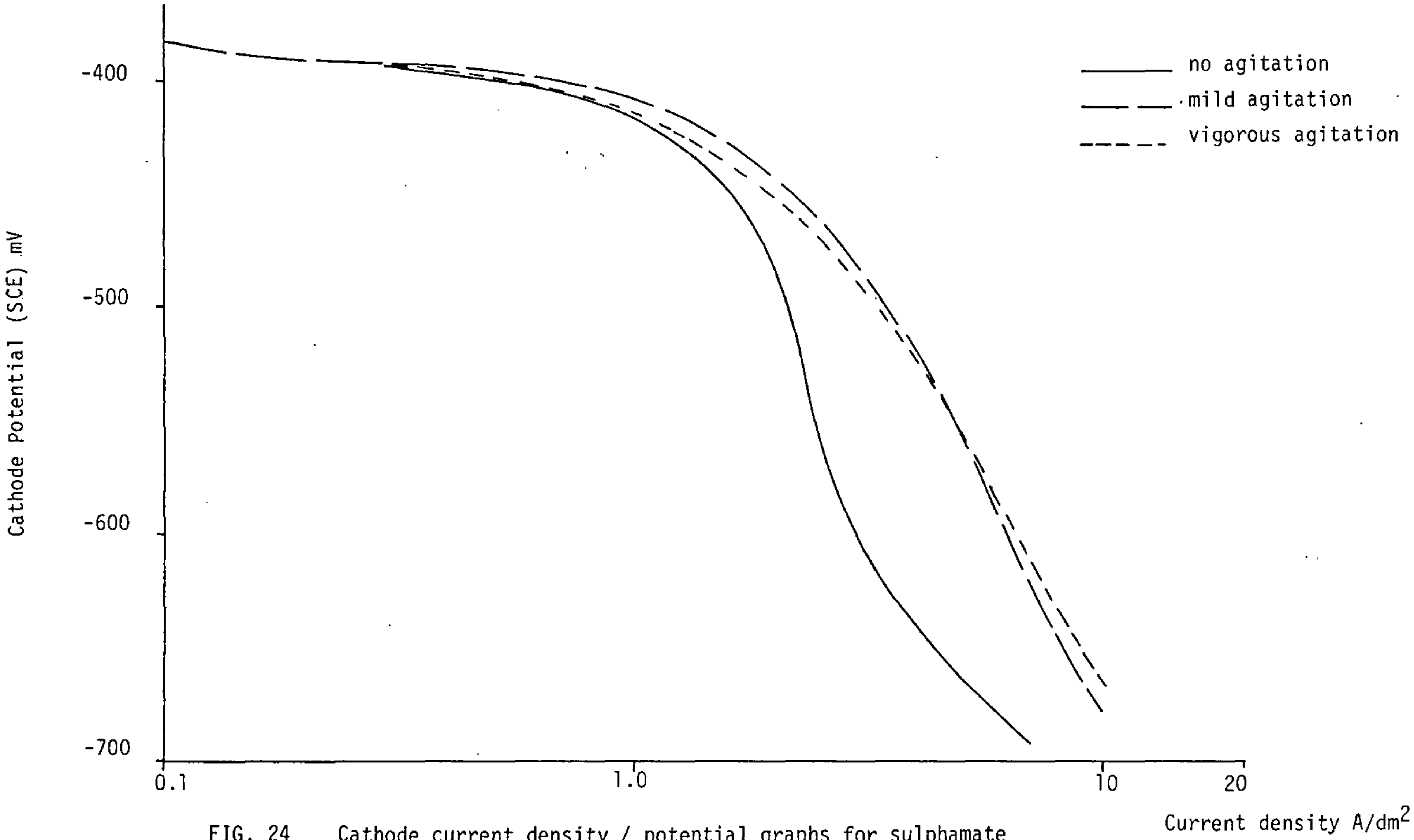


FIG. 24 Cathode current density / potential graphs for sulphamate alloy solution containing 220gl^{-1} Cd, 75 gl^{-1} Pb, 6 gl^{-1} resorcinol with varying degrees of agitation.

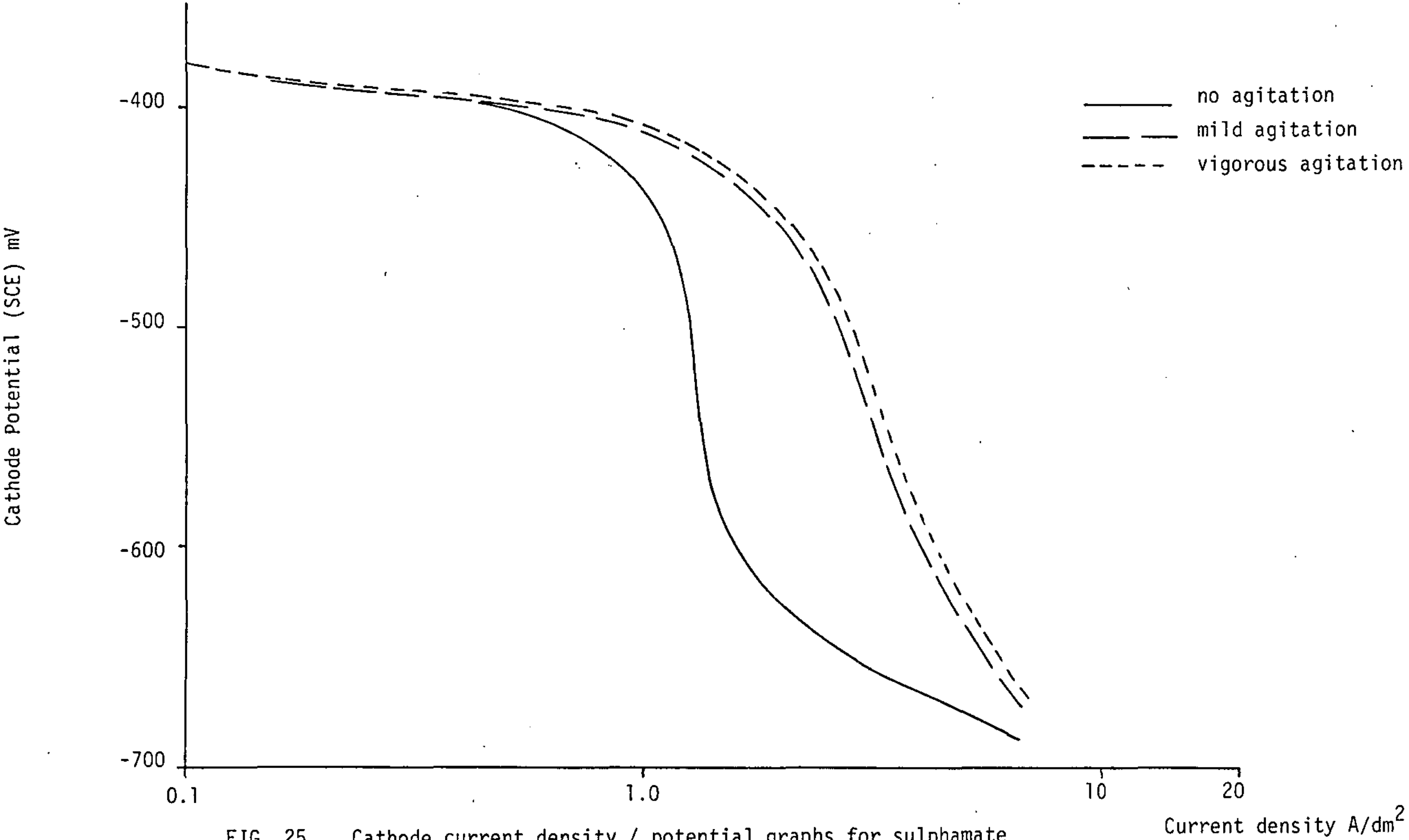


FIG. 25 Cathode current density / potential graphs for sulphamate alloy solution containing 220 gl^{-1}Cd, 50 gl^{-1}Pb and 6 gl^{-1} resorcinol with varying degrees of agitation.

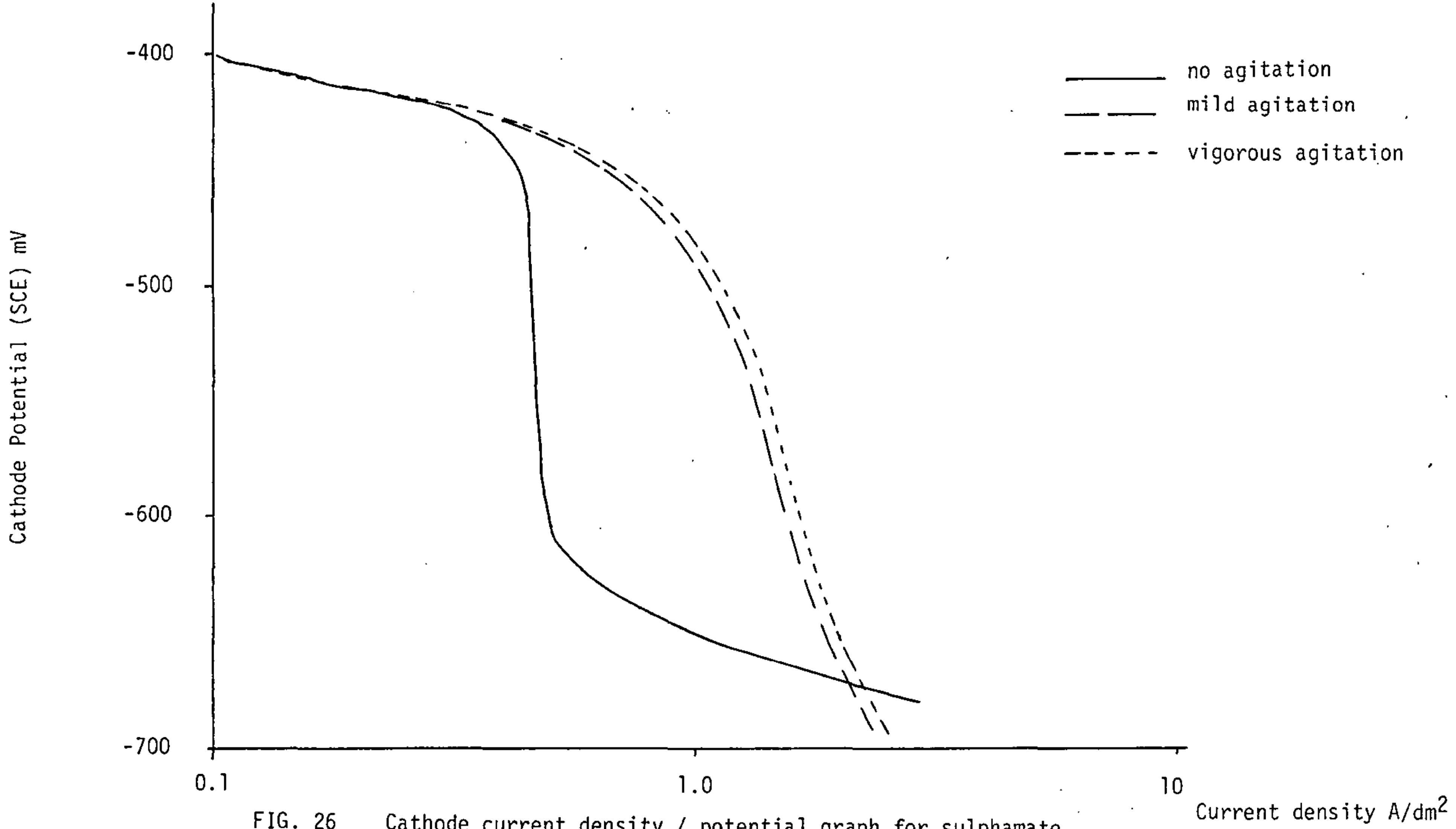


FIG. 26 Cathode current density / potential graph for sulphamate solution containing 220 gl^{-1}Cd, 25 gl^{-1}Pb and 6 gl^{-1} resorcinol with varying degrees of agitation.

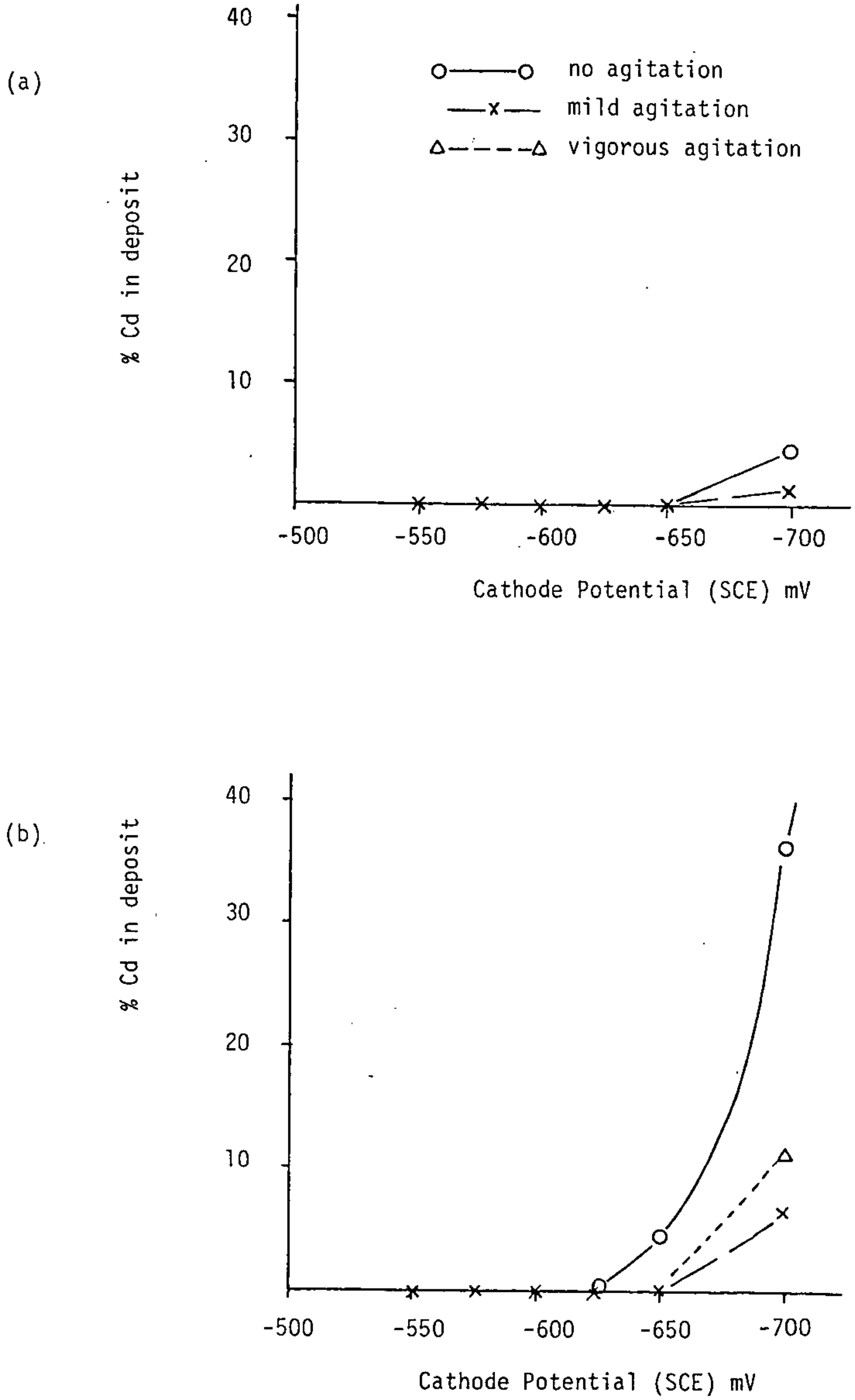
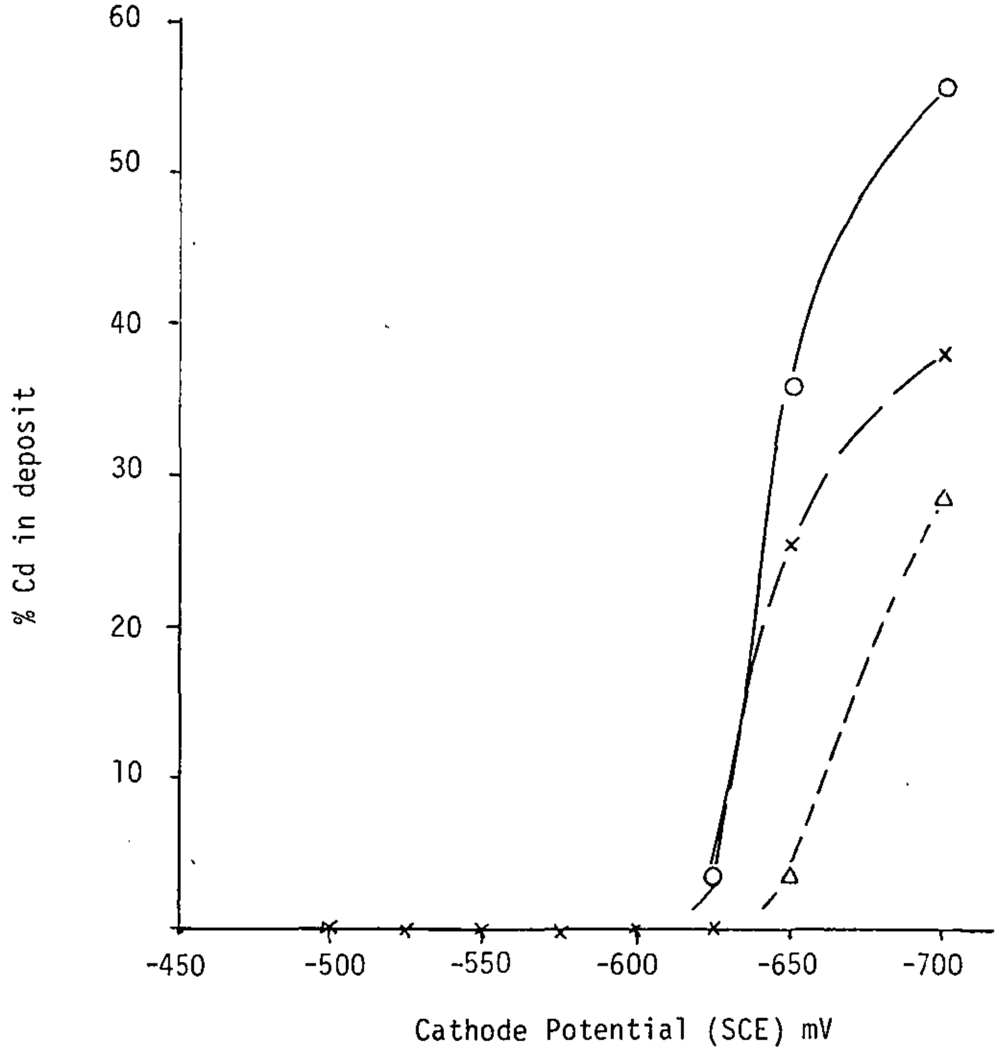


FIG. 27 Percentage cadmium in deposit v cathode deposition potential from alloy sulphamate electrolyte containing 220 gl^{-1} Cd, 6 gl^{-1} resorcinol and a) 75 gl^{-1} Pb, b) 50 gl^{-1} Pb, c) 25 gl^{-1} Pb.
Agitation of the electrolyte varied as shown.

(c)


60
50
40
30
20
10
% Cd in deposit
-450
-500
-550
-600
-650
-700
Cathode Potential (SCE) mV

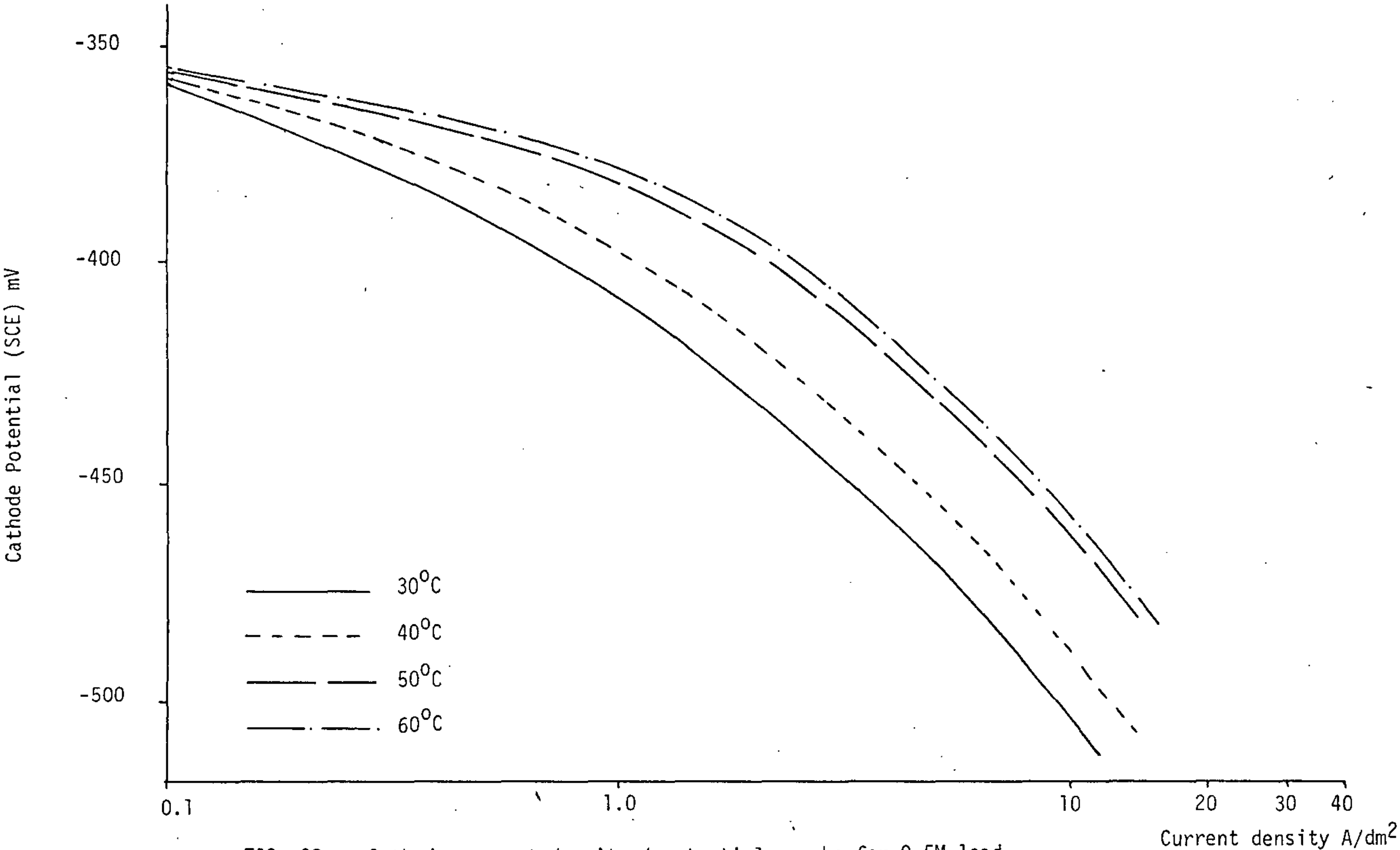


FIG. 28 Cathode current density / potential graphs for 0.5M lead fluorosilicate at various temperatures.

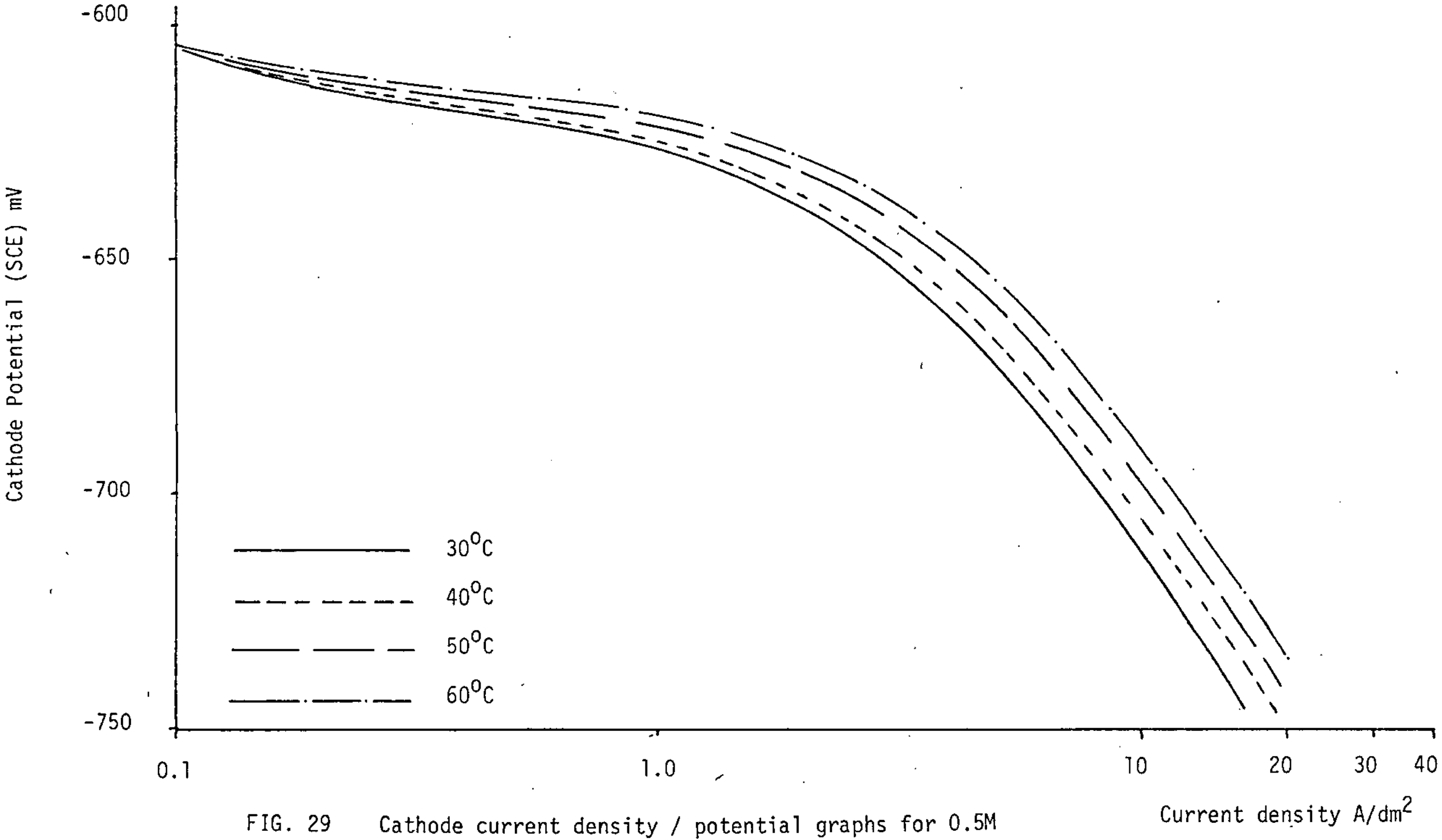


FIG. 29 Cathode current density / potential graphs for 0.5M cadmium fluorsilicate at various temperatures.

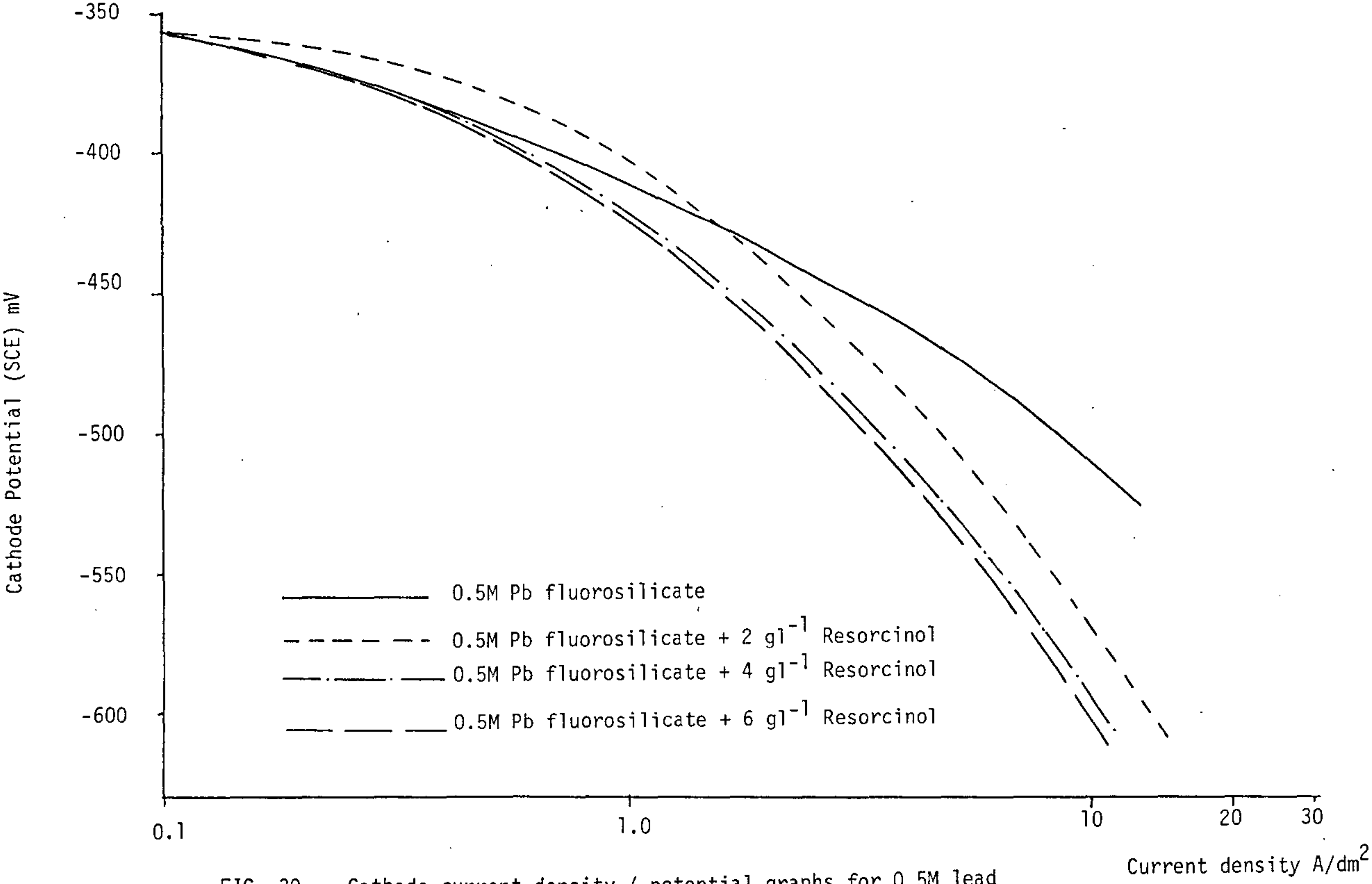


FIG. 30 Cathode current density / potential graphs for 0.5M lead fluorosilicate + addition agent at 30°C.

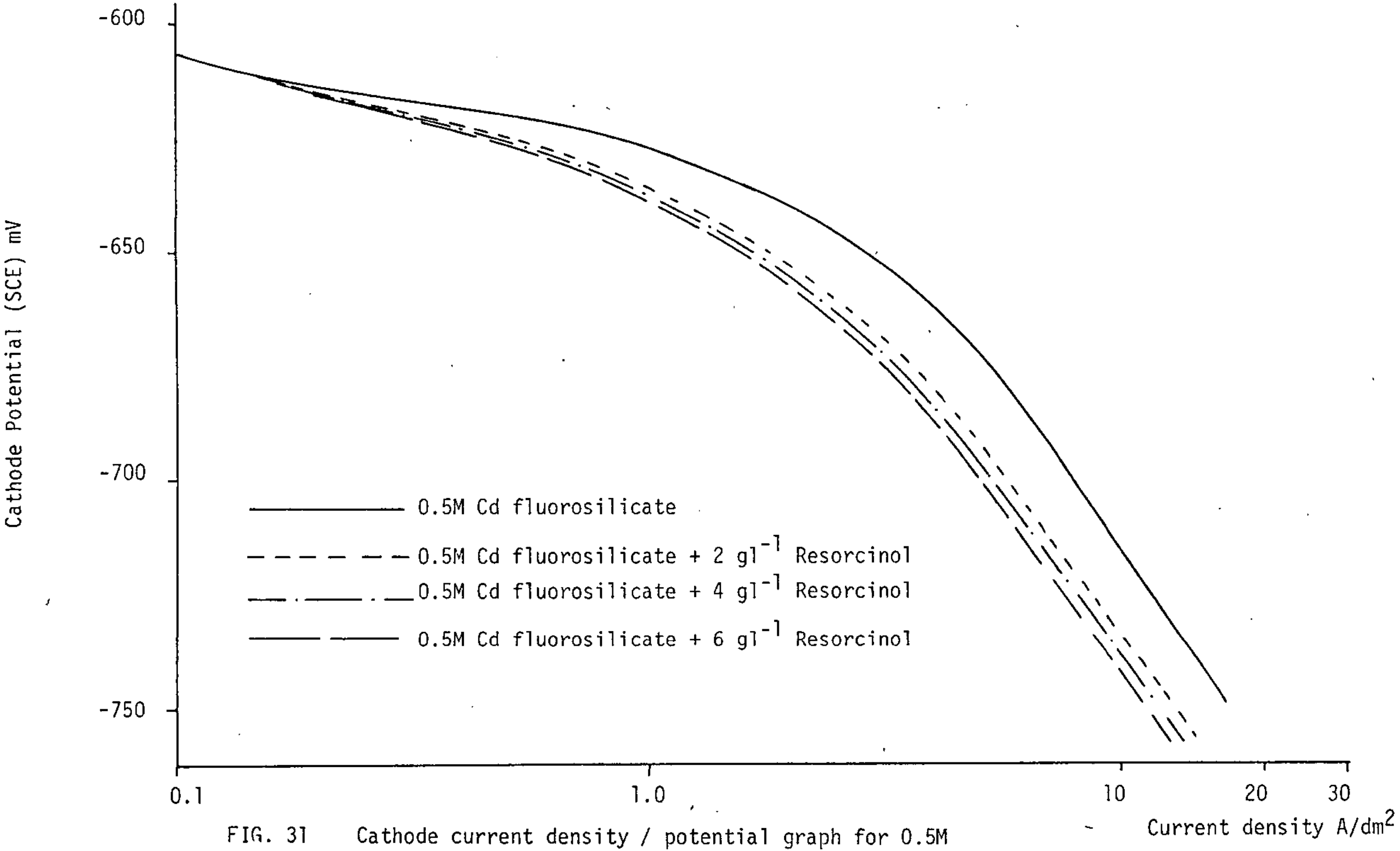


FIG. 31 Cathode current density / potential graph for 0.5M cadmium fluorosilcate + addition agent at 30°C.

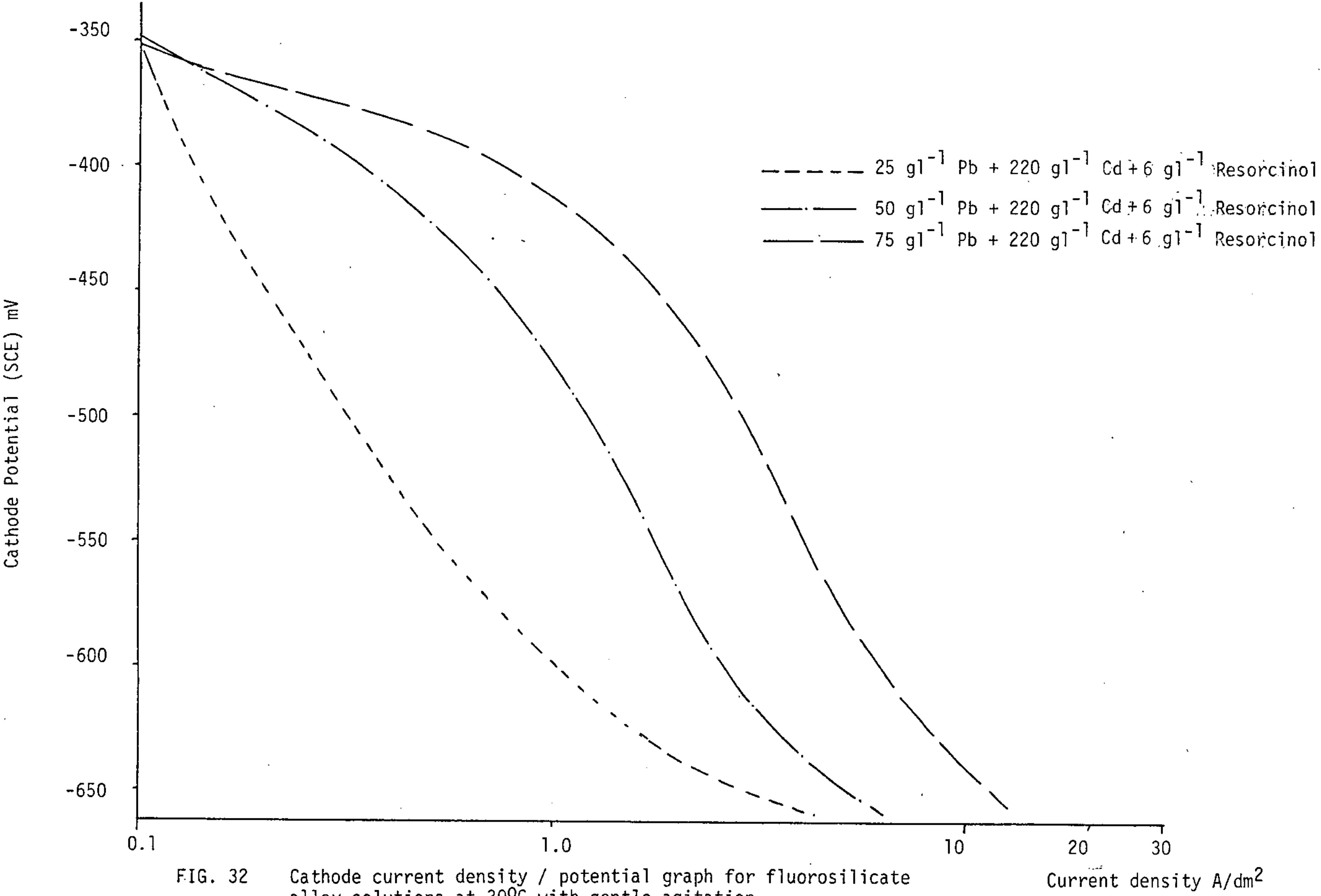


FIG. 32 Cathode current density / potential graph for fluorosilicate alloy solutions at 30^{O}C with gentle agitation.

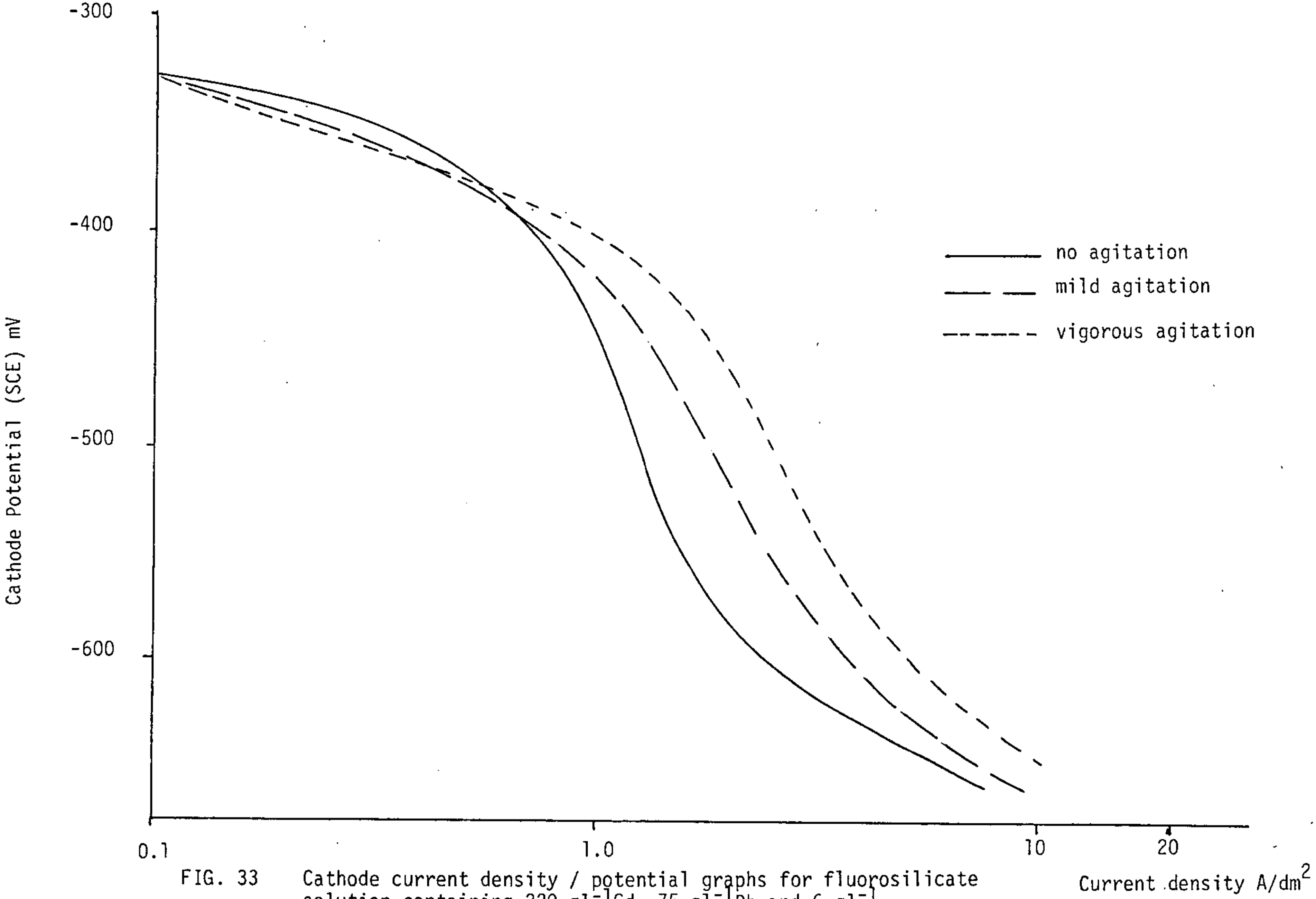


FIG. 33 Cathode current density / potential graphs for fluorosilicate solution containing 220 gl^{-1}Cd, 75 gl^{-1}Pb and 6 gl^{-1} resorcinol with varying degrees of agitation.

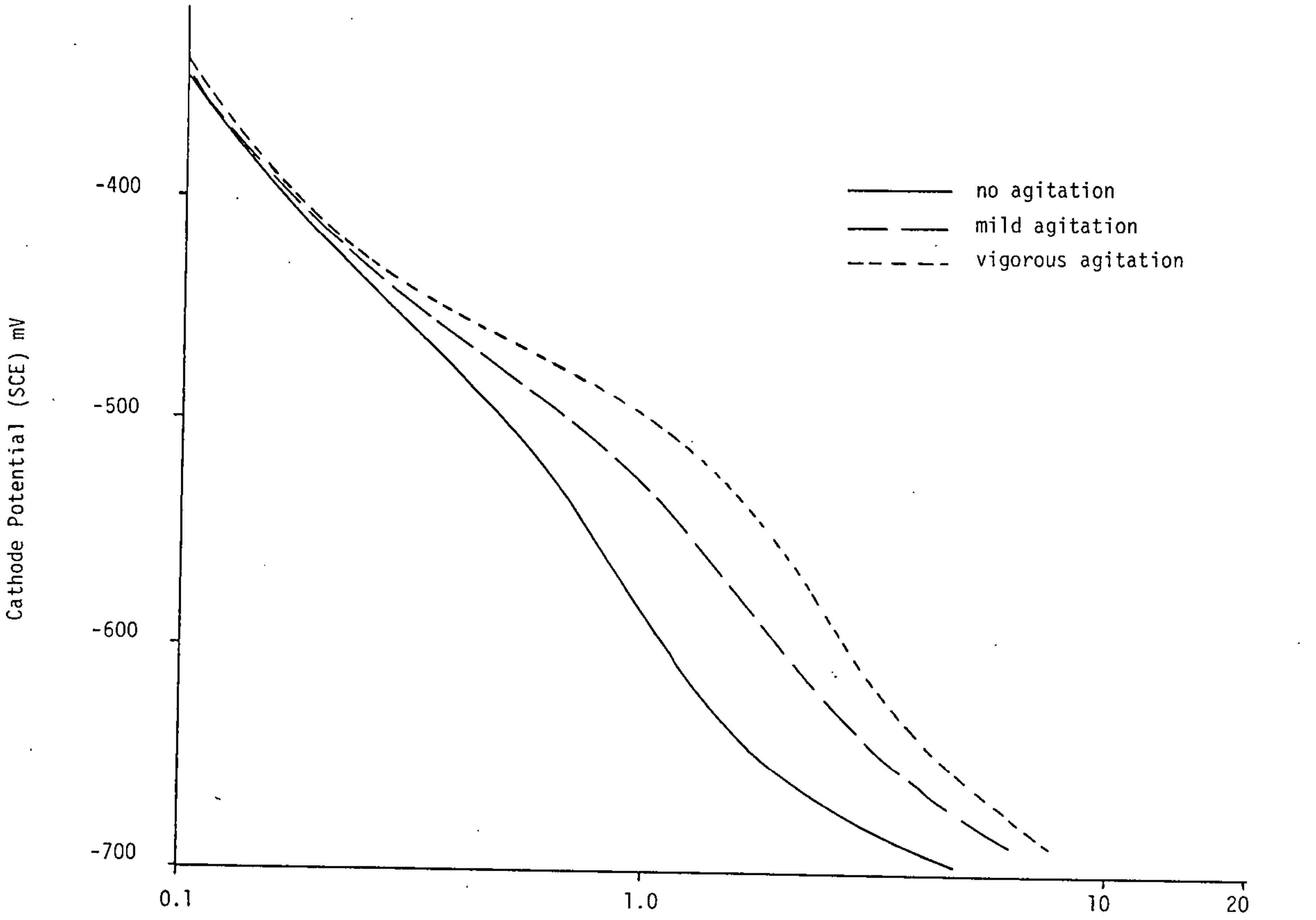


FIG. 34 Cathode current density / potential graph for fluorosilicate alloy solution containing 220 gl^{-1}Cd, 50 gl^{-1}Pb and 6 gl^{-1} resorcinol with varying degrees of agitation.

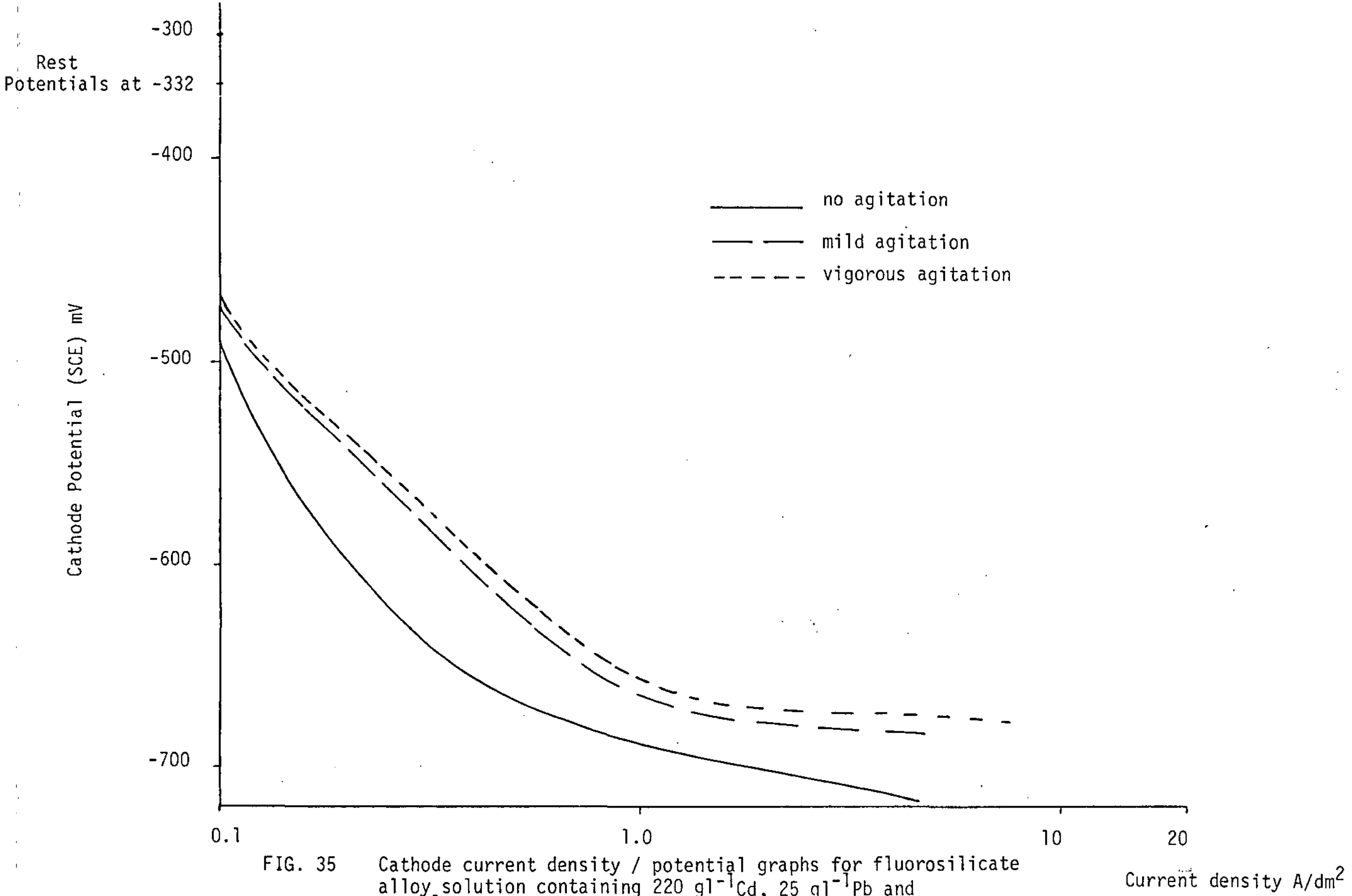


FIG. 35 Cathode current density / potential graphs for fluorosilicate alloy solution containing 220 gl^{-1}Cd, 25 gl^{-1}Pb and 6 gl^{-1} resorcinol with varying degrees of agitation.

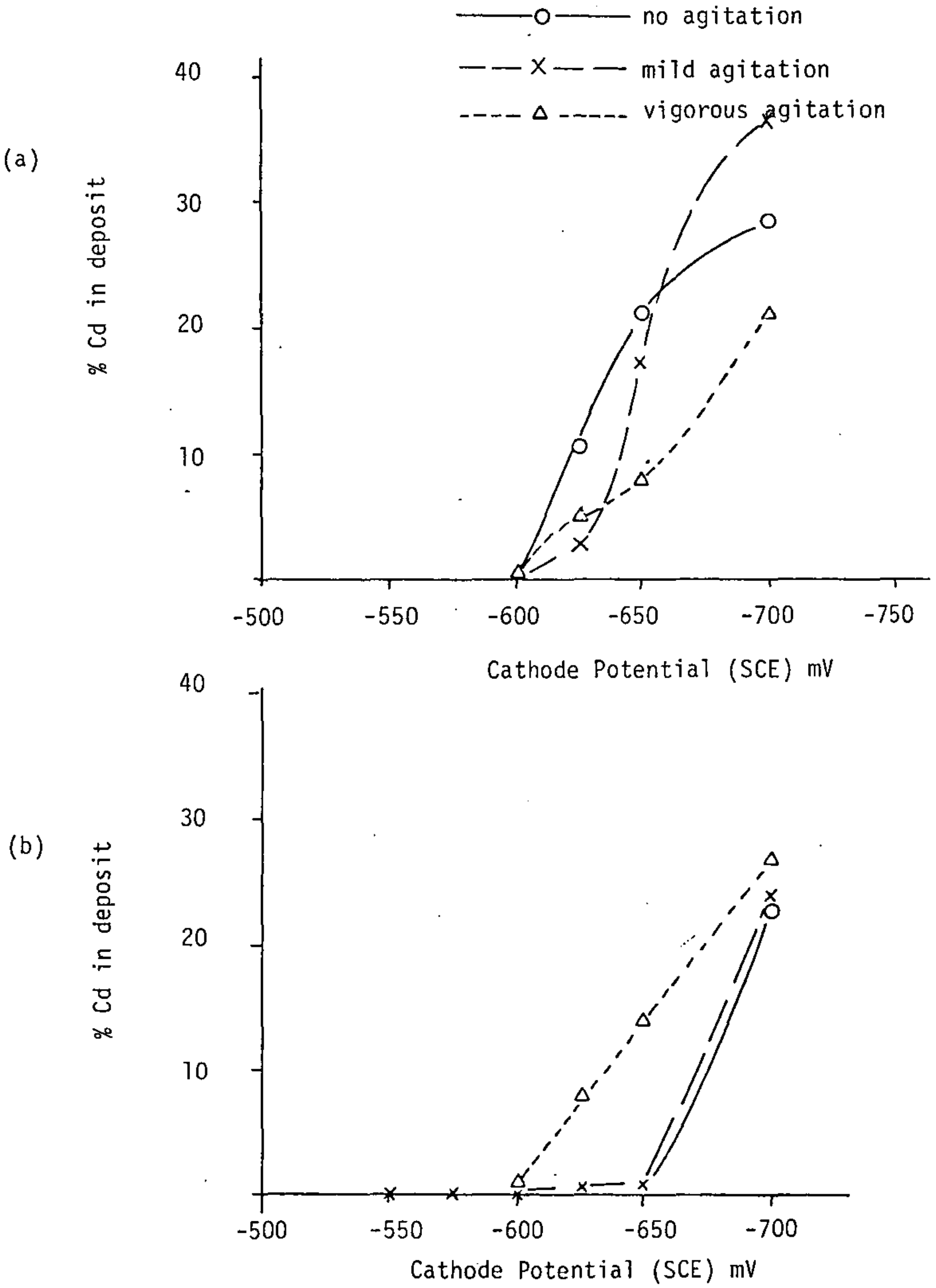
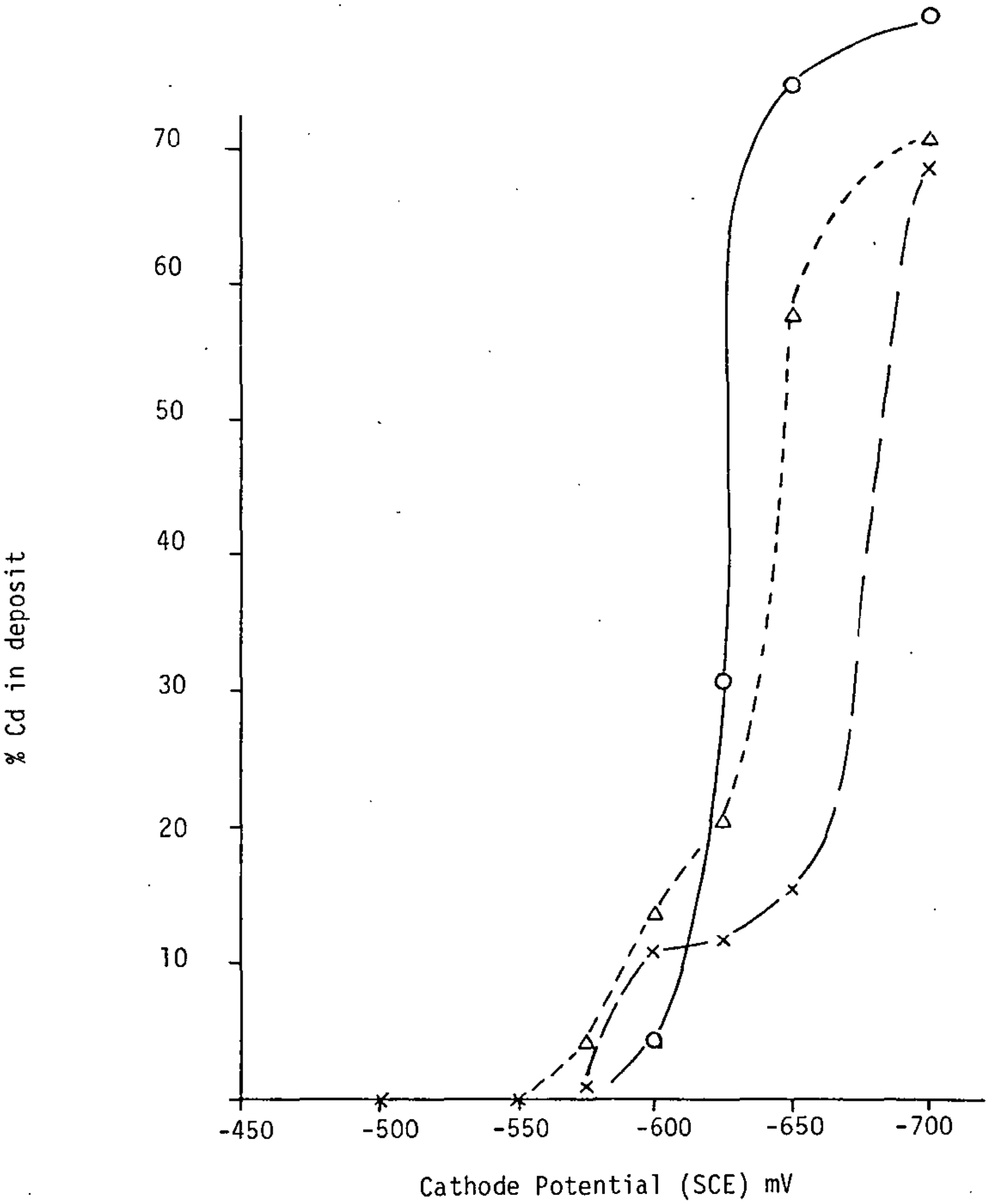


FIG.36 Cadmium in deposit v cathode deposition potential from alloy fluorosilicate electrolyte containing 220 gl^{-1} cadmium, 6 gl^{-1} resorcinol and a) 75 gl^{-1} Pb, b) 50 gl^{-1} Pb and c) 25 gl^{-1} Pb. Agitation as shown.

(c)


% Cd in deposit
70
60
50
40
30
20
10
-450
-500
-550
-600
-650
-700
Cathode Potential (SCE) mV

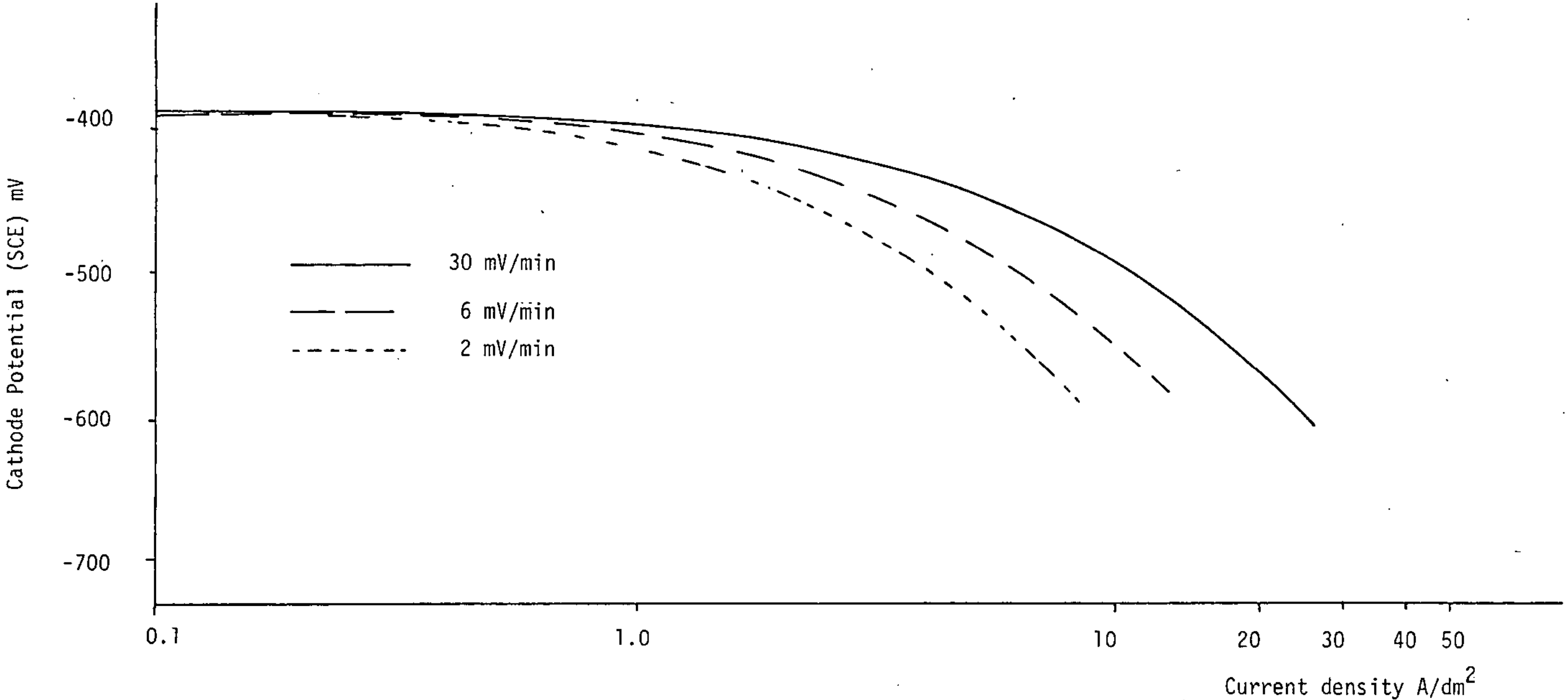


FIG. 37 Cathode current density / potential graphs for 0.1M lead fluoroborate using different sweep rates.

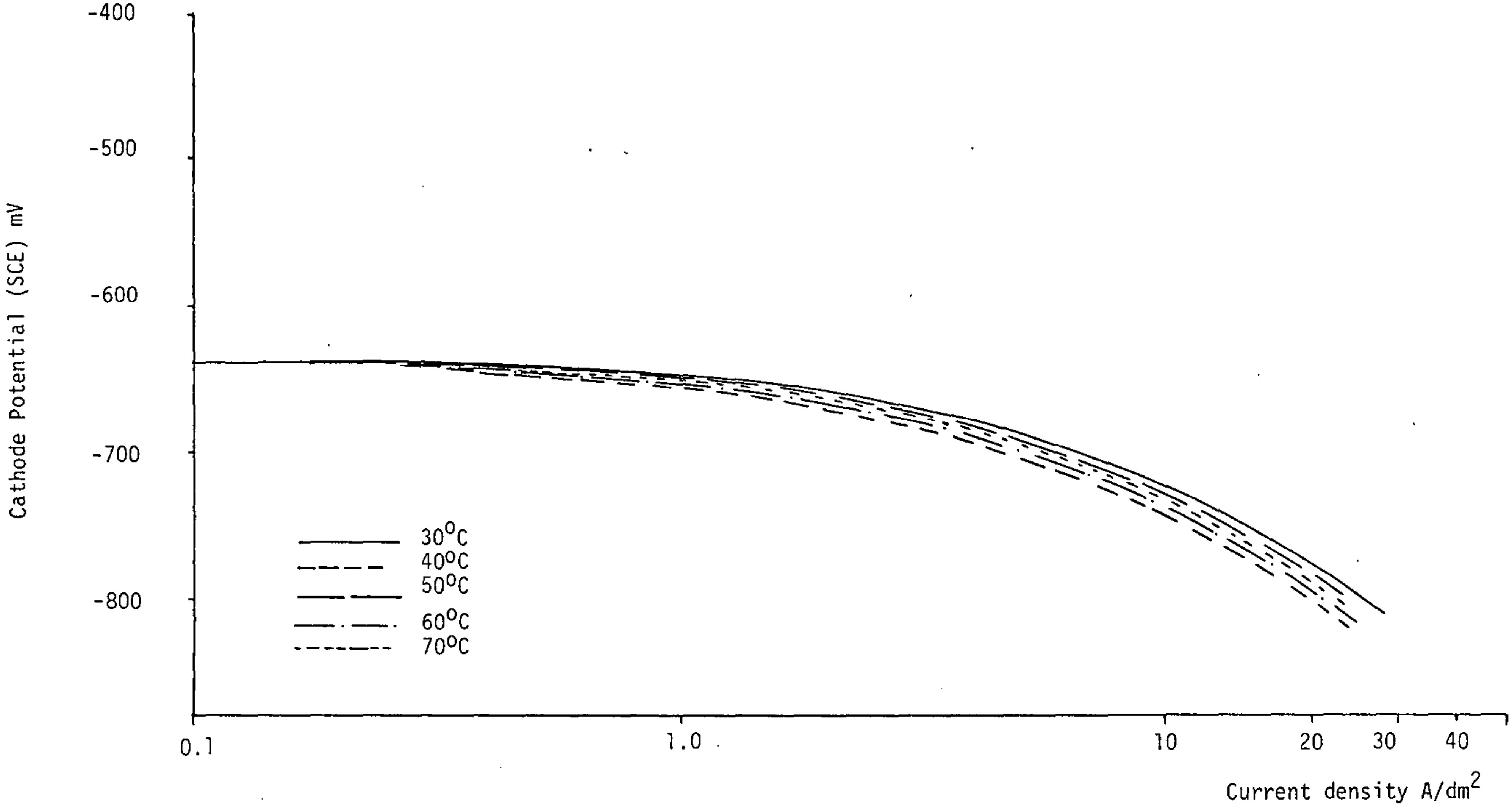


FIG. 38 Cathode current density / potential graph for 0.1M cadmium fluoroborate at various temperatures.

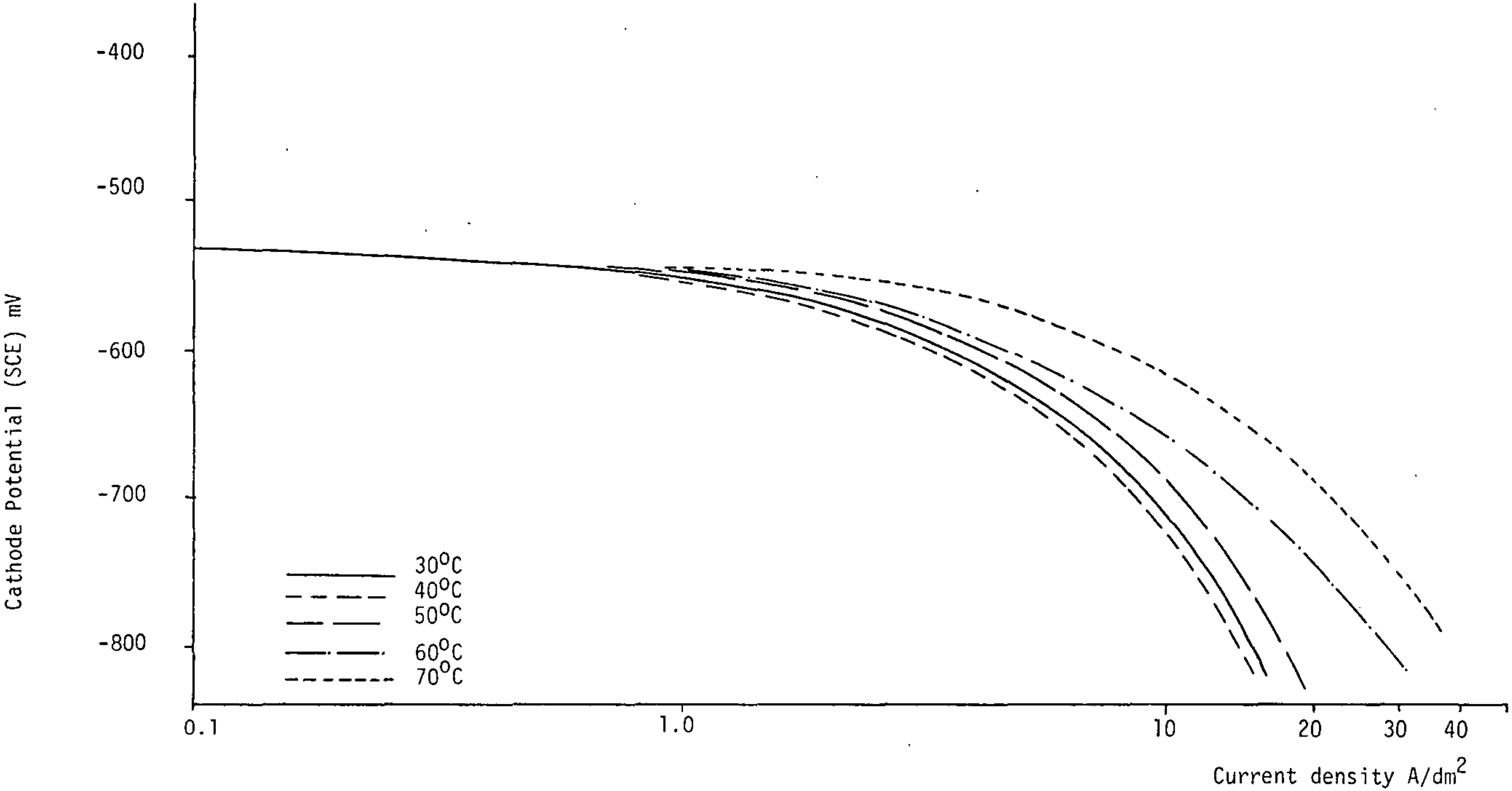


FIG. 39 Cathode current density / potential graph for 0.1M cadmium fluoroborate at various temperatures.

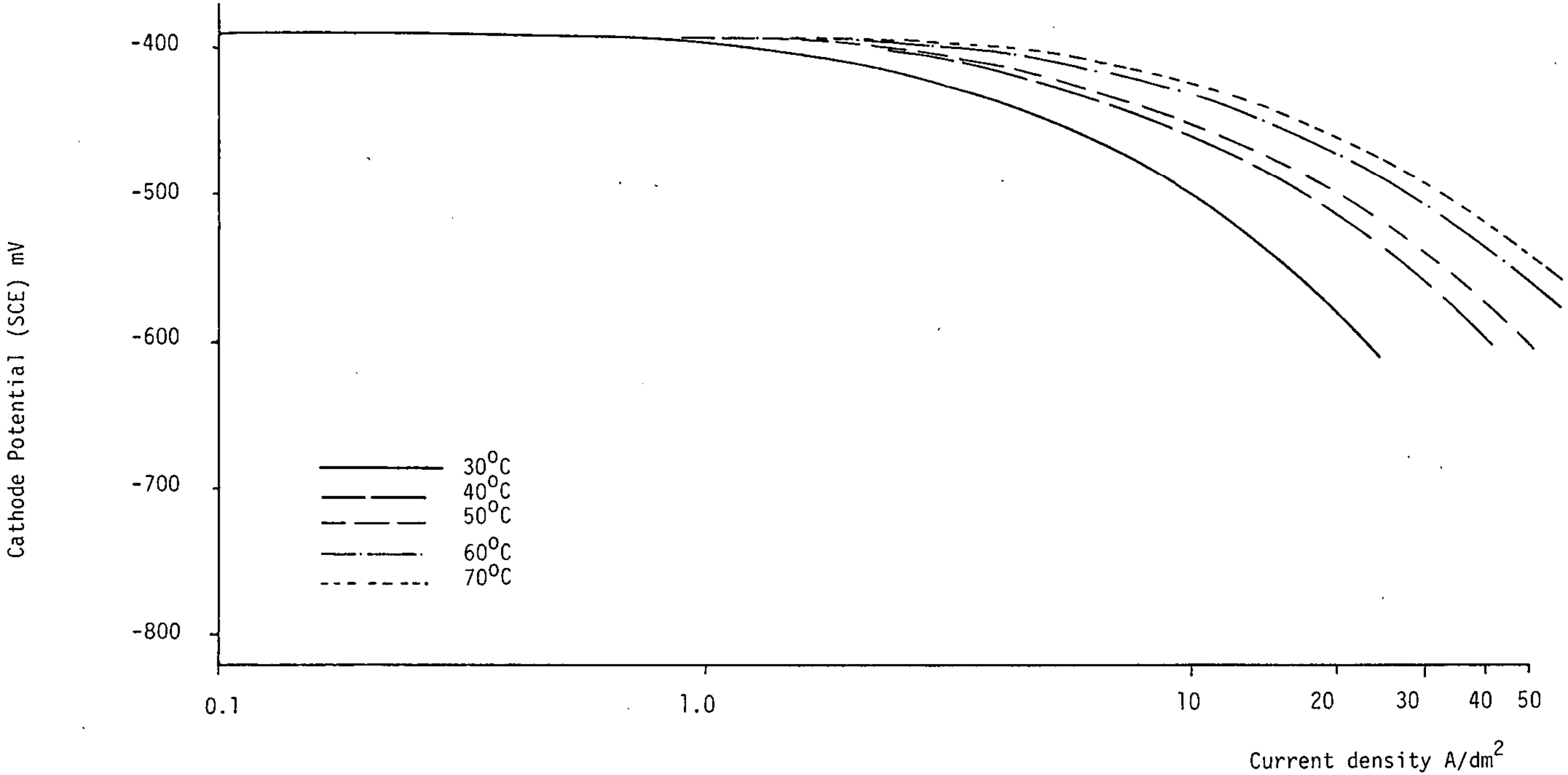


FIG. 40 Cathode current density / potential graph for 0.1M lead fluoroborate at various temperatures.

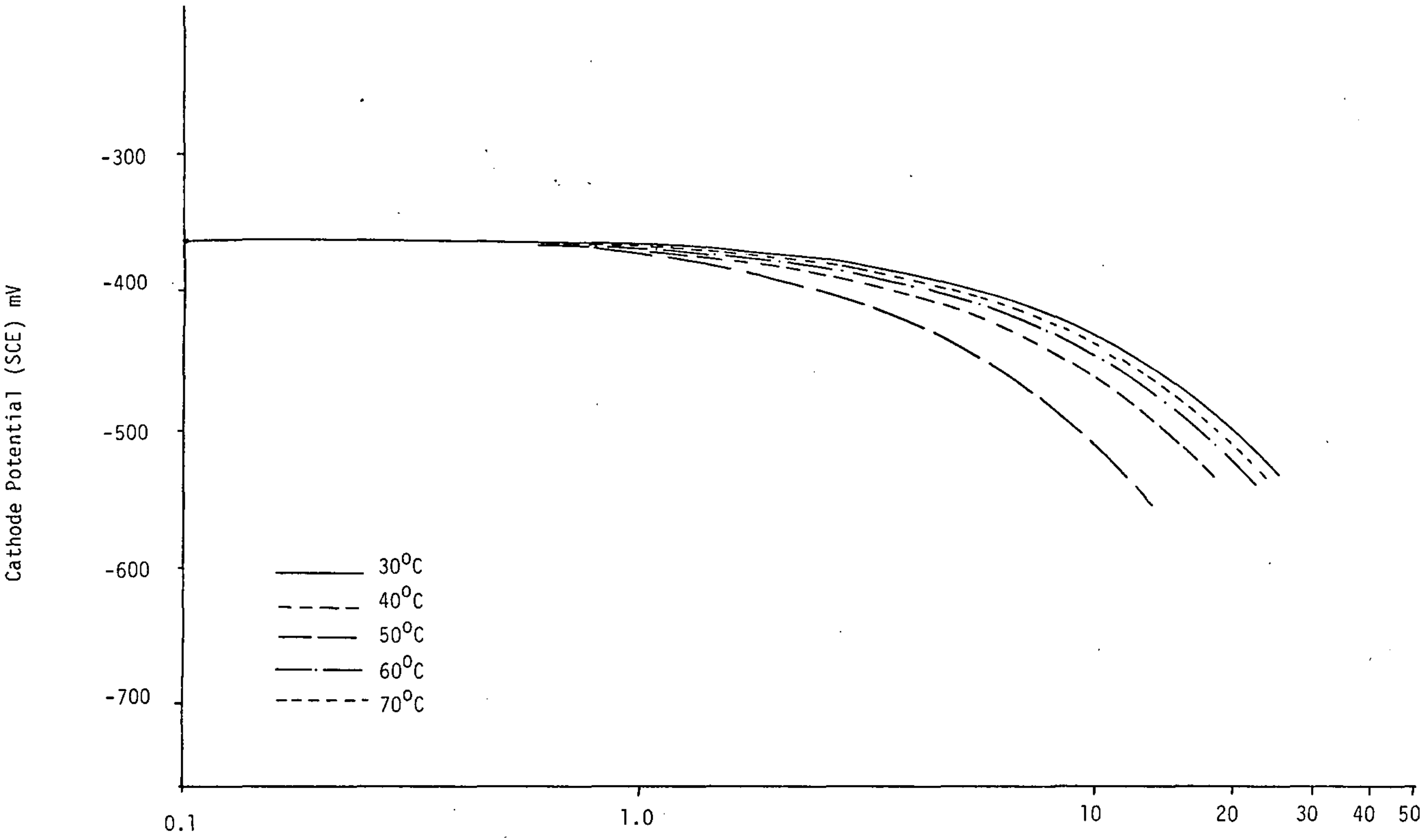


FIG. 41 Cathode current density / potential graph for 1M lead fluoroborate at various temperatures.

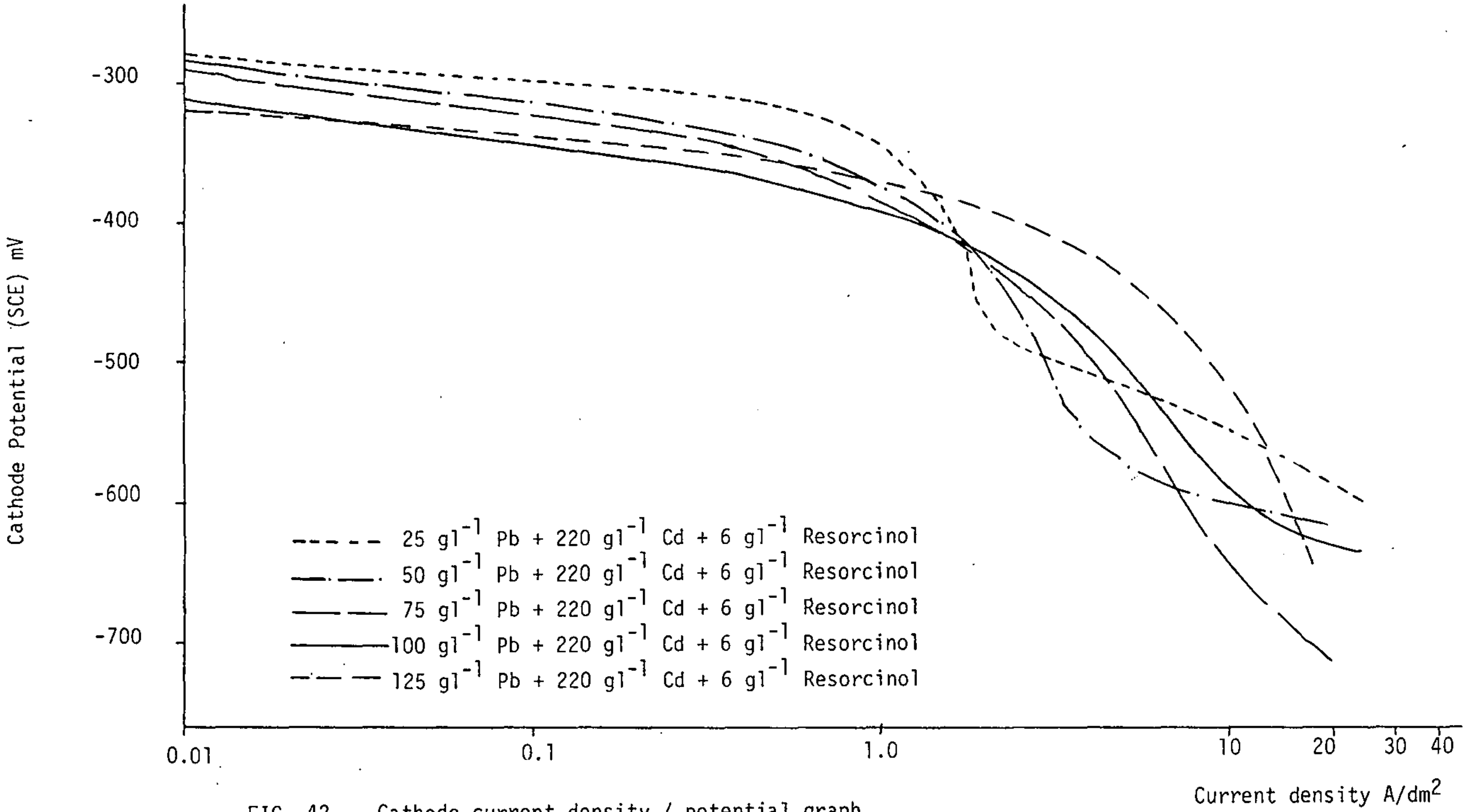


FIG. 42 Cathode current density / potential graph for fluoroborate alloy solutions at 30^{0}C with gentle agitation.

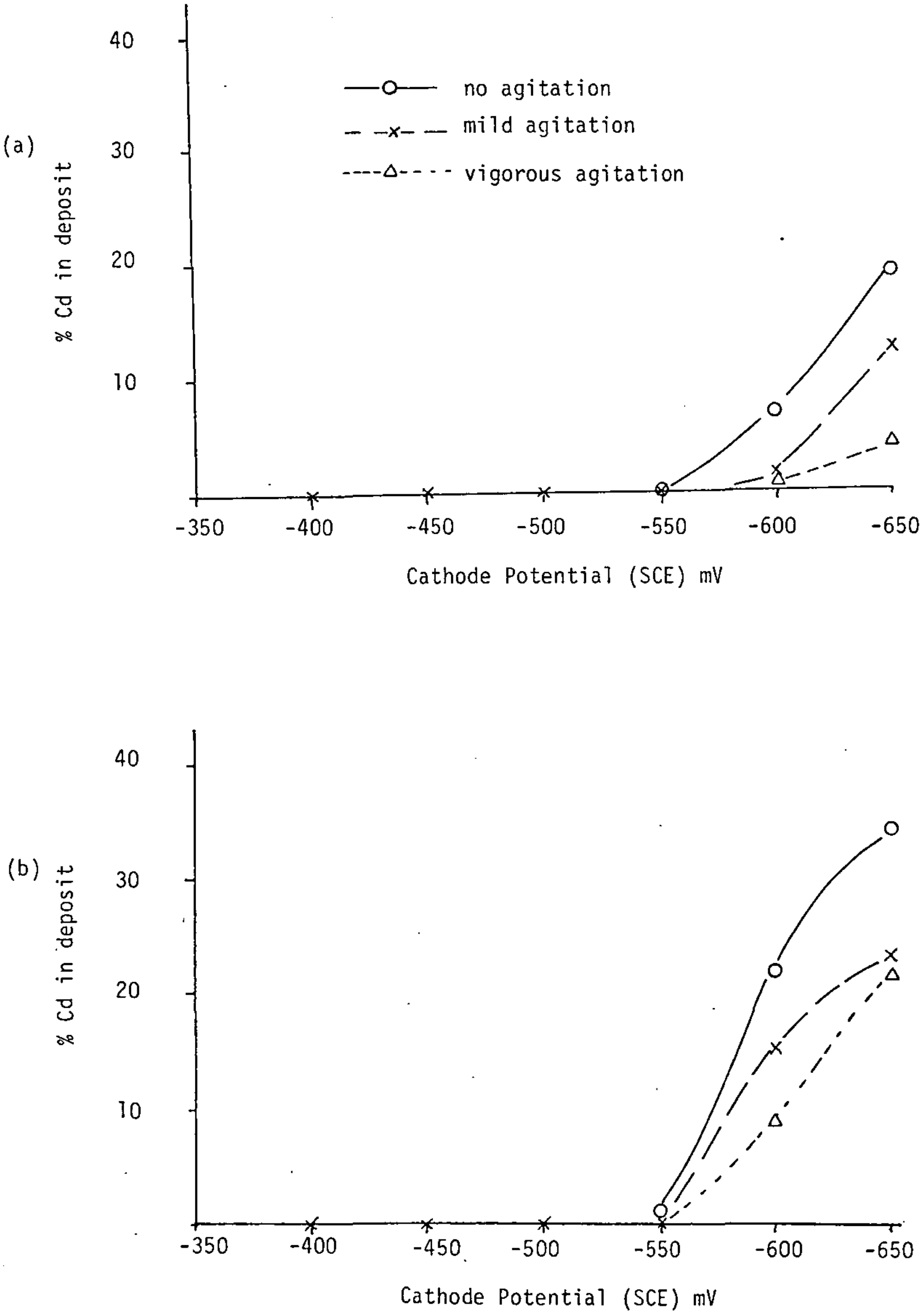
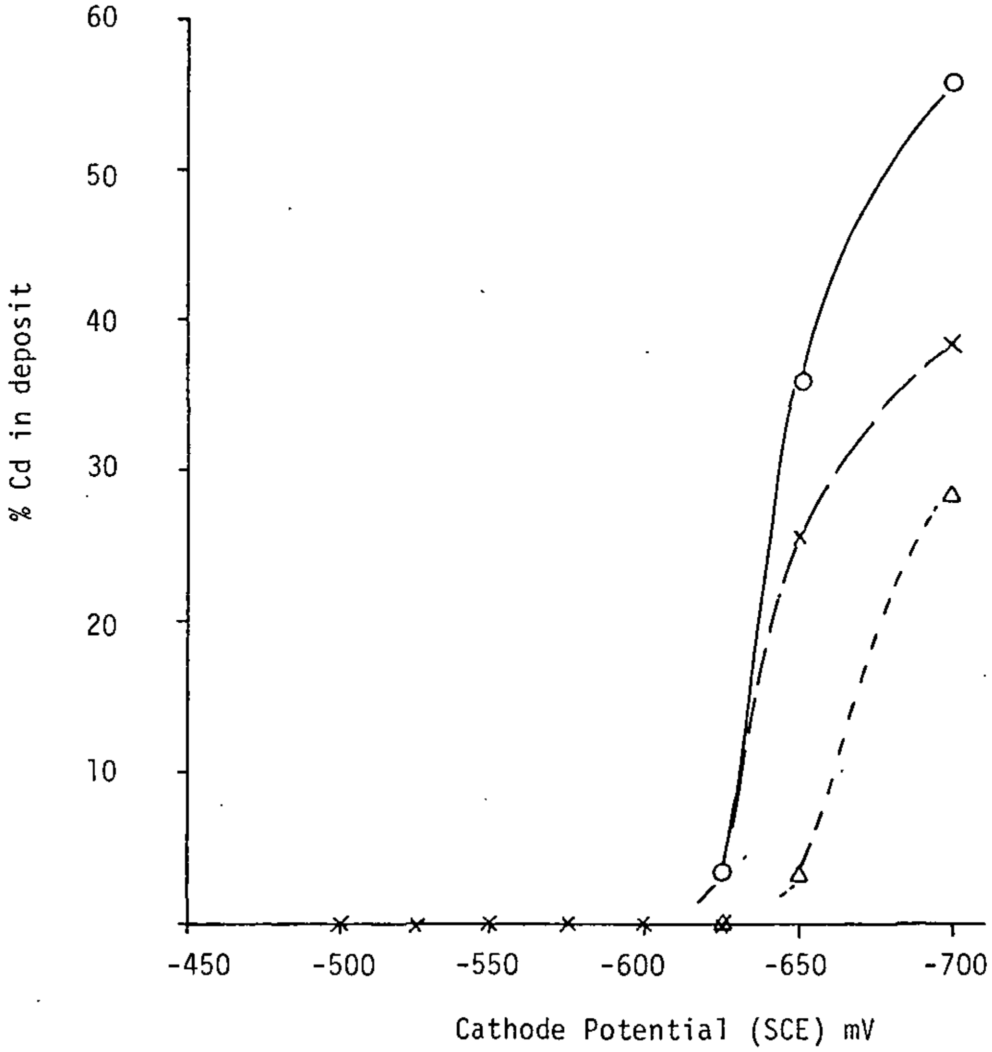


FIG. 43 Percentage cadmium in deposit v cathode deposition potential from fluoroborate electrolyte 220 gl^{-1} Cd, 6 gl^{-1} resorcinol, and a) 75 gl^{-1} Pb, b) 50 gl^{-1} Pb and c) 25 gl^{-1} Pb. Agitation as shown.

(c)


60
50
40
30
20
10
% Cd in deposit
-450
-500
-550
-600
-650
-700
Cathode Potential (SCE) mV

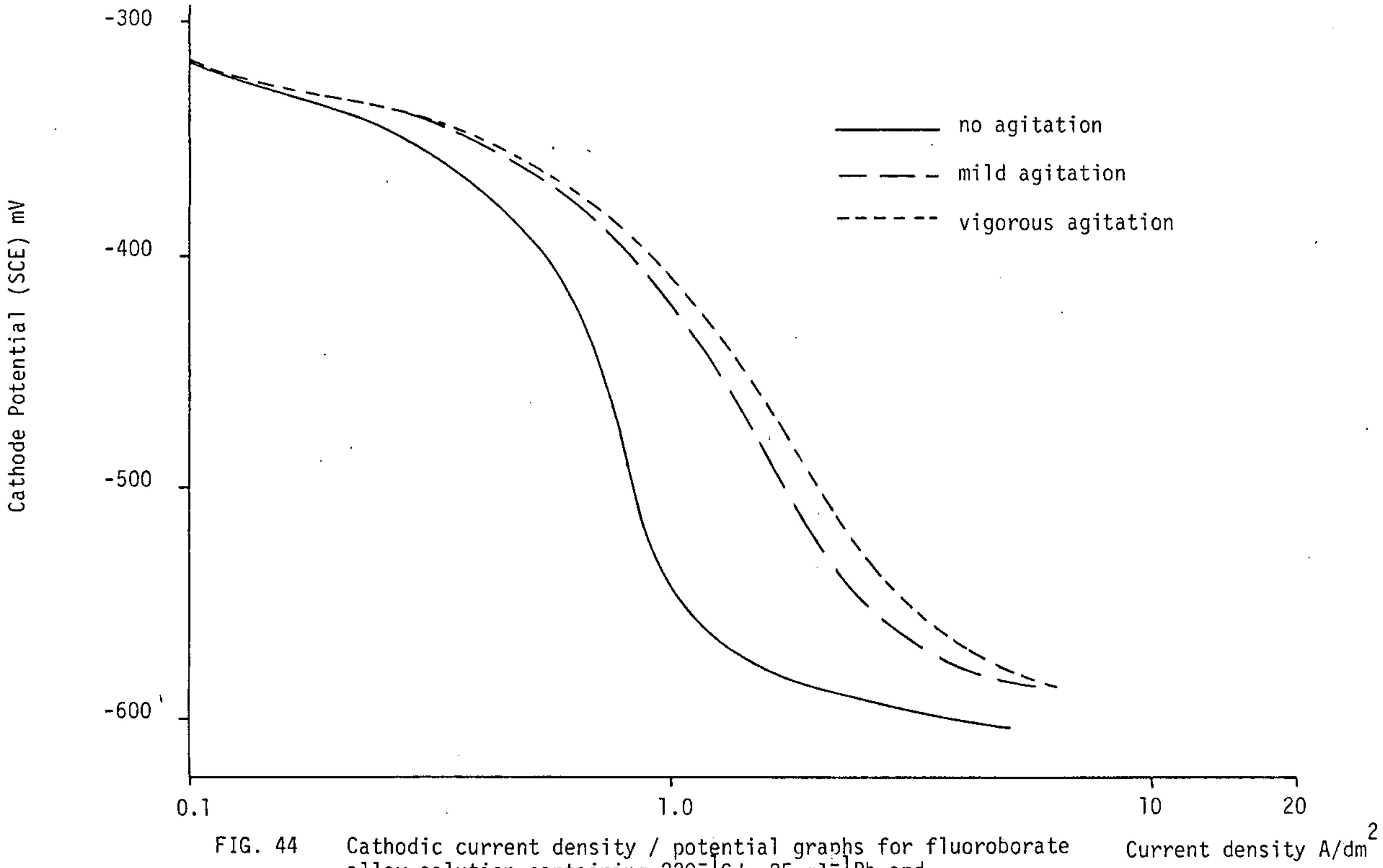


FIG. 44 Cathodic current density / potential graphs for fluoroborate alloy solution containing 220^{-1}Cd, 25 gl^{-1}Pb and 6 gl^{-1} resorcinol with varying degrees of agitation.

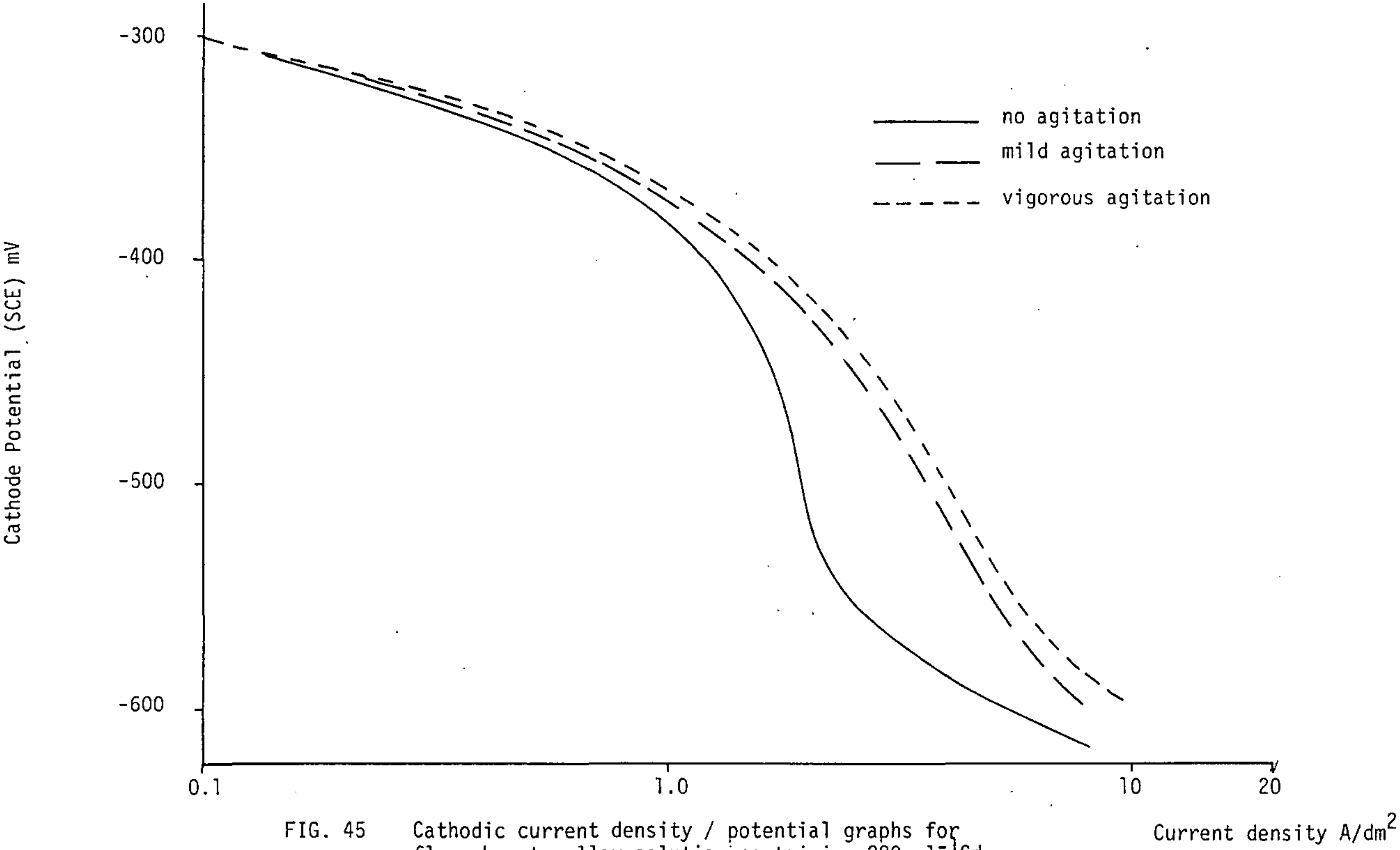


FIG. 45 Cathodic current density / potential graphs for fluoroborate alloy solution containing 220 gl^{-1}Cd, 50 gl^{-1}Pb and 6 gl^{-1} resorcinol with varying degrees of agitation.

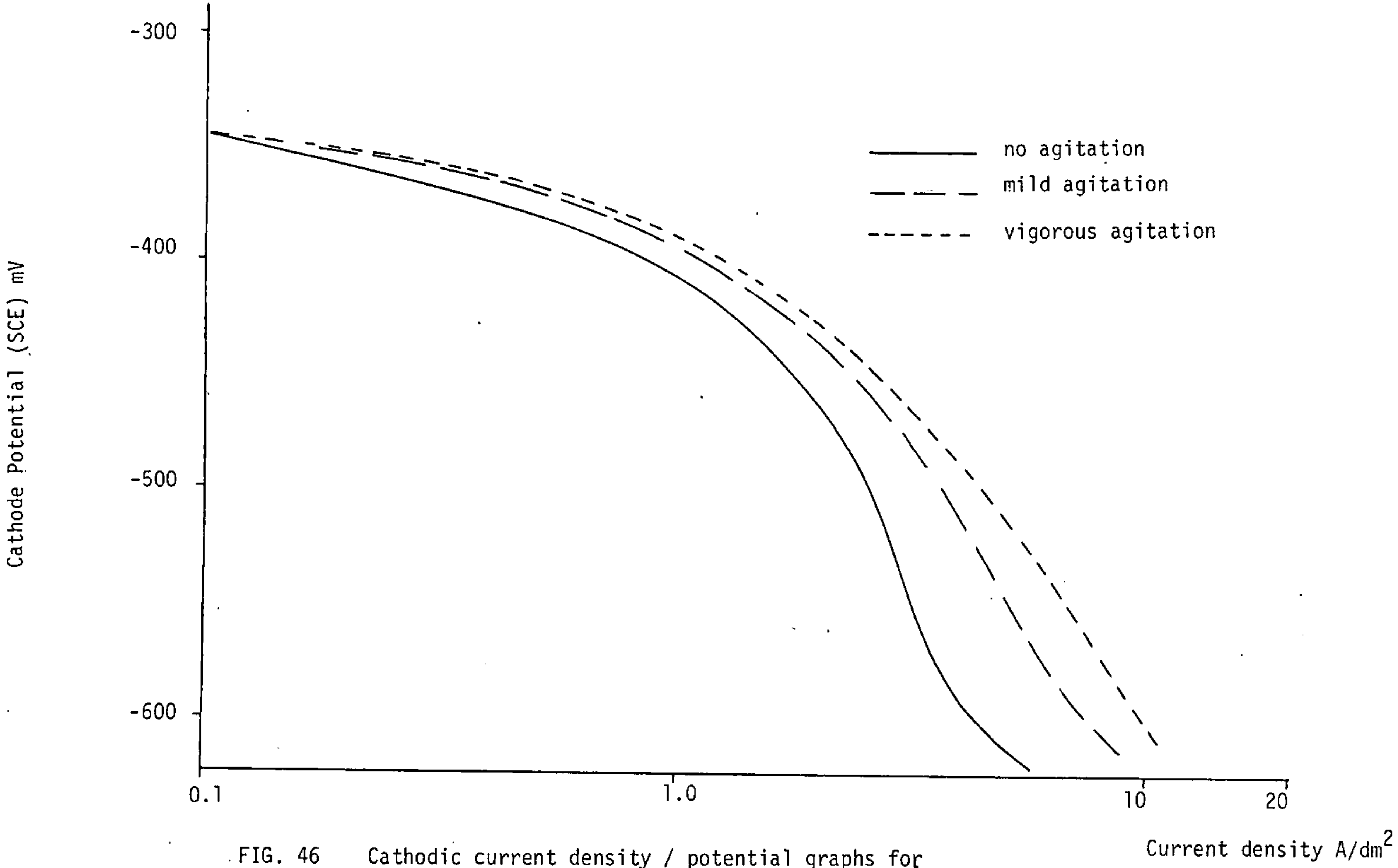


FIG. 46 Cathodic current density / potential graphs for fluoroborate alloy solution containing 220 gl^{-1}Cd, 75 gl^{-1}Pb and 6 gl^{-1} resorcinol with varying degrees of agitation.

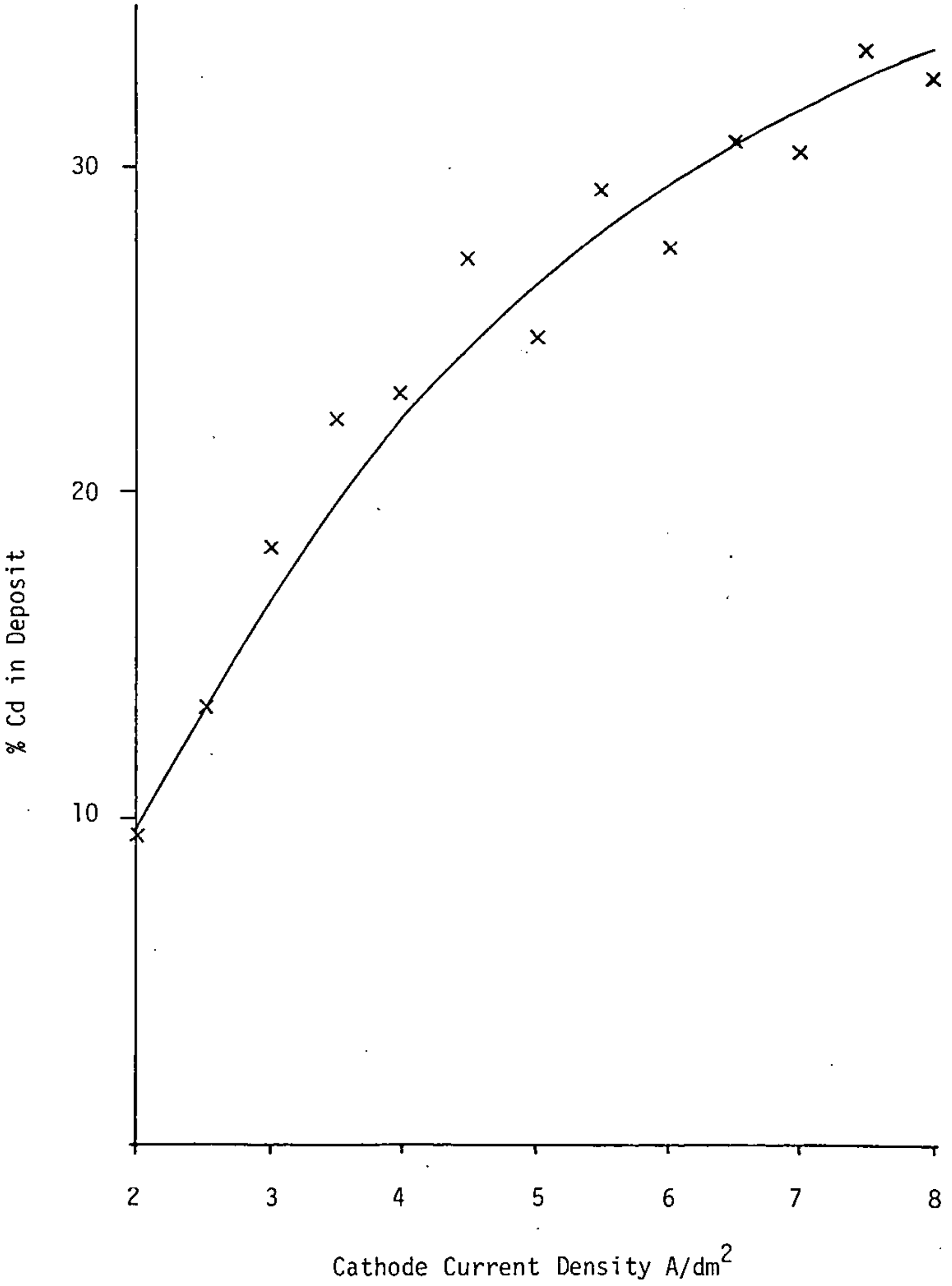


FIG. 47 Percentage cadmium in deposit plated galvanostatically from fluoroborate electrolyte containing 220 gl^{-1} cadmium, 50 gl^{-1} lead, 6 gl^{-1} resorcinol.

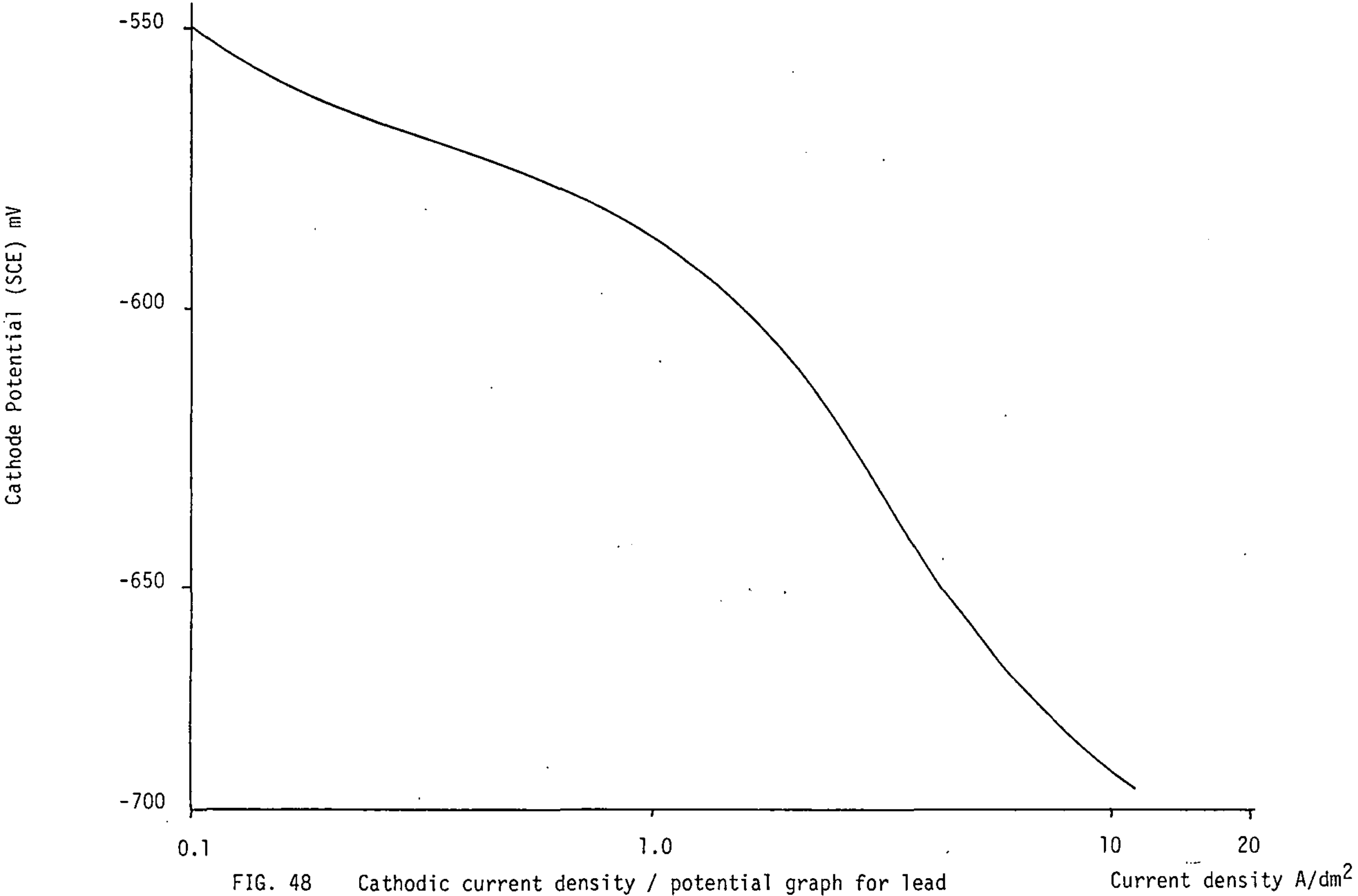


FIG. 48 Cathodic current density / potential graph for lead acetate - citrate solution at 60°C.

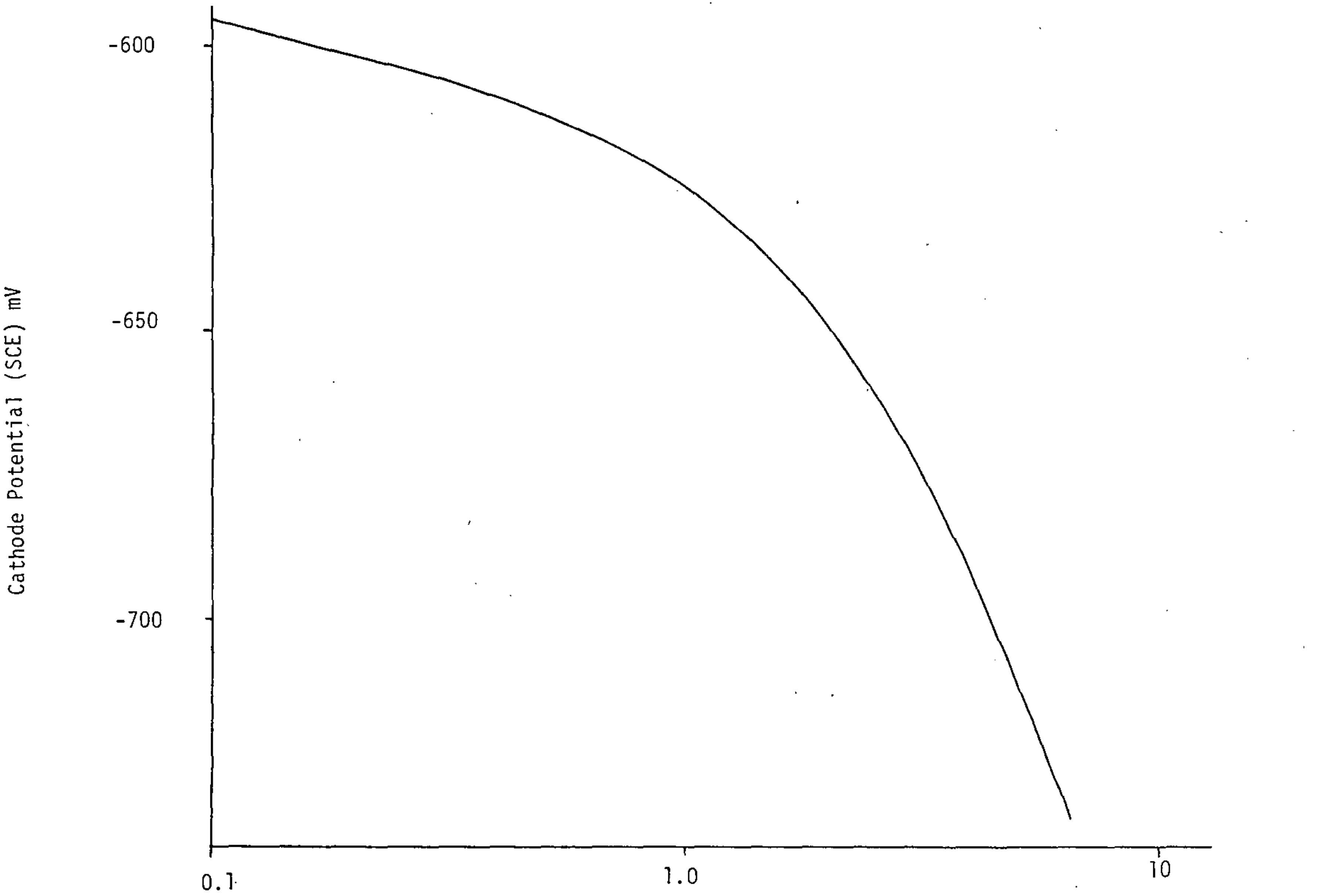


FIG. 49 Cathode current density / potential graph for acetate-citrate alloy solution at 60°C.

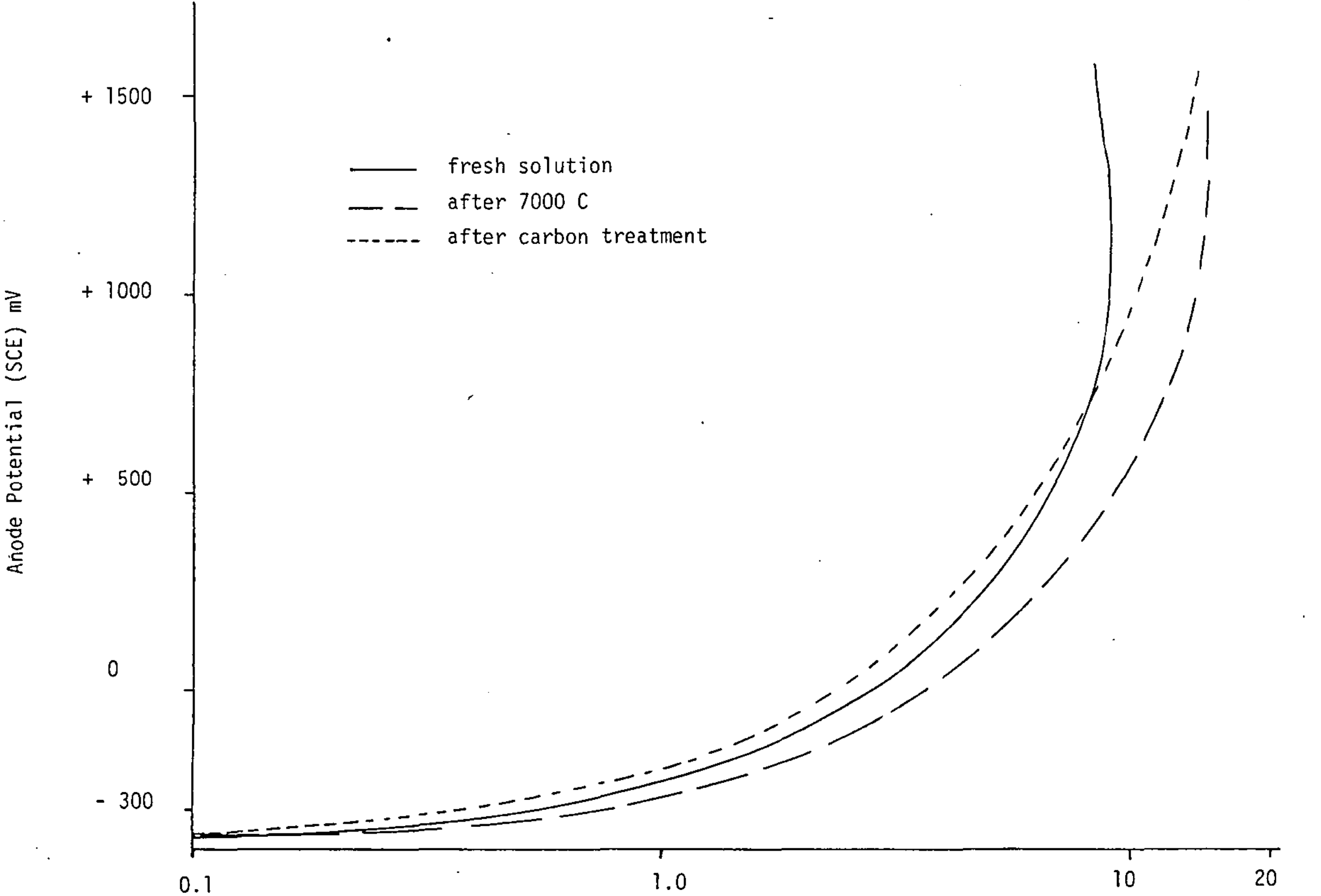


FIG. 50 Anodic current density / potential graph for fluoroborate solution containing 220 gl^{-1} cadmium, 50 gl^{-1} lead, 6 gl^{-1} resorcinol. Sweeps made on fresh solution, after 7000C and after carbon treatment.

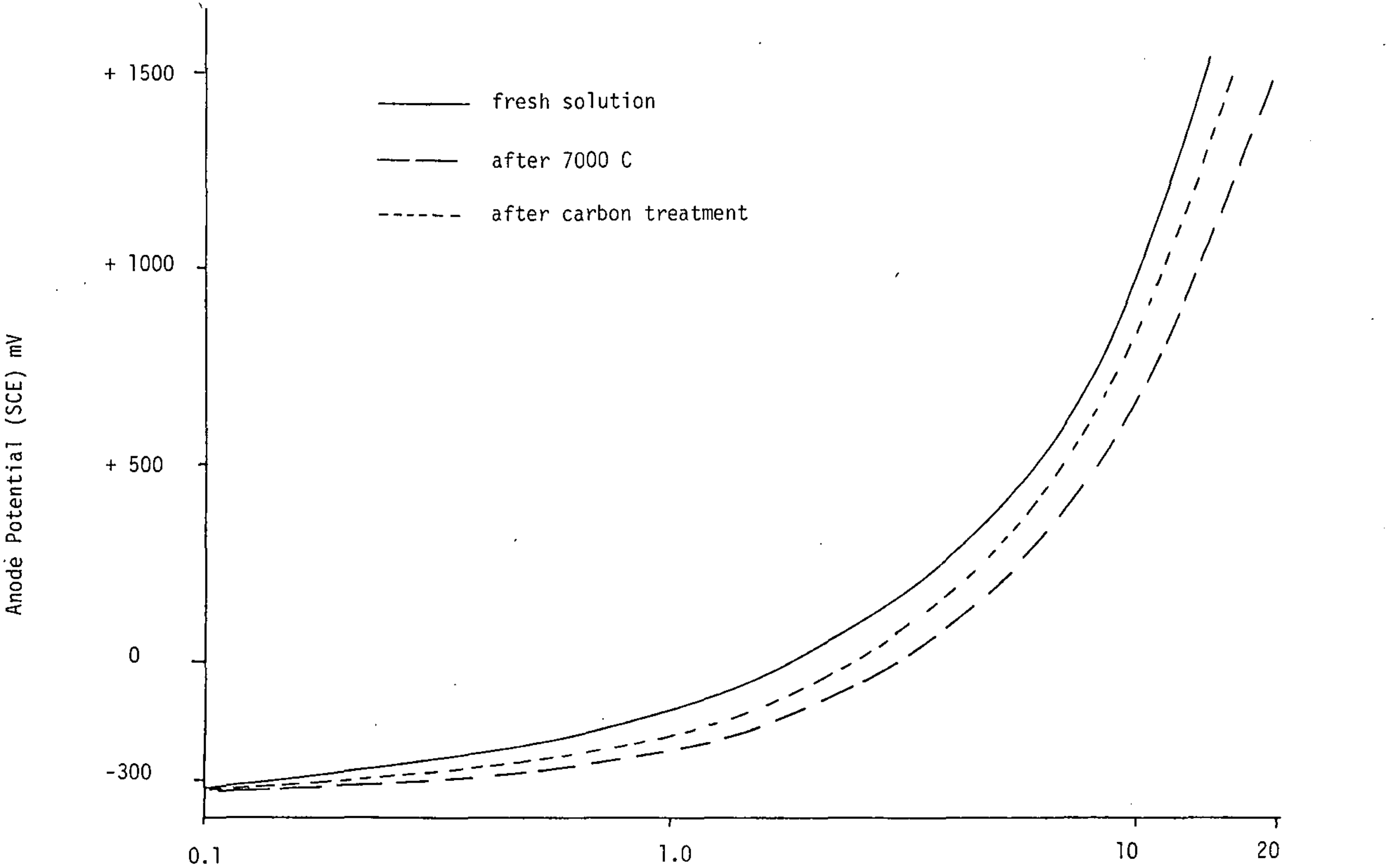


FIG. 51 Anodic current density / potential graph for fluoroborate solution containing 220 gl^{-1} cadmium, 50 gl^{-1} lead and 1 gl^{-1} peptone. Sweeps made for fresh solution, after 7000C and after carbon treatment.

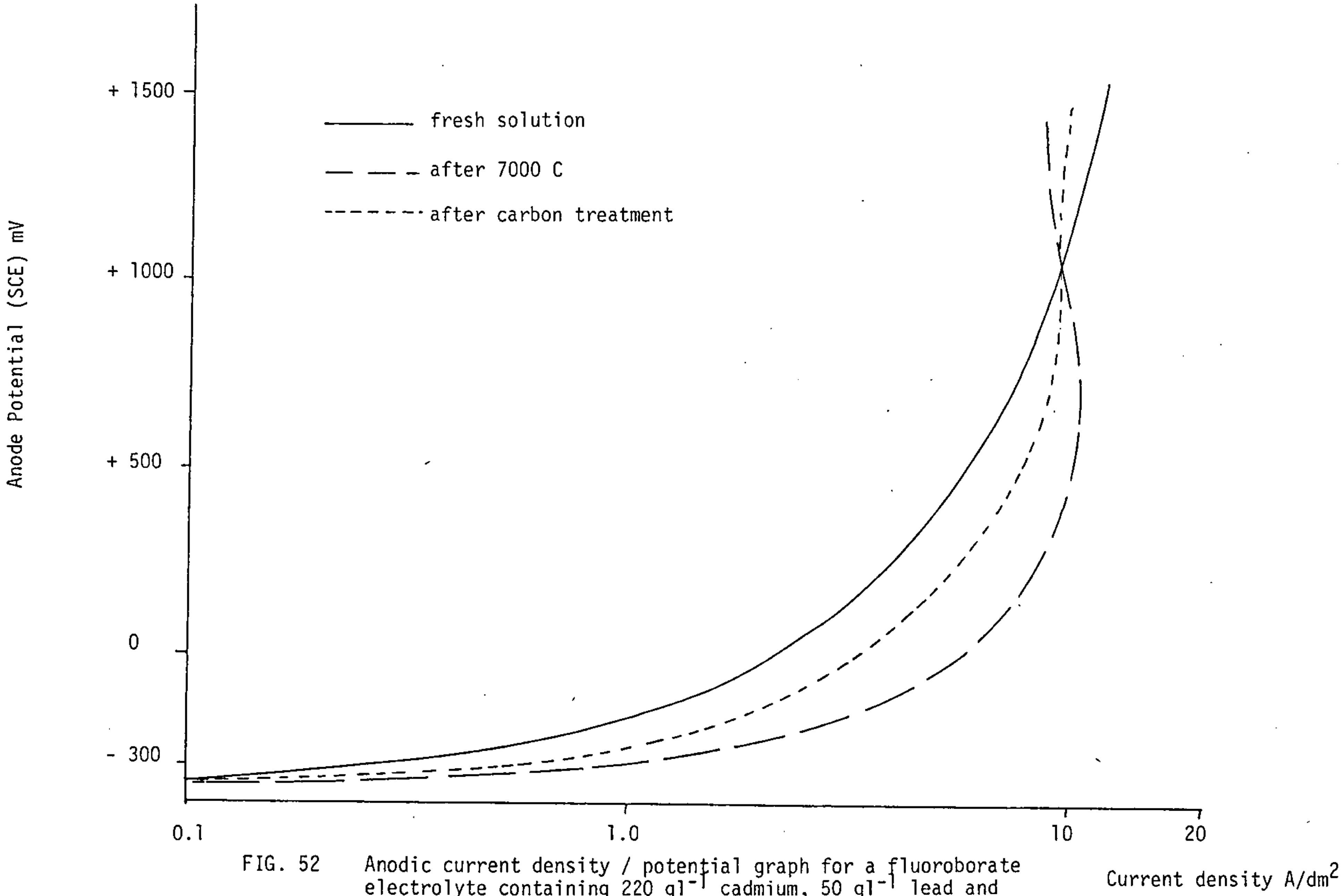


FIG. 52 Anodic current density / potential graph for a fluoroborate electrolyte containing 220 gl^{-1} cadmium, 50 gl^{-1} lead and 1 gl^{-1} polyethyleneglycol. Sweeps made on fresh solution, after 7000C and after carbon treatment.

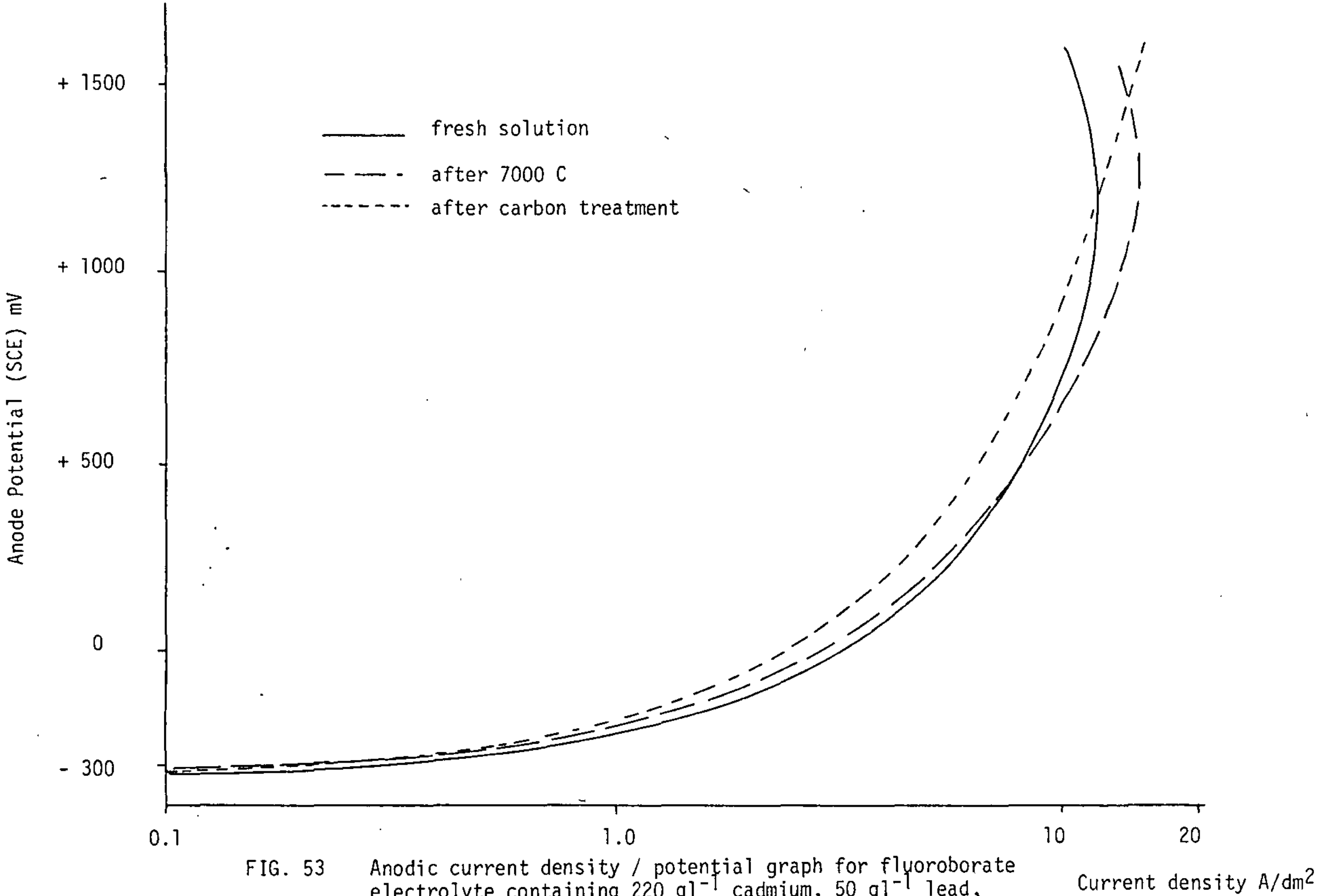


FIG. 53 Anodic current density / potential graph for fluoroborate electrolyte containing 220 gl^{-1} cadmium, 50 gl^{-1} lead, 6 gl^{-1} resorcinol, 1 gl^{-1} peptone, 1 gl^{-1} polyethyleneglycol. Sweeps made on fresh solution, after 7000C and after carbon treatment

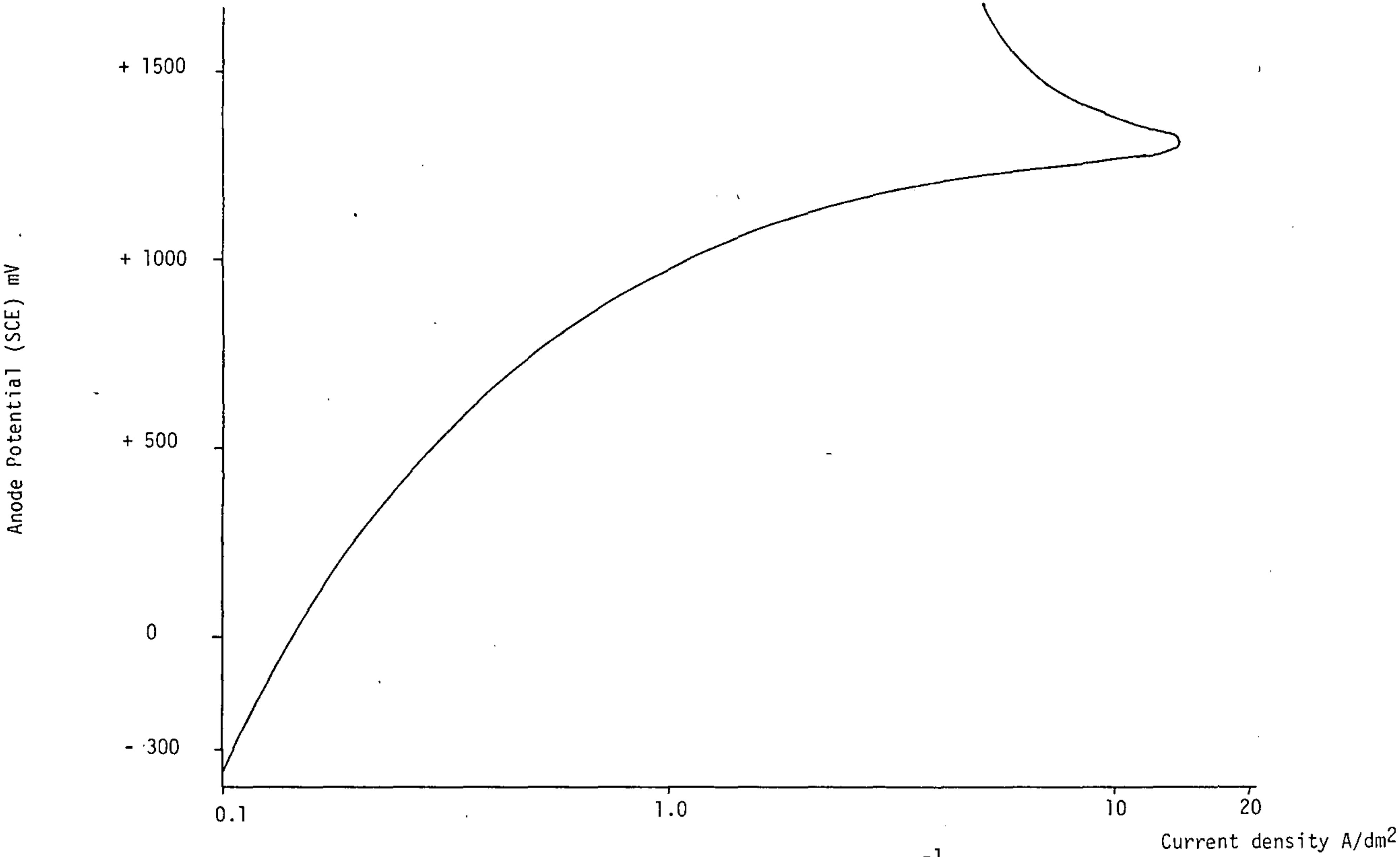


FIG. 54 Anodic current density / potential graph for 6 gl^{-1} resorcinol in 0.2M Na_2SO_4 pH adjusted to 2 by H_2SO_4.

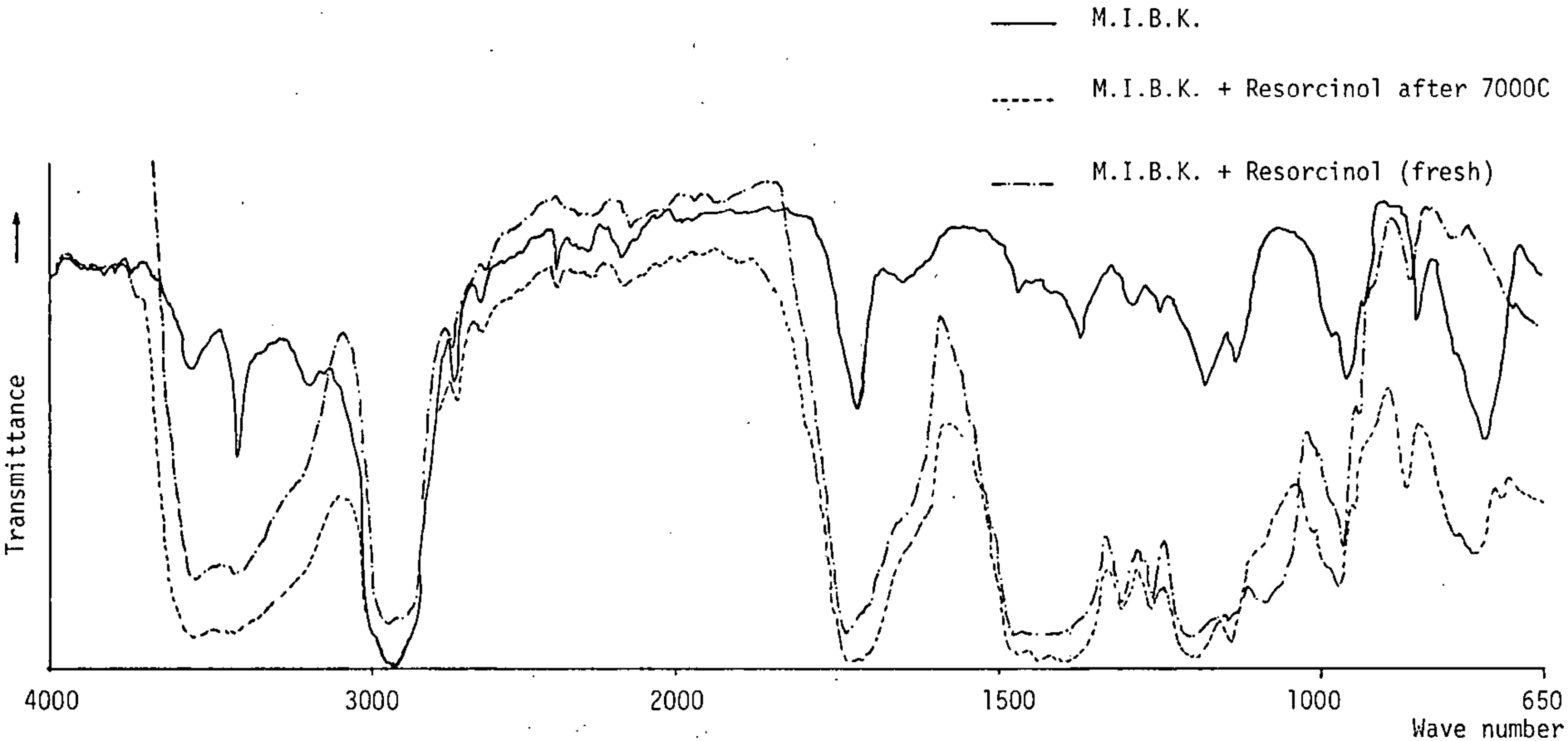


FIG. 55 Typical IR Spectra for M.I.B.K.; Resorcinol extracted into M.I.B.K. and Resorcinol after 7000C passed through plating bath then extracted into M.I.B.K.

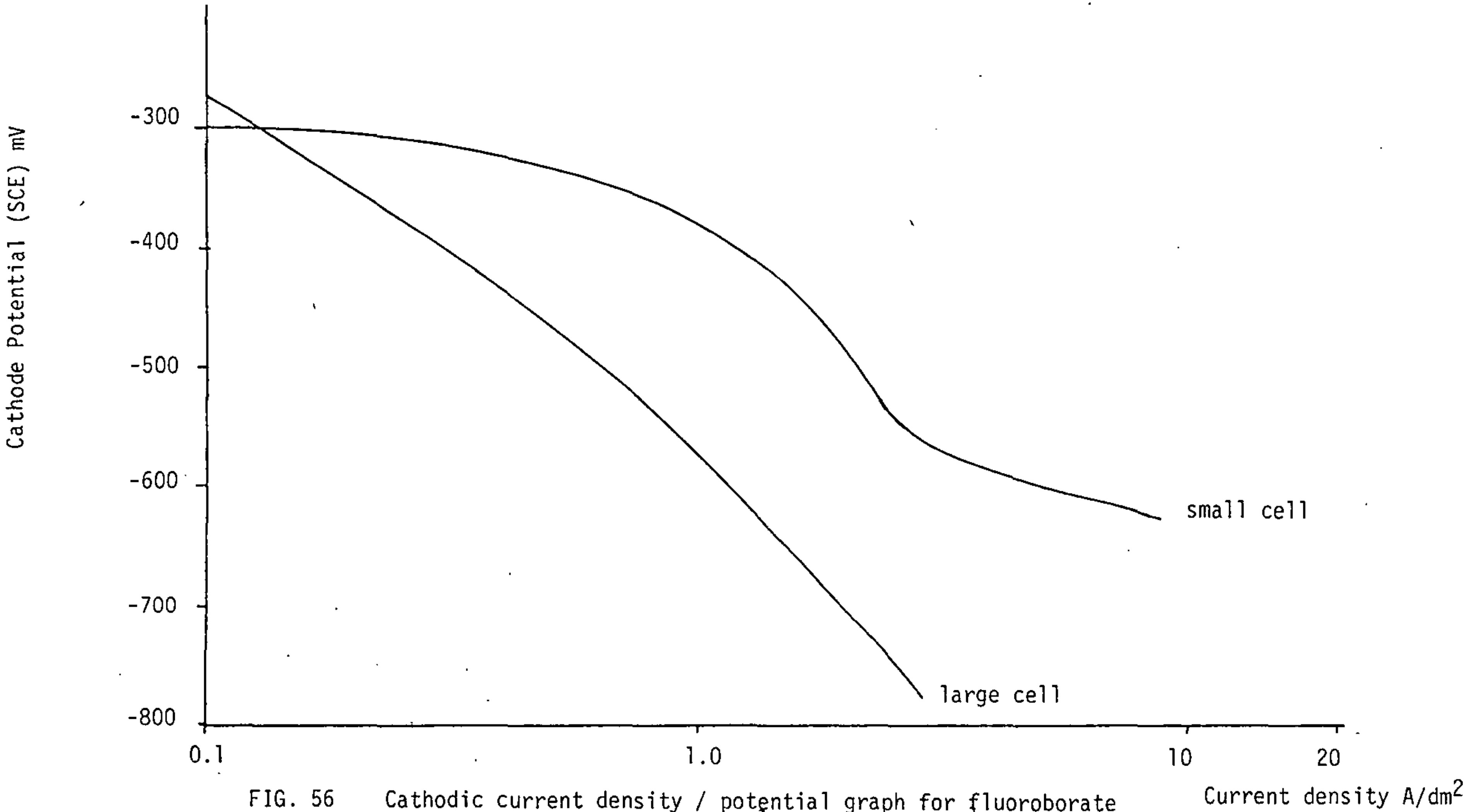


FIG. 56 Cathodic current density / potential graph for fluoroborate electrolyte containing 220 gl^{-1} cadmium, 50 gl^{-1} lead, 6 gl^{-1} resorcinol, 1 gl^{-1} peptone, 1 gl^{-1} P.E.G.. Sweeps made using small cell and large cell (effectively masked).

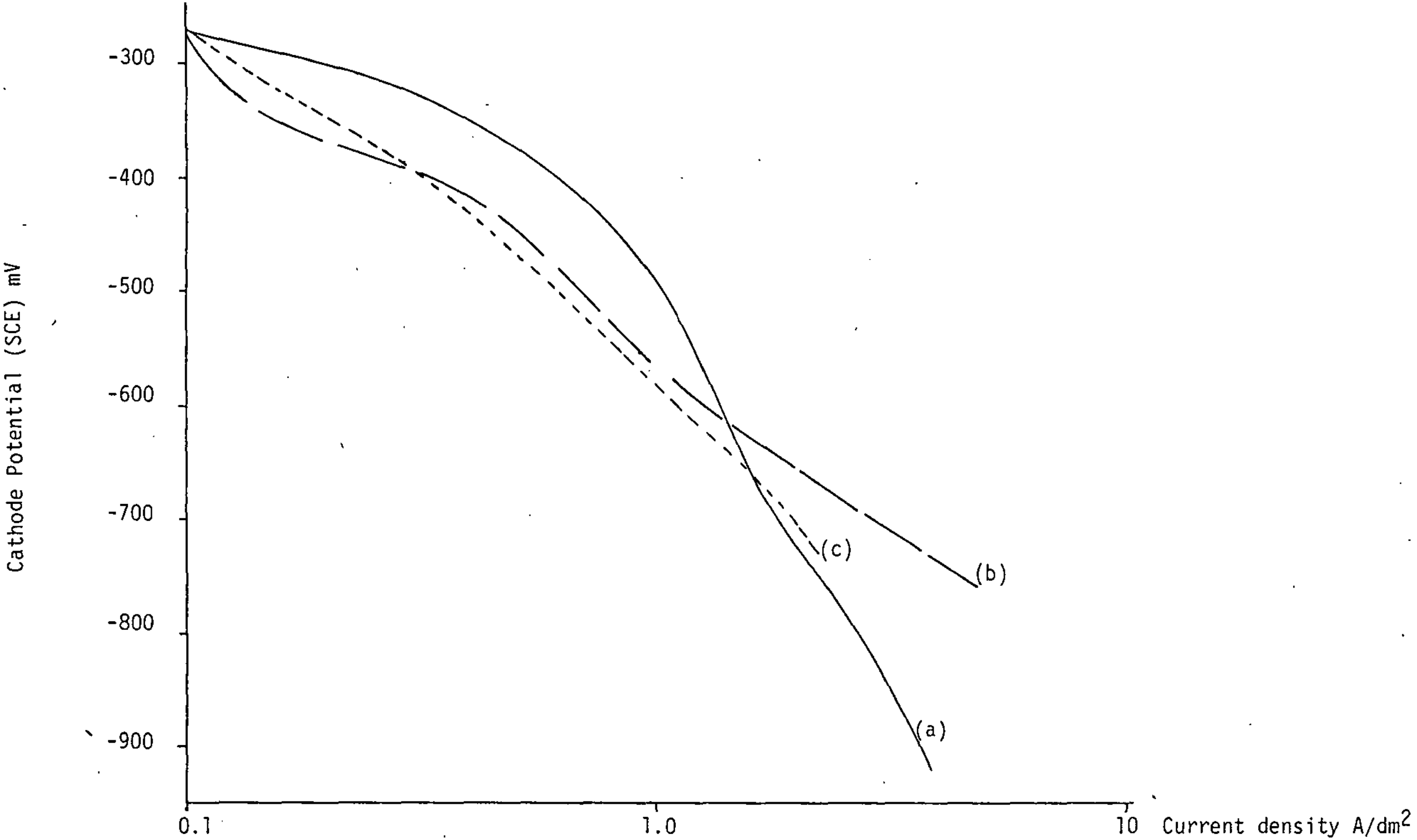


FIG. 57 Cathode current density / potential graphs for fluoroborate solutions containing 220 gl^{-1} cadmium, 50 gl^{-1} lead and addition agent. Addition agents were :
a) 6 gl^{-1} resorcinol
b) 6 gl^{-1} resorcinol and 1 gl^{-1} peptone
c) 6 gl^{-1} resorcinol, 1 gl^{-1} peptone and 1 gl^{-1} P.E.G.

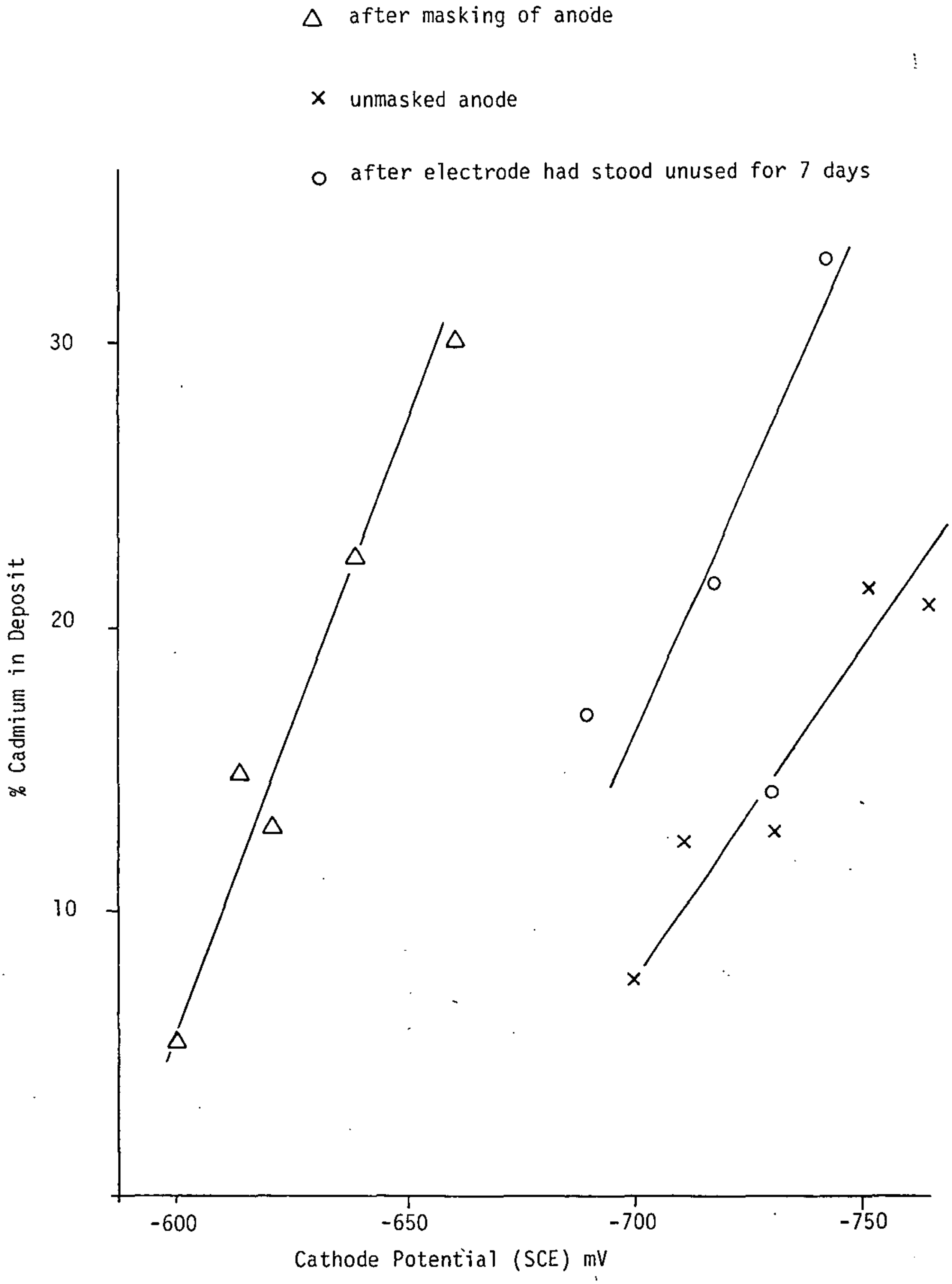
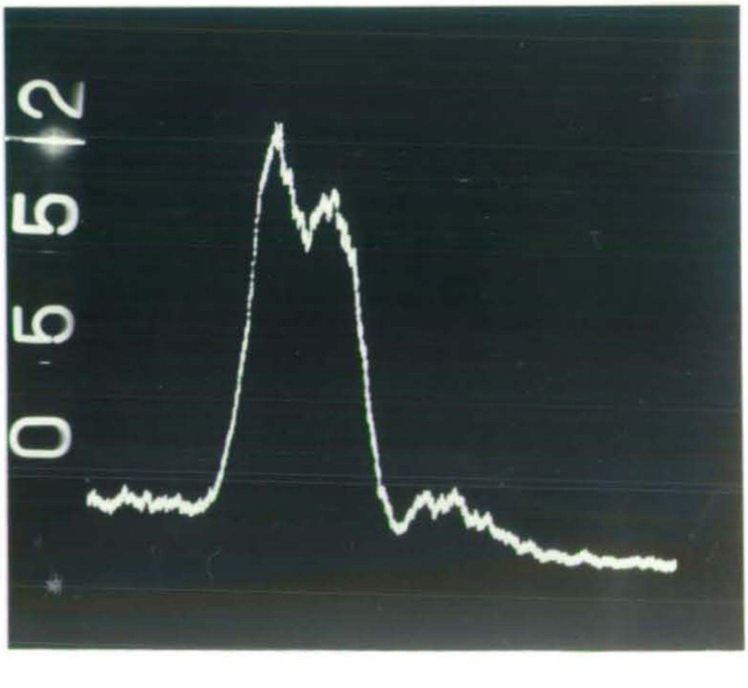


FIG. 58 Percentage cadmium in deposit plotted against deposition potential for the large cell.

FIG. 59 Electron micrograph of poor quality deposit plated from electrolyte which had stood unused for seven days. (Mag. x 500)

FIG. 60 Electron microprobe scan across raised lump in deposit shown in FIG. 59. Scan indicates cadmium rich areas


0 5 5 2

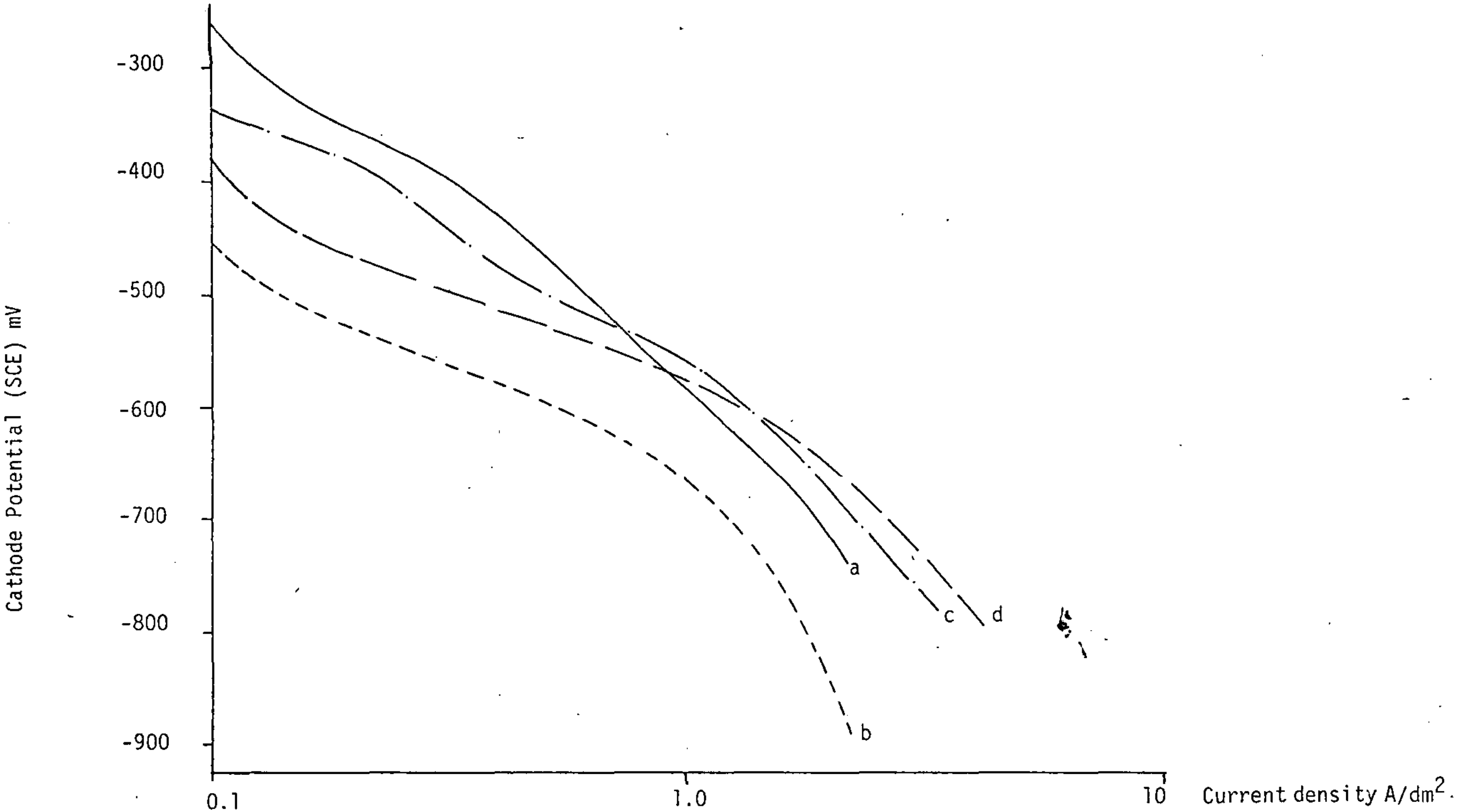


FIG. 61 Cathodic current density / potential graphs for fluoroborate electrolyte in large cell. Electrolyte composition 220 gl^{-1} cadmium, 50 gl^{-1} lead and 6 gl^{-1} resorcinol, 1 gl^{-1} peptone and 1 gl^{-1} P.E.G.

a) freshly made up solution, b) after standing 7 days unused, c) solution (b) with the addition of 1 gl^{-1} peptone, d) solution (c) with the addition of 1 gl^{-1} P.E.G.

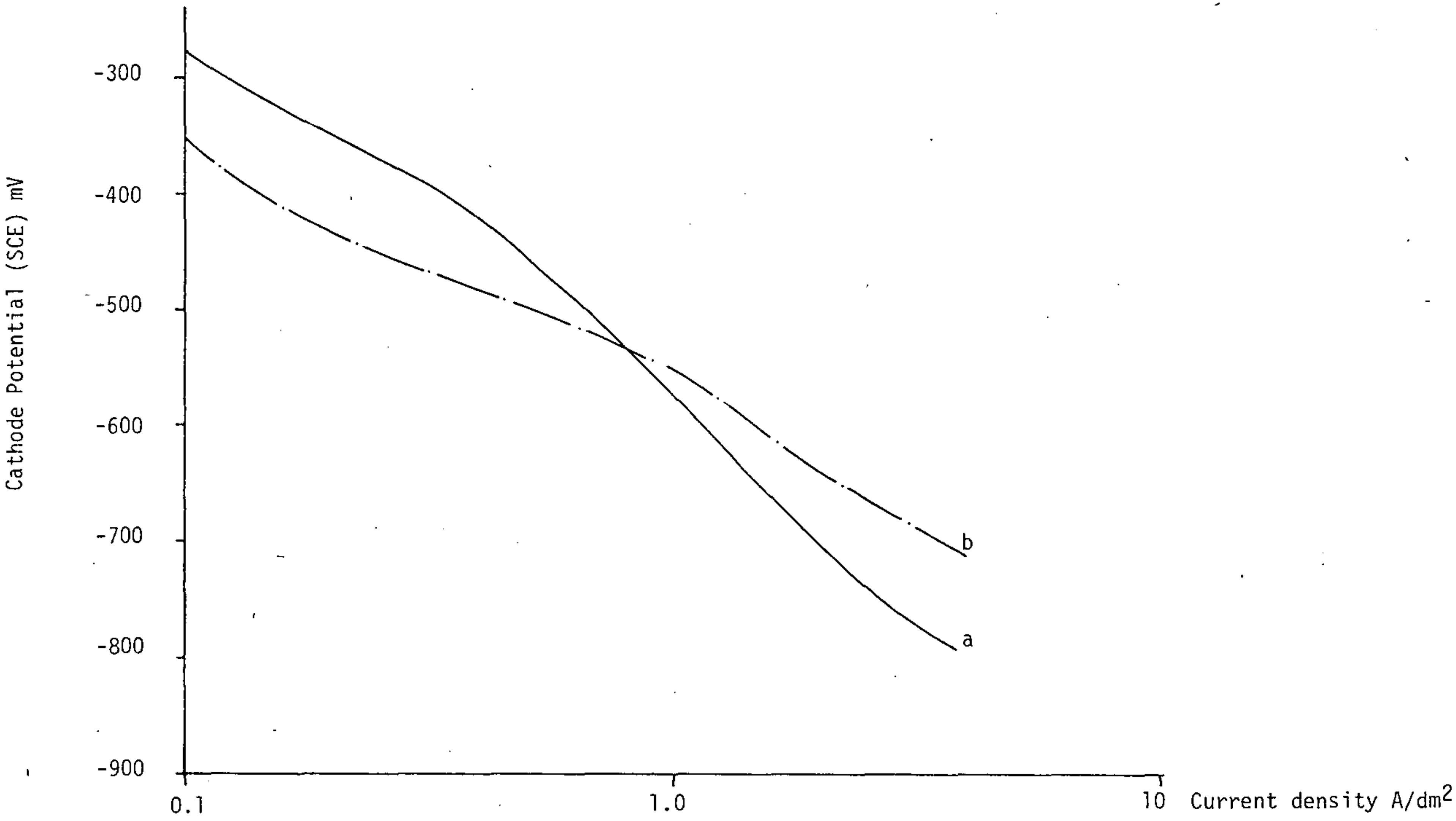


FIG. 62 Typical cathode current density / potential curves for large cell.
a) before the anode was properly masked, b) after masking the anode with P.T.F.E. tape.

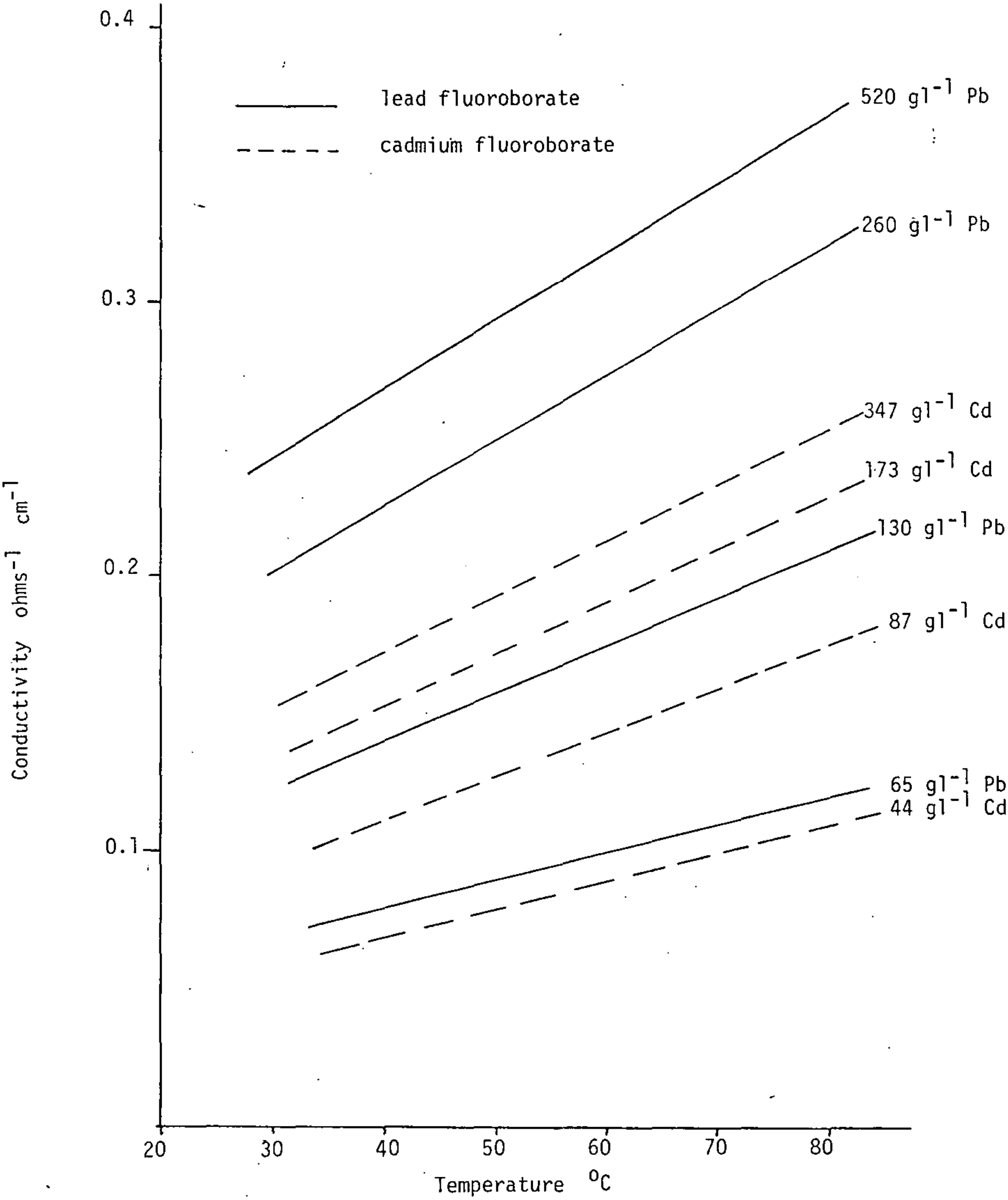


FIG. 63 Conductivity plotted agianst temperature for various concentrations of lead and cadmium fluoroborate.

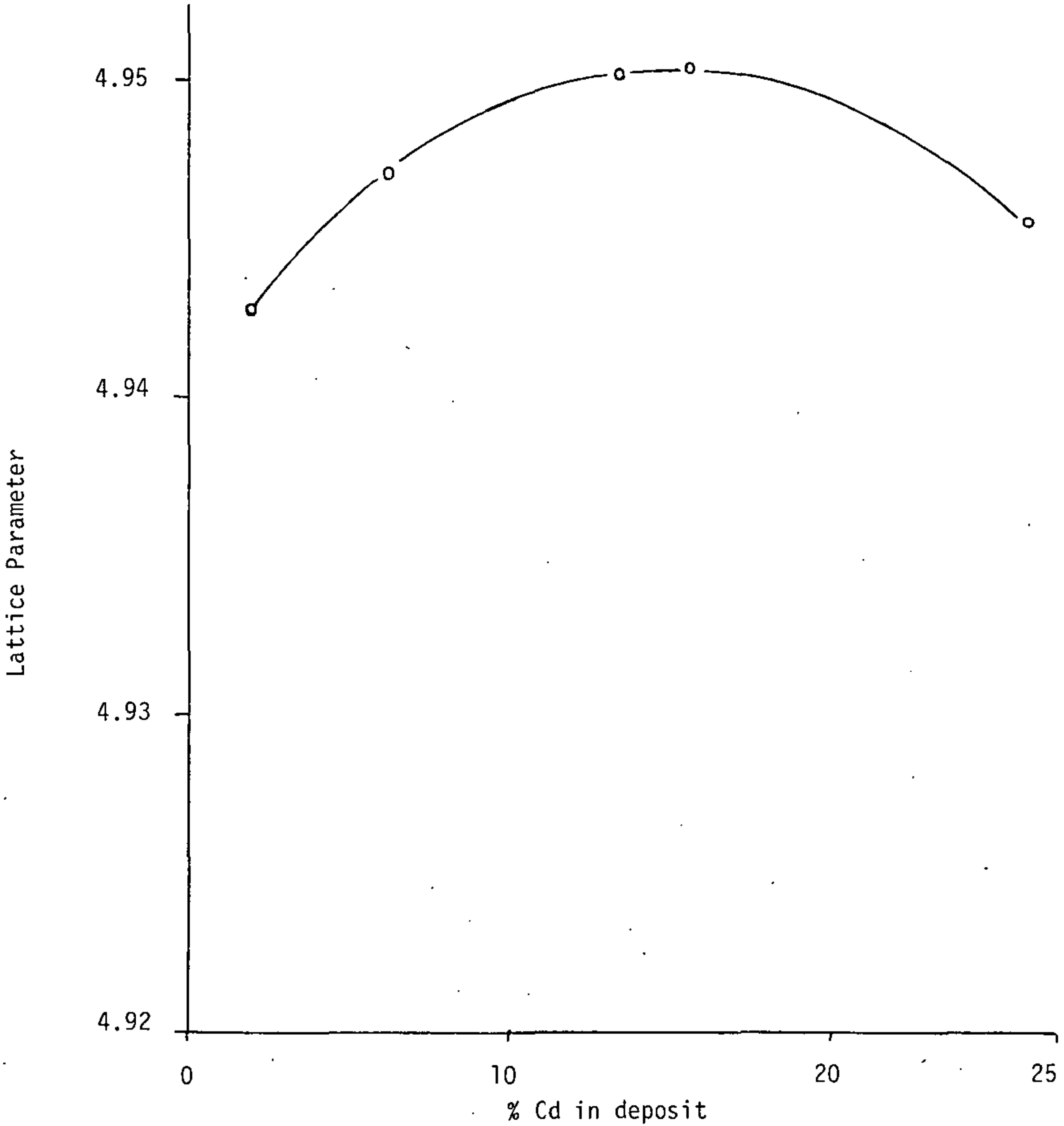
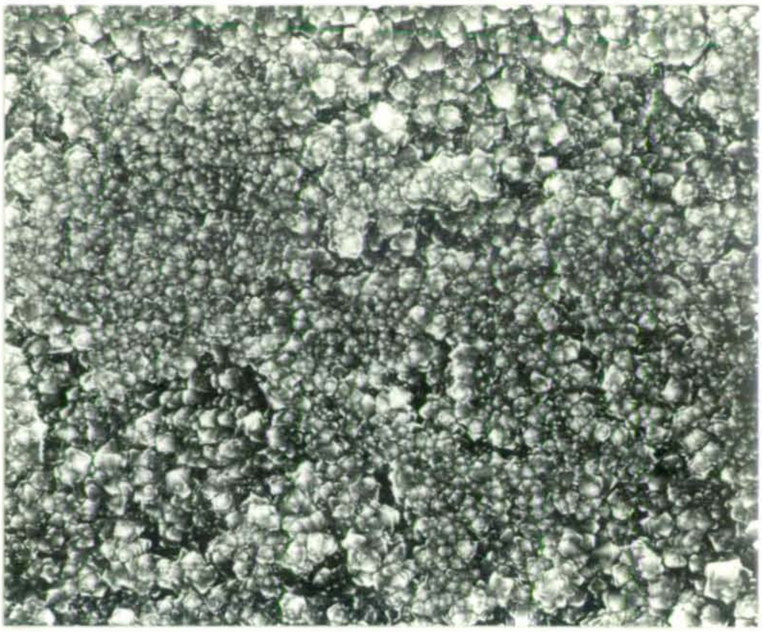


FIG. 64 Lattice parameter v percentage cadmium in deposit plated from fluoroborate electrolyte (220 gl^{-1} Cd, 50 gl^{-1} Pb, 6 gl^{-1} resorcinol, 1 gl^{-1} peptone, 1 gl^{-1} P.E.G.).

FIG. 65 Electron micrograph of lead-cadmium alloy deposit plated from a fluorosilicate electrolyte. (Mag. 2000 x)

FIG. 66 Electron micrograph of lead-cadmium alloy deposit plated from sulphamate electrolyte. (Mag. 2000 x)



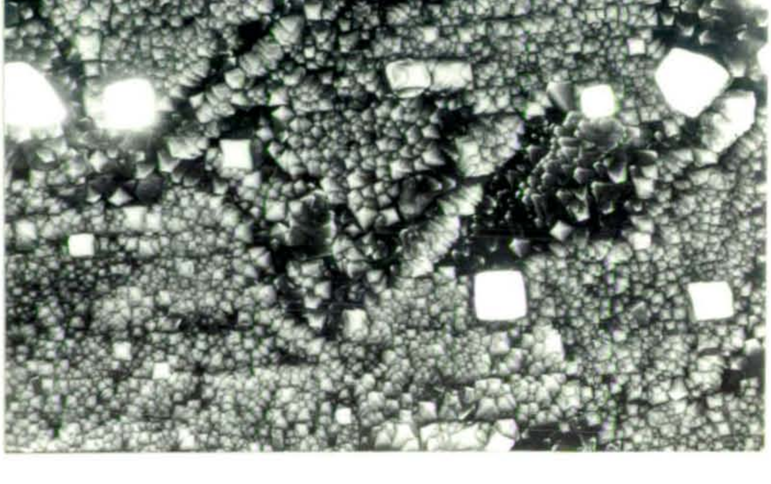
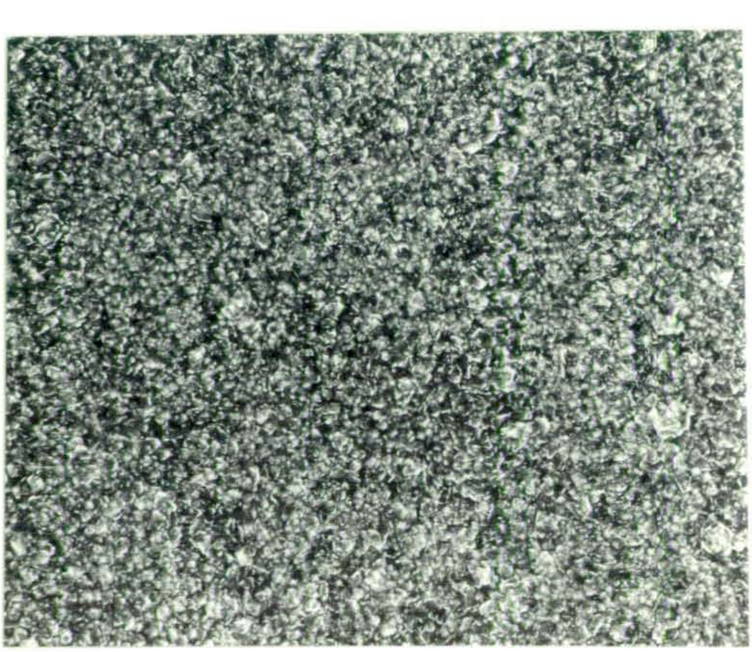


FIG. 67 Electron micrograph of lead-cadmium alloy plated from fluoroborate electrolyte containing resorcinol. (Mag. 2000 x)

FIG. 68 Electron micrograph of lead-cadmium alloy plated from fluoroborate electrolyte containing resorcinol, peptone and polyethylenglycol. (Mag. 2000 x)



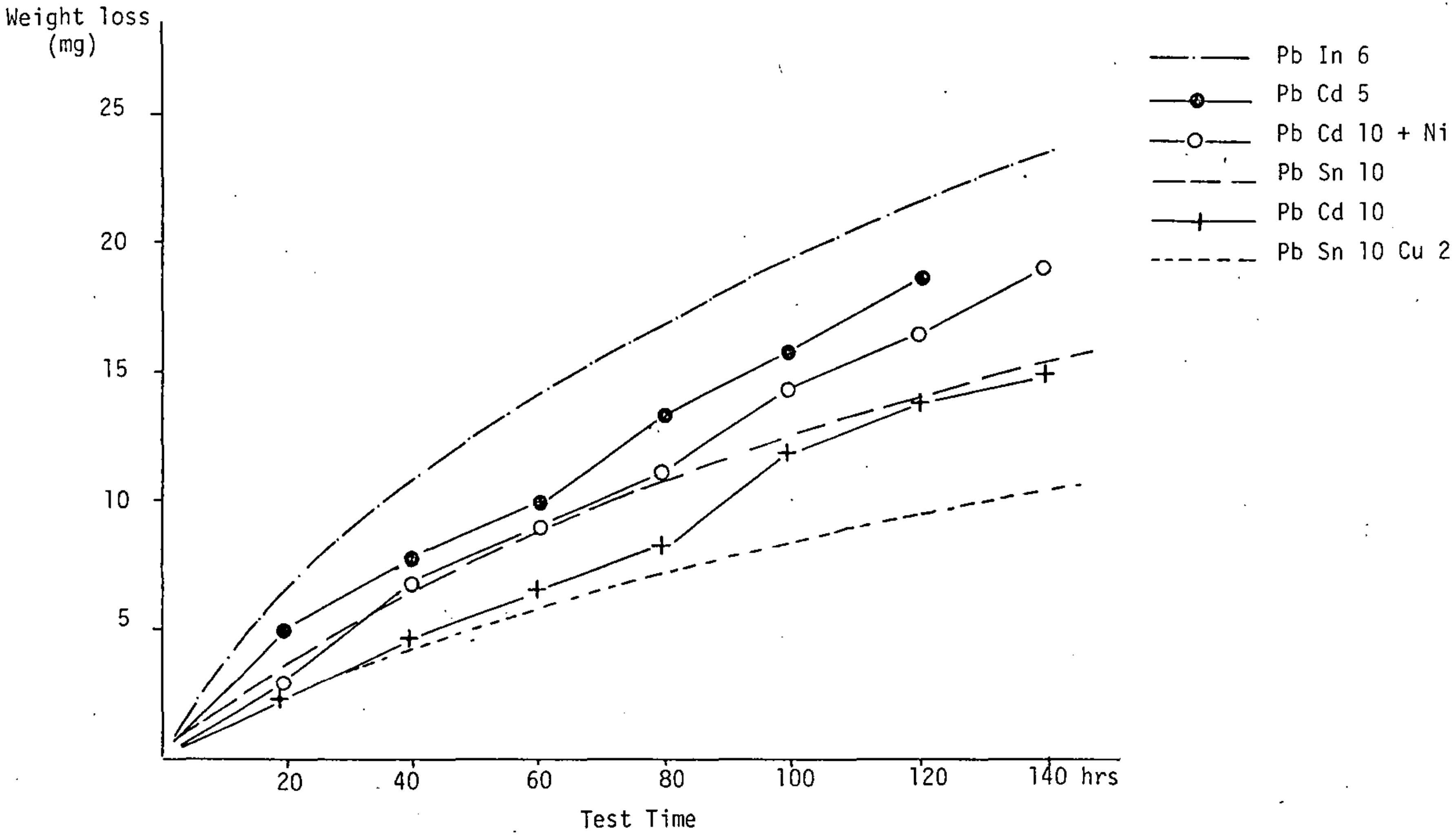


FIG. 69 Wear resistance for overlays of various compositions.[43]
Weight loss in mg plotted against test time in hours.

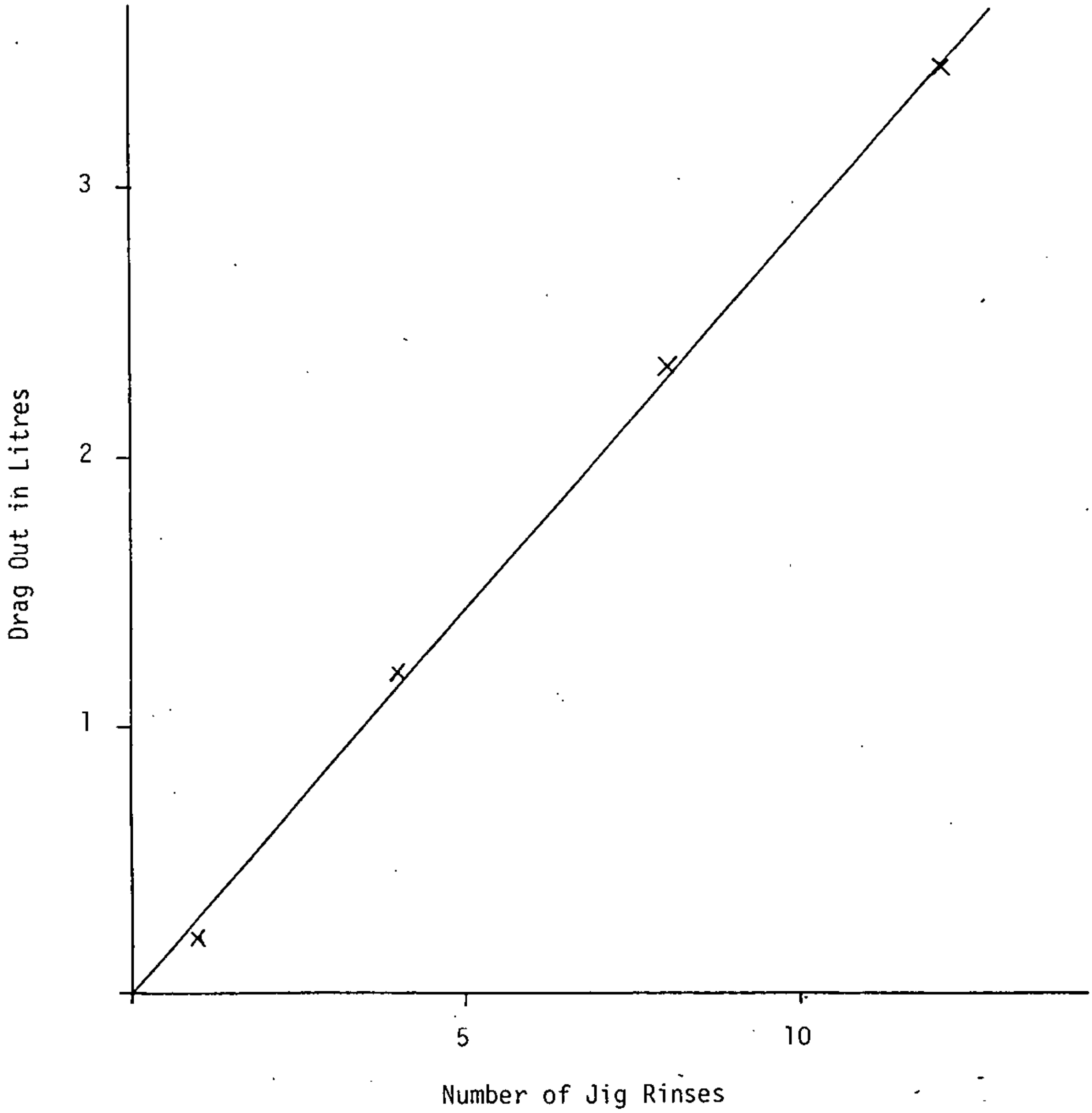


FIG. 70 Drag-out in litres from a Watts type nickel plating bath. 6 inch bearing jig used loaded with bearings.