

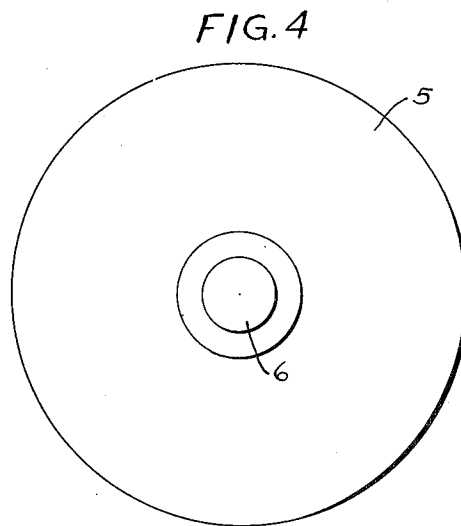
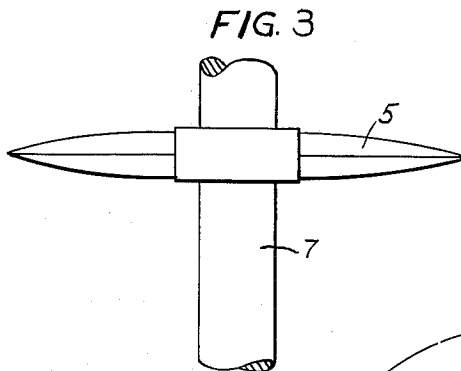
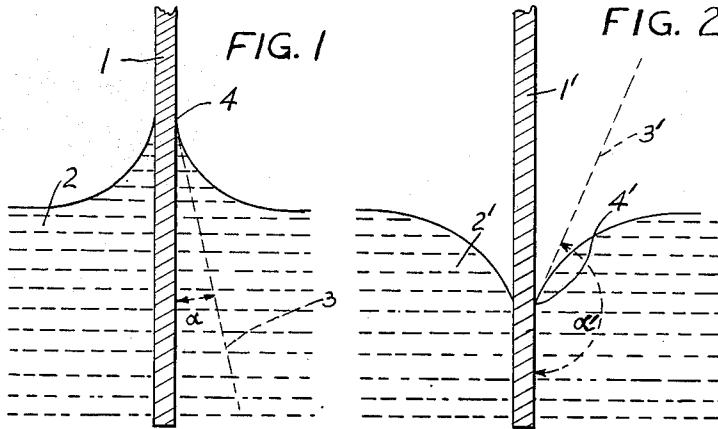
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PROCESS FOR THE PRODUCTION OF LEAD COATINGS

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## PROCESS FOR THE PRODUCTION OF LEAD COATINGS

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This invention relates to the production of lead coatings upon metallic surfaces by dipping; and more particularly to the production of coatings of lead upon iron, steel or copper by hot-dipping, and to the employment of such coated materials in the arts.

For many purposes it is desirable to protect with a coating of lead such metal surfaces as are exposed, for example, to the corrosive action of combustion products or of fumes from chemical processes, or of corrosive liquids, and one of the most convenient methods of coating is by hot dipping. Unfortunately it has not hitherto been possible to apply this method satisfactorily in the case of metals, such as iron, steel or copper, which are not readily wetted by liquid lead since in these cases "dewetting" of the lead almost invariably occurs and a continuous coating is not obtained.

By "dewetting" is understood in the art the spontaneous conversion of a more or less uniform continuous coating into a non-continuous coating with numerous "pores" and sometimes the agglomeration of the coating material into discrete globules. The time taken for a coating to dewet is a measure of the stability of the coating, and may be as little as a fraction of a second. A stable continuous coating is one which does not dewet in the time taken to remove the coated surface from the dipping bath and to cool it down to the solidifying point of the coating. The coating is said to be permanently continuous when the surface can be heated above the melting point of the coating and maintained at that temperature for periods of time sufficient to allow of any working operation being carried out, without dewetting intervening (such periods may, for example, be from 15 to 60 minutes).

It is usual, where dewetting occurs, to add to the lead a substantial proportion of a metal, such as tin, capable of forming an intermetallic compound with iron or copper. This may result in a reasonably permanent continuous coating, but the corrosion resistance of such coatings is considerably less than those of pure lead, and joints made between such coated surfaces are weak at elevated temperatures in comparison with joints between surfaces coated with pure lead. Attempts to overcome these defects by reducing the proportion of tin in the lead are unsuccessful because the coatings dewet.

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It is an object of this invention to provide smooth continuous lead coatings, having excellent adhesion and stability, by the hot dipping process on metals such as iron, steel and copper.

It is a further object to produce on metals such as iron, steel and copper by hot dipping lead-coated surfaces resistant to chemical corrosion. A still further object is to provide on such metals as iron, steel and copper by hot dipping lead-coated surfaces suitable for joining together by lead soldering or by sweating. A still further object is to provide on such metals as iron, steel and copper by hot dipping lead coatings which do not dewet on subsequent heat treatments even above the melting point of lead. Further objects will be apparent from the description which follows and from the accompanying drawings wherein

Figs. 1 and 2 illustrate metal objects partially immersed in liquid lead-containing baths;

Fig. 3 is a side elevational view of a portion of a heat exchange element; and

Fig. 4 is a plan view of the element shown in Fig. 3.

We have found that improved lead coatings on metals such as iron, steel and copper may be produced by hot dipping if there is used a lead bath containing a metal which, whilst forming no stable intermetallic compound with the metal to be coated, is sufficiently soluble in the metal to be coated and in lead to enable it to lower the "contact angle" between the solid metal and the liquid lead to below 15°, usually almost to 0°.

The expression "contact angle" can best be explained by reference to the accompanying drawings, in which 1 and 1' represent sections of a solid sheet dipped vertically into liquids 2, 2'. In Fig. 1 the meniscus is positive and reaches the solid sheet at 4. The contact angle,  $\alpha$ , is the angle made by the immersed portion of the solid sheet with the tangent 3 to the curve of the meniscus at the point 4. Similarly in Fig. 2, where a negative meniscus is shown, the contact angle,  $\alpha'$ , is the angle the tangent 3' makes with the immersed portion of the solid sheet. If the solid is perfectly wetted by the liquid, the meniscus is positive and the contact angle is 0°. At the other extreme the meniscus is negative and the contact angle exceeds 90° and approaches 180°.

In observing the wettability of a solid by liquid

lead, the solid should be dipped vertically into the liquid lead and then partially withdrawn. The meniscus between the liquid lead and that part of the solid which has been immersed and withdrawn indicates the true state of affairs, and the contact angle of this meniscus is a measure of the wettability.

A rapid and convenient method of measuring the contact angle is to suspend a sheet of metal vertically in a bath of liquid lead in an atmosphere of hydrogen, the suspension means including a length of resistance wire. The electrical resistance of this length of wire will vary according as the tension upon it varies, and the tension will increase as the angle of contact decreases. Measurement of the resistance of the length of resistance wire, e. g. by means of a Wheatstone bridge, gives a measure of the contact angle, and by reference to a scale of resistances graduated for the particular apparatus used the actual value of the contact angle can be read off.

From observations of the contact angle on withdrawal of a sheet of iron, steel or copper from a bath of liquid lead to which various additions have been made, we have discovered that the presence in the lead of even very small proportions of nickel, cobalt, manganese or chromium (or of silver in the case of copper sheets) is sufficient to increase the wettability of the solid metal by the liquid lead. A negative meniscus with pure lead becomes a positive meniscus with the modified lead bath; and where the meniscus was originally already positive, the contact angle is further reduced by the modification of the lead.

The most effective of these additions is nickel, probably on account of its ready solubility in lead, iron, steel and copper.

The present invention is based on the foregoing discoveries and consists in a dipping process for the production of lead coating on iron, steel and copper, which show in liquid lead a contact angle greater than 50°. According to the invention we use, when coating such metals by dipping, a bath of liquid lead containing nickel in solution which reduces the contact angle to below 15° and is soluble in but forms no stable intermetallic compound with the metal to be coated.

Any type of cast iron may successfully be lead-coated by the process of our invention. Where grey cast iron is to be coated, the surface must, of course be subjected to one of the usual treatments for the removal of graphite, and the best results are obtained with an iron in which the graphite is finely divided and uniformly disseminated.

Any plain carbon steel, including mild steel, ingot iron and low alloy steel, may successfully be lead-coated by the process of the invention. On high alloy steels improved lead coatings may also be obtained.

Under copper we include tough pitch, oxygen-free, and de-oxidised copper, and copper alloys containing a predominating proportion of copper. Improved coatings, compared with those of the prior art, are obtainable on such copper alloys, but certain copper alloys, for example aluminium- and beryllium-bronzes, are known to require special treatments when being soft-soldered and the same special treatments are necessary when coating with lead according to the invention.

The lead may be virgin lead, commercially pure

lead or "chemical" lead (i. e. lead suitable for protection of parts of plant from corrosive attack). It also includes those lead alloys which do not wet iron, steel and copper (as, for example, lead alloys containing tellurium or copper).

In addition to alloying elements as mentioned in the preceding paragraphs the iron, steel, copper and lead may, of course, contain minor portions of other elements commonly added during manufacture, and incidental impurities.

Throughout the specification and claims the words "iron," "steel," "copper" and "lead" are used with the significance hereinbefore defined, and the expression "solid iron, steel or copper" includes articles of all kinds made from these metals.

The nickel may be present already in the lead or may be added to the molten lead in the form of metallic nickel or as a nickel-lead hardener.

Where the lead bath is prepared by dissolving nickel in the molten lead, the added nickel may be as little as 0.01 per cent by weight of the lead, or may be as much as can be dissolved in the liquid lead at dipping temperature. For consistently satisfactory results we prefer to use 0.1 per cent of nickel.

The solid iron, steel or copper is prepared for lead coating by first degreasing and pickling in the usual manner. It has been found that the good coating properties of the nickel-containing lead are enhanced by prior roughening of the metal to be coated. For pickling iron or steel we therefore prefer hot sulphuric acid of 10 per cent concentration without the addition of an inhibitor (i. e. a substance which, when added to the pickling bath confines the attack of the acid to any oxide present and prevents attack and pitting of the metal), but mechanical methods of surface roughening, e. g. scratch brushing, may be used, followed by cleaning in inhibited acid. For roughening copper, acidified solutions containing ferric sulphate or ferric chloride have been found suitable.

The prepared solid metal is washed and treated with a flux. The flux may be, for example, aqueous zinc chloride or zinc ammonium chloride, but zinc salts are not essential. We have successfully used hydrogen gas or an aqueous solution of equal parts by weight of chlorides of lithium, potassium and ammonium.

A very convenient method of applying the flux in the case of zinc ammonium chloride is to float the melted flux on the surface of the molten lead so that the metal to be dipped passes through a layer of liquid flux into the liquid lead. The actual dipping is carried out in the usual manner.

The lead coatings produced by dipping according to the invention are smooth, continuous and relatively free from pores. No other method of lead coating by hot-dipping hitherto employed gives coatings so free from porosity in the case of iron, steel and copper. The coatings are ordinarily from 0.001 to 0.0002 in. thick and are not destroyed by subsequent working or by heating even above the melting-point of lead. The uniformity and nonporosity of the lead coatings produced according to the invention enables them to serve purposes for which much heavier coatings have hitherto been used, as, for example, for the lining of trunk pipes for the conveyance of corrosive gases in chemical works.

The proportion of nickel (0.1 per cent in the dipping bath) normally employed according to the invention compares very favourably with the

higher proportion of tin or other intermetallic compound-forming addition to the lead previously proposed, and the consequent economies are considerable.

The stability of the lead coatings produced according to the invention makes it possible to build upon them lead coatings of any desired thickness by burning on more lead. This "homogenising" process may be applied to the lead-coating articles of our invention in the usual manner, e. g. by melting a lead rod progressively by means of a blow-pipe flame whilst moving the rod in a series of parallel lines along the face of the article.

The process of the invention provides in the case of certain articles, e. g. heat exchangers, a useful method of simultaneously lead-coating and lead-soldering. In the manufacture of one type of heat-exchanger, for example, radial copper fins are fitted to a central hollow copper tube. Figs. 3 and 4 show in elevation and plan, respectively, a simplification of such a heat-exchanger. The fin 5 is provided with central hole 6 through which the tube 7 passes, forming a tight fit. When all the fins have been placed in position on the central tube, the article must be protected from corrosion by a lead-coating, and the joints between the fins and the central tube need to be made as solid as possible so as to facilitate the transfer of heat from the fins to the tube and vice versa. When such an article is coated with lead by dipping in a bath of molten lead containing nickel in accordance with the invention, it is found that the lead penetrates the difficultly accessible, fine spaces between the fins and the central tube and very satisfactory joints are produced. Other assemblies made of iron, steel or copper, may similarly be lead-coated and at the same time effectively joined by the dipping process of the present invention.

Surfaces of iron, steel or copper coated with lead according to the invention are particularly suitable for soldering together, using as solder lead or a lead alloy melting above 300° C. The use of such solders with iron, steel or copper has not been satisfactory hitherto, and it has been necessary to employ solders containing substantial proportions of tin, with consequent undesirable effects on the mechanical properties of the joints at elevated temperatures and on their service life. The present invention thus makes possible, in the soldering of iron, steel and copper surfaces, the use of lead and lead alloys hitherto found unsatisfactory.

Coated surfaces produced by the present invention can also be joined together by sweating.

A further advantageous application of the invention is found in the annealing stage in the wire-drawing of iron or steel. In the manufacture of such wire it is known that the material becomes hardened by the repeated drawing between the dies, and must at intervals be annealed by passing it through a bath of molten lead; particles of lead adhering to the wire provide lubrication for its passage through the dies. If the wire before annealing is suitably cleaned and the annealing bath is lead containing, say, 0.1 per cent of nickel, then the wire in addition to being annealed, acquires, in accordance with the invention, a uniform coating of lead, which not only acts as lubricant during the subsequent passage through the dies but provides a useful protective coating for the finished wire.

The following examples, in which the parts are parts by weight, serve to illustrate, but do not limit, the invention.

### Example 1

(a) A sheet of steel was degreased by swabbing with acetone, pickled by immersion for five minutes in 10% sulphuric acid at 80° C., washed, fluxed in an aqueous solution containing per litre 500 grams of zinc chloride, 50 grams of ammonium chloride and 6 ccs. of concentrated hydrochloric acid, and finally lead-coated by dipping into a bath of molten lead in which had been dissolved one part per thousand of nickel foil, the bath being maintained at a temperature of 375° C. The steel sheet was in this way coated with a smooth layer of lead. This layer was found to be entirely free from pores by the usual test, namely by maintaining the sheet for one hour in intimate contact with a sheet of filter paper soaked in a solution containing potassium ferricyanide and sodium chloride. This method of testing reveals the presence of any pores by the formation of blue spots at any point where the steel surface is exposed; such blue spots were absent in the case of the sheet coated by the procedure described above.

(b) In place of the flux described above, there was used an aqueous solution containing twenty parts of a mixture of equal proportions of lithium chloride, potassium chloride and ammonium chloride dissolved in 100 parts of water. The coated sheet was similarly free from pores.

### Example 2

A sheet of copper was degreased by swabbing with benzine, etched by immersion for five minutes in a solution containing 20% of ferric sulphate and 6% of hydrochloric acid, washed, and then fluxed in the solution containing lithium, potassium and ammonium chlorides described above in Example 1(b), and finally lead-coated by dipping into a bath of molten lead in which has been dissolved one part per thousand of nickel foil, the bath being maintained at a temperature of 380° C. The copper sheet was in this way coated with a smooth layer of lead 0.001" in thickness which was found by inspection through a low-power microscope to be free from pores.

We claim:

1. A process for the production of lead coatings on solid metal surfaces selected from the group consisting of the ferrous and cuprous metals which in liquid lead show a contact angle greater than 50°, which process comprises dipping the solid metal in a bath of liquid lead containing nickel in solution from at least 0.01% up to as much as can be dissolved in the liquid lead, said nickel in such amounts having the property of reducing the contact angle to below 15°, the bath being substantially free from any metal capable of forming a stable intermetallic compound with the solid metal, and withdrawing the solid metal from the bath whereby a corrosion resistant continuous and adherent lead coating is obtained.

2. A process for the production of lead coatings on solid wire which is made from a ferrous metal by drawing and which shows in liquid lead a contact angle greater than 50°, which process comprises passing the solid wire prior to a drawing operation into an annealing bath of liquid lead containing nickel in solution in amount from at least 0.01% up to as much as can be dissolved in the liquid lead, said nickel in such amounts having the property of reducing the contact angle to below 15°, the bath being sub-

stantially free from any metal capable of forming a stable intermetallic compound with the solid wire, and withdrawing the solid wire from the bath whereby a corrosion resistant continuous and adherent lead coating is obtained. 5

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