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IMMERSION Plating ~~ELECTROLESS DEPOSITION~~ OF TIN AND ITS ALLOYS ON STEEL WIRES

by

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INTRODUCTION

Large quantities of steel wire (tyre-bead wires, needle and pin-clip wire and cycle-spoke wire) and wire products are given a thin coating of tin or its alloys like copper-tin simply by immersing the coils or wire-products in a water solution of plating salts. No rectifier or electric current is required. These deposits obtained by electroless method, also known as immersion tinning or cementation process, on steel wires are used mainly for bright metallic surface, better adhesion to rubber and as good drawing lubricants. These coated steel wires are also an essential pre-requisite for subsequent electroplating processes. Although the deposits are normally thin, they still have several important industrial applications. Unlike most deposits produced by immersion, tin deposits are decidely adherent and bright, with some degree of resistance to corrosion of steel wires.

The advantages of immersion tinning are simplicity less capital expenditure for equipment, fast action and the ability to deposit tin in recesses. The process is especially useful for tinning such articles as safety pins, which owing to their design, might pose serious problems in normal electroplating processes. Most of the immersion processes have had little theoretical study. Some of the steel wire products thus coated are pins, paper clips, buttons, safety pins, hairpins, dress snap fasteness, small electrical and electronic parts. Important industrial uses are the"liquor-finish " (copper-tin alloy deposit) on steel wires[1], tyre-bead wires and bright wires. Though immersion plating of tin is an old art and several commercial processes are currently available, relatively little is published on all aspects in one place. The literature on this topic up to 1967 has been covered[2]. Immersion plating of tin and its alloys on various substrates like copper, aluminium, lead etc. has been communicated from this Laboratory[3]. The number of recipes appearing in the literature are quite large. Most of the work, is, however, covered by patents. This paper brings the developments concerning steel wire and wire products uptodate in the field. The objective is to introduce the subject and provide a " commercial need" for the process. All standard texts include information on various aspects of immersion tinning and formulae for practical operations[2,4-14A].

PRINCIPLES AND MECHANISM.

Immersion plating is the deposition of a metallic coating on a metallic substrate by chemical replacement from a solution of a salt of the coating metal. This is achieved by the simple immersion of the object to be plated in the plating solution. When the object is dipped into the solution, some of the basis metal is dissolved in the plating solution while an equivalent amount of metal ions from the bath is plated out onto the basis metal. This happens under the influence of the potential that exists between the metal ions in the solution and the immersed metal object. An external potential or electric current or a rectifier is not required . For example, if a piece of steel wire is immersed in a stannous chloride solution, some of the iron from the wire will go into

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solution while an equivalent amount of tin ions from the solution will deposit on the steel wire:

$$Fe + SnCl_2 \longrightarrow FeCl_2 + Sn$$

The above is basically an electrochemical reaction involving the transfer of electrons from iron (baser metal, $Fe \rightleftharpoons Fe^{+2} + 2e$ --- 0.44 volts) to tin ions (nobler metal, $Sn \rightleftharpoons Sn^{+2} + 2e$, − 0.13 V volts) and the exchange mechanism can be represented as

$$Fe \rightleftharpoons Fe^{++} + 2\bar{e} \quad \text{(anodic)}$$

$$Sn^{++} + 2e \longrightarrow Sn \quad \text{(Cathodic)}$$

Only very thin deposits are normally obtained, since the reaction ceases when the basis metal has been completely covered with the deposit. Beside the thinness of the deposits, it is obvious that every metal cannot be plated simply by dipping, as the metal being plated must be nobler than the metallic object being plated. Thus steel may be plated with gold, silver copper or tin, but not with zinc.

Immersion plating is different from "autocatalytic plating" of metals like copper or nickel where reduction of metal ions to metals is brought out with a chemical reducing agent like formaldehyde or sodium hypophosphite. It also differs from "contact" plating in not requiring a galvanic couple (e.g. with aluminium or zinc) to generate an internal flow of electrons. The reducing agent is the substrate metal itslef.

Although the coatings produced by immersion tinning are normally very thin, they are highly uniform, very fime-grained and bright. Unlike other deposits, like thatof copper on iron, produced by immersion, the tin deposits are very adherent. This is partly because of tin ion concentration in almost all the formulations used and partly because of less difference in potentials between tin and steel. Hence the rate of deposition is slow and treeing is effectively prevented. The production of dense, impervious deposits is aided by the relatively high overvoltage of hydrogen on tin[5].

THE PROCESS

DESIGN AND EQUIPMENT

It is possible to deposit tin or its alloys in recesses and on all types of complex or sharp shapes, including the inside of tubings, where electroplating is fraught with difficulty. Steel wires can be immersion tinned in the form of coils or in-line coated in a single strand or multiplicity of wires in parallel through the cell. In the former case, the coating cannot be uniform ;while in the letter case it would be more acceptable and uniform. Care should be exercised in steel selection, as different steels react differently with some recipes. The smoothest and brightest finish comes when the starting wire is also very smooth and bright.

No special plant and machinery is required. Only two vats are basically needed[15]. A rubber-lined steel tank may be used for large operations and an earthen-ware crack is satisfactory for small operations. Others mention tanks of enamelled iron[10], glass, PVC, polyethylene, polypropylene, and hot water or steam jackets, hot plate, quartz and tantalum heaters for heating purpose.[16]

PRETREATMENT

Articles for simple immersion tinning must be thoroughly and systematically cleaned.[7] Surface preparation will vary. Normally degreasing in alkaline solutions and etching with acid is the only pretreatment. Thorough rinsing before and

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and after tinning is an important step.

IMMERSION TINNING

Table-I gives details of some typical immersion tinning processes which are used in tinning steel wires. There are more patents, but details are lacking[26-28].

Several additions have been employed in the immersion tinning bath to obtain beneficial effects like better adhesion, brightness and control of thickness of tin deposits :

(i) INORGANIC : The main raw materials for one process[15] are sodium fluoride, antimony trioxide in addition to stannous chloride, thiourea and a surface active agent.

(ii) ORGANIC : Two solutions claim tinning of steel to render it solderable and use sulphamic acid or sodium bisulfate and a polyethylene oxide, producing a coating of 0.0025 mm thick in 5 minutes.[29] A complexing agent like citric acid or boric acid is added alongwith an enhancing agent like glutaric acid, succinic acid, glycolic acid into the immersion bath solutions of copper, nickel and tin to produce a brass-like finish on steel[30]. Addition of a long chain aliphatic amine is discolosed in a process for producing 'liquor finish' on steel[31]. A recent patent was granted for a smooth even tin coating from bath containing 15-30 g/l soluble stannous salt, 25-50 m/l of mineral acid, 0.1-10 g/l wetting agent and 15-20 g/l of two sulfur containing compounds, one selected from dithiols, thio derivative of alkyl glycols, thioamine acids and the other from alkali metal sulphides, thiocyanates and dithionates[32].

COMMERCIAL PROCESSES

Many proprietary formulations are currently available in the market for immersion tinning and liquor finish on steel wires.

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TABLE-I : TYPICAL IMMERSION TINNING PROCESSES FOR STEEL WIRES

Sl No.	Composition.	Temp. in°C	Immersion time in minutes.	Remarks.
1. i.	Stannous sulphate-0.75-2.25g/l Sulphuric acid - 5-15 g/l	80°-boiling.	5-20	For white " liquor finish" on steel wires
ii.	Stannous sulphate -7.5 g/l copper(II) sulphate hydrated -7.5 g/l Sulphuric acid(Con)-10-30 g/l	20°	a few minutes.	Variations in colour produced by varying the copper content; the higher the copper, the redder the deposit, Used as drawing lubricant and decorative finish
2.	Stannous sulphate -71.25 g/l Copper (II) sulphate hydrated -60.0 g/l Sulphuric acid(Con) -19 ml/l	Room	-	Suitable for highly finished iron or steel, as also basket plating of screws, nails and tacks.
3.	Stannous chloride- 3.75 g/l Cream of tartar - 90 g/l	Boiling	2-5 hours.	Work is placed in iron baskets and separate with thin sheets of perforated tin. Actually a contact process.
4.	Stannous chloride-15 g/l Ammonium alum -20 g/l	40°	a few minutes.	-
5. i.	Stannous sulphate -11.56 g/l Copper sulphate (monohydrate)-8.3 g/l Sodium bisulphate -14.9 g/l Gelatin powder -0.92 g/l Sulphuricacid(66° Be)-26 6.1 g/l	60°	5	pH 1.3, coating weight depends on immersi time, bath temp., solution concentration and acidity.
ii.	Stannous sulphate- 11.6 g/l Copper sulphate hydrated-10.6 g/l Glutamic acid- 0.9 g/l	49°	-	pH 0.5, Coating weight 4 g/m^2; Brassy coating with very good adherence on cold rolled steel wire.
iii.	Stannous sulphate-1.8 g/l Copper sulphate hydrated - 15.7 g/l Glycine - 1.0 g/l	38°	-	pH 1.3 coating weight 4 g/m^2; brassy coati with good adherence on cold rolled steel
6.	Stannous sulphate -13 g/l Nickel sulphate -200 g/l Tartaric acid -8 g/l Nickel chloride - 30 g/l Macconol MR (Wetting agent) - 1 g/l	65°	1-5 hours.	Suitable even for cast iron articles
7.	Stannous chloride - 1.5 g/l Potash alum $(KAl(SO_4)_2 \cdot 12H_2O)$ - 30 g/l	Boiling.	-	-
8.	Stannous chloride -15-20 g/l Lead acetate - 3-15 g/l Thiourea - 50-90 g/l Ammonium chloride - 45-65 g/l Ammonium thiocyanate - 40-60 g/l Hydrochloric acid - 15-20 ml/l	-	-	For immersion plating of tin-lead alloys
9.	Stannous chloride - 150 g/kg Ammonium sulphate - 150 g/kg Magnesium powder - 30 g/kg Powdered chalk - 670 g/kg	-	-	All the components are powdered and mixed intimately. The powder is rubbed with a we cloth on the surface to be tinned.
10.	Stannous chloride - 5 g/l Thiourea - 80 g/l Citricacid - 16 g/l	-	-	Other organic acids may be used in place of citric acid.
11.	Stannous chloride - 0.625 g/l Ammonium sulphate - 5 g/l Alum - 15 g/l	Boiling.	-	For getting a matt white deposit on iron and steel articles.
12.	Stannous sulphate - 10 g/l Copper sulphate (Hydrated) - 7.15 g/l E.D.T.A. - 0.85-1 g/l Sulphuric acid -(S.G.)1.84 - 2.5-6g/l	25°	3-4	pH 0.5 to 6. Well adherent bronze coating 1 to 2 µ thick on degreased iron and steel wire.
13.	Stannous chloride - 3.75 g/l Aluminium sulphate -15 g/l Cream of Tartar - 15 g/l	Boiling.	30-45	Addition of 1 drop of sulphuric acid hastens tin deposition.

Some of them are :

(i) Cuprodine SN by Anchem Products, Inc., USA

(ii) Cuprobond 100 and Straw-lacquered Finish by Pyrene Ltd., U.K. 2

(ii) Alstan and Related Processes by M & T chemicals, Inc., U.S.A. 3

(iv) Electroless Tin Plating Bath by National Aeronautical Laboratory, Bangalore, India[15] 4

(v) Electroless Tin ME-1010 by Circuit Services, Minneapolis, U.S.A. 5

POST TREATMENT

Following treatment in the tinning bath, steel wire and wire products are thoroughly rinsed in 6 clean cold water and dried with the aid of hot water. The brightness on the latter may be increased by tumbling for 7. a few minutes in saw dust, wheat bran or fine maple saw dust, after which they are tumbled in a barrel without any polishing agent[6], or leather scraps, whiting or other polishing agents[7]. 8. It should be clear that with immersion tinning, there may not sufficient deposit to reflow[33]. 9.

APPLICATIONS 10

Immersion tinning of steel wires and wire products is of significant industrial importance. It is extensively used 11 to provide a bright surface having better solderability. Tin or copper-tin coatings act as excellent drawing lubricants and offer considerable corrosion resistance.

As mentioned earlier, large quantitites of wire products such as pins, thimbles, eyelets, copper-coated steel dress pins and snap fasteners, paper clips, buttons, small electrical parts, as also hair pins, books, safety pins, nuts and screws etc. are coated with tin by the immersion processes.[1,2,6,7,10,12]

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It is customary to tin cycle-spoke wire (bright but not galvanized) and also the strings for musical instruments like guitars and banjos.

Liquor Finishing is normally a copper-tin alloy deposit and applied to steel wires basically for three purposes:as a drawing lubricantfor needle wire,pin-clip wire,as a decorative finish for hair-pins,clips,staple pins and on tyre-bead wires for increased adhesion with rubber[2,9,34].

FUTURE TRENDS

There have been marked developments in immersion tinning and tin alloy deposits on steel wires. A large variety of steel wires and wire products have been coated with tin simply by immersion.

In future,the variety of commercial finishes and areas of applications will grow. The search for even thicker coatings on all types of wires,including stainless steel,will continue and open new vistas for tinned wires.

It is concluded that the current and potential uses of immersion plating are abound with success when one has all the facts at one's disposal. It is hoped that the present paper will induce many people to benefit by these proven techniques and the future developments will be directed towards new types of baths so that immersion tinning can come fairly close to electrotinning.

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