

UNITED STATES PATENT OFFICE

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METAL PLATING

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1

This invention relates to metal coatings and is a continuation in part of my pending United States applications for Patent Serial Numbers 3537, now Patent No. 2,640,001; 14,639, now abandoned; 77,269, now abandoned; and 99,567 filed respectively January 21, 1948; March 12, 1948; February 18, 1949, and June 16, 1949.

This invention relates to the metal plating of objects from aqueous solutions without the application of melting heat or electricity, and particularly to the method of plating in which very small particles of metal are built up into continuous, dense, thick, metal coatings covering the surfaces of the object being plated.

An object of the invention is to provide a metallic coating which will be inexpensive in application, attractive in appearance and effectively adherent to the base surface and protective against weather, wear and corrosion.

Another object of the invention is to provide means for simplifying the operation and control of the process and to provide greater uniformity of coating thickness from batch to batch.

A further object of this invention is to provide means whereby any desired thickness of coat may be obtained in a predetermined time at a lower cost.

Further objects of the invention will appear from the following specification.

In the process described in my copending applications the objects to be plated, after being suitably cleaned, are tumbled, or rubbed, or impacted in a liquid medium containing finely divided metal in suspension, together with small amounts of certain surface active agents. The mechanical rubbing, rolling, tumbling or impaction may be done in a tumbling barrel, ball mill, tube mill or the like, or it may be done by imparting a velocity to the liquid suspension relative to the work being plated by means of an impeller or rapidly rotating wheel. The slurry may contain small metal grit, or metal balls to increase the rolling or rubbing action.

The surface active agents present in the liquid are retained in the coating in minute amounts, their presence is shown by photomicrographs and analysis which indicate that traces are so retained, just as traces of organic colloids or other addition agents may be retained in electroplated coatings. It is necessary therefore, that the surface active materials used for promoting plating should be non-injurious to the coating after it is laid down, and should preferably be protective and help inhibit tarnishing and corrosion.

My copending application Serial Number 3,537,

2

describes various oily and fatty surface active agents dissolved in suitable solvents that are acid or neutral in nature and may be used in the deposition of bright attractive tarnish resistant metal coatings. Copending application 14,639 describes various oily organic compounds alkaline or neutral in nature dissolved in either aqueous or non-aqueous solutions that may be used to provide continuous operation of the process whereby the same bath may be used for prolonged or indefinite periods to process batch after batch of objects. Application Serial Number 77,269 discloses that by raising the temperature at which the plating is done the oily acid type surface active materials disclosed in application 3,537 may be made to serve for continuous operation and the plating of successive batches of materials from the same bath. Application Serial Number 77,269 also discloses that at elevated temperatures certain metals that are difficult or impossible to plate at room temperatures may be successfully deposited when the temperature is raised to or above the recrystallization temperature and this is true of aluminum and brass.

In the continuous operation of the process as described, exact and predetermined control of coating thickness in successive batches of materials is important, calling for skill and experience and requiring certain tests made on the solutions, and certain addition of metal dust and surface active promoter to replace that lost by chemical reaction or in the coatings on objects removed from the operation.

The present invention simplifies the operation of the process and employs a medium for plating which may be used once and then thrown away, so that a fresh liquid containing fresh quantities of surface active materials is used for each run.

It is a further part and a purpose of this invention to reduce the quantity of metal dust required to that actually required for coating on the objects, or to a slight excess, so that each new run is made with all new dust or with a substantial addition of new dust.

It is a further part and a purpose of this invention to regulate the amount of metal dust for plating added to each cycle, whereby the thickness of coating applied to the objects being coated may be accurately controlled.

Any chemicals used with this disposable carrier liquid should be either very inexpensive or be present in the liquid in very minor amounts; furthermore when the quantity of dust used in each cycle is reduced to that actually deposited on the objects being plated, then the surface

active plating agents are extremely powerful to attain this result. It is a part and a purpose of this invention to provide plating promoters sufficiently powerful in their action to accomplish these purposes.

When in the treatment of each batch of articles in the same mill the quantity of surface active agents, of water, of grit and of objects for plating, is kept constant and when only the weight of metal dust is altered, and when all, or practically all, of the metal dust charged is plated out on the objects, then the amount of dust so charged determines the thickness of the coating deposited.

The coating thickness laid down under these conditions in unit time for different weights of dust, may be determined in advance in preliminary tests, and tables may be drawn up to show the thickness of coat deposited. These tables may then be used for the future operation of the process. Different sets of tables may be made for the principal systems of surface active materials used.

When the coating thickness is controlled in a mix which is used once and then discarded by limiting the amount of dust to that actually plated on the objects, with or without a small excess, then the ratio of shot or grit used for impacting or rubbing to dust present in the mix for plating may become very large.

For example, in one test in applying a cadmium coating .0002" thick to metal screws, the amount of cadmium dust added was $\frac{1}{2}$ of an ounce. The metal grit used weighed 12# or 192 ounces; thus making the ratio of grit to metal dust 384 to 1.

In another test plating 300# of nails 21 of the 25# of zinc dust added was used up in coating the nails, leaving 4# of zinc dust to be recovered from the liquid prior to its being discarded. In this example 700# of grit were used so that the ratio of grit to zinc dust was 28 to 1. In this example 4# of metal dust could be recovered to be used in the following run so that 21# of new dust would be required in the next cycle. Operating in this manner each charge would start out with a major percentage of new metal dust plus new promoting surface active materials. The use of such large ratios of shot or grit to metal dust calls for exceptionally efficient and suitable plating promoters.

When the coating is built up with a minimum quantity of metal dust for creating the deposit present, conditions of maximum attrition or rubbing result from the absence of the cushioning effect of a large circulating load of metal dust.

This invention overcomes the difficulties created by these very high loadings of coarse metal grit or shot relative to the finely divided metal dust used in building the coating by making the solution itself serve to cushion the impact. Certain film forming materials when added to the water have been found especially suitable.

Any protective films present on the particles and insulating them from the water and excessive abrasion must be parted to allow metal to metal contact with resulting "seizing" of the surfaces exposed. The tumbling action provides very high pressures over the extremely small surfaces of the particles and these forces act to scrub off the films and permit the solid surfaces to come into metal to metal contact.

These pressures exerted over very small areas appear sufficient to part strongly adherent films and some of the best surface active agents for use in the practice of this invention have pronounced and strong film forming characteristics

which coat the individual particles and shield them from attack by the water. Thus it is possible to eliminate gas formation and to operate closed mills with a vacuum. The formation of decomposition products of metal is avoided, or largely avoided, so that there is no appreciable loss of metal in waste products. This general class of surface active agents having very strong film forming characteristics with attendant ability to strongly coat individual metal surfaces with a mono molecular layer of strongly held material constitutes the preferred type of plating promoter in aqueous systems.

Another class of surface active materials suitable for use in the practice of the subject invention exhibits strong film removing properties and appears to excel in assisting the tumbling action to remove surface films from metal particles faster than they are created. The most suitable members of this class are the organic carboxylic acids such as citric acid and tartaric acid and the amino acids of which glycine is especially good. Other examples are the glycols such as ethylene glycol or polypropylene glycol. The use of these materials in the operation of the process gives very bright and attractive coatings. Their use is usually associated with substantial gas generation and sometimes with attack on the metal dust.

Any reaction products between surface active materials of this type and the metal dust used, are inert, insoluble and protective. Taking zinc for example, zinc citrate, zinc tartrate or zinc phosphate, are the end reaction products between the metal and citric, tartaric and phosphoric acid. These compounds are protective and inert to metals and are generally used to protect zinc. Any minute inclusions in the coating therefore are noncorrosive and non-injurious.

The best surface active materials which are preferred in the practice of this invention, are the strong film forming inhibitor materials which protect the metal from the carrier liquid water, prevent metal attack and which may be used in very small quantities. Of this class preferred types are selected from the group consisting of the protective colloids, such as the gums.

The gums are not soluble in water in the ordinary sense they disperse, swell and absorb water to form sols. The gum colloids include the water dispersible cellulose materials such as methyl cellulose, hydroxyethyl cellulose and carboxy methyl cellulose.

The gums include the tree exudations such as gum acacia, gum karaya and gum tragacanth. The gums also include the various colloids derived from sea weeds, such as agar and the alginates. Also included are starches, saponin, soluble silicates such as sodium silicate and certain seed extracts as well as certain proteins such as gelatines.

While there is some variation in efficiency among different members of this gum family, as a class they are especially suitable and desirable for the practice of this invention. In a liquid that is to be used once and then discarded they are ideal as they may be used in very small amounts. For example: the high viscosity form of sodium carboxy methyl cellulose may be used in a water solution down to $\frac{1}{10}$ of 1% by weight. A concentration of 0.25% in water is very suitable and provides a solution which has just the right viscosity and protective filming ability to provide exceptionally adherent and satisfactory coatings. The cost of the reagent added at the

5

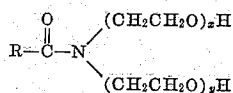
rate of $\frac{1}{4}$ gram to each 100 ccs of water is low enough to permit of its being used just once and then discarded, without appreciably increasing the cost of operating the process.

A 0.25% solution of high viscosity sodium carboxy methyl cellulose in water creates a water white somewhat thick and viscous solution which is utterly different from plain water. In general gums of the type just discussed function best in the presence of a detergent or wetting and cleansing agent. This requirement may be met in various ways such as by the addition of ammonium hydroxide, calcium hydroxide or sodium hydroxide. Of the various alkalisers, the one generally preferred is ammonium hydroxide.

The sols just discussed are not the only class of colloid in water which are suitable for use with this invention. Certain fatty acid derivatives may be used which provide a milky white solution in water. In this type of material a soluble phase is very effective such as a true solution in water, combined with a colloidal phase or emulsion.

The fatty acid derivatives such as the N-substituted fatty acid amides, the substituents being polyoxyethylene groups may be compounded with the fatty acids to provide milky emulsions in water. Some of these materials make extraordinarily rapid and effective plating promoters, and bright, shiny, smooth, dense coatings may be built up in periods as short as one hour.

For example, taking an eighteen carbon chain amide such as that just described with polyoxyethylene groups on the nitrogen, thus:



(x and y may each be defined as any number from 5 to 200. When the compound contains more than, say, approximately 80 moles of ethylene oxide, it begins to approach in properties the class of carbowaxes or polyethylene oxide waxes. These last materials are used successively in the plating process and appear to improve adhesion. The preferred range for x and y , however, falls generally in the range from 30 to 60) and mixing it at room temperature with caprylic acid in the proportion of $3\frac{1}{2}$ parts of caprylic acid to one of the substituted amide produces a material which is remarkably effective plating agent in water. The efficiency of this material is further increased by adding a wetting agent preferably a water soluble oil such as an alkanolamine condensate. The proportions listed above may be varied within fairly wide limits without materially effecting the efficiency of the material.

Another especially suitable surface active agent having proper characteristics to build up exceptionally brilliant, dense metal coatings may be compounded by mixing a fatty acid such as caprylic acid with a tertiary amine having one fatty alkyl group and two polyoxyethylene groups substituted on the nitrogen.

The effectiveness of this mix is increased when a small quantity of wetting agent preferably of the alkanolamine condensate type is used with it. With some of these materials a small amount of coupler or solubiliser may be of advantage in increasing the efficiency still further. The function of the coupler is to increase the degree in which the difficultly soluble material is actually dissolved in the water, or to increase the fineness of the dispersion.

6

For example: Ethyl alcohol may be used with caprylic acid in water solution to make a preparation suitable for plating under some conditions. It is obvious that a great many combinations of water soluble fatty acid derivatives in admixture with or combined with fats, oils, fatty acids, etc. is possible. A great many of these types have been investigated and have been found to be very effective in providing the right combination of outright solution, with or without a sol or an emulsion for excellent plating. These colloidal suspensions of one liquid in another are especially suitable where a fatty acid is involved, because the fatty acid when included in the coating in minute amounts provides tarnish resistance and tends to inhibit and retard corrosion. The coatings laid down from water carrying a solution or colloidal suspension of a fatty acid or fatty derivative are therefore in general brighter and more tarnish resistant than those laid down from a colloid of the gum family such as those described previously in which no fatty acid is used. Many combinations of the gums with fatty acid derivatives such as the tertiary amide are possible and many constitute suitable plating promoters.

The two examples of a fatty acid compounded with a fatty derivative described above are two that are especially good. The N-substituted amide is very suitable to use for solubilizing or emulsifying the fat oil or fatty acid. Caprylic acid is also particularly suitable but other fatty acids may be used. For example, a water soluble fatty acid such as acetic acid may be used with a water soluble oil such as an alkanolamine condensate. Very small amounts of the condensate and of acetic dissolved in water make very powerful plating agents which produce very adherent thick coatings in a short period of time, and are very suitable for use in the practice of this invention. While this combination appears to be an excellent film former it probably is more of a true solution rather than an emulsion or sol. The use of these plating agents reduces the activity of the water on the metal dusts to the point, where gas generation and attack on the metal dust no longer constitutes a problem. The film forming is particularly effective where one end of the molecule attaches itself to the metal surface as a metal accepting end. In this way the metal surface is protected entirely from contact with water.

These strongly film forming colloids in water solution function best as has been stated when a film removing agent is present. Thus, in the cellulose or gum type described, the ammonia or alkali serves as a solvent or film remover to assist the tumbling action in removing oxide or other films from the particle. In the fatty acid fatty derivative systems, the fatty acid serves the same purpose. The fatty acids have a definite and recognized property of dissolving metal oxides to form soaps.

Protective colloids exhibit the property of preventing agglomeration. This peptizing ability appears to be useful in preventing the particles from building up in size. This is important because any dust which is not plated out and which is recovered for use on a subsequent run, is more suitable if increase in particle size is avoided. The more nearly any dust recovered from one plating cycle and returned to the next approximates new dust in particle size, the less interference it will cause.

As typical of the working of the process and

the resultant plating attained the following examples illustrate specific variations:

Example 1.—Into a clean five quart porcelain jar mill, equipped with two stationary riser or lifter bars, went ten pounds of coarse zinc dust, approximately six mesh in size, which served as an impacting medium. Two pounds of acid pickled nails were added together with one-quarter pound of fine zinc dust, 1200 cc. of aqueous solution containing three grams of sodium carboxy-methyl cellulose, and two grams of a highly substituted water soluble tertiary amide based on an eighteen carbon chain and 15 cc. of ammonium hydroxide solution. The mill was closed and agitated for three hours at approximately sixty R. P. M. On opening the nails were found to be coated with a dull, light grey, smooth coating .002" thick. A physical examination of the nails showed the coating to be extremely adherent, and these nails, when subjected to the Preece test, easily passed the requisite of four one-minute dips.

Example 2.—A five quart jar mill, similar to the above, was charged with ten pounds of grit, one-quarter pound of zinc dust, and two pounds of acid pickled nails. The liquid in this example was composed of 1200 cc. of water, to which was added 24 cc. of a mixture composed of: one part of the tertiary amide used above, and three parts of caproic acid. This product was made by melting the tertiary amide and then stirring in the caproic acid. The mill was closed and agitated for three hours, and on opening the mill, a coating of .002" was obtained. This coating was bright and shiny in appearance.

Example 3.—A mill, similar to those used above, was charged with five-eighths of a pound of zinc dust, two pounds of acid pickled nails; and the liquid consisted of 1200 cc. of water, four grams of carboxy-methyl cellulose, and 36 cc. of ammonium hydroxide. The mill was run for two and one-half hours, and a coating thickness of .0018" was obtained on opening. The coating was dull grey in color, and was extremely adherent.

Example 4.—A five quart jar mill was charged as above except that one and one-half pounds of bronze nails, which had not been pickled, was substituted for the pickled steel nails, and sixty grams of fine, tin powder was added in place of the zinc dust. The mill was run for three hours and, on opening, a very attractive, smooth and highly polished, light tin coat had been obtained.

Example 5.—A five quart jar mill was charged with ten pounds of zinc grit, three-eighths of a pound of zinc dust, two pounds of acid pickled nails, and 1200 cc. of water containing 24 cc. of ethylbutyric acid. The mill was closed and run for three hours and, on opening, a very bright and lustrous coating—.0003" thick—was obtained.

Example 6.—Into a five quart jar mill went twelve pounds of lead coated zinc grit, 225 grams of lead powder, and, approximately, two pounds of assorted, acid pickled, steel objects. The liquid consisted of 1200 cc. of water, to which had been added 15 cc. of the caproic, tertiary amide mixture described above. After three hours the mill was opened and the objects were found to be coated with a substantial coating of lead. This was dark in color.

Example 7.—A five quart jar mill was charged, as above, except that the liquid consisted of 1200 cc. of water, two grams of a sodium alginate product (sold commercially as Kelgum) and 36

cc. of ammonium hydroxide. Three-eighths of a pound of zinc dust was added together with two pounds of acid pickled nails. The mill was run for three hours and, on opening, the nails were found to be coated with a thickness of .0006".

Example 8.—In an example exactly similar to the above, the liquid was composed of 1200 cc. of water containing twenty grams of starch, and 36 cc. of ammonium hydroxide. The nails were found to be coated with a zinc coating of .0014" thick.

These examples are illustrative of the effects achievable with different plating agents. It will be noted that the appearance, the adhesion and the quantity of dust for plating required, vary with the different promoters used. It will also be observed that the first two listed, provide the heaviest coating with the smallest addition of zinc dust.

The system of this invention thus employs an aqueous suspension in the coating of the particles in an efficient and effective manner. Plating is not achieved by the use of water alone and only water. The best that can be done with water is to smear a color on the surface to be plated. Particles of metal become lodged in surface irregularities and are rolled or smeared on. Such a "flash" when it is achieved at all imparts at best a very transitory and temporary protection to the base metal. Fluxes such as zinc chloride added to water in admixture with metal dust are unsuited and ineffective because they are incapable of building up coatings of requisite thickness even when the plating time is very prolonged. Such inorganic compounds retained in the final coating are highly corrosive and convert moisture into an electrolyte between the dissimilar metals with consequent deterioration of the deposited metal film. These effects are aggravated when the amount of metal dust used for plating is reduced and such metallic salts, especially inorganic salts, are not practically usable for permanent plating as attained by the present process.

The greatly expanded surface area of the metal dust requires protection from the water of the aqueous suspending medium and the adsorbed films of the plating agent must at the same time condition the dust particle surfaces for strong bonding to the base metal and to each other to desired depth of coating. All this is accomplished by the present procedure without any deleterious response of the traces of the plating agent retained in the final coating as used.

In this system the time of treatment is within a few hours and the processing as to character and depth of coating under predetermined control while the material is efficiently and economically applied. The resulting coating is tenaciously adherent and durably protective and readily applicable to a wide variety of articles.

I claim:

1. The method of metal plating successive batches of metal articles comprising mixing a batch of said articles with a quantity of particles of metal powder calculated in proportion to the amount of coating desired on said articles and less than thirty percent of the articles by weight and being in suspension in an aqueous solution from four to twenty times the particles by weight and containing between 0.1 and 2.0 percent of an organic, film-forming, plating agent, agitating said mixture and spreading said plating agent as organic molecular films on the metal surfaces and developing high pressures between the metal

surfaces of said articles and particles of said mixture parting said films at the areas of contact and bringing said surfaces together in metal to metal contact with each other and progressively depositing and attaching said particles to the article surfaces and to each other to gradually deplete said suspension and build up said particles into continuous dense metal coatings on the surfaces of said articles, and continuing said agitation of said mixture and the building up of said coatings to desired thickness thereof by deposit of at least 80 percent of said particles and with the depletion of the suspended particles to less than 20 percent, removing said batch of coated articles and separating and discarding said aqueous solution and mixing another batch of metal articles with less than thirty percent by weight of particles of metal powder in suspension in an aqueous solution four to twenty times the particles by weight and containing between 0.1 and 2.0 percent of an organic, film-forming, plating agent and repeating the agitation of said mixture and the filming of the metal surfaces and the progressive building up of the desired dense surface coatings as with the first batch of articles and removing the coated articles and discarding the aqueous solution as in the treatment of the first batch of articles, and similarly treating successive batches of articles to plate

dense adherent metal coatings on the surfaces of said articles of each batch.

2. The method of metal plating successive batches of metal articles as set forth in claim 1 in which a charge of impacting metal pieces is included with the articles in the aqueous suspension and in amount is less than four hundred times the weight of the powder particles.

3. The method of metal plating successive batches of metal articles as set forth in claim 1 in which the residue of powder particles remaining from the treatment of one batch of articles is used as a minor part of the charge of powder particles in the coating of the surfaces of the articles of a succeeding batch.

4. A method of metal plating successive batches of metal articles as set forth in claim 1 in which the solution includes an oxide film remover assisting in removing oxide films from the metal surfaces.

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