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COATING AND COLORING METALS

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This invention relates to the coating of metals either for preservative or decorative purposes and has for its object the provision of a simple, convenient and inexpensive process whereby certain common metals, and more particularly those subject to tarnish and corrosion, can be provided with a thin, adherent, coating which is permanent and non-corrodible under all ordinary conditions, which is artistically colored and of pleasing appearance, and which constitutes a satisfactory and enduring foundation for paint, enamel and other coatings; the provision of a process which does not require electric potential, either external or internal whereby coatings of different colors can be controllably produced; while further objects and advantages of the invention will become apparent as the description proceeds.

The invention is based upon the peculiar properties of certain molybdenum compounds and consists essentially in depositing upon the surface of the article to be coated or colored an adherent coating of substantial density and hardness, consisting apparently of one or more of the lower oxides of molybdenum formed thereon in situ. The formation of this coating offers varying degrees of difficulty depending to some extent upon the nature of the metal, but even more upon the contents of the bath, since the addition of certain chemical ingredients appears to activate or intensify the action, increases the density and adherence of the coating, and in conjunction with the time and temperature, controls the color. This action can also be intensified, and extended to ordinary non-active metals by the imposition of an electrical potential but it is an important feature of my invention that the common metals, iron, steel, tin, aluminum, zinc, cadmium, lead, and even magnesium, can be coated successfully without the employment of potential.

In the performance of my said invention I preferably employ a solution of one of the water-soluble molybdenum compounds such as the molybdate of one of the alkali metals, potassium, sodium, lithium or ammonium, the particular compound which I prefer being ammonium molybdate. This is used in aqueous solution of a very great range of concentration since a solution containing less than one-tenth of one percent of this compound is entirely operative, though slow, and a solution containing upwards of two percent of the same is likewise operative though more rapid. The only draw-back is that with undue concentrations (say upwards of 10%) a coating is obtained which is not so dense or closely adherent although I do not limit myself in this respect since there may be some cases wherein these qualities may be less important than speed. To this solution I preferably add a suitable activating reagent such as a soluble oxalate, or electrolyte such as the sulphate, chloride, etc., preferably of the same base i. e. ammonium, but on occasion even the pure acid itself. The proportion of this ingredient can be varied considerably according to the metal, the temperature, the time of treatment, and the nature and color of the coating desired. A coating of some kind can always be obtained within the limits of operation herein described, and such coating can be made darker in color by increase of molybdenum concentration or elevation of temperature or longer immersion or addition of such activating reagent (or electrical potential).

Articles made of or coated with iron, steel, tin, lead, aluminum, zinc, cadmium, or even magnesium, when carefully cleaned and immersed in such a solution become coated with a dense adherent protective coating generally of a glossy and shiny character (as compared with the dull black of most rust proofing processes), and exhibiting coloration of all kinds depending upon the concentration and temperature and composition of the liquid and the duration of treatment. These colors range through all gradations through yellow, red, green, and brown to black. It is not always possible to obtain the darker colors in the cold and in general it may be said that the higher the temperature and the greater the concentration the easier it is to obtain the darker shades. The colors depend almost entirely upon the composition and temperature of the solution and the duration of contact and only to a small degree upon the color of

the original metal; the colors are generally iridescent but very permanent. Alloys behave like the metal which predominates in their composition; thus zinc alloys, such as those employed in die casting, can be treated very successfully in this manner. A slight acidity is generally desirable.

The activity of the solution can be augmented by the addition of certain other substances. One class of substance having this effect is that of electrolytes, for example the water-soluble chlorides, nitrates, sulphates, etc. These salts may possess any desired base, although I prefer those on alkali bases, and I particularly recommend the use of the same base as already present in the solution e. g. ammonium chloride when ammonium molybdate is being used. Another class of substances exhibiting this energizing effect on the solution is found in the organic acids such as gallic acid, tannic acid, oxalic acid, or their salts. The proportion of the energizing ingredient can be varied very widely and same may be present in either greater or less proportion than the molybdenum compound. Articles of zinc, iron, lead and their alloys when immersed in this activated solution can be coated noticeably more quickly than in the plain solution first described, and in addition a coating can be obtained with convenient speed on certain other metals such as aluminum, copper, nickel, tin, and their alloys which exhibit too slow a reaction in the plain solution. The speed of reaction can be increased by heating, although the effect even of this solution on nickel and tin is rather unduly slow.

In order further to expedite the reaction and to extend it to other metals, thus facilitating the coating of nickel and tin and enabling coating of gold, silver, platinum, tungsten, chromium and the like I impress upon the article a slight negative E. M. F.; this may be done either by immersing it in contact with a sheet of electropositive metal contained in the same bath (such as zinc or magnesium) or by attaching the article to the negative pole of a battery, the positive pole of which is attached to a conducting plate of some kind suspended in contact with the liquid. In the former case, I obtain the best results by arranging the articles and contact plates successively, an article to be coated being located between and in contact with two zinc plates (for example). In case an exterior battery be employed as a source of E. M. F., its volume of current seems to have little or no effect. A common dry battery is sufficient to operate a large size tank, while a common storage battery can be employed for an indefinite time without appreciable loss of charge. The composition of the contact plate to which the positive pole of the battery is connected also appears not to be important. I generally make it of zinc since this substance is cheap, readily available and a good conductor; although it can equally well be made of carbon, iron, lead, or other metals, provided only that it be of some substance which does not dissolve with the production of ingredients which poison the bath such as copper which itself produces a flash coating on iron, aluminum, zinc, etc.

The reaction does not appear to depend upon the solution of any metal from the anode plate, and does not appear to constitute a galvanic deposition on the cathode plate although with a zinc anode solution occurs. While applicant does not desire to limit himself by any expression of theory, the readiest explanation appears to be that molybdenum tends to deposit a kind of flash coating by replacement on articles made of such substances as zinc, iron, cadmium and magnesium which tend to evolve hydrogen from acid or aqueous solutions; owing to secondary reactions this deposit would ordinarily be in the form of molybdic acid but the nascent hydrogen so far neutralizes that tendency as to give rise to a series of lower oxides which adhere closely to the surface of the article with the decorative and protective effects above described, Indeed it is possible that some of the coating consists of metallic molybdenum though this is doubtful.

By the process above described it is possible to color nearly every metal (excepting those like sodium and lithium which decompose water) for example gold, silver, platinum, tungsten, chromium, copper, zinc, nickel, tin, lead, magnesium, aluminum and their alloys. Furthermore these coatings are permanent, untarnishable, ornamental and very artistic. The color is iridescent and proof against handling, washing, rubbing etc. although it can be scraped away by abrasives or by hard tools. Aricles of iron and steel treated in this manner exhibit an increased resistance to weather and corrosive conditions; even a stick of magnesium is notably protected from salt water by this treatment. The coating thus produced also serves as a very satisfactory foundation for paint, enamel and the like by which the article is still further protected against corrosive influence, this being the preferred procedure in large scale treatment of iron and steel, as for example in connection with automobile bodies.

I do not limit myself to the use of such molybdenum compounds as are generally considered readily soluble, of which the molybdates are an example, inasmuch as I find it possible to operate successfully with baths containing excess amounts of other molybdenum compounds such as molybdic acid in intimate contact therewith as by being suspended therein. The small amount of this compound which goes into solution under such conditions serves to produce the result in

question even though its percentage in solution is very small. Also I do not limit myself to temperatures, nor to the duration of treatment, since one to three minutes immersion is generally sufficient in the case of a readily reactive solution while an increased time of immersion is desirable with the more attenuated solutions. This time element also depends upon the temperature and upon the color desired.

My improved process is useful both artistically and technically, artistically in enabling the production of pleasing and permanent colors on fittings, fixtures, and art objects made of inexpensive metals (such as electrical fixtures, biulders' hardware, interior decorations, plates, placques, statuary, bricabrac, etc.) or technically in rust proofing iron and steel, coating tin cans and other food containers, and producing a foundation to which paint and varnish will adhere more firmly than to the metal itself. Accordingly I do not limit myself in any respect except as specifically recited in my several claims.

Having thus described my invention what I claim is:

1. The process of coating articles consisting at least superficially of iron, steel, tin, aluminum, zinc, cadmium, lead, or magnesium which contains the step of simple immersion in a solution containing a soluble molybdate and a soluble oxalate.

2. A dipping solution for the purpose described containing a soluble molybdate and a soluble oxalate.

3. The process of coating metal articles which contains the step of immersion in circuit with a zinc anode in a dilute aqueous solution of ammonium molybdate, together with a larger qantity of second non-alkaline ammonium compound.

4. The process of coating metal articles which contains the step of immersion in electric circuit with a zinc anode in aqueous solution of a soluble molybdate, and a second non-alkaline salt which constitutes an electrolyte.

In testimony whereof I hereunto affix my signature.

ALADAR PACZ.