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ANODIZING IRON GROUP METALS IN LEAD SULFAMATE BATH

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This invention relates to electrodeposited coatings and is more particularly directed to the electrodeposition of black coatings containing lead oxide upon metals of the iron group by electrolyzing the iron group metal anodically in a lead sulfamate solution having a pH of about from 4.2 to 5.9, to articles having upon their surfaces black-lead oxide coatings so produced, and to compositions comprising lead oxide and sulfamic acid adapted to maintaining said lead sulfamate solutions during use at a pH of about from 4.2 to 5.9.

It is an object of this invention to provide processes and compositions for anodically treating metals of the iron group. A further object is to provide processes and compositions for the anodic electrodeposition of deposits containing lead oxide. A still further object is to provide articles comprising iron group metals having upon the surfaces thereof anodically electrodeposited black, lustrous, adherent, corrosion-resistant coatings comprising lead oxides. Further objects will become apparent hereinafter.

The foregoing and other objects of this invention are accomplished by processes in which an iron group metal is electrolyzed anodically in a solution having a pH of from about 4.2 to 5.9 and containing about from 75 to 450 grams per liter of lead sulfamate, and are further accomplished by the lead sulfamate compositions employed and by the coated articles produced.

The coatings obtained on metals according to this invention have a pleasing, lustrous, jet black color. They are strongly adherent and abrasion-resistant. They are likewise corrosion-resistant and afford the base metal substantial protection against corrosive influences. By reason of these properties the coatings are of outstanding value as both ornamental and protective finishes.

The coatings consist substantially of black lead oxides, but also contain appreciable quantities of the oxides of the iron group metal upon which they are produced. The amount of the base metal oxide may vary from a fraction of a per cent up to several per cent. For instance, a deposit of normal thickness (approximately .0002 inch) upon steel was found to contain iron oxides equivalent to 6.3 per cent iron, while a heavy deposit (.005 inch) upon nickel was found to contain nickel oxides equivalent to .3 per cent of nickel. Ordinarily the amount of base metal oxide will be found to be in the range from about .1 per cent up to about 10 per cent by weight.

Coatings such as above described may be produced upon metals of the iron groups according to

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this invention by placing the iron group metal, suitably prepared for plating according to conventional practices, in a solution comprising lead sulfamate and having a pH of about from 4.2 to 5.9, making the iron group metal the anode in an electrical circuit and passing a current through the circuit. The black, lead oxide-containing deposits are obtained as coatings on the anodes, while metallic lead is deposited upon the cathode. As lead is removed from the solution by the electrolysis, the solution may be replenished by the addition of a suitable bath-soluble lead compound, such as litharge.

Processes of this invention may be operated over a considerable range of current densities, densities in the range from about 5 to 30 amperes per sq. ft., for instance, giving excellent results.

Coatings of good character may be obtained by operating at room temperatures, but elevated temperatures may also be employed if desired.

The base metal upon which a black coating is anodically produced according to this invention may be a metal from the iron group of the periodic system, that is, iron, cobalt or nickel, or may be an alloy containing an appreciable proportion of an iron group metal. Thus coatings may be produced on ordinary steel or cast iron, nickel (either solid or plate), stainless steel, monel metal, and other alloys containing iron, cobalt, or nickel in appreciable proportion.

The surfaces upon which coatings are to be produced preferably should be prepared by suitable pickling and cleaning procedures. By dipping the metal to be coated in a chromic acid solution immediately before placing it into the electrodeposition bath, the electrodeposition may be facilitated, particularly in the case of such metals as cast iron or malleable iron or alloy steels.

A solution of this invention for producing anodic electrodeposits should have a pH of about from 4.2 to 5.9 and should contain about from 75 to 450 grams per liter of lead sulfamate. The pH may be adjusted independently of the lead sulfamate content by the addition of acidic or basic materials as required, but in general it is preferred to increase the acidity as desired by the addition of sulfamic acid and to increase the basicity as desired by the addition of a basic lead compound, such as litharge or lead carbonate. During operation of the solution it is well to maintain the pH and the lead sulfamate contents at an intermediate point within the ranges given above. Thus, excellent results are obtained when the pH is held at about 5.5 and

the lead sulfamate content is maintained at about 300 grams per liter.

A very satisfactory method for making up an electrodepositing solution of this invention is by dissolving a basic lead compound, such as litharge (PbO), in a solution of sulfamic acid. Such a solution of sulfamic acid may contain, for instance, from 37.5 to 225 grams per liter of sulfamic acid and in this may be dissolved from 50 to 300 grams per liter of litharge. A bath having the desired pH may, for instance, be made up by dissolving about 200 grams per liter of litharge in a sulfamic acid solution containing 150 grams per liter of sulfamic acid. Such a solution will have a pH of about 5.5.

Ideally, solutions made up to the composition above indicated and used according to this invention may be maintained during use by the addition of a composition of this invention comprising substantially basic lead compound together with a minor proportion of sulfamic acid. Suitable basic lead compounds are, for instance, carbonates, basic carbonates or hydroxides of lead, but particularly good results are obtained using oxides such as litharge. The minor proportion of sulfamic acid should be sufficient to compensate for the drag-out of sulfamic acid from the solution during use and may be, for instance, about from 1 to 10 per cent of the weight of the mixture. A composition comprising about 96.5 parts by weight of litharge and about 3.5 parts of sulfamic acid is particularly well adapted to the purpose. Such a composition is excellently adapted to maintaining the proper balance between bath constituents and pH, namely, a lead sulfamate content of about from 75 to 450 grams per liter at a pH of from 4.2 to 5.9, and should be used in amounts necessary to hold the pH at about 4.2 to 5.9 as above indicated. The proportions of litharge and sulfamic acid depend upon the rate of use of the solution relative to the rate of drag-out, high drag-out rates requiring a higher proportion of sulfamic acid, but in general the proportions indicated are highly satisfactory for normal operations.

The practice of this invention will further be made clear by reference to the following illustrative example.

Example

To a solution containing 150 grams per liter of sulfamic acid there was added 200 grams per liter of litharge and the solution was stirred until the litharge had all dissolved. The resulting solution had a pH of 5.5. In this solution well cleaned panels of steel were made anodes and

electrodeposition was effected by passing a current through the solution using lead cathodes. There was thus produced upon the steel panels a black deposit which was strongly adherent, abrasion-resistant, corrosion-resistant, and which upon analysis was found to contain lead oxide and iron oxide.

Electrolysis of the solution was continued for an extended period, a considerable quantity of steel panels being coated with a black deposit during this period of operation. As the bath was depleted by removal of lead and lead oxide constituents, the pH became lower, but was restored to the original value of 5.5 by the addition of litharge from time to time.

While in the foregoing description of this invention there have been shown certain specific processes and coated articles and certain electrodepositing compositions, it will be understood that without departing from the spirit of this invention one skilled in the art may readily employ numerous processes and compositions and produce numerous deposits.

I claim:

1. In a process for producing coatings upon iron group metals, the step comprising electrolyzing an iron group metal anodically in a solution having a pH of about from 4.2 to 5.9 and containing about from 75 to 450 grams per liter of lead sulfamate.

2. In a process for producing coatings upon iron, the step comprising electrolyzing the iron anodically in a solution having a pH of about from 4.2 to 5.9 and containing about from 75 to 450 grams per liter of lead sulfamate.

3. In a process for producing coatings upon nickel, the step comprising electrolyzing the nickel anodically in a solution having a pH of about from 4.2 to 5.9 and containing about from 75 to 450 grams per liter of lead sulfamate.

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