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METHOD AND COMPOSITIONS FOR PRODUCING SURFACE CONVERSION COATINGS ON ZINC

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This invention relates to methods of producing surface conversion coatings on zinc and other metals, and to baths and compositions for making up and for maintaining the baths, and provides improvements therein.

Surface conversion coatings produced in chromic acid and chromate solutions have been long known and used. Notable instances of such prior uses have been the production of surface conversion coatings on magnesium and on zinc. For producing surface conversion coatings on magnesium the method known as a "chrome pickle" and the method known as "specification PT13" (developed at the National Bureau of Standards by Buzzard and Wilson) have been those generally used. Neither of these methods give satisfactory surface conversion coatings on zinc, especially on zinc electrodeposits. The method which has been generally used with zinc is that described in volume 81, Transactions Electrochemical Society, page 354, as the Cronak treatment. This method is one in which zinc is dipped in a solution of sodium dichromate containing sulphuric acid. The disadvantages of said method are limited abrasion resistance, lack of color uniformity, and slowness of the conversion coating in hardening. A late review (1942) of the prior art is found in an article by Edwards "Anodic and Surface Conversion Coatings on Metals," page 341, volume 81, The Electrochemical Society.

According to the present invention, surface conversion coatings are obtained on zinc and on other metals, which are very adherent, so much so that they are not detached by sharp bending and will withstand cutting and shaping operations on the metal. The coatings are hard initially as they come from the bath, enabling articles to be handled immediately following the production of the coating. They may be rubbed with a cloth without removing parts of the coating. They have abrasion and corrosion resistance superior to coatings produced heretofore and have an evenness and liveliness of color such as to give them value as decorative coatings. The invention further provides a method which is readily controllable to give long service with uniform results in the coatings.

According to the present invention, we use a chromate solution containing one or more auxil-

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iary acid radicals having a proportional relation to the chromate content, adjusted to and maintained within a given range of hydrogen ion concentration or pH, and we electrolyse the bath, with the metal on which the coating is to be produced connected as anode, at current densities within a given range and related to the pH value within the pH range, and related also to the proportionality between the chromate concentration and the auxiliary acid radical concentration.

The chromate is advantageously an alkalimetal dichromate or other readily soluble dichromate, sodium dichromate being ordinarily used. It may be used as such or formed by the action of chromic acid and a hydroxide or other suitable alkaline substance.

Auxiliary acid radicals which have been found to give good results are simple and complex sulphate or selenate radicals, and simple and complex fluoride radicals.

We have further discovered that the dichromates and certain compounds containing the auxiliary acid radicals can be put together to form a composition of matter, which, when dissolved in water, gives a proportionality between the chromate and the auxiliary acid radicals, and also a pH, both within the limits of the present invention, and thereby enables the user to make an operating bath merely by dissolving the said composition in water.

The effectiveness of the auxiliary acid radicals varies, but in a general way by adopting one auxiliary acid radical as a standard a relative value can be obtained for the effectiveness, and thereby the proportionality to the chromate, of the other auxiliary acid radicals. Adopting the sulphate radical as a standard, the proportionality range of hexavalent chromium (the constituent of the chromate of interest from an analytical standpoint) to sulphate radical is 10:1 to 30:1 with optimum between 15:1 and 20:1. The proportionality range for any other effective auxiliary acid radical can be obtained by evaluating its effectiveness with reference to the effectiveness of the sulphate radical.

Using a sodium dichromate bath with sodium sulphate as the sulphate radical supplier, for a bath having a concentration of 100 g./l. of sodium dichromate, the range of the sodium sulphate is from 1¾ g./l. to 5½ g./l.

The fluoride radical has been found to have about five times the effectiveness of the sulphate radical and the silico-fluoride radical has been found to have about twice the effectiveness of the sulphate radical. The selenate radical has about the same effectiveness as the sulphate radical. A small amount of sulphate radical in the fluoride type bath improves the throwing power of the bath and makes the coating harder and more adherent.

Certain compounds of the auxiliary acid radicals have a limited solubility in chromate solutions and give a soluble content of the acid radical within the proportionality range, and by choice of such compounds of the auxiliary acid radicals, and the addition thereof in excess of the solubility thereof in the bath, a substantially constant concentration of the auxiliary acid radicals in the bath can be maintained over long periods of operation. For example, by the addition of calcium sulphate or sodium silico-fluoride to a sodium dichromate bath in excess of the solubility thereof in the bath, the amount of the calcium sulphate, or of the sodium silico-fluoride in solution, gives a concentration of the auxiliary acid radical of a value within the proportionality range of the chromate to the auxiliary acid radical, which concentration is maintained as long as calcium sulphate or sodium silico-fluoride is present to go into solution to take the place of sulphate or silico-fluoride radicals which are lost from this bath. A suitable amount of sulphate radical may be introduced into the fluoride type bath by adding sparingly soluble strontium sulphate in excess of the solubility thereof in the bath. Alkali metal sulphates or other soluble sulphates may also be used.

The overall hydrogen ion or pH range of the bath for all auxiliary acid radicals known to have effectiveness is from pH 2 to pH 7. The pH range for a bath with sulphate radicals is from pH 2 to pH 5. For a bath with the optimum chromate, sulphate radical proportionality, the optimum pH is from pH 3 to pH 4.5.

It is advantageous in keeping the pH at the optimum value to add to the bath a soluble buffer salt which is capable of buffering the solution in the desired pH range. The acetate radical and the trivalent chromium radical are examples of effective buffers for the sulphate auxiliary radical type bath. The trivalent chromium radical also improves the throwing power of the bath. The acetate radical may be added as alkali metal acetate, chromic acetate, or other soluble acetate. The trivalent chromium radical may be added as chromic acetate, chrome alum, or by reduction of chromate radical in the solution to trivalent chromium radical by zinc dust.

The pH range for a bath with silico-fluoride radicals is from pH 3 to pH 7, with the optimum from pH 5.5 to pH 6.0. In this type bath the optimum pH range is naturally buffered by the dichromate radicals in the solution and therefore additional buffers are unnecessary.

As the limits of the proportionality range and of the pH range are approached, the obtaining of deposits of good quality and even color becomes more critical, and beyond said limits the effects are unevenness of color, loss of throwing power, and stripping of the zinc or other surface metal especially at points of high current density.

The current densities generally used are from about 2 amperes per square foot to about 50 amperes per square foot.

The current density range which is used in the operation of the method is related to the proportionality between the chromate and auxiliary acid radical contents of the bath and to the pH of the bath. As the pH approaches the lower limit (acidity increases) the current density used is in progressively lower parts of the range. As the auxiliary acid radicals become greater in proportion to the chromate, the current density used is in progressively higher parts of the range, and as the auxiliary acid radicals become less in proportion to the chromate, the current density is in progressively lower parts of the range. However, the operating current densities are governed by both the pH of the bath and the auxiliary acid radical proportionality to the chromate in the bath. In general, when the proportionality between the chromate and auxiliary acid radical is regulated to an optimum, any pH within the range may be chosen and the current density may be regulated to obtain good results. With pH also in the optimum range, good results are obtained through the widest range of current densities, under which conditions the best throwing power is obtained.

The baths are used at room temperatures. A considerable increase of temperature decreases throwing power, or, otherwise expressed, decreases the evenness of the current distribution on the article being anodized.

The time of current flow is generally from 2 to 10 minutes.

The baths are maintained by additions from time to time of chromate, as such, or as chromic acid, as chemical analyses for hexavalent chromium or physical tests indicate. Ordinarily the auxiliary acid radical content is depleted by dragout, but less in proportion than the chromate, so that additions of the auxiliary acid radicals to maintain the proportionality between hexavalent chromium and the auxiliary acid radical may be less frequent. Certain compounds of the auxiliary acid radical may be used in the bath in excess of their solubility therein and when these are used a constant auxiliary acid radical content may be maintained in the bath over long periods of operation. In use the usual tendency is for the pH to rise, and adjustment to lower the pH is advantageously effected by adding chromic acid.

Steel is ordinarily used for the cathode.

The colors of the conversion coatings vary with the metal on which the coatings are developed and on the auxiliary acid radical used in the bath. On zinc a jet black color is obtained in baths of the sulphate radical type, and a yellow closely resembling brass in baths of the fluoride type. These coatings have, in addition to their other properties, high decorative value. On tin a semitransparent grayish coating is obtained in baths of both the sulphate radical type and of the fluoride type. On lead a yellow coating is obtained in both types of baths. On copper a bronze coating is obtained in both types of baths. On silver a red is obtained in both types of baths, the red being darker (maroon) in the sulphate type of bath. On zinc-base die-castings of good quality the coatings are of the same color as is obtained on zinc.

Examples of baths, and of modes of procedure in carrying out the method, according to the present invention follow.

EXAMPLE 1.—SULPHATE RADICAL TYPE

Bath solution

$Na_2Cr_2O_7.2H_2O$	200 g./l.
Na_2SO_4	5.0 g./l.
pH	3–4.5
Current density	3–30 amps./sq. ft.
Temperature	70° F.

EXAMPLE 2.—FLUORIDE RADICAL TYPE

Bath solution

$Na_2Cr_2O_7.2H_2O$	175 g./l.
Na_2CrO_4	25 g./l.
Na_2SiF_6	Excess of solubility
$SrSO_4$	Excess of solubility
pH	5.5–6.0
Current density	3–30 amps./sq. ft.
Temperature	70° F.

EXAMPLE 3.—SULPHATE RADICAL TYPE

Bath solution

$Na_2Cr_2O_7.2H_2O$	300 g./l.
$K\ Cr(SO_4)_2.12H_2O$	2.5 g./l.
$CaSO_4.2H_2O$	Excess of solubility
$CaCrO_4$	1.6 g./l.
CrO_3	1.0 g./l.
pH	3.0 to 4.5
Current density	3–40 amps./sq. ft.
Temperature	70° F.

The concentration of the solution may be varied widely and still have satisfactory film forming characteristics. Concentrations of sodium dichromate from 100 g./l. to 400 g./l. are preferred, though higher or lower concentrations may be used.

Before immersing in the electrolytic surface conversion baths, the metal surfaces are cleaned, and cleaning procedures like those practiced for preparing the metal article for electroplating other metals thereon are followed. No cleaning is required of articles on which metals have been freshly electroplated. A matte or nonreflecting surface conversion coating is obtained on a dull or etched surface, while a glossy surface conversion coating is obtained on a bright surface.

Chemical analysis of the coating on zinc indicates that the coating is in large part zinc chromate, with a small amount of zinc oxide. Our conclusion from this is that the coatings on other metals are composed mainly of a chromate of the metal with a minor amount of oxide of the metal.

What is claimed is:

1. A composition of matter for make-up of aqueous electrolytic baths for the production of surface conversion coatings on metals of the group consisting of zinc, tin, lead, copper and silver, having as its essential constituents a water soluble alkali-metal chromate and a water soluble compound containing auxiliary acid radicals of the group consisting of SO_4, F, SeO_4 and SiF_6 in the respective weight proportions

$$Cr^{VI}/SO_4=10:1 \text{ to } 30:1$$

$Cr^{VI}/SeO_4=10:1$ to $30:1$, $Cr^{VI}/F=50:1$ to $150:1$ and $Cr^{VI}/SiF_6=20:1$ to $60:1$, the amount of alkali metal in said composition being sufficient to impart a pH of 2 to 7 when dissolved in water.

2. A composition of matter according to claim 1, further characterized by the compound containing the auxiliary acid radical having limited solubility in water, the auxiliary acid radical in the dry compound being in excess of the amount required by said proportion range, the amount of the auxiliary acid radical which will go into water solution being within said proportion range.

3. A composition of matter according to claim 2, wherein the auxiliary acid radical containing compound is calcium sulphate.

4. A composition of matter according to claim 1, further characterized by the composition containing the auxiliary acid radical having limited solubility in water, the auxiliary acid radical in the dry compound being in excess of the amount required by said proportion range, the amount of the auxiliary acid radical which will go into water solution being within said proportion range and wherein the auxiliary acid radical containing compound is sodium silicofluoride.

5. An aqueous bath for the electrolytic production of surface conversion coatings on metals of the group consisting of zinc, tin, lead, copper, and silver, having as its essential constituents a water soluble alkali-metal chromate and a water soluble compound containing auxiliary acid radicals of the group consisting of SO_4, F, SeO_4, and SiF_6 in the respective weight proportions

$$Cr^{VI}/SO_4=10:1 \text{ to } 30:1$$

$Cr^{VI}/SeO_4=10:1$ to $30:1$, $Cr^{VI}/F=50:1$ to $150:1$, and $Cr^{VI}/SiF_6=20:1$ to $60:1$, and having a pH between 2 and 7.

6. A method of producing surface conversion coatings on metals of the group consisting of zinc, tin, lead, copper and silver, consisting essentially of passing electric current to an article having a metal surface of said group connected as anode, immersed in an aqueous bath solution having as its essential constituents a water soluble alkali-metal chromate and a water soluble compound containing auxiliary acid radicals of the group consisting of SO_4, F, SeO_4 and SiF_6 in the respective weight proportions $Cr^{VI}/SO_4=10:1$ to $30:1$, $Cr^{VI}/SeO_4=10:1$ to $30:1$, $Cr^{VI}/F=50:1$ to $150:1$ and $Cr^{VI}/SiF_6=20:1$ to $60:1$, and having a pH between 2 and 7.

7. A method according to claim 6, further characterized by the bath solution having room temperature, and the current density being between 2 amperes and 50 amperes per square foot.

8. A method of producing surface conversion coatings on zinc, consisting essentially of passing electric current to an article having a zinc surface connected as anode, immersed in an aqueous bath solution having as its essential constituents a water soluble alkali-metal chromate and sulphate radicals in the proportion

$$Cr^{VI}/SO_4=10:1 \text{ to } 30:1$$

and having a pH between 2 and 5.

9. A method of producing surface conversion coatings on zinc, consisting essentially of passing electric current to an article having a zinc surface connected as anode, immersed in an aqueous bath solution having as its essential constituents a water soluble alkali-metal chromate and fluoride radicals in the proportions $Cr^{VI}/F=50:1$ to $150:1$, and having a pH between 3 and 7.

10. A method of producing surface conversion coatings on zinc, consisting essentially of passing electric current to an article having a zinc surface connected as anode, immersed in an aqueous bath solution having as its essential constituents a water soluble alkali-metal chromate and silicofluoride radicals in the proportion

$$Cr^{VI}/SiF_6=20:1 \text{ to } 60:1$$

and having a pH between 3 and 7.

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