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PROCESS AND COMPOSITION FOR PRODUCING A DYEABLE CORROSION RESISTANT SURFACE ON ZINC AND HIGH ZINC ALLOYS

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This invention relates to dyed, corrosion resistant, metal surfaces of such metals as zinc and high zinc alloys, and more particularly it relates to a composition and process for filming or coating said metals and to the resulting product.

Zinc articles, when subjected to highly humid atmospheres or to actual contact with water, tend to develop a layer or crust of white zinc corrosion products which may be objectionable from the standpoint of appearance. More significantly, such corrosion products may interfere with the operation of articles which are designed to function with small tolerances. It is proposed, according to the invention, to produce a film on the surface of the articles by treating them with a solution or composition hereinafter described. The film acts as an inhibitor to protect the metal by preventing the formation of corrosion products, and in addition, the film thus produced is amenable to further processing, in particular to dyeing.

It is a principal object of the invention to provide corrosion resistant articles of zinc and high zinc alloys in a variety of attractive colors in which both the collar and the corrosion resisting film have good wash fastness and are resistant to wear. Other objects and advantages will appear as the description proceeds.

In general, the invention comprises subjecting the metal to be treated to the action of an aqueous solution comprising a chromium trioxide-containing compound, lactic acid and/or soluble lactates, and a mineral acid. The solution has a pH of approximately 1.0, which is kept within narrow limits and which, together with the lactic acid concentration, constitute more or less critical factors for obtaining satisfactory films and colors. After such treating step the metal is washed, dyed while still wet, dried, and subjected to a curing or heating step to fix the film and dye upon the surface of the metal.

Referring to the solution or composition in detail, and to the chromium compound in particular, it is required that the chromium trioxide-containing compound be a water-soluble material, preferably chosen from the class consisting of chromic acid and its salts, including dichromate salts. Salts of the alkali metals, such as sodium, potassium, and lithium, for example, are preferred, although other water soluble salts may be suitable. The preferred concentration of the chromium compound is about 150 g./l. of chromium trioxide, which corresponds to about 200 g./l. of sodium dichromate. At this concentration, films are produced which show good resist-

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ance to corrosion and which have good affinity for dyes. Commercially available chromium compounds may be employed for making up the composition. Where the expression "chromium trioxide" is recited in the specification and the claims, it is intended to embrace both that particular compound and also compounds inherently containing chromium trioxide, as may be determined by inspection of their chemical formula, an example of which is sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$.

The lactic acid concentration of the composition lies within narrow limits, the most suitable range being from about 0.24 to 2.17 g./l., with about 1.9 g./l. as the preferred concentration. Good dye affinity has been obtained at a concentration of 3.6 g./l., and higher concentrations up to about 9 g./l. may be employed, although at the higher concentrations the color shade may be somewhat light. For some purposes light shades, i. e., light in depth, may be suitable. Beyond about 9 g./l. the affinity for dyes rapidly decreases. Useful results may be obtained with concentrations as low as 0.12 g./l. The practice was to employ an 85% solution of lactic acid in water as a stock solution and to take a portion of this and dilute it as required. The stock solution had a pH of approximately 2.9 and 1 cc. of it weighed 1.122 grams. It was found useful to dilute this solution in the ratio of 75 cc. of water to 25 cc. of solution to form a working solution (hereinafter referred to as the 25% lactic acid solution), 1 cc. of which contained about 0.24 g. of lactic acid. Soluble lactates, such as sodium lactate, may be used in place of lactic acid in equivalent concentrations, and it is to be understood that references to lactic acid in the specification and claims are intended to embrace equivalent amounts of soluble lactates.

The preferred mineral acid is sulfuric, although other acids such as nitric, hydrochloric, and phosphoric have useful application. A sufficient amount of acid is employed to impart to the composition the required pH value. This amount is usually small and depends upon the concentration of lactic acid in the composition. For example, in a composition containing 200 g./l. of sodium dichromate and 1.91 g./l. of lactic acid, the amount of sulfuric acid required to produce a pH of 1.0 is about 5.63 g./l. In the case of sulfuric acid, the practice was to employ a 92% stock solution, 1 cc. of which weighed 1.68 g., and to dilute this solution as required. Preferably the solution was diluted in a ratio of 75 cc. of water to 25 cc. of the stock solution to form a working

solution (hereinafter referred to as the 25% sulfuric acid solution) containing about 0.42 g. of acid per cc.

As stated, the pH of the composition must be closely controlled, this being necessary in order to produce a film having optimum dye affinity. Excellent results are obtained at a pH of 1.0, and a variation of ± 0.1 or ± 0.2 is possible. Below a pH of 0.65 and above pH 1.5 the results are not satisfactory.

The composition may be made up by forming a solution of the chromium compound in water, adding the lactic acid to this solution, and then adding sulfuric acid to adjust the pH. Examples of various compositions and the results obtainable therewith are described below in Example 1.

Zinc and high zinc alloys are the preferred metals which may be treated according to the invention, and particularly good results are secured when these metals are in the form of castings and stampings. Other zinc-containing materials may be processed, such as zinc-plated brass formed by means of alkaline plating processes. Examples of high zinc alloys are (1) aluminum 4.01%, copper 1.00%, magnesium 0.03%, balance zinc; and (2) aluminum 4.01%, magnesium 0.04%, balance zinc. Alloys containing about 90 to 99.9% zinc are specially suitable to the treatment herein described. By the expression "high zinc alloys," as employed throughout the specification and claims, is meant alloys containing a major portion of zinc.

As stated, metal articles of the kind described may be made corrosion-resistant and dyed by subjecting the articles to the action of the above described compositions or solutions and then dyeing them in a bath containing the desired dye. As examples of articles suitable for processing according to the invention there may be mentioned slide fastener stringers, sliders, stops, and the like. It is important that the articles be clean before treating them, in order to avoid the presence of spots, blemishes, etc. in the final product. For this purpose a cleaning step, in which alkaline cleaners are generally used, is employed in advance of the solution-treating step, after which the articles are rinsed with water and/or dilute acid. They are then subjected to the treating or filming step, usually by immersing them in a bath of the treating solution. The film that is thus formed on the metal surface is insoluble, or substantially insoluble, in water and tends to act as a corrosion inhibitor to protect the bare surface. Thereafter the articles are rinsed with water and allowed to drain to reduce the drag-out loss attendant upon their removal from the treating bath. The articles should not be allowed to dry, as this would seriously affect the affinity of the film for the dye. They are, therefore, dyed a few seconds after draining in a solution of an organic, water-soluble dye. The articles are then rinsed, allowed to dry, and subjected to a curing or heating step to fix the dyed film upon the article.

The foregoing process may be described in greater detail, step by step, as follows. In the cleaning step it is necessary to completely remove from the articles all grease, oil, dirt, oxide or other surface contaminants. Dilute alkaline cleaners such as caustic soda, sodium hexameta phosphate, tri-sodium phosphate, etc. have been found satisfactory for this purpose. As an example, a 1% by weight caustic soda solution at a temperature of about 200° F. and a time of about 2 minutes gave excellent results. Temperatures

and times of treatment, however, may vary. Sodium hexameta phosphate in an amount of about 0.5%, or sodium oleyl alcohol sulfate, or both, may be added to the foregoing solution with good results. Preferably the articles are immersed in the cleaning solution and agitated during the course of the operation.

Following the cleaning, the articles are rinsed with cold water to avoid carrying over the alkaline cleaning agent into the acid treating solution. A dilute acid wash, for example, a 1 or 2% by weight solution of sulfuric acid for a few seconds at room temperatures, followed by a water rinse, is helpful to neutralize any alkali remaining on the articles. A small amount of free naphthalene sulfonic acid may be added to the sulfuric acid solution. Such acid wash also has a slight etching action on the metal surface and serves to keep the pH of the treating solution under better control.

The treating step is generally carried out for a time sufficient to produce the desired film or coating on the surface of the metal articles. The treating time is variable, but in practice may be about 15-20 seconds at room temperatures, with 20 seconds as the preferred period. Room temperatures, say 75° F. $\pm 5^\circ$ F., are preferred. Lower temperatures are permissible, although in this case the treating time may have to be increased proportionately. Mild agitation of the articles in the treating bath is desirable to obtain a uniform coverage.

After the treating step the articles should be drained to permit recovery of as much solution as possible without allowing them to dry. In practice, draining times up to 30 seconds may be permissible. Thereafter the articles may be rinsed with water to fully remove the treating solution, and in this operation care must be taken to avoid disrupting the film, which at this stage is rather soft. Preferably the rinsing is accomplished by immersing the articles in a bath of water at room temperatures, although lower and higher temperatures may be used. The rinsing period is usually on the order of about 10 seconds.

Following the rinsing, the articles, while still wet, are immersed in a dye bath for a time sufficient to dye the film, usually about 3 to 6 minutes, and preferably at room temperatures. The bath may be prepared by thoroughly dissolving the usual amount of dye, for example about 0.2% by weight, in a small amount of hot water and then adding this solution to the water in the dye bath. The pH of the dye bath is generally maintained at 4.0 ± 0.5 , and may be adjusted with suitable materials, say acetic acid or aqua ammonia according to the pH of the initial dye solution, which may vary from 2.0 to 11.0 depending upon the particular dyestuff. Agitation of the bath is helpful. A variety of colors are possible, such as black, violet, blue, green, red, walnut brown, chestnut brown, cinnamon brown, grey, and some of the dyes corresponding to these colors are as follows, the Color Index number, where known, being given in parenthesis: Palatine Fast Black WANA Conc., Supramine Fast Black BRA, Wool Violet 4 BN (698), Alizarine Sapphire (1054), Wool Blue C. G., Alizarine Fast Red S. Pdr. 110% (1034), Azo Fuchsine 6B New (57), Wool Red 40F (184), Azo Rubine (179), Milling Red R (430), Acid Anthracene Brown WSGA+Palatine Fast Black WANA, Chrome Fast Brown 3 B, Acid Anthracene Brown WSGA, Fast Acid Brown RG, Alphazurine A (714), Alkali Fast Green 2 G

(735), Alizarine Cyanone Green G Ex. (1078), Naphthol Green B (5), etc. Where articles such as slide fastener stringers attached to cotton stringer tapes are dyed, it is preferable that the dyes should have no affinity for cotton in order to avoid staining the tapes. In such case, dyes commonly used for dyeing silk, wool, or other protein fibers, such as acid, chrome, mordant, mordant-acid, and chromiferous dyes, may be employed. Rinsing off the excess dye from the articles is readily accomplished by employing one or two rinses with water at room temperature. If a dull finish is desired, the rinsing may be carried out at higher temperatures, say 140° F., for about 10 seconds. After rinsing, the articles may be dried at temperatures up to 140–150° F.

As a final step, the articles are cured by heating the same, a preferred treatment being at a temperature of about 200° F. for about 15 minutes. Higher or lower curing temperatures are permissible, say 150 to 250° F., provided the time is suitably adjusted. Higher temperatures will generally require lower times, and vice versa. The main consideration is to fix the film and the dye upon the metal surface to secure the optimum corrosion resistance and color effect.

It is desirable in many cases, particularly with pure zinc articles, to subject them in advance of the cleaning step to a pre-treatment with an acid such as dilute nitric acid to improve the shade of the dye, especially in the case of the lighter shades, and also to render the surfaces of the articles more suitable for filming, as by eliminating spots.

In the case of oily articles, or those containing residual soap, or which, in the manufacturing stage, have been under-burnished or over-burnished or have been subjected to various casting difficulties, it is desirable to subject them initially to a precleaning with dilute neutral or slightly alkaline cleaners at boiling or near boiling temperatures. They may then be rinsed, pretreated with dilute nitric acid, rinsed again, cleaned, subjected to the dilute acid wash (sulfuric acid) above described, then to the solution treating or filming step, etc. Such precleaning serves to remove the oil and soapy material adhering to the surfaces of the articles, while the nitric acid tends to etch the cleaned surfaces, to remove oxide films, etc.

The invention may be illustrated by the following examples:

Example 1

This example illustrates a number of treating solutions containing varying amounts of lactic acid, as listed below. In each case the solution contained 500 cc. of water and 100 gr. of sodium dichromate. The pH of each solution, prior to adjustment, is listed, and the amount of sulfuric acid required to adjust each solution to a pH of 1.0 is also listed.

Sohn. No.	Lactic Acid		Sohn. pH before Adjusting	Sulfuric Acid Required to Adjust Solution to pH 1.0	
	cc. 25% soln.	g./l.		cc. 25% soln.	g./l.
A25	0.25	0.12	4.18	6.2	5.21
A5	0.5	0.24	4.00	6.0	5.04
1A	1.0	0.49	3.72	6.3	5.29
2A	2.0	0.96	3.31	6.1	5.12
4A	4.0	1.91	2.92	6.7	5.63

Another solution, labeled 5A, was prepared containing 8.2 cc. of a mixture of 15 cc. 85% 75

lactic acid, 21 cc. 92% sulfuric acid, and 72 cc. water. Solution 5A contained 2.17 grams per liter of lactic acid, 5.23 grams per liter of sulfuric acid, and had a pH of 1.0. Zinc alloy castings in the form of slide fastener stringers, sliders, and handles were cleaned with an alkaline cleaner and then treated with these solutions. Thereafter they were dyed a variety of colors, including black, navy, walnut and chestnut. Good dye affinity was obtained in all cases, with the solutions containing the higher lactic acid content giving superior results.

Example 2

To illustrate the effect of the pH of the treating solution, eight solutions were prepared, each comprising 500 cc. of water, 100 g. of sodium dichromate, and 1 cc. of lactic acid (solution 1A of Example 1). Each solution was adjusted with sulfuric acid to the pH value listed below and then employed to treat slide fastener stringers. Thereafter the stringers were dyed, using black and walnut shades, and the dye affinity observed. The results are as follows:

pH of Soln.	Dye Shade	Results
2.0	Black	No affinity.
2.0	Walnut	Do.
1.5	Black	Poor affinity.
1.5	Walnut	Limited affinity.
1.0	Black	Good.
1.0	Walnut	Do.
0.65	Black	Fair.
0.65	Walnut	Fair to good.

Example 3

This example shows the variation that is possible in the choice of mineral acid for the treating solution. Zinc alloy slide fastener parts were cleaned with alkali, rinsed with acid, and then subjected to treatment with solution 4A described in Example 1, except that the pH of the solution was adjusted to pH of 1.0 with hydrochloric acid instead of sulfuric acid. Thereafter the parts were dyed navy blue, good results being obtained. The foregoing work was repeated with nitric acid and then with phosphoric acid substituted for the hydrochloric acid, and in each case the results were good.

Example 4

The corrosion resistance of zinc alloy articles treated according to the invention is illustrated by the following example. Zinc alloy slide fastener stringers and parts were processed with solution 4A (pH 1.0) described in Example 1, one sample of each article being left unprocessed for control purposes. Thereafter the samples, except the controls, were dyed a number of shades including black, navy blue, walnut and chestnut. The treatment of the stringers may be set forth as follows:

Clean: 1% sodium hydroxide, 45 sec. at 190–200° F., rinse.

Acid: 1% sulfuric acid, 15 sec. at 75° F., rinse.

Treat: Solution 4A, 20 sec. at 75° F., rinse.

Dye: Color as specified, 5 min. at 75° F., pH 4.1, rinse and dry.

Cure: 15 min. at 200° F.

The treatment of the parts is as follows:

Pretreat: 1% nitric acid, 15 sec. at 75° F., rinse.

Clean: 1% sodium hydroxide + 0.5% sodium oleyl alcohol sulfate + 0.5% sodium hexameta phosphate, 2 min. at 190–200° F., rinse.

Acid: 2% sulfuric acid, 15 sec. at 75° F., rinse.
 Treat: Solution 4A, 20 sec. at 75° F., rinse.
 Dye: Color as specified, 5 min. at 75° F., pH 4.1,
 rinse and dry.
 Cure: 15 min. at 200° F.

Three stringers and three parts were processed with each color. One stringer and one part of each color were then saved as processed control samples while all the other samples, including the unprocessed controls, were subjected to corrosion tests. The latter comprised the following procedure:

The test specimens were sealed in a container which had been adjusted by the use of a saturated potassium sulphate solution to produce a relative humidity of 95% at 120° F. The samples were exposed under these conditions for 22 hours a day and then allowed to cool, while still sealed, to room temperature for 2 hours a day, causing water vapor to condense on the parts. This test was conducted for twenty-eight days with weekly examinations. The degree of corrosion, after each examination, was visually evaluated and recorded.

All samples were examined at the end of 1, 2, 3 and 4 weeks. None of the processed samples showed evidence of corrosion, even after the fourth week of the test. The unprocessed samples all showed some corrosion after the first week of the test, in some cases bad corrosion, and after the second week all showed bad corrosion.

Example 5

In this example is shown the wash fastness of articles treated according to the invention. A number of zinc alloy slide fastener stringers were treated and dyed as described in Example 4. They were then subjected to two series of wash fastness tests. The first series comprised a group of four tests at 160° F., using 0.5% by weight of oleate soap and 0.25% by weight of sodium hexametaphosphate for 30 minutes. After each test, samples were taken out of the bath, rinsed and dried. Some of the test samples were removed and the remainder run again. The second series of tests was like the first series except that the temperature was 212° F.

The results showed excellent wash fastness of all the samples. In fact, the washed articles appeared to be brighter and to have a deeper shade of color than the unwashed articles.

Example 6

This example illustrates the steps of precleaning and pretreating metal articles prior to the alkaline cleaning, acid washing, filming, and dyeing of the same. A number of zinc alloy slide fastener parts were subjected to the following treatment, the dye shades including black, navy blue, walnut, and chestnut:

Preclean: 0.5% sodium salt of lauryl alcohol sulfate + 0.25% sodium hexameta phosphate for 45 sec. at 200-210° F. Rinse.

Pretreat: 3% nitric acid for 15 sec. at 75° F. Rinse.

Clean: 1% sodium hydroxide + 0.5% sodium oleyl alcohol sulfate + 0.5% sodium hexametaphosphate, 2 minutes at 190-200° F.

Acid: 2% sulfuric acid + 0.5% free naphthalene sulfonic acid, 15 sec. at 75° F.

Treat: Solution 5A, 20 sec. at 75° F.

Dye: Shades as required.

Good coverage of both the film and the dye were secured.

The process described above is well adapted to either continuous or batch operation, particularly the former.

It will be understood that, unless otherwise indicated, variations in the ingredients and conditions of the process are permissible within the scope of the invention.

In the light of the foregoing description, the following is claimed:

1. A composition for producing a corrosion resistant coating having good dye affinity on the surface of zinc and high zinc alloys which comprises essentially a water soluble chromium trioxide-containing compound selected from the class consisting of chromic acid and salts thereof, said compound being present in an amount equivalent to about 150 grams per liter of chromium trioxide, about 1 to about 9 grams per liter of lactic acid, an amount of strong mineral acid sufficient to impart a pH of 0.65 to 1.5 to the composition, and the balance water.

2. A composition for producing on zinc and high zinc alloys a corrosion resistant surface having good affinity for dyes which comprises essentially about 150 grams per liter of chromium trioxide, about 1 to about 9 grams per liter of lactic acid, an amount of sulfuric acid sufficient to impart a pH of about 0.65 to 1.5 to the composition, and the balance water.

3. A composition for producing a corrosion resistant surface having good affinity for dyes on zinc and high zinc alloy castings and stampings which comprises essentially a water soluble dichromate containing about 150 grams per liter of chromium trioxide, about 1 to about 9 grams per liter of lactic acid, an amount of sulfuric acid sufficient to impart a pH of about 0.65 to 1.5 to the composition, and the balance water.

4. A composition for producing a corrosion resistant surface having good affinity for dyes on zinc and high zinc alloy castings and stampings, which comprises essentially about 200 grams per liter of sodium dichromate, about 1.9 grams per liter of lactic acid, an amount of sulfuric acid sufficient to impart a pH of about 1.0 to the composition, and the balance water.

5. A process for rendering the surface of zinc and high zinc alloys corrosion resistant and amenable to dyeing which comprises subjecting the metal to the action of the composition described in claim 1 for a time sufficient to produce a film on the surface of the metal, and then washing said surface.

6. A process for producing corrosion resistant surfaces on zinc and high zinc alloys and coincidentally rendering such surfaces amenable to dyeing which comprises subjecting the metal to the action of the composition described in claim 3 for a time sufficient to produce a film on the surface of the metal, and then washing said surface.

7. A process for producing corrosion resistant surfaces on zinc and high zinc alloy castings and stampings and coincidentally rendering such surfaces amenable to dyeing which comprises subjecting the castings and stampings to the action of the composition described in claim 4 for a time sufficient to produce a film on the surface of the castings and stampings, and then washing said surface.

8. A process for producing a dyed, corrosion resistant surface on zinc and high zinc alloys which comprises subjecting the metal to the action of the composition described in claim 1 for a time sufficient to produce a film on the surface

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of the metal and then dyeing the treated metal before said filmed surface is dry.

9. A process for producing a dyed, corrosion resistant article of zinc and high zinc alloys which comprises subjecting the article to the action of the composition described in claim 2 for a time sufficient to produce a film on the surface of the article and then dyeing the treated article before said filmed surface is dry.

10. A process for producing dyed, corrosion resistant castings and stampings of zinc and high zinc alloys which comprises subjecting the castings and stampings to the action of the composition described in claim 4 for a time sufficient to produce a film on the surface of the castings and stampings, rinsing said composition from the castings and stampings, dyeing the treated cast-

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ings and stampings while still wet, and then curing the castings and stampings.

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