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METHOD OF COATING METAL

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This invention relates to the art of treating metal surfaces to improve their corrosion resistance and to prepare them to receive a siccative finish and is especially concerned with the treatment of ferriferous, zinciferous and aluminiferous surfaces.

Many different types of treatments have been proposed for these purposes such, for example, as the application of chemical conversion coatings of one kind or another by employing treating baths consisting essentially of aqueous acid phosphate or acid chromate solutions. Other procedures embody the addition of resinous vehicles to aqueous acid treating solutions containing such agents as chromic acid or soluble salts thereof. However, regardless of the particular system employed, the ultimate objective of such practices is essentially the same, namely, to secure maximum corrosion protection of the metal substrate while simultaneously achieving high levels of impact resistance, flexibility and paint bonding qualities. Naturally, the securing of such a desirable combination of properties is often difficult to achieve, as witness the many proposals which are familiar to the art, particularly as found in the patent and other literature now available in this field.

The principal object of the present invention is to provide an improved method as well as improved solutions for applying resinous, protective, flexible and impact-resistant paint-bonding coatings on the surfaces of ferriferous, zinciferous and aluminiferous surfaces.

It is also an object of this invention to provide stable coating solutions for the purposes described.

Another object is to produce articles having a final siccative finish which are greatly improved as to appearance, corrosion resistance and longevity.

Before describing the nature of the present invention I wish to call attention to the disclosure in my co-pending application Ser. No. 61,398, filed October 10, 1960, now Patent No. 3,063,877, because certain of the features described therein are utilized in connection with the present invention. In said earlier application I have disclosed a method of coating metal surfaces by treating them with an aqueous acid solution containing mixtures of hexavalent chromium as well as reduced forms of chromium. Solutions of such chromium compounds were referred to in the said application and will be hereinafter referred to as solutions of "mixed chromium compounds" and the preferred manner of preparing them, as disclosed in the said application, is by reacting an aqueous solution consisting essentially of from 50 to 800 g./l. of hexavalent chromium compound, expressed as CrO_3, with from 0.03 to 1 mol of formaldehyde, expressed as HCHO, for each mol of said hexavalent chromium compound. As pointed out in my earlier application solutions containing such mixed chromium compounds can be utilized to improve the corrosion resistance not only of a previously applied coating but also of the surface of a bare metal substrate itself.

In the procedure just described it is preferred that sufficient formaldehyde be reacted with the chromic acid

(CrO_3) to reduce at least 5% and preferably at least 20% of the total hexavalent chromium present. After the reaction, it has been found that the upper limit on the amount of total chromium present in reduced form is about 60% and that this holds true even though large excesses of formaldehyde and high temperatures during or following the use of formaldehyde are employed. As pointed out in my previous application referred to above, I have found it desirable to employ at least 0.03 mol of formaldehyde (calculated as HCHO) for each mol of hexavalent chromium (calculated as CrO_3) in order to reduce at least the minimum amount of chromium. For example, when a 33 percent CrO_3 solution is reacted with formaldehyde using the formaldehyde/chromic acid mol ratio of 0.03 to 1, there results a solution with about 5 percent of the chromium in reduced form. As an illustration of reaction ratios yielding a higher percentage of reduced chromium, I have found that by starting with the same 33 percent CrO_3 solution and reacting this solution with formaldehyde utilizing a formaldehyde/chromic acid mol ratio of 0.1 to 1, a solution containing about 20 percent of the chromium in reduced form is obtained. Thus, it can be seen that the use of a low formaldehyde/chromic acid ratio yields lower total reduced chromium. In addition, it has been found that decreasing concentration of the chromic acid results in lower reduced chromium values. Conversely, the amount of chromium obtained in the reduced state may be increased by utilizing more concentrated chromic acid or a higher formaldehyde to chromic acid ratio.

Because of the limitation on the maximum amount of chromium which can be reduced by the technique just described, it is not necessary, in general, to use more than about 1 mol of formaldehyde for each mol of hexavalent chromium. If higher mol ratios are used the resultant product may tend to gel on standing. Such gel causes no apparent harm and may be broken up by vigorous stirring.

It should be noted that, since the reaction of formaldehyde with chromic acid is exothermic, it is generally preferred to add aqueous formaldehyde solution to the chromic acid because this procedure permits close control of the temperature and it is best to operate without raising the temperature above 180° F.

I have now made a surprising additional discovery, namely, that, if there be added to an aqueous solution containing at least 0.25% by weight of mixed chromium compounds and at least 0.25% by weight of a polyacrylic acid compound, an admixture will be produced which, when applied to metal substrates and dried, will yield a coating which has greatly improved corrosion and impact resistance, flexibility and paint bonding ability.

In connection with the present invention, it should be noted that the polyacrylic acid compound may include both water soluble as well as water dispersible types. However, in this disclosure, the word "solution" is to be understood as meaning dispersions as well as aqueous solutions. Water soluble types are readily available as standard articles of commerce, among which are the products known under the proprietary name of Acrysol. For example, aqueous solutions of polyacrylic acids having different molecular weights and viscosities are designated as Acrysol–A–1 and Acrysol–A–3. Water dispersible emulsions of polyacrylic acids are also commercially available and among these are those known as the Rhoplex AC–200 emulsions. In addition, alkali metal and/or ammonium salts of polyacrylic acids are also available from various commercial sources. Acrysol and Rhoplex are trademarks registered in the name of the Rohm & Haas Company.

In addition to the polyacrylic acid compounds noted just above there also exist aqueous emulsions of acrylic esters called polymer latices such as those available under the designation EDX-1, the latter being the trademark of the Reichold Chemical Company.

While tests with all of these different types of polymeric acrylic acid products show that acceptable results may be obtained therewith, provided they are utilized in accordance with the teachings of this invention yet, I have found that somewhat improved corrosion resistance is obtainable where the coating solutions employed have been prepared from all acid systems. Where the alkali metal or ammonium salts of either the polyacrylic acid compound or the mixed chromium compounds have been excluded from the coating baths, it has been noted that humidity and water soak corrosion tests of the coatings show noticeable improvements in quality, uniformity and corrosion resistance. Accordingly, in order to secure maximum coating improvement with the process of this invention it is preferred to employ all acid systems to the exclusion of alkali metal or ammonium salts.

Hereinafter, in this specification and in the accompanying claims reference to "polyacrylic acid" is to be understood as applying to all of these types and grades of the product in question.

As noted hereinabove, the minimum amount of mixed chromium compounds which must be present in the aqueous coating solutions of this invention is 0.25% by weight of the coating solution. Where less than 0.25% by weight of these mixed chromium compounds is utilized, the subsequently produced coatings will not provide the increased corrosion resistance otherwise obtainable by use of the teachings of this invention.

So far as the polyacrylic acid content is concerned, this also must be present, as noted hereinabove, in an amount of at least 0.25% by weight of the coating solution. If less than 0.25% of polyacrylic acids are employed, no substantial improvement in coating properties will be realized. So far as the upper limit of polyacrylic acid is concerned, it has been found that no additional improvement, over those obtained initially, is experienced by the use of more than about 5% by weight of the polyacrylic acids based upon the weight of the coating solutions. A preferred upper limit of 2% (by weight based on the weight of the coating solution) of polyacrylic acids has been found on the basis of optimum results consistent with maximum economy of operation.

While the amount of mixed chromium compounds used may be as much as 10 parts thereof for each part of polyacrylic acid, it has been found, in the interests of economy, and to secure maximum efficiency of operation, that the amount of mixed chromium compounds should range from about 0.5 part to about 5 parts thereof for each part of polyacrylic acid employed in the coating solution.

When admixing the polyacrylic acid solution with the aqueous solution of mixed chromium compounds there is no apparent need to observe cooling precautions. However, the type of water used to dilute the mixed chromium compound solutions, or to dilute admixtures of polyacrylic acid and mixed chromium compound solutions should not be what is customarily termed "hard" water, since a measure of precipitation sometimes occurs when using such water. While many natural waters are entirely suitable for use in effecting dilution of either the mixed chromium compound solutions, or mixtures thereof with the polyacrylic acids, it is preferred, in the interest of avoiding any possible precipitation of coating constituents, to utilize either de-ionized or distilled water supplies. Where distilled or de-ionized water sources are not available, it is then recommended that the solution pH be maintained below about 2.3 since this pH level has been found to minimize substantially or to eliminate precipitation tendencies. The pH control may be accomplished through the addition of small increments of phosphoric or formic acids, and optimum blending is obtained when brisk agitation is employed throughout the mixing operation.

If desired, compatible co-solvents may be added to the coating solutions of the present invention in order to improve the spreadability and viscosity flow characteristics thereof. Such co-solvents which have been found to be especially suitable for use in this respect include aliphatic alcohols and ketones containing up to four carbon atoms, and aliphatic ether alcohols containing from 4 to 8 total carbon atoms. Typical examples of these are the methyl, ethyl and butyl alcohols, acetone, methylethyl ketone, and the mono and diethyl, propyl and butyl ethers of ethylene glycol.

The amount of co-solvent to be employed may range from as little as 0.1% to 20% based upon the weight of the coating solution. Generally, however, the use of from 0.1 to about 5% by weight of the coating solution will provide a maximum improvement in the flow characteristics of the coating solutions.

The solutions of this invention as described above are extremely stable and can be applied to reasonably clean metal surfaces. Where only slight oil films are present on the surface to be treated it is preferable to apply a solvent cleaning agent before the solution is applied. If the metal to be coated is heavily contaminated with oil or dirt a stronger cleaning agent, such for example as sodium orthosilicate is preferably employed. However, the cleaning stage itself forms no specific part of the present invention so it will suffice to state that conventional cleaning operations familiar in the art will be adequate for the purposes of this invention.

The coating solution is preferably applied at average living room temperatures, i.e., in the neighborhood of 72° F. which obviates a need for maintaining heated coating baths and heating equipment. Nevertheless, if desired, the baths of this invention may be applied at elevated temperatures without deleterious effect upon the quality of the resulting coatings.

The baths may be applied to the metal surfaces by dip, spray or roller coating techniques, the important consideration, of course, being that the entire surface area be adequately and thoroughly wetted by the bath. In this latter respect, it is quite permissible with this invention to incorporate in the coating solutions from 0.01% to 0.1% by weight thereof of a suitable wetting agent. While various cationic, anionic or non-ionic wetting agents have been found to be suitable for use in this respect, the preferred types are the non-ionics, typical of which are the polyethoxylated alkyl phenols containing from 6 to 12 ethylene groups, and from 8 to 9 carbon atoms in the alkyl group.

After the solution has been applied to the metal surface the surface should be subjected to a drying operation. This drying serves to cure the mixed organic-inorganic coating and, of course, the length of the drying step will depend upon the temperature utilized. Naturally, if the temperature is rather low a relatively long period of time will be necessary to effect a complete cure whereas, if the temperature is somewhat elevated, the drying and curing can be accomplished in less time. A preferred range of temperatures for the drying operation lies anywhere from about 200° to 350° F. because it has been found that temperatures within this range yield especially good results.

A coating produced in the manner just described is extremely useful per se and for some purposes will be all that is required. However, a siccative finish is generally applied to the coated surface and where this is desired the following technique may be employed. The coated surface, preferably, is at least surface dried but before drying is sufficiently complete to effect the required cure, the siccative film may be applied, following which a single baking step may be employed which will serve to completely cure the coating of the present invention while simultaneously effecting the customary baking of the siccative finish.

Certain specific procedures embodying the invention will now be described by way of example, but it is to be understood that these specific procedures should not be construed as limiting the scope of the invention except as defined in the accompanying claims.

Clean, cold-rolled steel panels were roller-coated at room temperature utilizing solutions of coating agents according to the present invention as identified below. After application of the coatings, each panel was dried for a 5-minute period at 350° F. After cooling, each panel was then painted with a standard automotive enamel and baked to cure the same. Corrosion tests are reported in Table I below and they include:

(*a*) Salt spray (336 hours) (ASTM-B-117-57T)
(*b*) Humidity (JAN H-792)
(*c*) Water soak (ASTM-D-870-54T)
(*d*) Bell adhesion test

The abbreviations used to characterize the coating agents employed are in accordance with the following table:

MCC—Mixed chromium compounds (in accordance with U.S. application Serial No. 61,398, filed October 10, 1960), now Patent No. 3,063,877. The total chromium content within the mixed chromium compounds was calculated as CrO_3 for purposes of making the comparisons in the following tables.

A-1—Acrysol A-1—Reported to be a water soluble solution of polyacrylic acids.

A-3—Acrysol A-3—Reported to be a water soluble solution of polyacrylic acids.

AC-200—Rhoplex AC-200—Reported to be a water dispersible emulsion of polyacrylic acids.

EDX-1—Reported to be an aqueous emulsion of an acrylic ester copolymer latex.

In all examples reporting the use of a polyacrylic acid compound, the amount used represents 100% of the respective compound.

Table I

Example No.	Coating system		Corrosion test results			
	Agent	Percent by wt.	Inch scribe failure in ASTM-B-117-57T	JAN H-792	ASTM-D-870-54T	Bell adhesion
1	CrO_3	0.25	Complete failure			Failed.
2	CrO_3	1	do			Do.
3	CrO_3	2	do			Do.
4	MCC	0.25	⅜	10	7.5	Do.
5	MCC	1	¼	10	7.5	Do.
6	MCC	2	3/16	10	8.0	Do.
7	A-1	0.25	Complete failure			Do.
8	A-1	2	do			Do.
9	A-3	0.25	do			Do.
10	A-3	2	do			Do.
11	AC-200	2	do			Do.
12	EDX-1	2	do			Do.
13	CrO_3 plus A-1	0.25 0.25	⅝	9.5	8.5	Do.
14	CrO_3 plus A-1	0.5 0.5	¼	9.5	8.5	Do.
15	CrO_3 plus A-1	1 1	⅛	10	8.5	Passed.
16	CrO_3 plus A-1	4 2	⅛	10	7.5	Do.
17	CrO_3 plus A-1	4 4	⅛	8	8.5	Do.
18	MCC plus A-1	0.25 0.25	⅛	10	10	Do.
19	MCC plus A-1	0.5 0.5	1/16	10	10	Do.
20	MCC plus A-1	1 1	Slight trace	10	10	Do.
21	MCC plus A-1	2 1	do	10	10	Do.
22	MCC plus A-1	1 2	do	10	10	Do.
23	MCC plus A-1	4 1	do	10	9.5	Do.
24	MCC plus A-1	4 2	do	10	10	Do.
25	MCC plus A-3	1 1	do	10	10	Do.
26	MCC plus A-3	4 2	do	10	10	Do.
27	MCC plus AC-200	2 1	do	10	10	Do.
28	MCC plus EDX-1	1 1	do	10	10	Do.
29	MCC plus EDX-1	4 1	do	10	10	Do.

In connection with Table II set forth below, clean, hot-dipped galvanized steel panels were roller-coated at room temperature utilizing solutions of coating agents according to the present invention as described in the examples included in the table. The coated panels were subsequently heated at 350° F. for 5 minutes and were then painted with a baking enamel. In each instance the test is listed opposite the example given in the table. The abbreviations employed are the same as those which were used in connection with Table I. The Bell adhesion test was replaced by an impact test wherein a ¾" ball is dropped upon a test panel under a given inch-pound force. The deformed surface is then examined for loose or cracked paint and ratings in inches of paint failure are reported.

Table II

Example No.	Coating system		Corrosion test results			
	Agent	Percent by wt.	Inch scribe failure in ASTM-B-117-57T	JAN H-792	ASTM-D-870-54T	Impact
30	CrO_3 plus A-1	0.25 0.25	1/8	9.0	9.0	No failure.
31	CrO_3 plus A-1	1 2	1/16	9.0	8.0	Do.
32	CrO_3 plus A-3	1 2	1/16	8.5	8.0	1/16.
33	CrO_3 plus A-3	2 1	3/16	8.0	7.5	3/16.
34	CrO_3 plus A-3	4 1	1/8	7.5	7.0	5/16.
35	MCC plus A-1	0.25 0.25	1/16	10	9.5	No failure.
36	MCC plus A-1	1 2	1/16	10	10	Do.
37	MCC plus A-3	1 2	1/16	10	10	Do.
38	MCC plus A-3	2 1	Slight trace	10	9.5	Do.
39	MCC plus A-3	5 1	1/32	10	10	Do.
40	MCC plus A-3	10 1	1/32	10	10	1/16.

In another test clean aluminum panels were treated with solutions according to the present invention containing (1) 1% Acrysol A-1 plus 4% mixed chromium compounds and (2) 2% Acrysol A-1 plus 4% mixed chromium compounds. These panels were dried and then painted with a baking enamel. The results in 5% salt spray corrosion testing (ASTM-B-117-57T) showed no failure after 1,000 hours.

From the test results reported above, it is clearly apparent that the production of coatings on ferriferous, zinciferous and aluminiferous surfaces by treating them with solutions according to the present invention containing mixed chromium compounds and polymers of acrylic acid results in the production of coatings having considerably enhanced flexibility and paint bonding characteristics as well as marked improvement in impact and corrosion resistant properties and that all of these improvements constitute a substantial advance over the results obtainable with prior art practices.

I claim:

1. The method of applying a coating to the surface of metal from the class consisting of iron, zinc and aluminum which method comprises treating the surface with an aqueous bath the coating-producing ingredients of which bath consist essentially of

(1) mixtures of chromic acid and its soluble salts and reduced forms thereof

and

(2) water-soluble and water-dispersible polyacrylic acid compound chosen from the class which consists of the said acid, the alkali metal and ammonium salts thereof and aqueous emulsions of acrylic esters known as polymer latices

the quantity of each of (1) and (2) in the bath being not less than 0.25% by weight, the treatment being continued until the surface is completely wetted by the solution, and then drying the surface.

2. The method of claim 1 wherein the mixed chromium compounds consist of approximately 40 to 95% hexavalent chromium with the remainder in reduced forms of chromium.

3. The method of claim 1 wherein the quantity of mixed chromium compounds employed in the bath is from 0.5 to 5 parts for each part of polyacrylic acid compound.

4. The method of claim 1 wherein the pH of the bath is maintained below about 2.3.

5. The method of claim 1 wherein the pH of the bath is maintained below about 2.3 by adding, as required, small amounts of acid from the class of phosphoric and formic acids.

6. The method of claim 1 wherein the bath is employed approximately at average living room temperature.

7. The method of claim 6 wherein the drying temperature is from approximately 200° to 350° F.

8. The method of claim 1 wherein a siccative film is applied to the coating after surface drying thereof but before a complete cure has been effected by the drying step.

9. The method of claim 8 wherein the drying temperature is from approximately 200° to 350° F.

10. An aqueous solution for coating metal surfaces, the principal coating-producing ingredients of which solution consist essentially of

(1) at least 0.25% by weight of reaction products derived from the admixture of an aqueous acid solution consisting essentially of from about 50 to about 800 gms./liter of hexavalent chromium, expressed as CrO_3, with from about 0.03 mol to about 1 mol of formaldehyde, expressed as HCHO, for every mol of hexavalent chromium

and

(2) at least 0.25% by weight of water-soluble and water-dispersible polyacrylic acid compound chosen from the class which consists of the said acid, the alkali metal and ammonium salts thereof and aqueous emulsions of acrylic esters known as polymer latices.

11. A solution according to claim 10 wherein component (2) consists of acid components from the said class.

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