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3,189,488

SOLUTIONS AND METHOD FOR COATING
METAL SURFACES

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No Drawing. Filed Sept. 24, 1962, Ser. No. 225,876
10 Claims. (Cl. 148-6.2)

This invention relates to the art of coating metal surfaces, and more particularly it relates to the art of applying, through use of stable coating solutions, polymeric, protective and adhesion promoting coatings to ferriferous, zinciferous and aluminum surfaces prior to the subsequent application of siccative type finishes.

Many different types of coatings have been proposed for treating metal surfaces. Some of these include chemical conversion coatings of the type which are obtained with the use of solutions containing such agents as acid phosphates and/or chromates. Others embody the addition of resinous vehicles to aqueous acid solutions containing such agents as chromic acid or salts thereof.

Regardless of the system employed, the ultimate objective remains unchanged, i.e., the desire to secure maximum corrosion protection of the metal substrate while simultaneously realizing high levels of paint adhesion, impact resistance and flexibility. That the ability to secure such a desirable combination of properties has proven difficult is evident from the host of literature, particularly patent literature, available in this field.

The principal object of the present invention is the provision of improved methods and solutions for applying resinous, protective, flexible and impact-resistant paint bonding coatings to ferriferous, zinciferous and aluminiferous surfaces.

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

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

In my co-pending application Serial No. 61,398, filed October 10, 1960, now U.S. Patent No. 3,063,877, which disclosure is hereby incorporated into this specification and made a part hereof, I disclosed a method of coating metal surfaces through use of an aqueous acid solution containing chromium compounds, which solution comprises not only hexavalent chromium but also reduced forms thereof. Such a solution of chromium compounds, which hereinafter will be referred to simply as "mixed chromium compounds," is obtained by the reaction of an aqueous solution consisting essentially of from 50 to 800 g./l. of a 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. Coatings resulting from such a solution provide high levels of corrosion resistance on either coated or bare metal surfaces.

In the procedure just described it is preferred that sufficient formaldehyde be reacted with the chromic acid (CrO_3) to reduce at least 5%, 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 is true even where large excesses of formaldehyde and high temperatures during or following the use of formaldehyde are employed. As indicated

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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 the 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/chromic acid ratio.

Due to 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 formation causes no apparent harm and may be broken 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 the surprising additional discovery that if there is added to an aqueous solution containing at least 0.25% by weight of mixed chromium compounds (as hereinabove described), at least 0.1% by weight of a water soluble polymer of hydroxyethyl ether of cellulose, an admixture will be produced which when applied to metal substrates and dried, will yield coatings having improved flexibility, paint adhesion and impact and corrosion resistance.

The cellulose polymers found to be suitable for use in accordance with the teachings of this invention are water soluble hydroxyethyl ethers of cellulose. These polymers are derived from the etherification of cellulose with hydroxyethyl groups, and are reputed to be nonionic in character. Such products are commercially available under the proprietary name Natrosol in several viscosity grades ranging from less than 100 centipoises (cps.) to several thousand cps. (Brookfield) at 25°C . for 1% solutions thereof.

Hereinafter reference to "cellulose polymers" will be understood as applying to water soluble polymers of hydroxyethyl ethers of cellulose.

As noted hereinabove, the minimum amount of mixed chromium compounds which must be present in the solutions of this invention must be 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 the use of the teachings of this invention.

So far as the cellulose polymer content is concerned, this must be present, as noted hereinabove, in an amount of at least 0.1% by weight of the coating solution. If less than 0.1% of the cellulose polymer is utilized, no substantial improvement in coating properties will be realized. With respect to an upper limit of cellulose polymer, it has been found that no additional improvements over those obtained initially are experienced by the use of more than about 2% by weight of the high viscosity types, or more than about 5% by weight of the lower viscosity types, based on the weight of the coating solution. A preferred upper limit of 2% by weight (based upon the weight of the coating solution) of cellulose polymer 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 cellulose polymers, 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 to about 5 parts thereof for each part of cellulose polymers employed in the coating solution.

In order to mix the cellulose polymers with solutions of the mixed chromium compounds it has been found desirable to dissolve the cellulose polymers in an aqueous system and to add this aqueous polymer solution to the aqueous solution of mixed chromium compounds. The addition of the aqueous polymer solution to the solution of mixed chromium compounds requires no cooling precautions. However, the type of water used to dilute the mixed chromium compound solution or to dilute admixtures of cellulose polymers with mixed chromium compound solutions should not be what is customarily termed "hard" water, since a measure of precipitation sometimes occurs upon dilution with such "hard" 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 cellulose polymers 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 acids such as phosphoric or formic, and the 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 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 0.1 to about 5% by weight of the coating solution will provide a maximum improvement of flow characteristics to the coating solutions.

Application of the stable cellulose polymer mixed chromium compound solution should be made on reasonably clean metal surfaces. Where only slight oil films are present on such metal to be treated, it is preferable to employ a solvent cleaning agent. If the metal to be coated is heavily coated with oil or dirt, a stronger cleaning agent, such as for example a sodium orthosilicate solu-

tion, is preferably employed. However, since the cleaning stage forms no part of the present invention, it will suffice to state that conventional cleaning operations will be adequate in freeing the metal surfaces of contaminants.

The coating application is preferably carried out at room temperature, thereby obviating the need for maintaining heated coating baths and heating equipment. However, if desired, the improved coatings of this invention may be applied at elevated temperatures with no deleterious effects upon resultant quality.

The solutions may be applied to metal surfaces by dip, spray or roller coating techniques, the important consideration being that the entire surface area be thoroughly wetted by the coating solution. In this latter respect, it is within the purview of this invention to incorporate into these coating solutions from 0.01 to 0.1% by weight thereof of a wetting agent. Use of such agents facilitates wetting of the metal surfaces to be treated. While various cationic, anionic or nonionic 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.

Following application of the solutions of this invention to base metal surfaces it is necessary to subject the treated surfaces to a drying stage. The drying stage serves to cure the mixed organic-inorganic coating and the length of such drying period will of course depend upon the temperature utilized. 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. It has been found that a preferred range of temperatures for the drying operation lies anywhere from about 200° to 350° F.

A coating produced in the manner just described is extremely useful per se and for some purposes will be all that is required in order to provide the proper level of corrosion protection. 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 cure completely the coating of the present invention while simultaneously effecting the customary baking of the siccative finish.

The invention will now be described in detail with reference to specific embodiments thereof, which embodiments are intended to be illustrative only and are not to be construed as in any way limiting the scope of this invention.

Clean, cold-rolled steel, galvanized steel and aluminum panels were roller-coated at room temperature utilizing solutions of coating agents as identified below. After application of the coatings, each panel was baked for five minutes at 350° F. After cooling, each panel was painted with a standard automotive enamel and baked to effect curing of same. Various corrosion test results were determined on these treated panels, and such tests included:

- (a) Salt spray (336 hours) (ASTM-B-117-57T)
- (b) Humidity (JAN H-792)
- (c) Adhesion—Conical Mandril (ASTM-D-522-41)
- (d) Impact—The test panel is impacted by a falling ¾" ball with a given force measured in inch-pounds, deforming the test specimen. After impact, the deformed surface is inspected for loose or cracked paint, usually on the reverse side of the impact, and rated descriptively. The degree of deformation, and accordingly the severity of any given force of impact is dependent upon the thickness of the specimen. Normally specimens heavier than 16 gage (0.0625") are not used, for the maximum impact

available, 86.7 inch-pounds, causes little deformation to these heavy sections.

The abbreviation "MCC" used in the following table comprises mixed chromium compounds (in accordance with U.S. application Serial No. 61,398, filed October 10, 1960). The total chromium content within the mixed chromium compounds was calculated as CrO_3 for purposes of making comparisons with CrO_3 formulations in the following table.

Example No.	Metal coated	Percent MCC	Cellulose polymer		Corrosion test results			
			Type	Percent	(a) Inch scribe failure in ASTM B-117-57T	(b) JAN H-792	(c) ASTM D-522-41	(d) Adhesion, impact (65 inch-lbs.)
1	Steel	None	Natrosol 250 H	0.1	Failed			Failed.
2	do.	do.	do.	1	do.			Do.
3	do.	do.	do.	2	do.			Do.
4	do.	0.25	do.	0.1	None	10	10	Passed.
5	do.	0.4	Natrosol 250 G	0.1	do.	8	9	Do.
6	do.	0.4	do.	0.25	do.	9	9	Do.
7	do.	1	Natrosol 250 L	0.1	do.	9	9.5	Do.
8	do.	1*	do.	0.1	Failed	8	9.5	Failed.
9	do.	1	do.	0.25	Trace	9.5	9.5	Passed.
10	do.	2	Natrosol 250 M	0.1	None	10	10	Do.
11	do.	2*	do.	0.1	Failed	8	9	Failed.
12	do.	2	do.	0.5	Trace	9.5	10	Do.
13	do.	2	Natrosol 250 L	1	do.	9	9	Do.
14	do.	2	do.	2	do.	9.5	9.5	Passed.
15	Aluminum	1	Natrosol 250 H	0.1	None	9.5	10	Do.
16	do.	2	do.	0.1	do.	10	10	Do.
17	do.	2	Natrosol 250 G	0.25	do.	9	10	Do.
18	do.	2	do.	0.5	do.	10	10	Do.
19	do.	2	Natrosol 250 L	2	do.	10	10	Do.
20	Galvanized steel	1*	do.	0.8	Failed	7	7.5	Failed.
21	do.	1	do.	0.8	Trace	9.5	10	Passed.
22	do.	2	do.	0.1	do.	9	10	Do.
23	do.	2	Natrosol 250 G	0.25	do.	10	10	Do.
24	do.	2	do.	0.5	do.	10	10	Do.
25	do.	2	Natrosol 250 L	2	do.	9	9.5	Do.

*Used CrO_3 rather than the mixed chromium compounds.

NOTE.—NATROSOL 250 H is reputed to have a Brookfield viscosity (at 25° C.) of from 1,500 to 2,500 cps. for a 2% solution, and of greater than 25,000 cps. for a 1% solution thereof. NATROSOL 250 G is reputed to have a Brookfield viscosity (at 25° C.) of 150-400 cps. for a 2% solution. NATROSOL 250 L is reputed to have a Brookfield viscosity (at 25° C.) of 75-150 cps. for a 5% solution. NATROSOL 250 M is reputed to have a Brookfield viscosity (at 25° C.) of from 4,500 to 6,500 cps. for a 2% solution thereof.

From the above results it is apparent that the use of mixed chromium compounds, same containing both hexavalent and reduced forms of chromium in combination with cellulose polymers such as hereinbefore defined, provides enhanced flexibility and paint adhesion, as well as impact and corrosion resistant properties to base metal surfaces, when such surfaces are treated in accordance with the teachings of this invention.

I claim:

1. The method of applying a coating to the surface of metals selected from the class consisting essentially 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) at least 0.25% by weight of a product comprising mixtures of chromic acid including its soluble salts and reduced forms thereof such as is derived from the reaction of an aqueous solution consisting essentially of from 50 to 800 grams/liter of a hexavalent chromium compound, expressed as CrO_3 , with from 0.03 to 1 mol of formaldehyde, expressed HCHO , for each mol of said hexavalent chromium compound, and
- (2) at least 0.1% by weight of water soluble polymers of hydroxyethyl ethers of cellulose,

the treatment being continued until the metal 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 being reduced forms of chromium.

3. The method of claim 1 wherein the quantity of mixed chromium compounds employed in the treating solution is from 0.5 to 5 parts for each part of water soluble polymers of hydroxyethyl ethers of cellulose.

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

5. The method of claim 1 wherein the pH of the treating solution is maintained below about 2.3 by adding, as

required, small amounts of acid from the class consisting essentially of phosphoric and formic.

6. The method of claim 1 wherein the treating solution is employed at average room temperature.

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

8. The method of claim 1 wherein a siccative film is applied to the surface prior to the drying step.

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

10. A solution for treating metal surfaces selected from the class consisting essentially of iron, zinc and aluminum, said solution consisting essentially of at least 0.1% by weight of water soluble polymers of hydroxyethyl ethers of cellulose, and at least 0.25% by weight of reaction products derived from the admixture of an aqueous solution consisting essentially of from about 50 to about 800 grams per 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, the balance of the solution being water.

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