

1

3,053,785

AQUEOUS ALKALINE SOLUTION COMPRISING VINYL ACETATE COPOLYMER, A CHROMATE AND WATER-SOLUBLE VOLATILE BASE

Harold Rosenbloom, deceased, late of Oakmont, Pa., by
Devorah Rosenbloom, executrix, Pittsburgh, Pa. (29
W. 10th St., New York 11, N.Y.)

No Drawing. Filed Feb. 18, 1958, Ser. No. 715,865
12 Claims. (Cl. 260—29.3)

This invention relates to novel solutions containing chromium compounds that may be applied to a surface to form a film thereon and provide corrosion protection and resistance to water spotting to the surface thus treated.

The problem of protecting the surfaces of metal products against corrosion is of great importance commercially and many attempts have been made heretofore to provide effective protection. For example, there are known various metal surface treatments that depend on the use of inorganic compounds. These have been found to solve some of the problems for which they are applied, but it has also been found that they are usually of a specific nature and therefore can be applied to but a single material, because on other metals they may, for example, accelerate corrosion rather than retard it, or otherwise create as much harm as they overcome.

There are also known for these general purposes materials that are essentially organic in composition. These, too, have been found to be unsatisfactory because they require a prompt top-coat or other treatment to supply the requisite protection for the metal to which they are applied. Several of the organic base coating compositions that are sold on the basis that they provide adhesion for top-coats actually accelerate corrosion of the metal surface and otherwise are not capable of general use.

It is, therefore, a major object of this invention to provide solutions which may be applied to metal surfaces to provide temporary corrosion protection thereof.

Desirable characteristics of a composition used to provide temporary protection for a metal are that it be relatively inexpensive, and it preferably should be usable in conjunction with high speed metal production processes. The composition also should form a suitable base for a subsequent treatment, such as painting or the like, and it should inhibit corrosion of the metal to which it is applied. Many applications also require that a protective coating resist substantially any attack by water, both to minimize corrosion and maintain sales appeal of the resulting product as by protecting the characteristic appearance of the base metal.

In accordance with the present discoveries, metals such, by way of example, as steel, galvanized iron and steel, electrolytic tin plate, zinc, brass and aluminum, can be provided with a thin coating that provides corrosion protection. This is accomplished by treating metal surfaces with an alkaline water solution containing an acidic copolymer or vinyl acetate and an aliphatic, alpha ethylenically unsaturated acid, a reducible hexavalent chromium-containing compound and ammonium hydroxide or other soluble, volatile base, all as more fully described herein-after. The resulting coating is on the order of but a few millionths of an inch in thickness; nevertheless it effectively provides corrosion protection for the metal. Moreover, it forms a fine base upon which to apply various top coats, such as paint and organic coatings, and it is resistant to attack by water, even to the extent of not being subject to water spotting. These coatings can be applied in a very simple, easily practiced process using skills fully available in metal treating industries today. The coatings can be produced without using high temperature applica-

2

tion procedures, and the rinsing and cleansing steps of known procedures also are not needed in practicing the present invention.

The solutions of this invention contain the copolymer, chromium component and volatile base in certain proportions. In general about 10 to 30 parts of the polymer per part of the chromium component, on a weight basis, are used. The water-soluble volatile base is included in amounts and at a concentration sufficient to bring, and maintain, the polymer and chromium component into solution and to result in an alkaline solution. The resulting solutions generally have a pH within the range of from 7 to about 9.5 and have a solids content of about 10 to 16 weight percent.

The film forming acidic copolymers used in this invention comprise copolymers of vinyl acetate and aliphatic, alpha ethylenically unsaturated acid of up to about 6 carbon atoms such, for example, as acrylic acid, crotonic acid, maleic acid, isocrotonic acid, methacrylic acid, tiglic acid, angelic acid, seneceioic acid, fumaric acid, itaconic acid or lower alkyl monoesters of maleic acid such as monoethyl maleate, monobutyl maleate and monomethyl maleate. These copolymers generally have a viscosity within the range of about 5 to 100 centipoises, measured as a molar solution in ethyl alcohol.

The preparation of these copolymers is well known and they are available commercially for a variety of purposes. Methods of preparation are disclosed in such United States patents as those to Stark No. 2,263,598, the Alien Property Custodian No. 417,808, Billig No. 2,317,725, Evans et al. No. 2,657,187, Pinkey No. 2,657,188, Wilson No. 2,643,245 and Wilson No. 2,643,246. The commercially available polymers usually are prepared from crotonic or maleic acid or a monoester of maleic acid, particularly monoesters of alcohols of 1 to 8 carbon atoms, and those constitute the preferred acidic copolymers for use in the invention. Crotonic acid copolymers with a viscosity of from 10 to 30 cp. are particularly satisfactory from the viewpoint of film formation, ease of solution and ease of polymerization. As commercially obtained the polymers are solid, or are a water emulsion containing on the order of about 55 weight percent of active component or polymer, and minor amounts of conventional emulsifying agents. Emulsion copolymers generally have a viscosity of about 5 to 20 cp. There are naturally occurring polymeric materials, such as shellac and casein, which are alkali soluble.

Generally the acidic copolymers are prepared with about 88 to 97 parts of the acetate and 3 to 12 parts of the acid, on a weight basis. Different ratios of the respective components, for example 93 to 97 parts of acetate for 3 to 7 parts of acid, may be used, if desired, as long as the characteristic solubility in alkali solution is retained. As is known, alkali solubility is imparted to these acidic copolymers primarily by their carboxyl groups. Consequently, at high degrees of polymerization, i.e. with high viscosity products, it is evident that the larger quantities of the acids must be used to characterize the polymer with the requisite carboxyl groups and therefore the requisite alkali solubility. The copolymer content of solutions of this invention normally comprises about 9.25 to 14.5 weight percent, measured as solid copolymer and based on the resulting solution. This factor also may be varied as long as a solution as herein described results.

Chromium is used in the solution of this invention in a reducible form that is in the hexavalent state and is soluble in alkaline water solution. It is present generally as an ammonium salt or in the form of an ammonium complex of zinc chromate that is stable in alkaline solution. A suitable ammonium salt can readily be prepared by mixing ammonium hydroxide (NH₄OH) and chromic

anhydride (CrO_3) in about stoichiometric amounts while using the hydroxide in the appropriate strength. The complex can be prepared by adding ammonium hydroxide to a zinc chromate pigment using the hydroxide in a strength sufficient to result in the desired alkaline solution. One suitable commercial ammonium complex of zinc chromate available for this purpose is hereinafter described in detail in Example II of this specification. Upon applying the solutions, the chromium, when used in the form of an ammonium salt, is believed to reduce to the trivalent state, in part, when the ammonia evaporates from a film formed thereof, decomposing the ammonium chromate salt. The resulting trivalent chromium is believed to react with the carboxyl groups of the resin to render it water insoluble. Where the complex is used, it is believed that the zinc reacts with the resin and, in effect, makes ammonium chromate available which then can perform the same function as it does when it is included as such. The ammonium chromate becomes available in proportion to the zinc which reacts. Measured as ammonium chromate this component generally is used in an amount of about 0.5 to 1.0 percent based on the weight of the resulting solution.

Ammonium hydroxide is the preferred watersoluble, volatile base that is to be used in preparing these solutions, in view of its economic advantage. However, water soluble organic bases, such as morpholine and triethanolamine, can be used when desired. Similar basic materials which have an evaporation rate on the order of that of water as well as mixtures of such bases can also be used. As noted above, the base must be volatile and is used in quantities and concentrations to solubilize the solid components and to result in an alkaline solution as described. Evaporation rate as used herein is intended to indicate the rate of evaporation in a solution of the invention in the form of a thin film, such as it made when the invention is used.

The solutions of this invention can be applied to metal surfaces that are to be coated by spraying, roller-coating or other known procedures. A particularly suitable method of application involves merely immersing the article being treated in a solution and then heating, as by directing a blast of warm air on the surfaces of the treated metal, to dry and cure the coat. In applying the solutions, it has been found that the solution temperature at the time of application should not exceed about 115°F . because at higher temperature a tendency of the resulting coating towards skinning has been observed. However, higher temperatures can be, and usually are, used to dry and cure the coating after it is on the metal.

Full commercial use of an invention such as the present one can be dependent upon the speed with which a coating can be produced and cured. Coatings in accordance with this invention are produced, dried and cured rapidly. However where the speed is considered to be marginal, or where greater speed is desired for any reason, it is within the scope of the present invention to include in the compositions a material that will accelerate cure without deleteriously affecting the desired results.

It has been found that certain reducing agents can be used to advantage as accelerators. Indeed, some reducing agents not only accelerate the cure but also have other advantages such as improving corrosion resistance and solution stability. Hexavalent chromium is well known to be a very strong oxidizing agent; it follows, therefore, that a large number of materials may be classed as reducing agents when used with hexavalent chromium. Of this large class of materials, those that are soluble in the described solutions and which do not impart water sensitivity to coatings made therefrom or detract substantially from the corrosion resistance provided by such coatings, may be used.

In general the preferred materials for this purpose are easily oxidizable, water soluble, hydroxy substituted hydrocarbons. Particularly satisfactory accelerators are un-

saturated primary alcohol or dihydric alcohol sometimes referred to as "diol" capable of forming a substantially volatile aldehyde upon oxidation. Representative examples of the foregoing include such materials as lower alkylene glycols, such as ethylene glycol, other hydrocarbon base compounds containing more than one hydroxyl substituent such as 2-butyne-1,4-diol, or 2-butene-1,4-diol, unsaturated or saturated primary alcohols such as propargyl alcohol, butanol, pentanol and hexanol, sugars and similarly water soluble, easily oxidizable materials. These hydroxy substituted hydrocarbons generally contain about 3 to 7 carbon atoms. Such materials as methyl and ethyl alcohols have been found to evaporate too rapidly at the temperature used in practicing the invention to be of best used for this purpose. Such inorganic reducing agents as sodium bisulfite and sodium hypophosphate actually detract from corrosion resistance and therefore cannot normally be used. The accelerators are used in small amounts on the order of 0.5 to 5 percent, and suitably about 0.5 to 2 percent, based on the weight of the solution to which they are added. If the water solubility of the material added is very pronounced, it should be used in the smallest amount possible to insure that no unreacted portion remains in the resulting coating film. For example, whereas ethylene glycol is satisfactory, it has been found that it should not be used in amounts materially greater than 0.5 percent because when quantities of 1, 3 or 5 percent were used, it was observed that the film would water spot, apparently due to unreacted glycol remaining in the film.

In addition to the foregoing, such other materials as are conventionally used in coating solutions containing resins may be used in this invention. The resin may, for example require a plasticizer; or a foam may develop that can be eliminated without deleteriously affecting the invention by adding an anti-foam agent. Those substances can be used in the conventional amounts in practicing this invention. The plasticizers may be the usually water soluble plasticizers for polyvinyl acetate and copolymers thereof. These materials are well known in the art and include polyesters, adipic acid resins, dibutyl phthalate, butyl benzyl phthalate and methyl phthalyl ethyl glycolate. These may be added as such or conveniently dispersed in the coating solution in an organic solvent solution thereof, for example, as a methyl ethyl ketone solution or other water soluble solution.

The invention will be described further in conjunction with the following examples. It should be understood that the details disclosed are given by way of illustration and are not to be construed as limiting the invention.

Example I

A chromate solution was prepared by adding ammonium hydroxide (28 percent concentration) to chromic acid in water until a pH of 8.5 was reached. The resulting mixture corresponded approximately to the composition, NH_4HCrO_4 , and had the following analysis, in parts by weight:

CrO_3	5.00
Ammonia (NH_4OH) 28%	6.00
Water	89.00

The acid polymer used was a copolymer of vinyl acetate and crotonic acid containing 100 parts of the acetate for each four parts of the acid. Its viscosity was 16 centipoises as determined on a molar solution (based on the weight of a monomeric unit) in ethyl alcohol. Water, ammonium hydroxide, and a plasticizer were admixed with the resin in the following amounts on a parts by weight basis:

Copolymer	9.81
Ammonia (NH_4OH) 28%	0.88

Water -----	88.33
Plasticizer (Resoflex R-296) ¹ -----	0.98

¹ High acid number polyester, dispersible in dilute alkali solutions, as disclosed in United States Patent No. 2,611,756, granted September 23, 1952.

The resin and chromate solutions were then mixed in a weight ratio of 9.2 parts of the chromate solutions with each 90.8 parts of the resin solution. The resulting solution was sprayed on the surface of hot dipped galvanized steel panels and then dried by heating to 550° F. for 7 to 10 seconds.

The panels were placed on Petri dishes containing hot water. This results in condensation of water vapor on the panels and would evidence a thin layer of that known as "white rust" if the coating were imperfect. This was repeated through several days to determine long term effects. No white rust or other failure of the coating was noted, thereby showing the effectiveness of the solution in providing films for effective corrosion and water resistance.

The invention may also be practiced with a solution in which the chromium content is provided as an ammonium complex of zinc chromate. This is demonstrated by the following example.

Example II

A resin solution containing the same components in the same amounts as set forth under Example I was first prepared. Then a zinc chromate complex was prepared by mixing a pigment, having a chemical composition in parts by weight within the following ranges:

ZnO -----	38-39
CrO ₃ -----	42.5-43.5
K ₂ O -----	10.7-11.7
H ₂ O -----	6.5-7.0
SO ₃ -----	nil
Cl -----	0-0.04
Moisture -----	0.03-0.04

with ammonium hydroxide and water in the following amounts, in parts by weight:

Zinc chromate -----	6.00
Ammonia (NH ₄ OH) 28% -----	12.60
Water -----	81.40

The chromate complex solution was added to the resin solution. The respective solutions were used in a weight ratio of 4.2 parts of the complex solution to 95.8 parts of the resin solution. The resulting solution was used to provide a coating on galvanized steel in the same manner as described in Example I above. After drying, it was noted that the coating was clear and transparent. This is believed due to the fine state of dispersion of the pigment that was added. Presumably, the chemical reaction occurring upon loss of the ammonia from the thin film reduced the pigment to colloidal size.

It has been found that the use of a complex occasionally causes gelation of the acidic resin. This can be overcome by adding more of the base, but that may result in viscosity instability. Consequently, it is preferred to form the coating solution in a manner which avoids this result. One procedure involves preparing the coating solution by dissolving the acidic resin in the zinc chromate complex solution, without first forming a separate resin solution, and then adding additional ammonium hydroxide to maintain the complex in solution. In this manner resin gelation may be avoided without inducing the problem of instability.

A very important application of the invention is to provide temporary protection for stacked galvanized sheets of iron and steel against the phenomenon called "white rust" which has been with the industry since its inception. The embodiments described thus far serve that intended purpose very satisfactorily. When a greater degree of metal protection is desired, such as is needed when salt water atmospheres are involved, the base com-

positions can be modified in accordance with an additional discovery.

It has been found that the addition of 0.5 to 5 weight percent of a thermosetting resin such as phenol-formaldehyde resins, resorcinol-formaldehyde resins, or an equivalent amount of a melamine resin or the like to a solution such as described in Example II provides the resulting film with salt spray resistance. This is of particular significance where ordinary steel, as distinguished from galvanized steel, is involved. This embodiment is demonstrated by the following example.

Example III

The acidic copolymer solution was prepared by mixing the acidic copolymer of Example I with ammonia, water and a plasticizer. The plasticizer, Resoflex R-296, was used in admixture, on a one to one basis, with methyl ethyl ketone (MEK). The various components were used in the following amounts:

	Gm.
Copolymer -----	392.4
Ammonia (NH ₄ OH) 28% -----	35.2
Water -----	3494.0
Resoflex R-296—ketone -----	78.4
Total -----	4000.0

A solution containing a thermosetting phenol-formaldehyde resin was then prepared. The resin was in liquid form containing 62½ percent solids. The liquid resin, ammonia and water were mixed in the following amounts.

	Gm.
Resin (62.5% solids) -----	128.0
Ammonia (NH ₄ OH) 28% -----	22.0
Water -----	650.0
Total -----	800.0

A solution according to the present invention was mixed as follows:

	Gm.
Acidic copolymer solution -----	3184.0
Resoflex R-296—MEK mixture -----	16.0
Ammonium chromate (10.97 concentration) --	365.0
Phenol-formaldehyde solution -----	800.0
Total -----	4365.0

The resulting solution has a solids content of about 10 to 11 percent. Experience has shown that the order of mixing these components affects the ease of obtaining a satisfactory solution. A suitable order is to add the plasticizer to the acidic copolymer solution, then incorporate the chromate solution and add the phenol-formaldehyde solution last. The utility of this embodiment of the invention was demonstrated on steel panels, in substantially the same manner as set forth under Example I, with satisfactory results.

Solutions in accordance with this invention also can be made with acidic copolymer emulsions as shown in the following example.

Example IV

The polymer used was composed of vinyl acetate and crotonic acid containing 94 parts of the acetate to six parts of the acid. This was in emulsion form in water and the resin formed about 55 weight percent of the emulsion. The resin viscosity measured as a molar solution in ethyl alcohol, was about 10 cp. The resin solution was prepared by diluting 15 parts of the emulsion with 84.6 parts of water, 0.4 part of 28 percent NH₄OH and a trace of a commercial anti-foam agent. Then 1.9 parts of a plasticizer solution, made of equal parts of Resoflex R-296 and methyl ethyl ketone, were mixed with 63.3 parts of the resin solution. To this mixture were added 9.1 parts of a chromate solution made from 5 percent of chromic acid, 6 percent of NH₄OH (28%) and 89 percent of water. One part of an accelerator

(propargyl alcohol) and 24.7 parts of water were added and the resulting solution mixed thoroughly. Ageing for about 2 hours completed manufacture; the completed solution had a pH of 7.5.

A solution prepared from a maleic acid ester copolymer with the acetate is shown in the following example.

Example V

For this example, separate solutions of zinc chromate complex, resin and plasticizer were prepared. Five and two-tenths parts of zinc chromate pigment, having an analysis within the range set forth in Example II, were mixed with 24.3 parts of 28 percent NH_4OH and 70.5 parts of water. The copolymer solution was prepared from 9.7 parts of acidic copolymer, 89.5 parts of water, 0.8 part of 28 percent NH_4OH and a trace of a conventional anti-foam agent. The resin used was an acidic copolymer, of 90 parts of vinyl acetate and 10 parts of monobutyl maleate, having a viscosity of 10 cp. as measured with a molar solution thereof in ethyl alcohol.

The coating solution was made by adding 1.7 parts of the plasticizer solution (equal parts of Resoflex R-296 and methyl ethyl ketone) to 90 parts of the resin solution. Then 8.3 parts of the zinc chromate-ammonia complex solution were added slowly while agitating. The resulting solution can be used for coating various metals to provide corrosion protection and water resistance in the manner described above.

The use of this invention in providing temporary protection, i.e., on the order of two weeks to a month or so, to materials produced in high volume, such as galvanized iron and steel, is particularly interesting. To be feasible for such application it is apparent that the use of the solution must be capable of integration in a commercial production line. Accordingly the invention was tested on a large pilot plant production line, in a preliminary and experimental fashion, to gain experience with problems that may be encountered in large scale production.

Example VI

The solution for the pilot plant runs was prepared with an ammonium chromate solution. The chromate solution contained, in weight percent, the following:

	Percent
CrO_3	5
Ammonia (NH_4OH) 28%	6
Water	89

A solution of plasticizer was made by mixing equal parts by weight of Resoflex R-296 and methyl ethyl ketone. The acidic copolymer was made with the copolymer of vinyl acetate and crotonic acid mentioned in Example I. This solution contained, in weight percent, the following materials:

	Percent
Water	88
Ammonia (NH_4OH) 28%	1
Acidic copolymer	11
Defoaming agent	trace

The coating solution was made by adding 2 parts by weight of the plasticizer solution to 88 parts by weight of the copolymer solution with agitation. Nine parts of the ammonium chromate solution were added, very slowly, to the copolymer-plasticizer mixture with agitation. Then one part of 2-butene-1,4-diol (an accelerator) was added and the resulting solution mixed thoroughly.

This solution was applied to galvanized sheet by flowing it through small pipes on to pinch rolls through which sheet was passed. The coated sheet then travelled under a bank of infra-red lamps to dry the coat and was then stacked. Each sheet was exposed to heat for about 25 seconds; the temperature was about 400° F.

Condensation tests were conducted on galvanized panels coated in the manner just described. The test procedure used was as follows: Pint jars with 2¼" di-

ameter top openings were half filled with hot water at a temperature of about 130° F. to 140° F. The metal panels to be tested were placed on the jars. Because of the temperature difference between the cool test panels and the warm water in the jars, water condensed on the bottom of the metal plates. Several uncoated panels were exposed to the same test conditions as controls. Within 12 hours, uncoated galvanized panels showed a white circle of white rust which became quite heavy within 24 hours. The panels were checked at 48 hour intervals and rated on a numerical basis of 10 being perfect to 0 representing complete failure over the entire circle of exposed surface as in the case of the uncoated panels. Exposures were run from 14 to 28 days or more, depending on the time necessary to get clearly comparative results on all coatings tested.

In a test of the galvanized panels coated as described in Example VI, it was 72 hours before corrosion spots began to show. Out of 12 panels in this test after 14 days, with a rating of 10 as perfect, two rated 9, one rated 8½, four rated 8, four rated 7 and one rated 6. In a similar test on 16 panels coated in a different run, one rated 9, ten rated 8½, two rated 8, one rated 7½ and two rated 7.

Stack tests were also made on panels coated in the manner of Example VI. The procedure for the stack tests was as follows: The panels under test, and uncoated control panels, were thoroughly wet with distilled water and stacked. Uncoated panels were placed in the stack with the coated ones. A weight of about 5 pounds was placed on the stack to insure contact of the wet surfaces. Some water was squeezed out when the weight was applied. The stack was opened and inspected after the first 12 hours, and every 48 hours thereafter. Corrosion, as shown by the formation of white rust on galvanized panels, usually started on the untreated panels within 12 hours. Progress of corrosion was noted by a visual inspection of both sides of each panel; in rating the results a panel free from corrosion was rated 10 and a panel showing complete failure was rated 0 as in the case of uncoated panels. The general pattern of satisfactory results reported in connection with the condensation tests just described was also found in the stack test experiments.

In making the pilot scale runs the primary object was to see whether the speed of drying of the coating was sufficiently rapid to permit use of the solution with high speed production processes. Particular efforts at maximizing corrosion protection were not made. For example, measurement of film thickness across the surface of treated panels indicated a lack of uniformity in coating by the procedure followed. The degree of corrosion resistance actually achieved in these runs was gratifying. Even better results will be achieved when the coating solution is applied uniformly and in the predetermined optimum thickness.

As noted above, the invention may be practiced with bases other than or in addition to ammonium hydroxide. The following example is representative of the invention where two different bases are used in preparing a coating solution.

Example VII

An ammonium chromate solution such as that used in Example I was prepared for this example. A polymer solution, using a copolymer of vinyl acetate and crotonic acid in a 25:1 ratio, was prepared with the following components.

	Gms.
Copolymer	92.50
Morpholine	9.50
Water	778.25
Resoflex 296—MEK	18.50
Total	898.75

The chromate solution was slowly added, with agitation,

to the polymer solution along with an accelerator and an anti-foam agent. The resulting solution was constituted as follows:

	Gms.
Copolymer solution -----	898.75
Chromate solution -----	91.16
Accelerator (2-butene-1,4-diol) -----	10.00
Antifoaming agent -----	.10
Total -----	1000.01

The solution was aged 24 hours. Then 3" x 3" galvanized panels were immersed in this solution and then withdrawn at a rate of 4" per minute. The panels were immediately dried by subjecting them to a temperature of 550° F. for 10 seconds.

These panels, along with uncoated control panels, were placed on Petri dishes containing hot water to conduct a test such as was noted under Example I above. Using 10 as a perfect rating indicating no "white rust," after 17 days the three panels coated with the polymer solution were rated as 9. The uncoated control panels showed 100% light corrosion in 24 hours and were very heavily corroded, and rated 0, in 17 days.

While propargyl alcohol and 2-butene-1,4-diol have been exemplified as the accelerators in most of the examples, it should be apparent that any of the other accelerators, for example 2-butyne-1,4-diol, could be used, if desired, with satisfactory results being obtained.

The procedure of Example VII was then repeated, essentially, substituting a zinc chromate complex solution, such as in Example II, for the ammonium chromate solution. Two galvanized panels were coated by immersion in this solution; one was dried immediately at 550° F. for 10 seconds, and the other was dried at 550° F. for 25 seconds. In the Petri dish test and with the same rating system already described, the panel dried 10 seconds rated 6 after 17 days. The panel dried 25 seconds rated 8 after 17 days, and two control panels showed 100 percent light corrosion in 24 hours and were heavily corroded and rated 0 in 17 days.

From the foregoing discussion and examples it is evident that the present invention is of particular value in providing metal with a film that acts as a temporary protective coating. Other advantages of the resulting coating are that if it becomes contaminated with oil, grease, soil or the like, it can be readily cleaned with such well known cleaners as aqueous acidic detergents without affecting the utility of the coating material because it is substantially inert to such materials. If it is desired to remove the coating so that the base material may be treated or worked on, such as by being electroplated, the coating can be removed by applying a solution of a strong alkali. Furthermore, these coatings are substantially colorless and do not alter the characteristic appearance of the surfaces to which they are applied. This latter point is of particular importance in galvanized products where the characteristic star-like crystals contribute to the sales appeal.

According to the provisions of the patent statutes the principle of the present invention has been explained and the invention has been illustrated and described with what are now considered to represent its best embodiments. However, it should be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

What is claimed is:

1. An aqueous alkaline solution consisting essentially of an alkali soluble, acidic copolymer of vinyl acetate and an aliphatic alpha ethylenically unsaturated organic acid, a member selected from the group consisting of ammonium chromate and ammonium complex of zinc chromate in a range from about 0.5 to 1.0% by weight of the final solution measured as ammonium chromate, water and

a water-soluble volatile base sufficient to dissolve the solid components in the water.

2. A solution of claim 1 in which said organic acid of said acidic copolymer is crotonic acid.

3. A solution of claim 1 in which said chromate is ammonium chromate.

4. An aqueous alkaline solution consisting essentially of an alkali soluble, acidic copolymer of vinyl acetate and an aliphatic alpha ethylenically unsaturated organic acid containing up to about six carbon atoms, a member selected from the group consisting of ammonium chromate and ammonium complex of zinc chromate in a range from about 0.5 to 1.0% by weight of the final solution measured as ammonium chromate, water, a water-soluble volatile base in a concentration sufficient to solubilize the solid compounds, and a readily oxidizable water-soluble hydroxy substituted hydrocarbon in an amount of the order of 0.5 to 5.0% by weight of the solution.

5. A solution of claim 4 in which said hydroxy substituted hydrocarbon is an aliphatic hydrocarbon of 3 to 7 carbon atoms and contains at least one hydroxy group.

6. An aqueous alkaline solution consisting essentially of an alkali soluble acidic copolymer of about 88 to 97 weight percent of vinyl acetate and 3 to 12 weight percent of an aliphatic, alpha ethylenically unsaturated, organic acid, a member selected from the group consisting of ammonium chromate and an ammonium complex of zinc chromate in a range from about 0.5 to 1.0% by weight of the final solution measured as ammonium chromate, water, and a water-soluble volatile base in a concentration sufficient to effect solution of the solid compounds in water and selected from the group consisting of ammonium hydroxide, morpholine and triethanolamine.

7. A solution of claim 6 in which said acid is selected from the group consisting of crotonic acid, maleic acid and lower alkyl monoesters of maleic acid.

8. A solution of claim 7 in which said solution includes a water-soluble aliphatic, hydroxy substituted hydrocarbon in an amount of the order of 0.5 to 2.0% by weight of the solution.

9. A solution of claim 8 in which said hydroxy substituted hydrocarbon is a dihydric alcohol.

10. An aqueous alkaline solution consisting essentially of an alkali soluble, acidic copolymer of vinyl acetate and an aliphatic alpha ethylenically unsaturated organic acid, about 0.5 to 1 percent, measured as ammonium chromate and based on the weight of the resulting solution, of a member selected from the group consisting of ammonium chromate and ammonium complex of zinc chromate, water, and a base selected from the group consisting of ammonium hydroxide, morpholine and triethanolamine in an amount sufficient to effect the solution of the said copolymer and chromate in the water.

11. An aqueous alkaline solution of claim 10 in which said organic acid is selected from the group consisting of crotonic acid, maleic acid and lower alkyl monoesters of maleic acid.

12. An aqueous solution of claim 10 to which there is added between 0.5 and 5% of a thermosetting resin selected from the group consisting of phenol-formaldehyde resin, resorcinol-formaldehyde resin and melamine resin.

References Cited in the file of this patent

UNITED STATES PATENTS

2,351,716	Smith -----	June 20, 1944
2,356,879	Pense -----	Aug. 29, 1944
2,612,481	Cone -----	Sept. 30, 1952
2,871,213	Graulich et al. -----	Jan. 27, 1959
2,902,390	Bell -----	Sept. 1, 1959
2,902,459	Teppema -----	Sept. 1, 1959