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3,647,567 POST-DIPPING OF ACIDIC DEPOSITION COATINGS

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10 Claims

ABSTRACT OF THE DISCLOSURE

Metallic articles are coated with an adherent polymer film by the acidic deposition process which comprises contacting these metallic articles with an aqueous bath containing a synthetic resinous film forming emulsion and an oxidizing acid system. By subjecting these acidic deposition coatings to a solution, about 0.25 to 7.0 weight percent of which contains a material selected from phosphoric acid, chromium trioxide and water or acid soluble chromates and dichromates, the resistance properties—especially water and salt spray resistance—of these coatings are enhanced.

BACKGROUND OF THE INVENTION

This invention pertains to the deposition of coatings on a metal substrate and to the improvement in the properties of such coatings by a post-dipping process. The coating of metallic articles by acidic deposition is disclosed in copending patent application Ser. No. 880,914 filed Nov. 28, 1969.

Generally the acidic deposition process involves coating a metallic article from a bath which contains an oxidizing acid system and a synthetic film forming emulsion stabilized by nonionic or anionic surfactants. The oxidizing acid system must be capable of producing metal ions at the surface of the metallic article. The emulsion, on the other hand, must be stable to this acid system but coagulatable onto the surface of the article by the action of the acid system produced metallic ions.

Films prepared by acidic deposition generally contain at least a small amount of water soluble species along with various metal ions such as those of the substrate which has been coated. It is thought that these water soluble species contribute to the poor water and salt spray resistance often exhibited by acidic deposition films.

SUMMARY OF THE INVENTION

This invention relates to an improvement in the acidic deposition process. Specifically it has been found that the resistance properties of acidic deposition films, especially to salt spray and water can be improved by contacting "un-baked" or "uncured" acidic deposited coatings with a solution of about 0.25 to 7.0 weight percent (based on the total solution weight) of a material selected from phosphoric acid (H_3PO_4), chromium trioxide (CrO_3), and water or acid soluble chromates and dichromates. Following this step the acidic deposition films or coatings are then baked or dried according to standard methods.

DESCRIPTION OF THE INVENTION

Acidic deposition as referred to in this invention involves the addition of an oxidizing acid system to an aqueous emulsion (also called a latex or an aqueous polymeric dispersion) and the subsequent coagulation of this emulsion onto a metal substrate in the form of an adherent coating or film.

Generally any aqueous, synthetic, resinous, film forming emulsion is satisfactory in forming the acidic deposition bath used therein. In particular however, the emulsions used should be formed of vinyl or ethylenically polymerizable monomers. Furthermore it is desirable that

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these emulsions be prepared in an aqueous medium by addition polymerization in the presence of anionic or nonionic surfactants or both.

The preparation of these synthetic film forming emulsions can be accomplished by any of the standard emulsion processing techniques. Thus it is common to charge a portion of the polymerization catalysts or initiators into the reaction flask. The temperature of this mixture is then increased to about 100° F.—200° F. at which time separate additions of the remainder of the monomers and catalysts are carried out. Following these additions the emulsion mixture is held a reaction temperature until substantially complete monomer conversion is attained.

Variations on this procedure include the use of a separate surfactant feed to be carried out during the monomer addition, the use of pre-emulsified monomers, the use of a water alcohol mixture as the emulsification medium and other well known variations.

The compositions of these emulsions can vary. Generally any of the normal emulsion monomers can be used. For example, the vinyl esters of fatty acids having from 1 to 18 carbon atoms including vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl oleate, and vinyl stearate can be used. Likewise, the various vinyl polymerizable acids such as acrylic, methacrylic, crotonic, itaconic and fumaric acids or maleic anhydride, etc., are useful. Esters of acrylic acid, methacrylic acid, maleic acid, or of other vinyl polymerizable acids with alcohols, glycols or epoxides having from 1 to 18 carbon atoms can likewise be employed. Examples of such esters include methyl acrylate or methacrylate, ethyl acrylate or methacrylate, propyl acrylate or methacrylate, isopropyl acrylate or methacrylate, the various butyl acrylates or methacrylates, cyclohexyl, acrylate or methacrylate, benzyl acrylate or methacrylate, isobornyl acrylate or methacrylate, phenyl acrylate or methacrylate, n-hexyl, n-octyl, 2-ethyl hexyl, t-octyl, dodecyl, hexadecyl, or octadecyl acrylates or methacrylates. Acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, styrene, α -methyl styrene, vinyl toluenes, allyl acetate, glycidyl methacrylate, t-butylaminoethyl methacrylate, hydroxylalkyl acrylates or methacrylates, such as hydroxyethyl methacrylate, hydroxy propyl methacrylate or acrylate, hydroxyethyl vinyl ether, hydroxyethyl vinyl sulfide, vinyl pyrrolidone, N,N-dimethylaminoethyl methacrylate, ethylene, propylene, vinyl chloride, vinyl fluoride, vinylidene fluoride, hexafluoropropylene, chlorotrifluoroethylene, and tetrafluoroethylene, can also be used as the monomers herein.

Several of the above monomers give preferred results when incorporated into the emulsions hereinafter described. In particular, isobornyl methacrylate, styrene and hydroxyl propyl methacrylate produce films which have superior wet adhesion. Wet adhesion is defined as the adhesion of the unbaked coating to the particular metallic substrate. When emulsions are prepared having poor wet adhesion, their acidic deposited, unbaked films tend to sag and drip off the panel onto which they are coated. On the other hand superior emulsions, including those prepared using the above monomers, when plated, generally adhere tightly to the metal substrate and do not sag on the coated article prior to baking.

Since almost all emulsions are prepared containing water sensitive surfactants, the resistance of films prepared from these emulsions to water is a problem. The incorporation of about 15 to 60 solids weight percent of acrylonitrile or methacrylonitrile into the emulsions as prepared herein gives improved water resistance.

Water resistance is expressed herein as percent water up-take. It is determined by immersing a baked coated panel in a bath of boiling water. The heat is then removed and the bath allowed to cool at room temperature

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for 3 hours. Prior to immersion in the bath, the panel is weighed and the area of its coated surface determined.

$$\text{Specific film weight} = \frac{\text{total weight of film}}{\text{total area coated}}$$

Likewise after the 3 hour immersion period the panel is weighed and the area that was immersed in the bath is determined.

$$\text{Specific water up-take} = \frac{\text{weight of water absorbed}}{\text{area of film immersed}}$$

Using these two determinations the percent water up-take can be calculated.

$$\text{Percent water up-take} = \frac{\text{specific water up-take}}{\text{specific film weight}}$$

In addition to the above preferred monomers it is desirable, but not required, to include in the emulsions herein prepared various acid functional polymerizable monomers. Preferred among these monomers are acrylic acid, methacrylic acid and itaconic acid. The incorporation of these acid monomers serve to improve film adhesion to the particular metallic substrate. However, if too large an amount of these acids is used, the water resistance of the resulting films can suffer. Therefore, it is desirable to have from about 0.25 weight percent to about 5.0 weight percent of these acids present based upon the total emulsion solids content.

Finally, in order to prepare films having increased solvent resistance properties, it is desirable to incorporate into the above emulsion monomer compositions from about 0.25 to about 10 weight percent of a cross-linking monomer. Included are monomers containing epoxide functional groups, e.g., glycidyl methacrylates and acrylates, methylol functional monomers, e.g., methylol acrylamide or methacrylamide and alkylated methylol monomers, e.g., methylated, ethylated or butylated methylol acrylamide or methacrylamide.

Examples of preferred aqueous, emulsion, film forming compositions useful herein include:

(1) Homo or copolymers of 1-8 carbon alcohol esters of an acid functional monomer.

(2) Copolymer of 1-8 carbon alcohol esters of an acid functional monomer and an acid functional monomer.

(3) Copolymers of a 1-8 carbon alcohol ester of an acid functional monomer, an acid functional monomer and acrylonitrile or methacrylonitrile.

(4) Any of the above having as an additional component methylol acrylamide or methacrylamide.

(5) Any of the above having as an additional component isobornyl methacrylate.

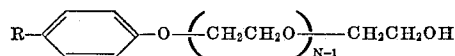
(6) Any of the above having as an additional component a vinyl aromatic monomer such as styrene or vinyl toluene.

Most preferable among the composition useful herein is a copolymer of about 0.5 to 15 weight percent of isobornyl methacrylate, about 0.5 to 10 weight percent of methylol acrylamide or methacrylamide, about 15 to 60 weight percent of acrylonitrile or methacrylonitrile, about 30 to 80 weight percent of a 1 to 8 carbon alcohol ester of an acid functional polymerizable monomer and about 0.25 to 5.0 weight percent of an acid functional polymerizable monomer.

The emulsions as are useful in the processes of this invention can be either anionically or nonionically stabilized. However, if nonionic surfactants are used, the emulsion preferably should include, as one of its co-monomers, a polymerizable acid. Generally, when nonionically stabilized emulsions are prepared, any of the common nonionic surfactants can be used with advantage. These nonionic surfactants generally are polyethylene or polypropylene oxide derivatives having pendant hydrophobic groups such as phenoxy, or phenyl groups. Illustrative of these ethylene oxide or propylene oxide derived

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surfactants are the "Igepals," which are members of an homologous series of alkylphenoxypoly(ethyleneoxy) ethanols, which can be represented by the general formula:



wherein R represents an alkyl radical and n represents the number of mols of ethylene oxide employed. Included among this series are alkylphenoxypoly(ethyleneoxy) ethanols having alkyl groups containing from about 7 to about 18 carbon atoms inclusive, and having from about 4 to about 100 ethyleneoxy units, such as the heptylphenoxypoly(ethyleneoxy) ethanols, nonylphenoxypoly(ethyleneoxy) ethanols and dodecylphenoxypoly(ethyleneoxy) ethanols; the sodium, potassium or ammonium salts of the sulfate esters of these alkylphenoxypoly(ethyleneoxy) ethanols; alkylpoly(ethyleneoxy) ethanols; alkylpoly(propyleneoxy) ethanols octylphenoxyethoxy ethyldimethylbenzylammonium chloride; polyethylene glycol t-dodecylthioether; the "Pluronic," which are condensates of ethylene oxide with a hydrophobic base, formed by condensing propylene oxide with propylene glycol; the "Tritons"; the nonionic "Tergitols"; and the like.

When anionically stabilized emulsions are prepared, the anionic stabilizers can be used alone or in admixture with the above nonionic surfactants. Generally any of the standard anionic stabilizers can be used in the emulsions herein prepared. These stabilizers (also called emulsifiers or surfactants) are salts—generally alkali metal salts of organic acids particularly the sulfates, phosphates or carboxylates. Examples include Triton 770 conc. or Triton X-200—the sodium salt of alkyloxy polyether sulfate; Triton GR 5 or GR 7—dioctyl sodium sulfosuccinate; Triton QS 44—phosphate surfactant in free acid form; sodium lauryl sulfate; Dowfax 2A1 (Benax2A1)—sodium dodecyl diphenyl ether disulfate; Dowfax 3B1—sodium n-nonyldiphenyl ether disulfate; Daxad 30—sodium salt of a polymerized carboxylic acid; Daxad 23—sodium salt of polymerized, substituted, benzoid alkyl sulfonic acid; Daxad 11KLS—polymerized potassium salts of alkyl naphthalene sulfonic acids; and the like.

Particularly useful in the emulsions of this invention are the co-reactive anionic surfactants which can be used either alone or in combination with nonionic surfactants, anionic surfactants or both. These co-reactive surfactants can be prepared by forming the alkali metal, amine or ammonia salt of sulfonic, phosphoric or carboxylic acids having sites of polymerizable unsaturation. Examples include the sodium salt of 2-sulfoethyl methacrylate, sodium vinyl sulfonate, the sodium salt of styrene sulfonic acid, as well as the sodium salts of the various polymerizable acids, e.g., acrylic acid, methacrylic acid, itaconic acid, maleic or fumaric acids, or ester acids, etc.

In preparing emulsions from any of the above anionic or nonionic surfactants it is desirable to use the least amount of surfactant that will produce oxidizing acid stable emulsions. Thus if surfactant levels in excess of 6-8 percent based upon the total emulsion monomer content are used, the rate of acidic deposition is greatly slowed. In fact in some instances the surfactant level can be increased to such a level that the emulsion will be too stable to coagulate onto a metal article exposed to the acidic bath. On the other hand, the level of surfactant should be sufficient to maintain emulsion stability in the presence of the dilute, oxidizing acid systems.

It can readily be seen that the absolute amount of surfactant required can vary greatly. This amount is controlled by many factors including the emulsion monomers, polymer molecular weight, surfactant solubility, and surfactant unit charge. However, the preferred emul-

sions are prepared using the above described co-reactive surfactants. These surfactants can be used at very low levels (0.5 to 5%) and still produce oxidizing acid stable emulsions. In particular the use of these surfactants produces cured films having excellent water and solvent resistance properties.

Furthermore the surfactants that can be used in preparing the emulsions of this invention preferably should not be substantially degraded in the presence of the dilute oxidizing acid systems. For example, sugar (sucrose, dextrose, etc.) or starch based surfactants are in many instances unsatisfactory as emulsion stabilizers for nitric acid containing acidic deposition baths.

Among the above surfactants several systems are preferable. In one about 0.5 to 1.5 weight percent of the sodium salt of 2-sulfoethyl methacrylate based on the total emulsion solids is mixed with a like amount of sodium vinyl sulfonate. In another preferred system from about 0.25 to 1.5 percent of sodium lauryl sulfate is used. In yet another system a mixture of about 2.5 to 6.0 percent of an anionic phosphate surfactant is used. Finally, in another system, nonionic surfactants derived from nonylphenoxy poly(ethyleneoxy)ethanol are used.

The monomers used herein are polymerized in the usual manner, i.e., by means of a catalytic amount of a conventional free radical polymerization catalyst or catalyst system (which can also be referred to as an addition polymerization catalyst, a vinyl polymerization catalyst or a polymerization initiator). An illustrative but by no means exhaustive enumeration of such catalysts includes inorganic peroxides such as hydrogen peroxide, sodium perchlorate and sodium perborate, inorganic persulfates such as sodium persulfate, potassium persulfate and ammonium persulfate, and redox systems such as sodium metabisulfite-potassium persulfate, and the like.

In addition other initiators can be used. These include tertiary butyl hydroperoxide, benzoyl peroxide, tertiary butyl perbenzoate, tertiary butyl peroctoate, lauryl peroxide, azo-bis-isobutyronitrile (AIBN) and any of the other commonly used initiators.

In order to prepare the acid deposition baths as are used herein, the emulsion which has previously been prepared is placed in a non-metallic container and an oxidizing acid system is added thereto. The solids of the resulting bath can vary from about 2% to about the solids level of the emulsion itself. However, when controlled film thicknesses are desired, it is preferred that the bath contain about 5-20% of the solid emulsion copolymer—the remainder being acid and water.

The oxidizing acid systems which are used in this bath comprise those acid systems which act upon the particular metallic substrate to be coated producing a concentration of substrate metal ions at the bath-substrate interface sufficient to cause coagulation of the emulsion onto the metal. When the metallic substrate contains iron, zinc or tin, nitric acid and in some cases sulfuric acid will cause the emulsions herein described to coagulate onto these substrata. Most preferred among the above acid systems is nitric acid. When the substrate is either copper or aluminum more vigorous conditions are required. For example, by using a mixture of fluoroboric acid, hydrofluoric acid, chromic anhydride and potassium ferricyanide either aluminum or copper can be coated by acidic deposition. This mixture can also coagulate emulsions onto normal iron, tin or zinc type substrata. The amount of the oxidizing acid system that is used herein can vary depending on the stability of the particular emulsion and on the substrate that is to be coated. For example tin plate requires lower acid level baths than does steel. In general the amount of acid can vary from about 1.0% to 50% by weight based upon the solids weight of the emulsion that is used. Preferably this acid content should be in the 2.5 to 15 weight percent range.

Although the preferred method of incorporating the desired acid system into these baths is to add the diluted

emulsion to a solution of the oxidizing acid system, it is also possible to prepare the emulsions in the presence of the dilute acid system itself. This method then eliminates the necessity of post-adding acid to the diluted emulsion.

Generally any metallic substrate can be used in the process of this invention. Included are cold rolled steel, phosphatized steel, sand blasted steel, tin free steel, galvanized steel, iron, zinc, tin-plated steel, tin, copper, aluminum, etc. The only requirement of the substrate is that it produces sufficient ions to coagulate the particular emulsion on its surface when it is immersed in the oxidizing acid system containing bath. Among the various substrata, tin is coated the most rapidly. For example, in a bath containing about 5 to 15 weight percent based on emulsion solids of nitric acid, a tin plated panel will be plated in about 10-40 seconds. On the other hand when steel panels are immersed in a bath containing a like amount of the same acid, plating can take from about 1 to 20 minutes.

When baths are prepared as above, substrate coating can be carried out at room temperature or lower without difficulty. Likewise the bath temperature can be increased to 50° C. or higher with a corresponding decrease in substrate plating time. Surprisingly, as the bath temperature is increased, the water resistance of the plated panels also increases. In general, plating can be carried out between just above the freezing point of the bath and just below its boiling point.

The baths as prepared herein can be used repeatedly to coat a large number of metal articles. For example, a 10% solids emulsion bath placed in a 500 ml. beaker can be used to plate as many as 150 or more 3" x 6" steel panels. However, as increasing numbers of articles are coated the bath emulsion solids tends to decrease while the bath pH increases. Thus additional amounts of the acid system and the emulsion must periodically be introduced into the coating bath. Furthermore, as more panels are coated residual metal ion content in the bath increases due to the surface dissolution of the metallic articles. This metal ion content can be controlled by any conventional means of metallic ion separation, e.g., electrodeposition, precipitation, ion exchange, etc.

The process herein disclosed is not limited to the coating of metal panels. Thus, car bodies, siding material, appliance bodies, metal containers, or any other metallic substrate can be coated with advantage. Moreover, in a variation of this process a metal tank or container can be coated by pumping the bath as described above into this container and then removing the bath after a coating of sufficient thickness is obtained. In general any metallic substrate can be coated simply by contacting it with the baths herein prepared. Furthermore using normal pigmentation techniques, the emulsions of this invention can be formed into paints. The pigments which are useful, however, are preferably limited to those pigments which are nonreactive with oxidizing acid systems. For example: barytes, red iron oxide, titanium dioxide, magnesium silicate, calcium silicate, carbon black, etc., are useful. These pigmented emulsions can be employed to coat metallic articles by the processes described herein in the same manner that non-pigmented emulsions can be used.

Following the above deposition step, the coated metal articles are contacted with the solution described herein-after, preferably washed with water, and then either air dried or baked using standard methods. Although not required it has been found particularly advantageous when baking to carry out a two step baking process. In the first step the substrate is baked at a low temperature (about 85° F.-175° F.) for about 1 minute to 25 minutes. This step allows the removal of water trapped in the coated films. Following this step a higher temperature bake (about 225° F. to 400° F.) is carried out over a like period to insure complete cure of the coating. When "cure" is used herein it is meant to be synonymous with crosslinking or drying.

In preparing the post-dip solutions of this invention (also referred to as wash solution or bath) any solvent which will solvate the materials hereinafter described can be used with the proviso that this solvent not act to dissolve the acidic deposition films during immersion. However, it is preferred that a major portion of the solvent be water.

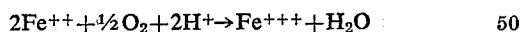
The active portion of this post-dipping bath is about 0.25 to about 7.0 weight percent (based upon the total post-dip bath content) of a material selected from chromium trioxide, phosphoric acid, and water soluble or acid soluble chromates and dichromates. Included among these materials are the following chromates; potassium, sodium, ammonium, calcium, cesium, lithium, magnesium, zinc, etc., and dichromates; sodium, ammonium, lithium, etc. Preferred among these chromates and dichromates is zinc chromate.

When phosphoric acid is used in the post-dipping bath it is preferred that it be added to the bath at about the 0.25 to 3.0 weight percent level. However, when the chromates are used, e.g., zinc chromate or chromium trioxide, this level preferably can range from 0.25 to 5.0 percent. Most preferable results, in general, are obtained when any of the above bath materials are present at about the 0.5 to 1.5 weight percent level.

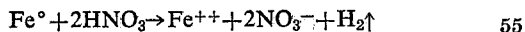
The amount of time that the "uncured" or "unbaked" acidic deposited film is exposed to this bath can vary from about 5 seconds to 5-10 minutes. However it is preferred that bath exposure generally be in the 15-90 seconds range. Exposures of greater than 15 or 20 minutes generally cause redispersion of the uncured film and result in baked films which are highly discolored.

The "unbaked" acidic deposited films can be exposed to the above bath by any convenient method. For example, a tank or container which has been coated by acidic deposition can be subjected to this bath by pumping the bath solution into the container itself. Likewise, this bath can be applied by spraying or brushing. However the preferred method of bringing the acidic deposited, coated metal substrate into contact with this bath is by dipping.

Although the exact mechanism by which the emulsions as used herein coagulate onto the surface of a metal article in the presence of an oxidizing acid system is not known, it is thought that the particular acid systems which are useful react with the metallic substrate to produce metal ions. This can be illustrated for iron and nitric acid as follows:



The ferrous ions (Fe^{++}) can then be further oxidized to ferric ions (Fe^{+++}) in the presence of oxygen and acid:



These metal ions in turn can act to coagulate the emulsion. Since this coagulation effect occurs at the interface of the metallic article and the emulsion, a film of the emulsion is thereby deposited onto the surface of the metallic article.

It is thought that this interfacial coagulation is caused by the metal ions acting to reduce the absolute electrochemical potential or zeta potential of the emulsion particles. Zeta potential is defined as the difference between the movable outer layer emulsion particle charge and the overall charge of the emulsifying liquid. When the magnitude of this charge is reduced sufficiently by a high concentration of metal ions as are found at the emulsion-substrate interface, the individual emulsion particles are then caused to coagulate. This explanation is offered only to clarify the process of the invention herein described. It is not included as a limitation upon this invention. In the following examples parts unless otherwise specified are understood to mean parts by weight.

EXAMPLE 1

An aqueous emulsion was prepared by the following procedure:

(1) Into a reaction flask equipped with a mechanical agitator, thermometer, three addition funnels and reflux condenser were added 720 grams of water, 64.8 grams of a 5% aqueous solution of the sodium salt of 2-sulfoethyl methacrylate and 4.8 grams of sodium vinyl sulfonate.

(2) A mixture was prepared containing 64.8 grams of a 5% aqueous solution of the sodium salt of 2-sulfoethyl methacrylate, 4.8 grams of sodium vinyl sulfonate, 47.4 grams of a 60% aqueous solution of N-methylol acrylamide and 120 grams of water.

(3) 7.8 grams of potassium persulfate and 16.2 grams of itaconic acid were dissolved in 240 grams of water.

(4) A solution of 28.2 grams of isobornyl methacrylate, 367.8 grams of acrylonitrile and 658.2 grams of butyl acrylate was prepared.

#1 was heated to 149° F. with a continuous nitrogen flow. When the temperature became stable at 149° F., 7.8 grams of sodium metabisulfite were added. Separate three hour additions of #2, #3, and #4 were begun. At the end of the addition, the reaction temperature was increased to 167° F. and 60 drops of tertiary butyl hydroperoxide were added. 1½ hours later an additional 60 drops of tertiary butyl hydroperoxide were added and the resulting mixture was held 2½ more hours. An emulsion resulted having no free monomer, a density of 1.02 grams/ml., a pH of 2.72 and a #1 spindle, 20 r.p.m., Brookfield viscosity of 24 cps.

An acidic deposition bath was prepared by adding 40 ml. of the above emulsion to 150 ml. of water and 10 ml. of a 10% aqueous nitric acid solution. Seven duplicate sets of panels were dipped in the above bath for five minutes producing uniform coatings thereon. Immediately after the coating process, one of the coated panels from each set was dipped for 30 seconds in water while the other panel of the set was dipped for 30 seconds in a 0.5% aqueous chromium trioxide solution. Both panels were then baked for 5 minutes at 140° F. followed by 5 minutes at 300° F. The water up-take of all panels was determined with the following results.

Set #	Post-dip	Water up-take, percent
1.....	Water.....	1.04
1.....	Chromate.....	0.43
2.....	Water.....	0.97
2.....	Chromate.....	0.65
3.....	Water.....	1.25
3.....	Chromate.....	1.01
4.....	Water.....	1.07
4.....	Chromate.....	0.51
5.....	Water.....	1.61
5.....	Chromate.....	0.45
6.....	Water.....	0.81
6.....	Chromate.....	0.75
7.....	Water.....	0.90
7.....	Chromate.....	0.55

Following the above tests all chromium trioxide dipped panels showed much less surface discoloration than did the water dipped panels.

EXAMPLE 2

Using the same procedure as described in Example 1 an emulsion was prepared having a pH of 2.9, a density of 1.03 g./ml. and a #1 spindle, 20 r.p.m., Brookfield viscosity of 23 cps.

20 ml. of this emulsion were mixed with 5 ml. of 10% aqueous nitric acid and 75 ml. of water producing an acidic deposition bath. Two sets of cold rolled steel panels were each dipped into this bath for 5 minutes. One panel

from each set was then immersed in a 1% aqueous phosphoric acid solution for 30 seconds and then baked for 5 minutes at 140° F. followed by 5 minutes at 300° F. The other panel in each set was baked as above immediately after its removal from the acidic deposition bath. Water up-take was evaluated with the following results:

Set #	Phosphate post-dip	Water up-take, percent
1-----	No-----	1.07
1-----	Yes-----	0.34
2-----	No-----	2.60
2-----	Yes-----	1.00

All phosphoric acid post dipped panels exhibited very little discoloration after the water up-take test. However, the non-dipped panels discolored severely.

EXAMPLE 3

An emulsion was prepared as described in Example 1. An acidic deposition bath was prepared by adding 20 ml. of this emulsion to 10 ml. of a 5% aqueous nitric acid solution and 70 ml. of water. A zinc chromate containing solution was prepared by adding an excess of zinc carbonate to a 10% aqueous chromium trioxide solution. For a 3.0% zinc chromate post-dip bath 60 ml. of this zinc chromate-chromium trioxide solution were added to 140 ml. of water. For a 0.5% post-dip solution 10 ml. were added to 190 ml. of water. Two cold rolled steel panels were dipped into the above acidic deposition bath for 5 minutes, washed, and one was post-dipped in the 3% zinc chromate solution for 30 seconds while the other was similarly dipped in the 0.5% zinc chromate post-dip solution.

A normal water up-take test was run except that both panels were allowed to remain in the room temperature water for 20 additional hours. The 0.5% zinc chromate post dipped panel exhibited a water up-take of 1.6% while the 3% zinc chromate post dipped panel gained no weight at all.

EXAMPLE 4

Using the same procedure as described in Example 1, an emulsion was prepared which exhibited a #1 spindle, 20 r.p.m., Brookfield viscosity of 23 cps., essentially no free monomer, a pH of 2.90 and a solids content of 48.5% (48.1% theoretical). At the same time a pigment paste was prepared comprising 12 parts of a mixture of magnesium silicate and calcium silicate, 24 parts of barytes, 24 parts of red iron oxide, 24.0 parts of water, 1.6 parts of Daxad 30, an anionic surfactant derived from the sodium salt of a polymerized carboxylic acid obtained from W. R. Grace and Company, 1.6 parts of Igepal CO-610 a nonionic surfactant derived from nonyl phenoxy poly(ethyleneoxy)ethanol obtained from the GAF Co., and 0.8 part of an anti-foaming agent AF-100 obtained from the NOPCO Company.

An acid deposition bath was prepared by mixing 10 ml. of a 10% aqueous nitric acid solution, 10 ml. of the above pigment paste, 20 ml. of the above emulsion and 60 ml. of water. A cold rolled steel panel was dipped into this bath for 5 minutes and then dipped into a bath containing 0.5 weight percent chromium trioxide. This panel was then baked for 15 minutes at 140° F. followed by 15 minutes at 300° F. A red coating resulted which had excellent appearance and exhibited a water up-take of 2.41%.

EXAMPLE 5

Using the same procedure as in Example 1, a similar emulsion was prepared except that #3 contained 90 additional grams of water, and 16.2 additional grams of

itaconic acid and that #4 contained 16.2 less grams of butyl acrylate. The resulting emulsion exhibited a solids content of 45.6% (47.0% theoretical), less than 0.2% free monomer, a density of 1.03 g./ml. and a pH of 3.05.

A 100 ml. acidic deposition bath was prepared by mixing 20 ml. of the above emulsion with 5 ml. of a 10 weight percent aqueous nitric acid solution and 75 ml. of water. Six pairs of cold rolled steel panels were dipped in this bath for 5 minutes. Out of each pair one was dipped in a bath containing 10 ml. of a 10% by weight aqueous chromium trioxide solution and 190 ml. of water. Both the dipped and the non-dipped panels were then baked for 5 minutes at 140° F. followed by 5 minutes at 300° F. Water up-take tests were performed on each set of panels with the following results:

Set #	Chromate post-dip	Water up-take, percent
1-----	No-----	9.62
1-----	Yes-----	4.80
2-----	No-----	6.67
2-----	Yes-----	4.23
3-----	No-----	6.23
3-----	Yes-----	5.08
4-----	No-----	5.11
4-----	Yes-----	4.44
5-----	No-----	8.05
5-----	Yes-----	4.44
6-----	No-----	7.83
6-----	Yes-----	2.37

EXAMPLE 6

An emulsion was prepared according to Example 1. 600 ml. of this emulsion were added to a mixture of 2250 ml. of water and 150 ml. of a 10% aqueous nitric acid solution. In addition a 0.5% chromate bath was prepared by adding 5 grams of chromium trioxide to 1000 grams of water. 2 sets of cold rolled steel panels were coated for 5 minutes in the above acidic deposition bath. Out of each set one panel was dipped for 30 seconds in the chromate post dip solution and baked with the non-post-dipped panel for 5 minutes at 140° F. followed by 5 minutes at 300° F.

The first set of panels were placed in 70° C. salt spray for 24 hours and removed. The chromate post-dipped panel showed little evidence of degradation. On the other hand the non-post-dipped panel was completely blistered and discolored after this period of salt spray. The post-dipped panel was kept in salt spray for 23 additional hours before substantial film degradation occurred. But even after this 47 hours of total salt spray exposure no blistering of the film was evident.

The second set of panels as prepared above-one non-post-dipped and one post-dipped was placed in boiling water. After 2 hours' immersion the film on the post-dipped panel was still tough with no evidence of discoloration. However, after only ½ hour's immersion in boiling water, the film on the non-post-dipped panel was severely discolored. One hour's immersion resulted in a bubbling of the film while after 1½ hours' immersion, the non-post-dipped film peeled off its steel substrate.

EXAMPLE 7

Using the same procedure as in Example 1 a similar emulsion was prepared except that part #4 contained 629 grams of butyl acetate, 59 grams of isobornyl methacrylate, and 368 grams of acrylonitrile. The resulting emulsion exhibited a solids content of 47.6% (47.7% theoretical), and a percent monomer conversion of 99.6.

An acidic deposition bath was prepared by adding 20 ml. of the above emulsion to 5 ml. of a 10% aqueous nitric acid solution and 75 ml. of water. Two sets of steel panels were dipped in the above bath for 5 minutes and one set was post-dipped for 30 seconds in a 1.0 weight percent chromium trioxide solution while the other set was dipped for a like amount of time in a 3.0 weight percent chromium trioxide solution. These panels were then baked

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for 5 minutes at 140° F. followed by 5 minutes at 300° F. and water up-take tests were run with the following results:

Set #	Percent	
	Chromium trioxide	Water up-take
1.-----	1.0	0.603
2.-----	3.0	0.708
2.-----	1.0	0.880
2.-----	3.0	1.874

Film appearance and general water resistance were excellent.

In the same manner a series of comparisons between water post-dipped and chromate post-dipped acidic deposition coated panels was made for levels of chromium trioxide of 0.5%, 1.0%, 3.0%, and 5.0%. On the average post-dipping in the chromate bath improved the water resistance of these acidic deposited films by 50% over the water post-dipped films.

It is understood that the foregoing detailed description is given merely by way of illustration and that many variations can be made therein without departing from the spirit of this invention.

The embodiments of this invention in which an exclusive privilege or property is claimed are:

1. An improvement in the process of coating metallic articles by acidic deposition which comprises:

contacting an unbaked or uncured acidic deposited coating of a synthetic film-forming resin on a metallic article with a solution comprising about 0.25 to 7 weight percent, based on the total solution weight, of a material selected from the group consisting of phosphoric acid, chromium trioxide, and water or acid soluble chromates and dichromates.

2. An improvement in the process of coating metallic articles by acidic deposition which comprises:

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contacting an unbaked or uncured acidic deposited coating of a synthetic film-forming resin on a metallic article with a solution comprising about 0.25 to 7 weight percent based on the total solution weight, of a material selected from the group consisting of phosphoric acid, chromium trioxide, and water or acid soluble chromates and dichromates; and baking said article for a time sufficient to cure the coating thereon.

3. The process of claim 1 wherein said solution is aqueous.

4. The process of claim 1 wherein said material is selected from the group consisting of phosphoric acid, chromium trioxide and zinc chromate.

5. The process of claim 1 wherein said solution comprises about 0.25 to 5.0 weight percent of chromium trioxide.

6. The process of claim 1 wherein said solution comprises 0.25 to 3.0 weight percent of phosphoric acid.

7. The process of claim 1 wherein said solution comprises 0.25 to 5.0 weight percent of zinc chromate.

8. The process of claim 1 wherein said material is present in an amount equal to about 0.5 to 1.5 weight percent based on the total solution weight.

9. The coated article obtained by the process of claim 1.

10. The coated article obtained by the process of claim 2.

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