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(54) **Stable Latex Rust Converting Primer**

(57) Storage stable metal primer compositions for converting rust to inert iron complexes and for depositing residual adherent protective latex primer coatings

thereon comprise an acid stable non-ionic surfactant free oil-in-water emulsion of a film forming latex having covalently bound acid groups (carboxyls or sulfonates) and a chelating agent selected from polyhydroxy phenols or polyhydroxy phenol carboxylic acids, e.g. tannins and/or tannin derivatives.

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SPECIFICATION

Stable Latex Rust Converting Primer**Technical Field**

This invention relates generally to chemical compositions and coatings which have the ability to complex metals and convert rust in the form of storage stable latexes and to protect underlying metallic surfaces from progressive rusting or corrosion; and more particularly, to such chemical compositions which utilize polyhydroxyphenyls and/or polyhydroxyphenyl carboxylic acids and derivatives capable of metal ion chelation such as tannins and tannin-like derivatives in combination with ionically stabilized, water/alcohol insoluble latexes containing covalently bound acid groups.

10 Background of the Invention

Iron and iron based alloys have, for centuries, constituted the major class of metallic materials utilized for the construction of the vast majority of objects in the world's civilizations. Use of iron and ferrous alloys is universal. However, objects constructed of ferrous materials are subject to a serious defect which affects their usefulness and long term durability i.e., the phenomenon of rust. When exposed to the atmosphere and moisture, iron materials are subject to rusting which can cause severe corrosion of the surface and ultimately may destroy the object. Attempts to control rust may take several courses among which are the substitution of nonrusting materials; utilization of special rust resistant iron alloys; and the provision of protective coatings on the iron surface to isolate the rust-prone metal from the oxidizing influence of the atmosphere. However, it is not always feasible nor economical to provide nonrusting substitutes for the iron material; and protective coatings are not always effective in preventing the eventual rusting of the iron surfaces.

Once an iron surface has rusted, it is very difficult to effectively protect the unrusted underlying metal without the mechanical removal and cleaning of the rusted portions. Because of the expense and labor involved in completely removing rust from the metallic surface and reapplying protective materials to the newly exposed metal, various techniques have been devised for reducing and/or preventing further deterioration of the rusted surfaces, i.e. phosphating. One technique which has been attempted with some degree of success is the conversion of the rust (which is a hydrated iron (III) oxide) into a more inactive ferric chelate derived from the action of compounds such as polyphenols tannins or tannin-like derivatives.

The production of black oxide (magnetite) anti-corrosive coatings on steel by high temperature treatments has been known for many years. Attempts to convert iron and steel, particularly rusty steel, to magnetite at ambient temperatures have been the subject of much research. Two general approaches have been taken. Conversion due to the incorporation of special pigment systems in oil based coatings for example, combinations of zinc tetroxochromate, barium chromate and zinc phosphate in the presence of basic organic inhibitors such as guanidine salts (reference G. Meyer "D. T. Farben-Zeitsch, 18 (1964) p. 352) and combinations of iron powder, an aluminum alloy pigment and small amounts of zinc and magnesium oxide (British Patent 821,133). This approach results in slow conversion (9 months—1 year) and is not applicable to water based systems. Thus it is necessary to employ organic solvents which are often undesirable.

Although it had earlier been used for corrosion inhibition and descaling in circulating water systems, Shreir discovered in 1955 that tannins, when combined with phosphoric acid, caused rapid conversion of iron or steel to a black coating and proposed such systems as "wash primers" under conventional coatings with better durability than either ingredient alone (U.S. Patent 2,854,368 issued 9/30/58). In 1958 Knowles and White published more detailed results on the Shreir invention showing that the corroded steel withstood only 1—3 weeks weathering and required topcoating relatively soon to avoid a reoccurrence of the rusting (J. Oil Color. Chem. Assn, 41 (1958) p.10).

In 1959 Coales was granted a patent (German 1,049,518, issued 1/20/59) on an apparently water-in-oil emulsion of tannin solution emulsified with lanolin and dispersed in mineral oil with fillers as a metal protective coating. In Indian Patent No. 60684 (5/20/59), Ramanujam et. al. describe compositions similar to Shreir's work. Their Patent No. 60612 (5/6/59) describes low cost oil-in-water emulsions from polymerized cashew nut shell phenols and formaldehyde condensates of same that were emulsified in water with tannins and bentonite. Coatings from those emulsions on steel withstood nine weeks immersion in water compared to unmodified acidified tannin which required topcoating within one week. In 1961 Seligman reported in *Elektroteck u Maschinebau*, 78(1961) p. 296, that the Plus-Gas Co., London, UK was marketing tannin compositions for corrosion coating, two of which were "wash primers" and the third a tannin solution coating containing film forming resins. (Plus-Gas Solution B).

An extensive development program was reported by Stephan in *Farber Lack*, 68 (1962) p. 701—777. Stephan took two different approaches in an attempt to produce longer lasting primers using tannin-like rust conversion, one involved resin like condensates from chelating monomers such as methylene disalicylic acid and salicylic acid condensed with formaldehyde (British Patent 913,157). The polymers were dissolved in alcohol and neutralized with dilute ammonia to a pH of 6.5. The second approach involved addition of neutralized alcohol/water solutions of tannin to polyvinyl acetate

emulsions. Stephan reported that the emulsifiers in the PVA latexes evaluated tended to destabilize the tannin. Cellulosic derivatives were preferred. For stability it was necessary to adjust the pH of the tannin modified latexes to around 7. These compositions did not perform as expected being no better in corrosion resistance after 4 weeks weathering than simple tannin "wash" primers without polymer.

5 Ishra and Sokolov were granted a Russian Inventors Certificate No. 172587, published 6/29/65 5
which is more understandable if read in conjunction with their article published that year in
"Sudostroenie" (Leningrad) 12 (1965) p. 65—69, which was translated by the U.S. Dept. of Navy and
published as NTIS Report AD 638897. Iskra et. al. observed that tannins/phosphate or phosphoric acid
10 wash primers, both with and without polyvinyl butyral in solvent require sealing (painting) within a 10
short time (few days) after application. In an attempt to overcome the problem, tannic/phosphoric acid
solutions were added to a GP (General Purpose, unmodified, alkaline pH) grade of styrene (65%)
butadiene (35%) latex. Acidified tannin was unstable and thus had to be neutralized with alkali before
addition. Due to the weakness of the resulting films and lack of conversion, a simple blend of aqueous
15 tannin and the above emulsion, however, a very high level (20%) in polymer weight was necessary for 15
wetting and conversion of the steel.

British patent 1,045,118 to Faulkner examined the use of tannin derivatives and tannin-like chemicals as rust converters when incorporated into conventional oil based solvent containing coatings.

20 Several publications including Franiau's article in Chimie des Peintures (Brussels) v. 33 (11) p. 20
383—90 (1970) and Langenaeck article in Peintures, Pigments, Vernis (Paris) v. 46(6) p. 625—32
(1970) and Kelate News S. A. PRB Brussels (Industrie-Lockier-Betrieb) V.40,207 May 1972 and
Franiau's U.S. Patent 3,753,924, issued August 21, 1973 describe tannin based products. There is
some indication of the use of an acidic natural rosin, soluble in alcohol, but insoluble in water, in
combination with alcohol/water blends.

25 Hengelhaupt's U.S. Patent 4,086,182, issued April 25, 1978 discusses rust converting 25
compositions including latexes and chemically modified gallic acids.

The prior art formulations, some of which are noted above, although capable of converting rust into the complexes, suffer from one or more defects which have impaired their full acceptance into the market place. Among the defects exhibited by such prior art formulations are temporary nature of the
30 thin "wash primer" type converters without additional coats of conventional primers and/or limited 30
conversion of rust where latex is incorporated, poor bond of the film to the underlying metal surfaces,
and/or poor shelf life because of coagulation of the tannin modified-latexes and/or poor resistance of
the applied primer to penetration by moisture to the underlying metallic surfaces due to the nature of
the polymer, excess surfactants or presence of external acids.

35 The present invention is directed to overcoming the defect, i.e., insufficient protection of the prior 35
art formulations, as set forth above.

Disclosure of the Invention

In its broadest aspect, the present invention provides compositions including polyhydroxyphenyls and polyhydroxyphenyl carboxylic acids and their derivatives as rust converting components with film
40 forming, ionically stabilized, latexes incorporating acid groups within their molecular structures. Such 40
compositions are oil-in-water emulsions with the rust converters contained in the aqueous phase and
conversion catalysed by acid groups covalently bonded to the latex polymer oil phase. Stability is
achieved by careful selection of emulsifiers used in latex manufacture. Durability is achieved by
selection of polymers that are stable in low pH aqueous media and are essentially insoluble in water or
45 in mixtures of water soluble alcohols, such as ethanol and water, where the latter is the major 45
component.

Additional components may be incorporated into the rust converting compositions, among which may be included materials to aid in the coalescence of the latex particles into the films; plasticizers to improve the physical properties of the films; thickeners or thixotropes; freeze-thaw stabilizers; wetting
50 agents; defoamers; fillers or selected pigments; other water dispersable resins, dispersing aids, 50
protective colloids, flow control agents, etc.

Detailed Description of the Invention

The rust converter formulations of the invention comprise oil-in-water emulsions having as the essential components metal chelating agents selected from the class comprising polyhydroxyphenyls and polyhydroxyphenyl carboxylic acids and their derivatives, especially tannins and tannin derivatives;
55 and acid stable, ionically stabilized latex of low pH in aqueous emulsion brought about by the 55
incorporation of acid groups as a portion of the polymer molecules; and water. The chelating agents are
dissolved in the latex-aqueous phase to form the invention product.

The major fraction of the polymer forming the solids content of the latex must comprise an
60 organic natural or synthetic material, that is sufficiently solid or semi-solid that, alone or when modified 60
by admixing with other ingredients in the compositions, will form a relatively non-tacky film over the
range of ambient temperatures. Furthermore, the polymers must exhibit a measurable acid value due to
the inclusion of acid groups, preferably carboxyls incorporated by covalent bonding within the polymer

molecules in the range of 0.5—50% by weight (preferably 1—20%); as well as exhibiting stability in storage in the form of aqueous emulsions; and being essentially insoluble in water or mixtures of water and water miscible alcohols where water is the major component. The polymer should be emulsifiable in the essential absence of non-ionic emulsifiers and protective colloids.

5 The surfactants can be anionic or cationic in nature, stable at low pH. The surfactants can be 5
chosen from any of a large group of generic types some examples of which are: Anionic-sodium,
potassium, calcium, or magnesium salts or partial salts of alkyl sulfates, alkyl sulfosuccinates, acylalkyl
laurates, alkyl aryl sulfonates such as, alkyl naphthalene sulfonates and linear alkyl benzene sulfonates;
10 alkyl phosphates, sulfosuccinates, alkyl oxydibenzene sulfonates, aryl sulfonates, perfluoro carboxylic 10
acid salts and perfluoro alkyl sulfonates and proprietary types such as Sipexes from Alcolac Inc. Some
specific examples are Sodium oleyl sulfate, sodium dihexyl sulfosuccinate, sodium N-cyclohexyl-N-
palmityl laurate, sodium linear or secondary dodecyl benzene sulfonate, sodium isopropyl naphthalene
sulfonates, sodium dodecyl oxydibenzene disulfonate, sodium xylene sulfonate, and Zonyl FSB from
Dupont Chemical.

15 The surfactants may be used alone or in blends and also in conjunction with anionic protective 15
coloids such as carboxy methyl cellulose, alginic acid carboxylated polyvinyls, methyl vinyl ether/maleic
acid copolymers, refined argar, cellulosic acid, carboxy methyl guar, carboxy methyl carob, and
polyacrylic acid and their salts or partial salts. Cationic salts of the following generic types can also be
used: N-alkyl trimethylene diamine salts, N-alkyl imidazolinates, quaternary ammonium salts, alkyl
20 guanidine amine complexes, collamide derivatives, sulfonium derivatives, and alkyl pyridinium salts. 20
Specific examples of these are: N-octyl trimethylene diammonium chloride, heptadecyl-N-benzyl
benzimidazole, N-N-di benzyl dimethyl ammonium chloride, ethanolated alkyl guanidine amine
complex, sodium salts of sulfated lauryl alcohol and myristyl, collamide, dodecyl ethyl methyl sulfonium
chloride and lauryl pyridinium chloride. The more preferred types of surfactant being the anionics,
25 specifically alkyl aryl sulfonates. 25

Note that cationic and anionics cannot be used together due to instability of the mixtures.

Acid salts such as sodium hydrogen phosphates are not considered to be emulsifiers for the purposes of this invention since such salts do not significantly lower the interfacial tension at the latex particles sufficiently in the absence of a true anionic surfactant.

30 Such materials may be an ancillary part of the emulsifier system of this invention in the role of a 30
buffer or dispersant.

As will be discussed in greater detail subsequently, a large number of additional components may be added to the rust converting emulsions for a number of purposes. However, their inclusion in the compositions is not intrinsic to the basic function of producing stable emulsions which convert rust and
35 for producing a durable primer on the iron surfaces. Among the additives are such materials as 35
coalescing agents; plasticizers; thickeners and freeze-thaw stabilizers; wetting agents; defoamers;
fillers; preservatives; dispersing aids, flow control aids, pigments and other acid stable, emulsifiable
dispersible resins. The addition of such additives, however, is principally done for the purpose of
modifying and adjusting the secondary characteristics of the composition.

40 It is important to note that the advantages of the compositions of the invention are brought about 40
by the inclusion of ionically stabilized latexes having acid groups covalently bound to the polymer
molecules, thereby eliminating the need for any external acids. External acids or their acid salts are
defined as inorganic acids forming true solutions in water, as opposed to organic colloidal solutions
such as formed for example by polyacrylic acid and other protective colloids and thickeners, and
45 emulsions, for example, the acid latexes described above. External acids are further distinguished from 45
acidic emulsifiers, dispersants, or wetting agents due to their lack of interfacial and surface activity
when a true surfactant is absent.

The use of the term "Latexes having acid groups" is meant to refer to latexes which incorporate
acid groups, e.g. the carboxylic or sulfonate group, within the structure of their molecules by covalent
50 bonds and are stable in aqueous solution. The incorporation of the acid structures within the molecules 50
imparts acidity to the aqueous phase, initiating conversion by the chelating agent. Films having
excellent adhesion are produced due to the tendency to form secondary bonds on metal. When such
polymers are dispersed within aqueous solution, the acid properties are manifest by low pH's of the
latexes. The pH's are definitely on the acid side ranging from a high of somewhat more than 4 down
55 to 2 and even lower, the preferred range being 2.0—3.5 since the ferric ion tends to precipitate as pH 55
rises. Such acid functional latexes are commercial products readily available from a number of
manufacturers and are used for adhesives, laminating and the like, rather than as coatings.

However, typical latexes may be prepared as follows on a lab scale in small quantities in a pressure bottle:

Example 1

		<i>by weight</i>	
	Water	47.6%	
5	Sodium dodecyl oxydibenzene disulfonate	2.1	5
	Styrene	29.2	
	Acrylic acid	1.5	
10	Potassium persulfate	0.2	
	Butadiene	19.4	10

The water, surfactant, styrene, and acrylic acid were added to a pressure bottle. The bottle was shaken well and after a short period in cold storage, potassium persulfate and butadiene were added. The bottle was capped and placed into a bottle reactor and allowed to thaw at 10—20° for 1/2 hour. Upon completion of thawing the water bath was increased to reaction temperature of 50°C, held 6 hours, then heated to 70°C and held for a further 2 hours.

The latex obtained had the following characteristics:

Non-volatiles—49%

Coagulum 1%

pH 3.5

20 Example 2

	<i>Initial Charge</i>	<i>by weight</i>	
	1) Water	35.2	
	2) Sipex JKB	5.7	
	3) Ethyl Acrylate	5.0	
25	4) Methacrylic Acid	1.7	25
	<i>Pre-emulsion</i>		
	5) Water	17.6	
	6) Sipex JKB	1.4	
	7) Ethyl Acrylate	28.9	
30	8) Methacrylic Acid	4.3	30
	9) Potassium persulfate	0.13	
		<hr/> 99.93	

(a) Items 1—4 were added to the reaction flask in the order listed, however, allowing the Sipex JKB to dissolve before adding the monomers.

(b) Agitated sufficiently to form an emulsion.

(c) Added 9 to the flask and heated with stirring to 70°C.

(d) Prepared the pre-emulsion 5—8 and began the addition of this mixture to the reaction flask as soon as an exotherm was noted. Maintained the temperature at 70—75°C throughout the addition period which was 1 3/4-2 hours.

(e) When the addition was completed, the contents were heated to 85°C and maintained for 1/2 hour.

(f) Cooled to room temperature and discharged.

The resultant latex typically had the following characteristics:

Non-volatiles—42%

Viscosity at 77°F—125 cps (Brookfield RVF #2 spindle 20 RPM)

pH—2.3

The noted latexes in un-neutralized form are not normally formulated into surface coatings due to their tendency to corrode metal containers, create pigment instability and cause "flash" rusting of steel. Instead they are utilized for the purposes of adhesives, laminating and flock binders. However, when used in the rust converting compositions of this invention, these acid functional latexes not only initiate the conversion process, but produce tough, durable and adherent coatings on iron surfaces, which coatings have shown excellent resistance to moisture and salt spray since additional, external, water soluble acids are not required.

The latexes which are suitable for use in the rust converter formulations can be chosen from a broad range of polymer forming molecules of which the following are an illustration:

Vinylchloride/acrylate copolymers

Vinylidene chloride/acrylate copolymers

Vinyl acetate/acrylate copolymers

Vinyl acetate/vinyl chloride/acrylic acid copolymers

Vinylidene chloride, butadiene acrylic acid

Cyclic hydrocarbon polymers (sulfonated)
 Acrylate copolymers
 Methacrylate copolymers
 Vinyl acetate/ethylene/acrylic acid copolymers
 Styrene/butadiene/acrylonitrile/acrylic acid copolymers
 Styrene/butadiene/acrylic acid copolymers

5 5

In general, unsaturated acids are employed for copolymerization with polymers prepared by free-radical reactions typical of which are itaconic, fumaric, acrylic and methacrylic acids. Sulfonation of, for example, hydrocarbons is performed with sulfuric acid.

10 10
 Polymers of any of the above individual monomers copolymerized with acidic materials are also useful as are other related acidic polymers and combination of polymers. The specific selection generally depends upon the polymer's ability to form a water resistant film in the anticipated environment in which the chelating composition is to be used, is stable, e.g. hydrolysis resistant in a low pH aqueous media, and/or availability and cost.

15 15
 As noted above, all of the latexes are produced with varying amounts of acid, however, those latexes exhibiting a pH of from about 2 to 3.5 and containing 1—20% by weight acidic monomers are most preferred in the invention compositions.

20 20
 The latexes are secured from commercial sources or produced in the form of an aqueous oil-in-water emulsion in which the polymer solids content may range in the area of about 35—65% by weight, more or less, of the latex. See for instance the latex preparations, set forth in Examples 1 and 2, above.

25 25
 The commercial emulsions are stabilized with surfactants which are normally included in the products as manufactured. The surfactants may be either anionic or cationic all of such surfactants being compatible in the invention compositions. However, for the purposes of the invention, those emulsions which are stabilized with nonionic surfactants and/or nonionic protective colloids are not useful in the invention compositions. Such nonionic stabilized emulsions coagulate during manufacture or during storage in the presence of the rust converting chelating agents. The most preferred emulsifiers are the anionics, specifically alkyl aryl sulfonates. However, other surfactants which are acid stable and do not cause coagulation or precipitates in the presence of chelating agents during storage are also suitable.

30 30
 Suitable materials for producing a chelated iron in the hexaquo (Fe^{3+}) state are in general the polyhydroxy phenols and polyhydroxy phenyl carboxylic acids and their derivatives. The most common source of this class of compound is tannins which are widely distributed in nature. Tannins are loosely classified into two types (1) hydrolysable types (or pyrogallol) tannins and (2) condensed (or catechol) tannins according to the products they yield on hydrolysis with mineral acid, i.e., water soluble products from hydrolysable, and a precipitate (phlobathene) from condensed types. Also there are "mixed" types.

35 35
 Hydrolysable tannins contain metapolygallic acid (or gallic acid glucosides), ellagic acid glucosides, and quinic esters of gallic and metapolygallic acid. Tannins may have a molecular weights over 2000 and a phenol hydroxyl functionality of 23 or more. The specific tannin is usually defined by vegetable source from which it was extracted. Thus hydrolysable tannins may be from gall (or nut gall), hydrabolan, chestnut wood, divi-divi-pods, valonea, sumac or chinchona. Condensed tannins may be derived from quebracho, mimosa (also acacia or wattle), mangrove bark (cutch), oak, gambier and chestnuts. Certain natural resins and gums also contain tannins or similar polyhydroxy phenol chelating agents such as cashew gum accroides (*Yucca*) and polymerized urushinol.

40 40
 For the purposes of the invention both classes of tannins are satisfactory provided their particular grade is water soluble. The hydrolysable types are preferred since, in general, due to their higher hydroxyl functionality.

45 45
 Synthetic derivatives of tannin and from other sources also show chelating ability. This appears to be related to the presence of two or more phenolic-oxy substituents for example, in benzoic or benzoic acid, where at least two hydroxyls are ortho to each other. Examples of such derivatives are 2,3-dihydroxy benzoic acid (*o*-pyrocatechuric acid); 3,4-dihydroxy benzoic acid (protocatechuic acid) and pyrocatechol.

50 50
 Also 2,3,4-trihydroxy benzoic acid; 2,4,5-trihydroxy benzoic acid; and 3,4,5-trihydroxy benzoic acid (gallic acid) and pyrogallol are useful; as well as other tannin derivatives such as ellagic acid.

55 55
 Particularly preferred of the above groups due to the proximity of hydroxyl substituents are pyrocatechuric acid; 2,3,4-trihydroxy benzoic acid; and gallic acid.

60 60
 Preferred due to commercial availability is gallic acid. Combinations of tannic acid and gallic acid are advantageous since tannic acid increases the solvency of water for gallic acid. Such mixtures also display solution stability, as well as greater resistance to moisture of the latex films.

The third essential component of the rust converting formulation is water, which is by definition, the liquid portion of a latex and which further serves as the solvent for the rust converters. Thus, the rust converting compositions comprise an ionically stabilized acid functional latex of low pH, tannins and related materials, and water. As will be noted subsequently in the following examples, a

formulation comprising only the above-noted components provides a very useful and operable rust converting primer.

5 Generally speaking, the percentages of the principal components in the composition, i.e., the latex, the rust converting agent; and water, are not critical. However, water comprises the largest component, being present in most of the preferred compositions in the area of 30—80% by weight. The latex is the second most prominent component normally being present in the vicinity of about 20—65% by weight. The metal chelating component may be present at considerably less percentage than the other two components e.g. in the neighborhood of perhaps 1—15% by weight, with a more preferred range of 2—8%. The ratio of component weights may vary from the percentages as stated above without greatly affecting the rust converting and film forming properties of the compositions. 10

Although these three components provide perfectly satisfactory and operable compositions, the formulation's secondary characteristics may be adjusted by the addition of other components. For instance, it may be desirable to formulate a thickened and/or thixotropic composition; plasticizers may be added to increase the flexibility of the residual latex film; coalescing aids may be desirable in order to ensure proper film formation; freeze-thaw stabilizers may be added and wetting agents, defoamers, fillers, pigments, preservatives, dispersing aids, flow control aids and other acid stable water dispersible resins, or emulsified resins. 15

In order to aid in the coalescing properties of the latexes, such materials as ethyl ethers of diethylene glycol acetate; the butyl ether of diethylene glycol acetate, the propyl ether of 1,2 propylene glycol; or hexylene glycol may be added. The ethyl ether or diethylene glycol acetate is the preferred coalescing agent for use in the formulations of the invention. When added, however, such coalescing aids will be most useful at perhaps 1 to 5% by weight. 20

Plasticizers such as phthlate esters, adipate esters, sebacate esters, or azalate esters may also be added to the formulation in order to increase the flexibility of the resultant latex films. If desired, anionic thixotropes and thickeners such as carboxylated polyvinyls; polymethyl vinyl ether/maleic acid copolymers; alginic acid; carboxymethyl cellulose; refined agar; cellulosic acid, carboxy methyl guar; carboxy methyl carob; and polyacrylic acid may be added. These materials may be employed as their partial salts if desired. The most preferred types of thickeners are the alginic acid and its partial salts. 25

Freeze-thaw stabilizers, such as glycols or other materials may be used. Glycols such as ethylene, propylene, and hexylene glycol are examples, as are other materials such as salts of N—COCO beta amino butyric acid, or the proprietary product Dalpad A from Dow Chemical Co.; or Nopco 2225-C from Nopco Chemical Co. ethylene or propylene glycols being preferred. 30

Wetting agents, such as the surface active agents listed above under emulsifiers, especially the acetylinic derivatives and fluorochemical surfactants. 35

Defoamers such as 2,4,7,9-tetramethyl-5 decyn-4,7-diol or proprietary types such as Hodag PU218 from Hodag Chemical Co; Colloid 581-B from Colloids, Inc.; Nopco JMY and Nopco NXZ from Nopco Chemical Co., Nilfoam C from Naftone Inc. may also be added, usually in percentages of less than 1%. Fillers such as barytes, clays, tales, mica, and silicas may be also added to lower the cost, and increase hardness and water resistance of the resulting films. Selected pigments can also be added to improve the corrosion resistance of the dried films. They are limited due to the nature of the system but black iron oxide and or titanium oxide (rutile), may be employed. 40

Dispersing aids may also be employed to aid in pigment and/or filler dispersions. Lecithin derivatives such as Kelesin 1081 from Spencer Kellog Co.; Daxas 21 from Dewey and Almy Co.; and Tamol 731 from Rohm and Haas Co.; the latter two being salts of condensed naphthalene sulfonic acids are preferred. Flow control aids may also be employed to ensure a smooth even flow of the coating on application, to give a uniform film thickness on the substrate, and eliminate surface defects such as pin holes, fish eyes, and brush stroke marks. Many of the wetting aids and stabilizing surfactants mentioned above will also perform this function. Other acid stable water dispersed or emulsified resins can be blended with the primary latexes to modify the film properties or reduce costs. 45

Emulsions such as Picopale A101 from Hercules Inc. (a sulfinated high molecular weight cyclic petroleum hydrocarbon) and Witcobond W106 (urethane latex) from Witco Chemical Co. are useful. 50

The rate of conversion of rust into the iron complex in the presence of the tannins and similar chelating agents is highly dependent upon the pH of the rust converter formulation. The lower the pH the more rapid the conversion takes place. Since the rust converter formulations of the invention are at acid pH's of 3.5 or less, the conversion takes place at an acceptable rate. Higher pH's result in reduced solubility of ferric ions and slower reaction rates. 55

In order for these rust converting primers to afford maximum long term protection from further rusting certain precautions must be taken. Rusted surfaces must be abraded to remove all rust and/or other coatings that are not firmly bonded to the substrate. Millscale must be removed. The surface must be cleaned of water soluble chlorides or sulfates and degreased. Enough coats of material should be applied to give a dried film thickness of approximately 2—4 mils and each coat should be touch dry before applying another coat. The primer should be allowed to dry 16—24 hours before topcoating and the topcoated item should be allowed to dry for 7—10 days before exposure to corrosive environments. 60

The following examples will illustrate various rust converter formulations falling within the invention and will also illustrate the process for producing the rust converter formulations.

Example 3

A simple three component rust converter formulation in accordance with the invention was prepared utilizing tannic acid, a carboxylated vinyl chloride/acrylic copolymer, and water. The carboxylated vinyl chloride/acrylic copolymer was a latex stabilized with anionic surfactant. The latex emulsion has a pH of 2.2, a glass transition temperature of +7°C, and was 50% by weight in nonvolatiles. 5

The rust converter formulation was produced by dissolving tannic acid in water heated to 130—140°F. The tannic acid-water solution was thereafter cooled to 85—90°F and then blended with the latex emulsion using agitation. 10

The resultant formulation comprised, by weight, 60% latex 6% tannic acid and 34% added water. The pH of the rust converter formulation was 2.0—2.5 and contained 36% by weight nonvolatiles.

The resultant composition was milky white in color and after being allowed to reach room temperature was painted onto a lightly rusted panel which had been wire brushed to remove loose rust. Within 5 minutes the panel surface was coated with a blue-black coating which on drying for 48 hours had excellent adhesion, was tough, and had good resistance to water and salt fog. 15

Example 4

A formulation prepared having the same component percentages as set forth in Example 3 with the difference being that a carboxylated vinylidene chloride/acrylic ester copolymer emulsion was substituted. The copolymer emulsion had a pH of 2.0, glass transition temperature of +7°C, and nonvolatiles of 51.0%. After being prepared by the same method as utilized in Example 3, the resultant formulation was painted onto a lightly rusted panel after loose rust had been removed. As in the case of Example 3, a blue black coating was formed on the panel surface within 5 minutes. However, the residual film formed on the panel surface was improved over the film formed by Example 3 in its resistance to moisture. This result was expected since the polymer was selected for its excellent resistance to moisture vapor transmission. 20 25

Example 5

A rust converter formulation was prepared with plasticizer, coalescing aid, and thickener additives. A carboxylated acrylic copolymer containing acrylonitrile in which the aqueous emulsion was stabilized with an anionic surfactant was utilized in the composition. The latex emulsion had a pH of 2.5, glass transition temperature of +33°C, and nonvolatiles of 50%. 30

The rust converting composition had 60.6% by weight latex emulsion; 3.0% tannic acid; 3.1% dioctyl phthalate (plasticizer); 2.5% ethyl ether of diethylene glycol acetate (coalescing aid); 0.4% acid salt of alginic acid (thickener); and 30.8% added water. 35

The formulation was produced by first dissolving tannic acid in water at 130—140°F. The thickener was premixed with the coalescing aid and thereafter added to the tannic acid solution with agitation. When the thickener was all dissolved, the latex was added with further agitation. After all of the latex was well mixed into the tannic acid and water, the plasticizer was added slowly with high speed agitation. 40

The resultant formulation had a pH of 2.7 and a nonvolatile content of 35.0%.

A sample of the above formulation was painted onto a lightly rusted panel which had previously been wire brushed to remove loose rust. The coating was allowed to dry overnight. A second coat was applied and after drying overnight was overcoated with one coat of an oil-based enamel. After drying one week, the panel was exposed to 5% salt fog for 200 hours. At the end of salt fog exposure, there was very little sign of new rusting, and no blistering. The residual coating still have excellent adhesion when tested by applying tape, over a cross-hatched area of the panel, and then pulling off. 45

Example 6

Another sample of a rust converter formulation was prepared utilizing a combination of tannic and gallic acids as well as a carboxylated styrene/butadiene latex. The styrene/butadiene latex aqueous emulsion was stabilized with an anionic surfactant. The latex emulsion had a pH of 4.3, a glass transition temperature of 27°C, and a nonvolatile content of 46.0%. 50

The sample was produced by dissolving tannic and gallic acids in water at 135—145°F. An acid salt of alginic acid thickener and an ethyl ether of diethylene glycol acetate coalescing aid were premixed and added to the acid solution with agitation. When the thickener was dissolved, the latex emulsion was added with agitation followed by a phthalate plasticizer using high speed agitation. 55

The resultant sample had the following composition: Latex emulsion, 62.1% by weight, tannic acid 0.5%, gallic acid 1.5%, algin salt 0.3%, as thickener, 2.5%, coalescing aid phthalate plasticizer 3.1%, added water 30.0%. The sample had a pH of 3.5 and a nonvolatile content of 34.0%.

A lightly rusted previously wire brushed steel panel was painted with the sample, and upon initial drying was painted with a second coat. After drying 24 hours the panel was covered with a tough black 60

coating which was then top coated with one coat of an oil based maintenance enamel. After drying one week, the panel was scribed with an X and then exposed to salt fog for 200 hours. There was less than 1/16" undercutting along the edges of the scribe, very little blistering or rust spotting in other areas of the panel. The coating had excellent adhesion when tape was applied to a cross hatched area and pulled off. The black prime coating could not be removed even after several applications of paint stripper. 5

Example 7

A sample exactly similar to Example 6 was prepared with the exception that the gallic acid was eliminated and tannic acid was made up to a percentage of 2.0. The test as in Example 6 was repeated and similar results were obtained with the exception that more blistering was noted on the test panel. It is postulated that the increased blistering was due to the fact that tannic acid is soluble in cold water and is more leachable, whereas gallic acid is soluble only in hot water. It appears therefore that a film containing tannic acid alone may be more water sensitive than a film containing gallic acid or a combination of gallic acid and tannic acid. 10

15 Examples 8—11 15

Results similar to those obtained with the formulation of Example 6, were obtained when other samples were prepared whose only change in components were different carboxylated latex emulsions. Percentages were the same as in Example 6.

8. Vinyl chloride/acrylic acid copolymer—Final composition pH 3.3; nonvolatiles 35.0%
 20 9. Styrene/acrylic ester/acrylic acid copolymer—Final composition had a pH 2.5; nonvolatiles 37%
 10. Styrene/butadiene/acrylonitrile/acrylic acid copolymer—Final composition had a pH 3.1; nonvolatiles 36.0%
 11. Vinyl acetate/acrylic acid copolymer—Final composition had a pH 3.5; nonvolatiles 35.0%

25 Example 12 25

In order to determine the effect of nonionic surfactants on the rust converter formulations, samples similar to Examples 6 and 11 were prepared utilizing latexes stabilized with blends of anionic and nonionic surfactants. The presence of the nonionic surfactants the materials could be processed to completion since on addition of the latex emulsion to the tannic acid solution, lumps of coagulant formed. 30

As a further test of the suitability of the nonionic surfactant, tannic acid solutions were treated with nonionic surfactants commonly used during the manufacture of latexes. The tannic acid solution coagulated immediately thus indicating that nonionic surfactants should not be utilized in the formulas of the invention.

35 Example 13 35

In order to evaluate whether pH is important to the action of rust converting formulations, a sample was prepared similar to that shown in Example 7 above, with the exception that the alginate thickener was eliminated and the latex emulsion was neutralized with ammonium hydroxide to a pH of 7.5—8.0. The ammonium hydroxide was added slowly with good agitation. Considerable thickening occurred as the carboxylic acid functionality of the latex was neutralized. The resultant basic pH material was painted onto rusted steel, however, blackening did not occur even after standing for several hours. 40

Example 14

A sample exactly similar to that set forth in Example 7 was prepared with the exception that an acid stable, non-carboxylated styrene/butadiene latex emulsion was utilized. However, in order to approximate the Example 7 formula as closely as possible, formic acid was added to give a final pH of 2.7—3.0. Samples of Example 7 and Example 13 compositions were then painted on rusty steel and allowed to dry. The resultant films were then checked with adhesive tape over a cross hatched area of the panels. The carboxylated latex formula i.e., Example 7 gave much superior adhesion. 45

In another test, the material from Example 7 was painted on a glass plate and also on a wire brushed rusty panel. After drying 48 hours, both panels were exposed to boiling water. The sample on the glass plate softened considerably; whereas the sample on the rusty panel was unaffected. In fact the toughness of the coating on the rusty panel actually increased after the exposure. 50

The test indicates that ferric chelate formation may actually cross link the resultant latex film coating. 55

Example 15

In order to test several other characteristics of the invention compositions, several additional tests were performed. A sample of Example 7 was painted on wire brushed unrusted steel. A black

coating was formed rapidly but the adhesion of the resultant film was much less than the same material on a wire-brushed rusted panel.

5 A sample of Example 7 was painted on a very heavily rusted panel with some of the loose rust removed. Although a tough black coating was rapidly formed, on further examination it was found that 5 some unconverted rust still remained under the polymer film. The adhesion of the coating to this very heavily rusted panel was also poorer than adhesion on a panel free of all loose rust. The result of this test indicates that it is advisable to wire brush loose rust before application of the rust converter formulations.

10 Samples of Examples 3—7 were stored for one week at 140°F along with a commercial rust converting latex primer. The samples of Examples 3—7 showed no signs of thickening or coagulation 10 whereas the commercial rust converting latex formula coagulated and became unstable.

A sample of Example 7 was painted on a tarnished copper pipe which was degreased and areas of green salts abraded. The material brightened on application and remained so on drying. The film was strongly adherent, and remained intact on exposure outdoor for 6 months, without topcoat.

15 An aluminum panel, (alloy type 2024—T3) was degreased and coated with material from 15 Example 7. No apparent change occurred on the surface but the composition gave an extremely well bonded coating (probable due to slight etching of the surface by the acidic polymer) which showed no signs of deterioration after 6 months exterior exposure without topcoat. A galvanized sheet with heavy excrescences was coated with Example 7. A foamy cloudy film was formed which had poor adhesion. 20 When the sheet was abraded with abrasive paper and coated a clear coating formed which had 20 excellent adhesion and showed no signs of deterioration after 6 months outside without a topcoat.

Applicability of the Invention

From a review of the above disclosure, it will be apparent that the rust converting formulations of the present invention, which include ionically stabilized carboxylated latexes and polyhydroxyphenyl 25 carboxylic acids and derivatives such as tannin and/or gallic acid in the formulation have the ability to 25 convert rusted surfaces into iron complexes. In addition, the resultant films offer good protection against further rusting of the underlying metal surfaces when topcoated. The compositions of the invention are also useful as etch primers on copper, aluminum and zinc surfaces acting as a tie-coat for subsequent painting.

30 Although considerable variation in the formulations are possible, it is important that ionically 30 stabilized latexes having acid groups covalently bound into the polymer molecule be utilized. The formulations of the invention should find utility wherever it is desired to arrest rust; and to reduce, or eliminate further rusting and corrosion of the underlying surfaces or enable protective coatings to adhere to the difficult to paint metals such as aluminum, copper, zinc or their alloys.

35 Other aspects, objects and advantages of the invention can be obtained from a study of the 35 disclosure and the appended claims.

Claims

1. A method for producing a storage stable anti-corrosive metal primer composition comprising the steps of dissolving a chelating agent selected from polyhydroxy phenols or polyhydroxyphenyl 40 carboxylic acid and their derivatives in water, and blending the resulting aqueous solution with an 40 ionically stabilized film forming latex which is (1) substantially insoluble in water or water containing a minor amount of alcohol, and (2) has acid groups covalently bonded to the latex polymer molecule.

2. A method according to claim 1 wherein said film forming latex comprises a nonionic 45 surfactant-and protective colloid-free oil-in-water emulsion, and including the step of stabilizing said 45 latex by the addition of an anionic or cationic surfactant.

3. A method according to claim 1 or 2 and including the step of adding one or more of the following components: a coalescing aid; a plasticizer; a wetting agent; an inorganic extender; a freeze-thaw stabilizer; a thickener; a thixatrop; and a pigment.

4. A storage stable anti-corrosive metal primer composition comprising a chelating agent 50 selected from the polyhydroxy phenols or polyhydroxyphenyl carboxylic acids and their derivatives, an 50 ionically stabilized film forming latex which is (1) substantially insoluble in water or water containing a minor amount of alcohol, and (2) has acid groups covalently bonded to the latex polymer molecule, and water as a medium for said composition.

5. The composition according to claim 4 wherein said film forming latex comprises a nonionic 55 surfactant-and protective colloid-free oil-in-water emulsion containing an anionic or cationic 55 surfactant.

6. The composition according to claim 4 or 5 and comprising one or more of the following features:

- (a) said aqueous emulsion has a pH of less than about 4.5;
- 60 (b) said polyhydroxyphenyl carboxylic acid is selected from tannins and gallic acid, and mixtures 60 thereof;
- (c) said acid groups are selected from carboxyl and sulfonic acid groups;
- (d) said latex comprises a carboxylated latex having a pH of about 4 or less; and

(e) said anionic surfactant is an alkyl aryl sulfonate.

7. The composition according to any of claims 4 to 6 wherein said latex is selected from vinyl chlorides, acrylates, vinylidene chlorides, methacrylates, vinyl chloride-acrylate copolymers, vinylidene chloride-acrylate copolymers, vinyl acetate-acrylate copolymers, vinyl acetate-vinyl chloride-acrylic acid copolymers, vinyl acetate-ethylene-acrylic acid copolymers, styrene-butadiene-acrylonitrile-acrylic acid copolymers, styrene-butadiene-acrylic acid copolymers, styrene-acrylate-acrylic acid copolymers, styrene-methacrylate-acrylic acid copolymers, and mixtures thereof. 5

8. The composition according to any of claims 4 to 7, and comprising one or more of the following additional components: a coalescing aid; a plastizicer; a wetting agent; an inorganic extender; a freeze-thaw stabilizer; a thickener; a thixatropo; and a pigment. 10

9. In a rust converter and metal-protective film forming storage stable aqueous emulsion composition, a polyhydroxyphenylcarboxylic acid chelating agent, and a film forming latex, the improvement comprising selecting the film forming latex from those ionically stabilized latexes which (1) incorporate carboxylic or sulfonic moieties into the latex molecules by covalent bonding, which produce acid pH's upon being emulsified into water and, (2) are storage stable in the presence of the rust converting agents. 15

10. An essentially nonionic surfactant-and protective colloid-free ionically stabilized film forming latex, said latex having measurable acid values due to the inclusion of acid groups, preferably carboxylic or sulfonic moieties covalently bonded into the latex molecules and which produce acid pH's upon being emulsified into water, and a rust converting agent. 20

11. An article of manufacture comprising a metallic substrate having film of an anti-corrosive metal primer composition as claimed in claim 1 covering said substrate at least in part.