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COMPOSITIONS AND METHODS FOR PRESERVATION OF METALS

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This invention relates to compositions of matter and methods for their application for the preservation of metals, and has particular reference to the preservation of metals that are sensitive to atmospheres which exhibit a deleterious or corrosive attack. In addition to ferrous alloys, this includes such metals as the alloys of iron, zinc, cadmium and certain alloys of magnesium and aluminum.

It is well known that certain ferrous alloys such as the low carbon steels of the SAE 1000 series readily form oxygen rich oxides, commonly known as rust, when exposed to moist air and atmospheres containing oxygen, acid anhydrides and other impurities such as are commonly encountered in industrial atmospheres. Other metals such as zinc develop basic carbonate deposits commonly known as white rust under similar conditions of exposure. Still other metals or alloys such as aluminum, cadmium and their alloys develop stains. Other metals such as magnesium undergo erosion under these same conditions.

The chemical treatment of sensitive metals to provide surfaces resistant to the deleterious effects of corrosive atmospheres has for many years received scientific attention. Accordingly, many chemical treatments intended for this purpose have been developed and have been reduced to widespread commercial practice. For example, ferrous alloys have been treated with phosphoric acid compositions to provide surfaces that resist corrosion both before and after imparting organic finishes such as lacquers, paints, enamels and primers. Other chemical treatments providing similar protection have been developed for zinc, aluminum, cadmium and magnesium alloys.

Enhancement of the corrosion behavior of such alloys beyond that imparted by water-soluble inorganic compounds reactive with the metal to provide a corrosion-resistant coating, commonly termed inorganic conversion coatings, such as phosphate coatings, chromate and fluoride coatings, has been taught in applicant's earlier United States Patent No. 2,885,312 and in the application for reissue thereof, Serial No. 824,759, filed July 2, 1959, now Reissue No. 24,875. This patent discloses the deposition of an organic seal coating comprised of a strongly anionic water soluble polymer compound capable of deposition on the metal or phosphatized metal surface or chromatized metal surface from an aqueous bath. It has been shown that resistance to weathering of phosphatized steel is improved by this means by a factor of the order of 2 or 3.

It is a primary object of the present invention to provide novel and improved compositions and methods for the preservation of metals.

Another object of this invention is to provide a process for imparting a corrosion-resistant coating to metals which is superior to those heretofore proposed and used.

Other objects and advantages of the present invention it is believed will be readily apparent from the following detailed description of preferred embodiments thereof.

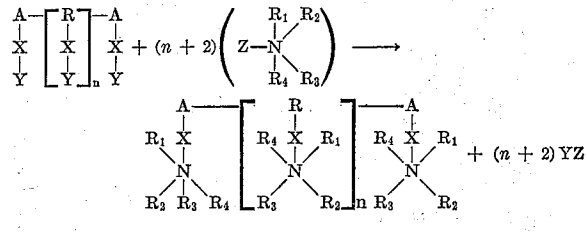
Briefly, this invention comprehends within its scope the discovery that organic seal coatings formed by the deposition of a strongly anionic polymer can be made to impart improved corrosion behavior by a treatment with a strong cationic agent such as a cetyl dimethyl ammonium chloride, other quaternary compounds, cationic amines or amphoteric reagents such as N-methyl taurine. Also, water soluble polymeric substances capable of strong cationic behavior such as polyvinyl pyridine and polymerized ethylene imine can be used.

This can best be accomplished by reacting the anionic polymer with a high molecular weight cationic reagent immediately after the reaction of the organic anionic polymer seal coating component with the basic metal or inorganic conversion coating. For example, low carbon steel sheet is continuously treated with phosphatizing-anionic polymer seal composition using conventional rollercoat coating equipment whereby the sheet is conveyed through two applicator rolls over which there is flowed a phosphatizing composition embodying an anionic reactive polymer to comprise the first step in preservation of the metal. After the steel sheet or strip is conveyed from the applicator roll it is passed through a second set of applicator rollers over which is flowed the cationic reactants, then through squeegee rolls to remove the excess and finally dried with warm air to comprise the second step of the preservation reaction.

The steel thusly treated shows resistance to rusting in moist air, improved by a factor of 6 times over steel which has been treated by phosphatizing alone. The improvement in resistance to rusting is 2 to 3 times greater than steel which has been phosphatized and seal coated with an anionic polymer without subsequent cationic treatment.

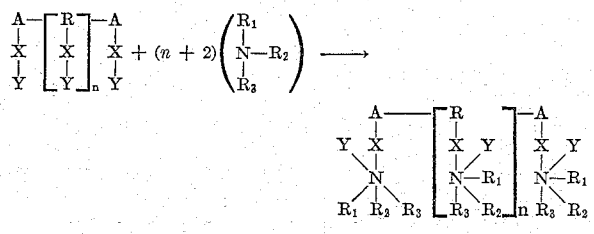
The reaction between the anionic polymer and the cationic reagent results in the formation of a copolymer of approximately double the molecular weight of the anionic polymer. These cationic agents are broadly defined as organic cationic substances having a basic nitrogen atom. In this reaction the co-polymer is rendered insoluble and more adherent to the inorganic conversion or basis metal.

The following represents a generic typical reaction which occurs between the anionic polymer and a quaternary cationic reactant:



where R is an organic grouping with a free valence such as, for example a vinyl-substituted aryl group capable of polymeric reaction, X is a strong polar group such as a sulfonic acid, carboxylic acid, or phosphonic acid

group and Y is hydrogen, an ammonium radical or a metal, N is a nitrogen atom, R_1, R_2, R_3 and R_4 are alkyl, aryl or alkyl substituted aryl groups or hydrogen atoms, Z is a halogen ion, A is a hydrocarbon terminal group and n is an integer greater than 1. When the cationic reactant contains nitrogen with a valance of three, the reaction with the anionic polymer may be represented by the equation:



where R, X, N, R_1, R_2, R_3, Y, A and n have the meanings given above.

It will be understood that the foregoing formulas for the cationic reactants are given merely for the purpose of the representative equations and do not embrace all of the cationic substances within the scope of the invention. Thus, as will be seen hereinafter, various heterocyclic amines, imines, imidazoles, and polymerized amines may be employed. In general, however, the cationic substances react in the manner illustrated by the equations.

The preferred classes of polymers are strongly anionic and include polystyrene sulfonic acid, its ammonium and metal salts, polyvinyl toluene sulfonic acid, its ammonium and metal salts, phosphatic acid and salt derivatives of polystyrene and polyvinyl toluene, methylacrylic acid polymers, co-polymers and their salts, heteromaleic acid polymers of styrene and salts thereof, and polyvinyl sulfonic acids and their salts. The preferred average molecular weights of the anionic polymers are in the range of 80,000 to 5,000,000. There exists a wide variety of cationic substances capable of reacting with the preferred classes of anionic polymers to produce the desired types of insoluble co-polymers. These cationic substances may be employed in the form of monomers or in the form of polymers capable of undergoing cationic reactions. The following are cited as typical examples:

Class of cationic substances:	Typical compound
Acetic acid salts of alkyl amines.	Olyl dimethyl amino hydrogenacetate.
Salts of fatty acid tertiary amines.	Dodecyl dimethyl amine hydrogen phosphate.
Ethanolated alkyl guanidine amine complexes.	Ethylated lauryl carbamyl guanidine.
Fatty acid amines.	Dimethyl hexadecyl amine.
Alkyl hetrocyclic tertiary amines.	Stearyl hetrocyclic ethyl amine.
Alkyl dimethyl amine oxide.	Tetradecyl dimethyl amine oxide.
Fatty diethanol amides.	Lauryl diethanol amide.
Tertiary amine ethylene oxide condensates of primary fatty amines.	Dodecyl ethoxylated amine.
Quaternized polyvinyl pyridine.	Polyvinyl pyridine polymethyl chloride.
Polyvinyl pyridine.	Polyvinyl pyridine, molecular weight 40,000 to 400,000.
Alkyl quaternary ammonium halide.	Cetyl trimethyl ammonium chloride.

Class of cationic substances:	Typical compound
Alkyl aryl quaternary ammonium halide.	Dimethyl benzyl cetyl ammonium chloride.
Hydroxy ethyl alkyl imidazo lines.	Heptadecanyl (1) hydroxyl ethyl (2) alkyl imidazoline.
Amine esters of long chain fatty acids.	Stearyl amidoacetate trimethyl chloride.
Substituted amide of alkyl phosphate.	Dodecyl imine phosphate ester.
Quaternized alkyl polyvinyl pyridinium.	Polyvinyl pyridinium methyl chloride.
Polymerized ethylene imine.	Polyethylene imine (average mol. weight 40,000).

The following examples are illustrative of the compositions and processes of the present invention, but it is to be understood that the invention is not to be limited to the specific details thereof:

EXAMPLE I

This example illustrates the co-deposition of an inorganic phosphate-anionic polymeric coating followed by cationic insolubilization of the anionic polymer to form an adherent co-polymer wherein the following typical baths and processing steps are employed.

Bath No. 1

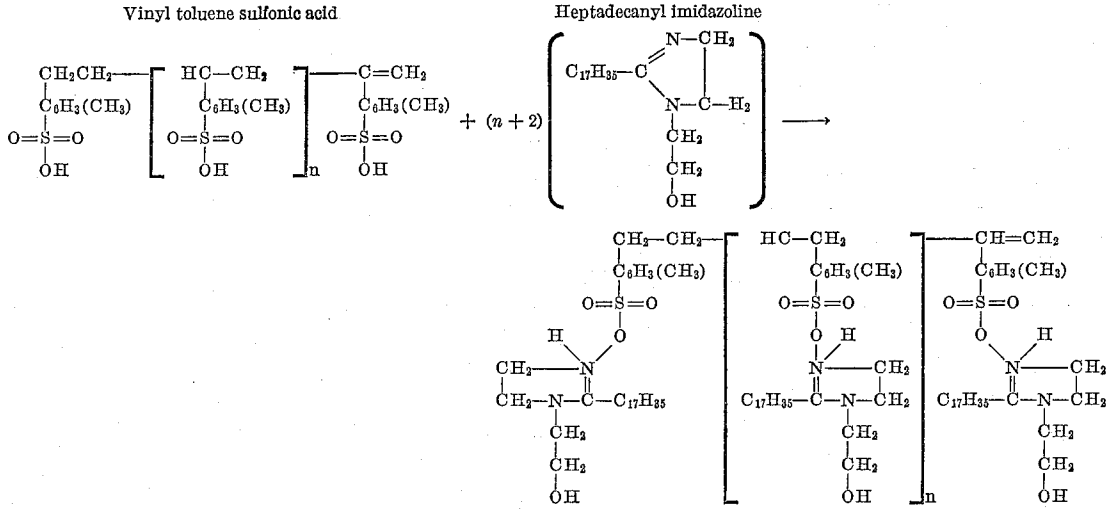
Material component:	Weight percent
Sodium acid pyrophosphate	1.0
Water	91.5
Polymeric vinyl toluene sulfonic acid (molecular weight, 400,000)	1.0
Zinc oxide	1.0
Orthophosphoric acid (75%)	5.0
Nitric acid (60%)	0.5

Bath No. 2

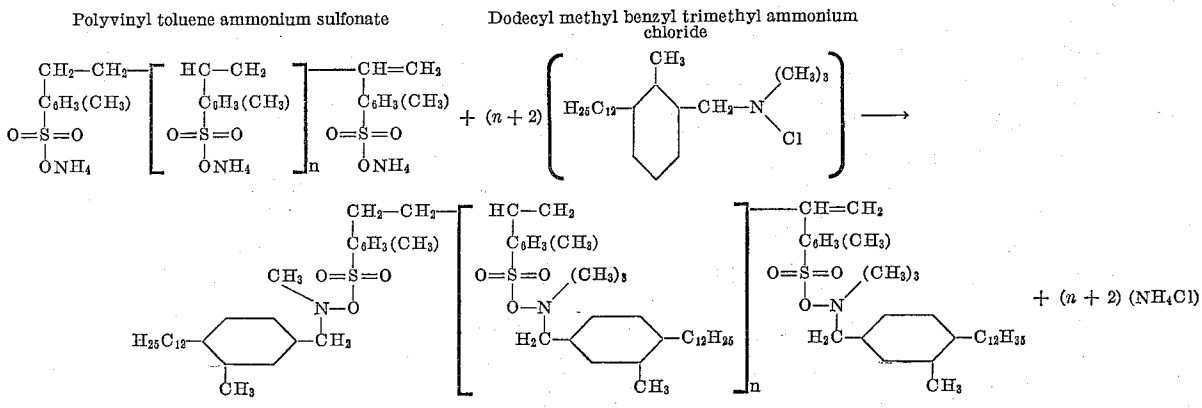
Material component:	Weight percent
2-hydroxyethyl heptadecanyl 2-imidazoline	1.0
Orthophosphoric acid (75%)	0.5
Ammonium hydroxide (28%)	0.5
Water	98.0

The following variations in concentrations (percent by weight) may be observed in bath No. 1: sodium acid pyrophosphate, 0.6–2.0; water 97.0–85.0; vinyl toluene sulfonic acid, 0.55–1.60; zinc oxide 0.5–2.0; orthophosphoric acid 3.0–7.0; nitric acid, 0.25–0.85. The following variations in concentrations (percent by weight) may be observed in bath No. 2: imidazoline, 0.72–1.8; orthophosphoric acid, 0.0–1.5; ammonium hydroxide, 0.03–1.2; water 99.25–96.0. The pH of bath 1 was 2.0 and the pH of bath 2 was 6.0. Ranges of 2.0–2.8 and 5.8–8.5, respectively, may be utilized. Application of these baths was as follows: Descaled hot rolled steel or cleaned cold roll steel of the low carbon series in the form of sheet was heated to 140° F. and conveyed at speeds of 200 ft. per minute through applicator rolls which were flooded with a composition corresponding to bath No. 1. The excess of bath No. 1 was squeegeed off by passing through a set of squeegee rolls. The reaction with the steel was allowed to proceed for an interval of about 20 seconds. Then the strip or sheet is passed through another set of applicator rolls flooded with solution corresponding to bath No. 2 to form the insoluble copolymer. This was followed by a pass through squeegee rolls to remove the excess reactants, followed by a water rinse. The work was then dried in warm air at 200° F. The steel was thus rendered preserved for storage and/or application of organic finish. The reaction taking place between the mono-

mer group of the anionic polymer and the cationic reagent is illustrated as follows:



A similar reaction occurs when the cationic reagent is dodecyl methyl benzyl trimethyl ammonium chloride and the anionic polymer is a salt of polyvinyl toluene sulfonic acid.



EXAMPLE 2

In the treatment of phosphatized steel, zinc or cadmium coated steel, it has been found that unpainted corrosion behavior is improved with the embodiment of a minor but effective amount of a molybdate such as ammonium molybdate, sodium molybdate, ferro molybdate or zinc molybdate. A typical bath for this purpose has the following composition.

Material component:	Weight percent
Polyvinyl toluene sulfonic acid (molecular weight 400,000)	1.0
Zinc carbonate	0.25
Ammonium molybdate	0.25
Phytic acid (70%)	0.1
Orthophosphoric acid (75%)	0.2
Water	98.2

The following variations in concentrations (percent by weight) may be utilized; vinyl toluene sulfonic acid, 0.5–2.5; zinc carbonate, 0.1–0.5; ammonium molybdate, 0.1–0.5; phytic acid, 0.0–0.2; orthophosphoric acid, 0.0–0.5; water 99.3–95.8. The pH of this bath was 6.0 (it can be adjusted to the range of 5.0–6.8 with ammonium hydroxide or orthophosphoric acid as required). After application to the zinc strip by roller-coating, the metal received a subsequent treatment with the cationic reagent of Example 1, also by roll on application. The metal was rinsed with water and then dried with warm air. Both baths and the metal are maintained at a temperature of about 125° F. during the application cycle.

EXAMPLE 3

A similar bath produces a desirable finished coating which provides protection of galvanized steel strip from the formation of white rust and simultaneously prepares it for painting.

Material component:	Weight percent
Polyvinyl styrene sulfonic acid (molecular weight 350,000)	1.0
Ammonium molybdate	0.25
Phenyl glycol ether	0.5
Zinc carbonate	0.25
Water	98.0

The ingredients may be varied in concentration (weight percent) as follows: vinyl styrene sulfonic acid, 0.5–2.5; ammonium molybdate 0.1–0.5; phenyl glycol ether, 0.0–1.0; zinc carbonate, 0.0–0.5; water 99.2–99.5. The pH of this bath was adjusted to 6.8 using orthophosphoric acid. Application was by roll on at 140° F. and was followed by a subsequent roll-on application of the cationic reagent with final dry-off in warm air. The cationic reagent bath had the following composition.

Material component:	Weight percent
Dodecyl methyl benzyl trimethyl ammonium chloride	1.0
Ammonium hydroxide (28%)	0.05
Orthophosphoric acid (75%)	0.05
Water	98.9

The following variations in the ingredients of the cationic reagent bath can be observed: quaternary am-

monium compound 0.5–2.0; ammonium hydroxide, 0.0–0.1; orthophosphoric acid, 0.0–0.1; water 99.5–97.7. The pH of this bath was 6.0 (it can be adjusted to the range of 5.0 to 8.1 using ammonium hydroide or orthophosphoric acid as may be required).

EXAMPLE 4

Another example of treatment for the preservation of galvanized steel sheet is disclosed as follows.

Material component:	Weight percent
Polyvinyl sulfonic acid (molecular weight 1,200,000)	1.0
Ammonium molybdate	1.0
Calcium hydroxide	0.25
Ammonium hydroxide (28%)	0.1
Water	97.65

The following variations in concentration (percent by weight) may be observed: polyvinyl sulfonic acid, 0.75–2.5; ammonium molybdate, 0.25–1.5; calcium hydroxide 0.0–0.5; ammonium hydroxide, 0.0–0.25; water, 98.9–95.25. The pH of this bath was 5.5 (it can be adjusted to 5.0–6.5 using ammonium hydroxide or orthophosphoric acid as may be required). The cationic reagent bath had the following composition.

Material component:	Weight percent
Cetyl trimethyl ammonium chloride	2.0
Orthophosphoric acid (75%)	0.1
Water	97.9

The following variations in concentrations (weight percent) can be utilized: cetyl trimethyl ammonium chloride, 0.5–2.5; orthophosphoric acid, 0.1–0.25; water, 99.4–93.25. The pH was 6.0 (it can be adjusted in the range of 5.5–8.3 using ammonium hydroxide or orthophosphoric acid as may be required).

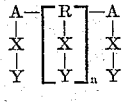
It is possible to reverse the treatment steps and still secure desirable preservation of metal surfaces. This can be accomplished by first treating the metal or the conversion coated metal with the cationic reagent in monomeric or polymeric form and then reacting it with the anionic reagent in monomeric or polymeric form. It is preferred to use the sequence of first treating with the anionic polymer since cationic substances frequently exhibit a passivating action on the metal surfaces and thereby reduce their ability to enter into a subsequent reaction. It is further possible to utilize the anionic polymers and cationic reagents in the treatment of phosphatized steel, zinc, cadmium and other disclosed metals and alloys by conventional immersion or spray wash treatments.

Having fully described my invention, it is to be understood that I do not wish to be limited to the details set forth, but my invention is of the full scope of the appended claims.

I claim:

1. A process for the preservation of metal surfaces comprising the steps of applying to such surfaces an acidic aqueous solution containing an amount of a water-soluble inorganic component selected from the group consisting of compounds of phosphorous, compounds of molybdenum and mixtures thereof, said component being reactive with said metal to provide a corrosion-resistant coating thereon and a minor proportion of an anionic metal reactive synthetic organic polymer derived from an unsaturated monomer capable of polymeric reaction, followed by the application to such surfaces of an aqueous solution containing a minor proportion of an organic cationic substance having a basic nitrogen atom effective to react with said anionic polymer.

2. The process of claim 1 wherein the anionic polymer has the generic formula:



where R is an organic group with a free valence capable of polymeric reaction, X is a strong polar group selected from the group consisting of a sulfonic acid group, a carboxylic acid group and a phosphonic acid group; Y is selected from the group consisting of hydrogen, an ammonium radical and a metal, A is a hydrocarbon terminal group and n is an integer greater than one.

3. The process of claim 2 wherein the anionic polymer is selected from the group consisting of polystyrene sulfonic acid, ammonium and metal salts of polystyrene sulfonic acid, polyvinyl toluene sulfonic acid and ammonium and metal salts thereof, polystyrene phosphonic acid and ammonium and metal salts thereof, polyvinyl phosphonic acid and ammonium and metal salts thereof, methylacrylic acid polymers, co-polymers and salts thereof, hetero-maleic acid polymers of styrene and salts thereof, and polyvinyl sulfonic acid and salts thereof.

4. The process of claim 2 wherein the aqueous solution containing an anionic polymer includes phytic acid.

5. The process of claim 4 wherein the inorganic component includes a phosphate.

6. The process of claim 1 wherein the inorganic component includes a phosphate.

7. The process of claim 1 wherein the inorganic component includes orthophosphoric acid.

8. The process of claim 7 wherein the inorganic component includes a molybdate.

9. The process of claim 1 wherein the inorganic component includes a molybdate.

10. The process of claim 1 wherein the anionic polymer comprises polyvinyl toluene sulfonic acid.

11. The process of claim 1 wherein the anionic polymer and the cationic substance are each present in said solutions in amounts within the range 0.5 to 2.5% by weight.

12. The process of claim 1 wherein the anionic polymer comprises polyvinyl toluene sulfonic acid and the cationic substance comprises a quaternary ammonium compound.

13. The process of claim 12 wherein the inorganic component includes a phosphate.

14. A process for the preservation of metal surfaces comprising the steps of applying to said surfaces an acidic aqueous solution containing an amount of a water-soluble inorganic component selected from the group consisting of compounds of phosphorous, compounds of molybdenum and mixtures thereof, said component being reactive with said metal to provide a corrosion-resistant coating thereon and a minor proportion of an anionic metal-reactive synthetic organic polymer derived from an unsaturated monomer capable of polymeric reaction having a substituent selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxylic acid group and salts of said acid groups followed by the application to said surfaces of an aqueous solution containing a minor proportion of an organic cationic substance having a basic nitrogen atom, said cationic substance being reactive with said anionic polymer.

15. An article of manufacture comprising a basis metal having a protective coating comprising the reaction product, in situ on the surface of said basis metal, of a water-soluble inorganic component selected from the group consisting of compounds of phosphorous, compounds of molybdenum and mixtures thereof, said component being reactive with said metal to provide a corrosion-resistant coating thereon and an anionic metal reactive synthetic organic polymer derived from an unsaturated monomer capable of polymeric reaction having a substituent selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxylic acid group and salts of said acid groups with a cationic substance containing a basic nitrogen atom.

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