

1

3,118,793

METHOD OF PRETREATING AND PHOSPHATIZING A METAL SURFACE FOR SICCATIVE COATINGS

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This invention relates to the protective coating of metals, and more particularly to a composition and method for improving the corrosion resistance of ferrous metal surfaces which are treated with phosphate coating compositions, and subsequently have applied thereto a coating of siccative material. This is a continuation-in-part of our copending application, Serial No. 860,332, filed December 18, 1959, now abandoned.

It has been recognized for some time that the corrosion resistance of metals such as iron and steel may be increased materially by subjecting the metal to preliminary treatment with phosphate coating compositions. Such treatment is intended to deposit an integral adherent phosphate coating on the surface of the metal, which coating tends to prevent corrosion by resisting the action of moisture or other oxidizing influences.

In the metal finishing industry where ferrous metals are usually phosphate coated as above described prior to the application of a siccative coating, such as varnish, lacquer, paint, japan or the like, a major problem exists in that a certain percentage of the metal has a surface which is passive in the respective that it will not accept a phosphate coating suitable for the application of an overlying siccative coating. A further percentage of such metal has surface characteristics which will admit of the acceptance of a phosphate coating suitable for the application of a subsequently applied siccative coating, but the corrosion resistance of the phosphate siccative coating combination is inadequate and far below the average result desired upon the subsection of such steel coated surfaces to a standard accelerated salt spray test.

It is an object of this invention to provide a composition and method for pretreating ferrous metal surfaces prior to the formation thereon of an integral adherent metal phosphate coating and the subsequent application thereto of a siccative material which will result in an improved and uniform corrosion resistance of such coated metal surfaces.

It is another object of the invention to provide such a composition and method which results in a greatly increased corrosion resistance as measured by the standard accelerated salt spray test.

It is a further object of this invention to provide a composition and method whereby light rust and scale may be removed from metal surfaces simultaneously with the pre-treatment of said surfaces in accordance with this invention.

Further objects and advantages of the composition and method of this invention will become apparent from the reading of the following description and claims.

It has now been discovered that the application of solutions or emulsions containing certain substituted short chain mono-carboxylic acids to ferrous metal surfaces such as iron and steel activates such metal surfaces, renders them uniformly receptive to the formation thereon of a moderately refined, uniform and adherent phosphate coating which when subsequently treated with a siccative coating gives salt spray accelerated corrosion results which are superior to the results obtained in the past by any other known method of treatment. Among those acids which are suitable for use in accordance with the method and compositions of this invention are the

2

hydroxy-substituted mono-carboxylic acids such as glycolic, lactic, hydroxy propionic, hydroxy butyric, hydroxy valeric, hydroxy caproic and glyceric (2,3, dihydroxy propionic) acids; diglycolic acid; thioglycolic and thiodiglycolic acids; chloro-substituted mono-carboxylic acids such as monochloroacetic acid, dichloroacetic acid, trichloroacetic acid and α -chloropropionic acid; as well as aminoacetic acid and cyanoacetic acid.

It has additionally been discovered that the composition and process when used in accordance with this invention will remove light rust and scale from ferrous metal surfaces simultaneously with the above-described activation of said surface.

Subsequent to the preliminary activation treatment utilizing the composition and process of this invention, the treated metal surface is phosphate coated by the application thereto of conventional phosphate coating chemicals which may be selected from a wide variety of well-known solutions which produce fine grain integral adherent phosphate coatings on the metal. One such coating composition has as its essential ingredients, zinc dihydrogen phosphate, a nitrate and free phosphoric acid. Similarly other dihydrogen phosphates such as manganese may be utilized. Also, instead of using nitrates as an accelerator, other substances such as chlorates may be used. Activators such as nickel, copper, cobalt, fluorides, etc., may be at times usefully employed. The phosphate coating chemicals as well as the methods by which they are applied are well-known in the phosphating art. Among the conventional methods for applying such compositions are dipping, spraying or the like.

It is also preferable when applying the pre-treating compositions in accordance with the method of this invention to include in the composition a solvent, detergent, wetting agent, or other surfactant material. Organic detergents having desirable wetting and emulsifying powers for example are sodium alkyl sulfates, such as sodium allyl sulfate; sulfonated hydrocarbons such as alkyl naphthalene sulfonic acid; and certain "non-ionic" detergents such as the polyethylene glycol derivatives including among others the alkyl aryl polyether alcohols. It will be readily appreciated that the surfactant chosen must be one of those compatible with acid systems. It is not indispensable to the effective utilization of the composition and process of this invention that any surfactant be utilized, and other chemicals in addition to those mentioned may be added to the composition of this invention, where such chemicals tend to improve the performance of the system without affecting or inhibiting the subsequently applied coating materials.

The glycolic acid solutions which are effective in accordance with this invention may have the following range of compositions:

	Percent by weight of solution
55 Glycolic acid (hydroxy acetic acid)-----	1-70
Solvent -----	30-99

The diglycolic acid solutions which are effective in accordance with this invention may have the following range of compositions:

	Percent by weight of solution
60 Diglycolic acid (a,a'-dicarboxyl dimethyl ether) _ _	5-40
Solvent -----	60-95

The above compositions may have suitably included therewith an appropriate amount of solvent, detergent, wetting agent, or other surfactant. The above solutions may be utilized as concentrated solutions although all but the most dilute are more economically further diluted with a solvent in the proportions of from 1:2 to 1:10 and are effective as so diluted. It is to be understood that the term "solvent" includes but is not limited to water. For example, mineral spirits may effectively be

3

used as such a solvent. The mineral spirits solution may be removed from the treated surface by water overflow as a consequence of its ready emulsification with water. The mineral spirits solution above may also be used as the basis for an emulsion by substituting a blend of alkylaryl polyether alcohols and organic sulfonates for the dioctyl ester of sodium sulfosuccinic acid. A suitable concentration would then be a 30% emulsion in water.

The following examples will indicate the application of the composition and method of this invention; however, it will be obvious to one skilled in the art that various modifications may be made without departing from the composition and process of this invention as hereinafter claimed.

Example 1

A slightly rusted steel sheet was immersed for thirty seconds in an aqueous solution of glycolic acid containing 25% by weight glycolic acid per total weight of the solution. The sheet was removed from the glycolic acid and rinsed with water for thirty seconds. The treated sheet was then conventionally treated with phosphate coating chemicals by immersion in a cleaning solution for sixty seconds, rinsing with water for thirty seconds, immersion in a zinc dihydrogen phosphate solution for sixty seconds, rinsing with water for thirty seconds, and finally rinsing with a chromic rinse for thirty seconds. A siccative coating consisting of a gilsonite primer and a gilsonite top coat was then applied to the treated sheet and dried. The coated sheet was then subjected to an accelerated salt spray test for a period of 336 hours, at the end of which time no failures of the siccative coating were observed.

Example 2

A steel sheet similarly lightly rusted as that utilized in Example 1 was treated in accordance with Example 1 with the exception that the pretreatment with the aqueous glycolic acid solution was omitted. This coated sheet was subjected to a standard accelerated salt spray test for a period of 240 hours, at the end of which time complete failure of the siccative coating was observed with excessive blistering and creepage of the combined coating.

Example 3

A group of lightly rusted steel test panels was pretreated by wiping with a solution of glycolic acid in mineral spirits. The solution used had the following composition; parts being expressed as percent by weight of the total weight of solution:

Mineral spirits.....	70.0
Dioctyl ester of sodium sulfosuccinic acid.....	13.0
Pine oil.....	7.0
Glycolic acid (70%).....	10.0

Good rust removal was observed as a result of the wipe. The panels were then rinsed with water for thirty second. The treated panels were then conveniently treated with phosphate coating chemicals and painted as in Example 1. A group of control panels were treated in the same way except that a plain mineral spirits wipe was substituted for the wipe with the mineral spirits solution of glycolic acid. The panels were then all subjected to a 336 hour accelerated salt spray test. Those panels which had been pretreated showed no failures and a total paint creepage from a score line of $\frac{1}{2}$ to $\frac{3}{16}$ inch. The control panels showed $\frac{1}{3}$ total failures and total paint creepage from a score line of $\frac{1}{4}$ to $\frac{1}{2}$ inch (ignoring the total failures).

Example 4

A group of lightly rusted steel test panels was pretreated by spraying for one minute at 80° F. with a 5% solution of a composition made up as follows; parts

4

being expressed as percent by weight of the total weight of solution:

Glycolic acid (70%).....	80.0
Water.....	15.5
Alkylaryl polyether alcohol.....	4.5

A further group of steel test panels was pretreated by wiping for one minute with a 25% solution of the above composition. Good rust removal was observed as a result of the acid wipes.

A further group of steel panels was treated only by wiping with kerosene.

All panels were then rinsed with water for thirty seconds and then conventionally treated with phosphate coating chemicals and painted as in Example 1.

The panels were then all subjected to a 336 hour accelerated salt spray test. All of the pretreated panels showed no failures and a total paint creepage from a score line of $\frac{1}{2}$ to $\frac{3}{16}$ inch. The control panels showed $\frac{1}{3}$ total failures and total paint creepage from a score line of $\frac{1}{4}$ to $\frac{1}{2}$ inch (ignoring the total failures).

Example 5

A group of lightly rusted steel test panels was pretreated by wiping with a solution of diglycolic acid. The solution used had the following composition; parts being expressed as percent by weight of the total weight of solution:

Diglycolic acid.....	36.0
Water.....	59.5
Alkylpolyether alcohol.....	4.5

The time required for removal of light rust was longer than was required by solutions of glycolic acid, but the results were good. The panels were rinsed with water and then conventionally treated with phosphate coating chemicals as in Example 1.

The panels took a very good integral, fine-grained, adherent phosphate coating.

Example 6

A group of lightly rusted steel test panels was pretreated by wiping with a solution of diglycolic acid. The solution used had the following composition; parts being expressed as percent by weight of the total weight of solution:

Diglycolic acid.....	25.0
Water.....	74.0
Alkylpolyether alcohol.....	1.0

Good rust removal was observed as a result of the wipe. The panels were rinsed with water and then conventionally treated with phosphate coating chemicals as in Example 1. Two groups of control panels were treated in the same way as the test panels except that the pretreatment with diglycolic acid was omitted. The test panels had coating weights of 470-490 mgm./ft.². The control panels had coating weights of 470-550 mgm./ft.². A siccative coating consisting of a gilsonite primer and a gilsonite top coat was then applied to all panels.

The coated and painted panels were then subjected to an accelerated salt spray test with the following results:

Test panels.....	288 hours, moderate blistering and total paint creepage from a score line $\frac{1}{8}$ inch.
Control panels.....	120 hours, severe blistering and loss of adhesion over 50 to 100% of the total area.

Example 7

Six lightly rusted steel test panels were pretreated by wiping with a solution of monochloroacetic acid having

the following composition, parts being expressed as percent by weight of the total weight of solution:

Monochloroacetic acid.....	10.0
Isooctyl phenoxy polyethanoxy ethanol.....	.5
Water	89.5

A further group of steel panels was given no pretreatment. Three of the test panels were then rinsed with water for thirty seconds, and three of the test panels were allowed to dry completely without a water rinse. All of the panels were then conventionally treated with phosphate coating chemicals and painted as in Example 1. The panels were then all subjected to a 336 hour accelerated salt spray test. All of the untreated panels were badly corroded, while the treated panels were rated as having fair to good corrosion resistance.

Example 8

Six lightly rusted steel test panels were pretreated by wiping with a solution of thioglycolic acid having the following composition, parts being expressed as percent by weight of the total weight of solution:

Thioglycolic acid.....	10.0
Isooctyl phenoxy polyethanoxy ethanol.....	.5
Water	89.5

A further group of steel panels was given no pretreatment. Three of the test panels were then rinsed with water for thirty seconds, and three of the test panels were allowed to dry completely without a water rinse. All of the panels were then conventionally treated with phosphate coating chemical and painted as in Example 1. The panels were then all subjected to a 336 hours accelerated salt spray test. All of the untreated panels were badly corroded, while treated panels were rated as having good corrosion resistance.

Example 9

Six lightly rusted steel test panels were pretreated by wiping with a solution of thiodiglycolic acid having the following composition, parts being expressed as percent by weight of the total weight of solution:

Thiodiglycolic acid.....	10.0
Isooctyl phenoxy polyethanoxy ethanol.....	.5
Water	89.5

A further group of steel panels was given no pretreatment. Three of the test panels were then rinsed with water for thirty seconds, and three of the test panels were allowed to dry completely without a water rinse. All of the panels were then conventionally treated with phosphate coating chemicals and painted as in Example 1. The panels were then all subjected to a 336 hour accelerated salt spray test. All of the untreated panels were badly corroded, while the treated panels were rated as having fair to good corrosion resistance.

Example 10

Six lightly rusted steel test panels were pretreated by wiping with a solution of cyanoacetic acid having the following composition, parts being expressed as percent by weight of the total weight of solution:

Cyanoacetic acid.....	10.0
Isooctyl phenoxy polyethanoxy ethanol.....	.5
Water	89.5

A further group of steel panels was given no pretreatment. Three of the test panels were then rinsed with water for thirty seconds, and three of the test panels were allowed to dry completely without a water rinse.

All of the panels were then conventionally treated with phosphate coating chemicals and painted as in Example 1. The panels were then all subjected to a 336 hour accelerated salt spray test. All of the untreated panels were badly corroded, while the treated panels were rated as having fair to good corrosion resistance.

Example 11

Six lightly rusted steel test panels were pretreated by wiping with a solution of lactic acid having the following composition, parts being expressed as percent by weight of the total weight of solution:

Lactic acid.....	10.0
Isooctyl phenoxy polyethanoxy ethanol.....	.5
Water	89.5

A further group of steel panels was given no pretreatment. Three of the test panels were then rinsed with water for thirty seconds, and three of the test panels were allowed to dry completely without a water rinse. All of the panels were then conventionally treated with phosphate coating chemicals and painted as Example 1. The panels were then all subjected to a 336 hour accelerated salt spray test. All of the untreated panels were badly corroded, while the treated panels were rated as having fair to excellent corrosion resistance.

While in the above examples, water is shown as the solvent component of the compositions utilized in accordance with this invention, as indicated above, mineral spirits may effectively be used as such a solvent. For example, VM & P naphtha, kerosene and xylene may be suitably incorporated together with the organic acids above disclosed.

Having thus described our invention, we claim:

1. In a method of producing a corrosion resistant coating on a ferrous metal surface including the steps of forming an integral adherent metal phosphate coating on said surface, and subsequently applying a coating of siccativ material upon said metal phosphate coated surface, the improvement which comprises pretreating said metal surface prior to the formation of said metal phosphate coating by applying to said metal a pretreating solution consisting essentially of a substituted short chain monocarboxylic acid selected from the class consisting of glycolic, lactic, hydroxy propionic, hydroxy butyric, hydroxy valeric, hydroxy caproic, glyceric, diglycolic, thioglycolic, thiodiglycolic, monochloroacetic, dichloroacetic, trichloroacetic, α -chloropropionic, aminoacetic and cyanoacetic acid, and a liquid diluent for said acid, said acid constituting at least about .001 percent by weight of said solution.
2. The method of claim 1 wherein said solution additionally contains a compatible surfactant.
3. The method of claim 1 wherein said acid is glycolic acid.
4. The method of claim 1 wherein said acid is lactic acid.
5. The method of claim 1 wherein said acid is hydroxy propionic acid.
6. The method of claim 1 wherein said acid is hydroxy butyric acid.
7. The method of claim 1 wherein said acid is hydroxy valeric acid.
8. The method of claim 1 wherein said acid is hydroxy caproic acid.
9. The method of claim 1 wherein said acid is glyceric acid.
10. The method of claim 1 wherein said acid is diglycolic acid.
11. The method of claim 1 wherein said acid is thioglycolic acid.
12. The method of claim 1 wherein said acid is thiodiglycolic acid.
13. The method of claim 1 wherein said acid is monochloroacetic acid.
14. The method of claim 1 wherein said acid is dichloroacetic acid.
15. The method of claim 1 wherein said acid is trichloroacetic acid.
16. The method of claim 1 wherein said acid is α -chloropropionic acid.

7

17. The method of claim 1 wherein said acid is amino-acetic acid.

18. The method of claim 1 wherein said acid is cyano-acetic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,067,215	Tanner	Jan. 12, 1937
2,164,042	Romig	June 27, 1939

5

2,383,800
2,554,972
2,793,191
2,809,906
2,837,449
2,981,634

731,882

8

Johnson	Aug. 28, 1945
Alquist et al.	May 29, 1951
Streicher	May 27, 1957
Baecker et al.	Oct. 15, 1957
Blaser	June 3, 1958
Davis	Apr. 25, 1961

FOREIGN PATENTS

Great Britain	June 15, 1955
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,118,793

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James E. Maloney et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 32, for "respective" read -- respect --;
column 3, line 30, strike out "sheet and dried. The
coated sheet was then subjected"; line 59, for "second"
read -- seconds --; same column 3, same line 59, for
"conveniently" read -- conventionally --.

Signed and sealed this 30th day of June 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents