United States Patent Office 3,021,228
Patented Feb. 13, 1962

3,021,228

INHIBITION OF WET STORAGE STAIN

Paul Gibson, South Holland, and John E. Farbak, Chicago, Ill., and Philip D. Murphy, Highland, Ind., assignors to Swift & Company, Chicago, Ill., a corporation of Illinois

No Drawing. Filed Oct. 14, 1960, Ser. No. 62,524
10 Claims. (Cl. 117—71)

This invention relates to a method for treating metallic surfaces to protect such surfaces against deterioration and more particularly to the protection of zinciferous metal surfaces and the articles thereby provided.

Zinc-containing metal surfaces such as galvanized iron surfaces are subject to deterioration upon exposure to air and/or moisture, and it is consequently necessary, unless the galvanized metal is to be used immediately, to subject the galvanized articles to further treatment before storage in order to inhibit tarnishing or what is known in the art as "wet storage stain." Wet storage stain is the discoloration or tarnish which develops on the surface of zinc-containing metal coatings as a result of the reaction between zinc and moisture, oxygen, salts and/or acidic substances. The smooth zinc-containing surface, when this objectionable reaction takes place, becomes marred with a greyish, white, powdery substance thought to be a zinc carbonate of variable composition. This powdery substance, in addition to detracting from the appearance of the surface, also interferes with bonding ability of coatings such as paint, adhesives, plastics, etc.

In the past various chromic acid treatments have been employed to protect zinciferous surfaces against wet storage stain, but such treatments have not provided adequate protection over an extended period of time or have required subsequent treatments which, of course, add to the cost of protection.

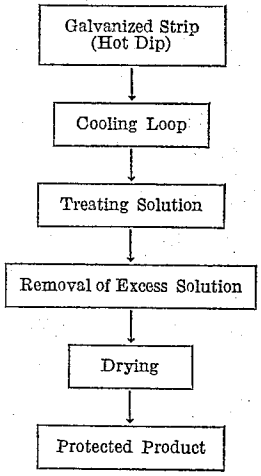
It is therefore an object of this invention to provide zinciferous materials having improved resistance to wet storage stain over a long period of time.

Another object of the invention is to provide a method for treating objects having zinc-containing metallic surfaces to provide an improved resistance to deterioration of the surface appearance.

Still another object is the provision of a wet storage stain inhibiting composition adapted to protect zinciferous surfaces against deterioration.

Other objects, if not specifically set forth herein, will be readily apparent to one skilled in the art from the following detailed description of the invention.

A simplified flow diagram of the process involving the treatment of galvanized steel strip is as follows:



The treating solution contains a chromium ion source and a fatty alkylolamide or a phosphate supplying element, and the fatty alkylolamide.

In accordance with this invention it has been found that zinc-containing surfaces such as galvanized metal objects can be protected against deterioration by treating such objects with a composition containing a chromium ion supplying component such as chromic acid or water soluble alkaline earth and alkali metal salts thereof and a fatty alkylolamide. The fatty alkylolamide is a condensation product of an alkylolamine and a fatty acyl component having in the alkyl chain thereof an alkylolamine reactive group such as an oxirane group or a halohydroxy group.

The treating composition is used desirably, although not necessarily, in a water carrier and can be prepared in the form of a concentrate which may be diluted with water. Maximum protection of the zinc-containing surface is attained if the treating solution is maintained at a pH of around pH 5–9.

The protective composition is applied to the surface being treated either by brushing, spraying or by immersion of the article in a liquid carrier containing said composition. The immersion procedure is preferred since this method of application is readily adaptable to inclusion in conventional galvanizing operations. The treatment can be carried out at ordinary room temperature although much higher temperatures are usually encountered, particularly when the treatment is part of a galvanizing operation. In galvanizing operations where sheet iron is passed through a bath of molten zinc and the sheet is air cooled before passage into the treating bath, the galvanized object enters the bath at elevated temperatures around 180° F. or above. While some additional cooling of the sheet takes place in the bath, the temperature of the bath rises as a result of continual passage of hot sheets therethrough, and after a period of operation there is little cooling of the zinc-coated sheet by the treating bath. Nevertheless, the fact that the object leaves the treating bath at an elevated temperature is not undesirable since this higher temperature insures a more rapid evaporation of the liquid carrier from the object when it leaves the treating bath.

The chromium supplying component of the mixture is preferably chromium trioxide (CrO_3) which hypothetically provides the hydrate H_2CrO_4 in solution. Water soluble alkali metal or alkaline earth chromium salts such as sodium dichromate or potassium dichromate may be employed as the chromium supplying element. Other water soluble chromium supplying salts such as magnesium chromate, calcium chromate, sodium chromate or potassium chromate can also be used. Usually about 0.1–2% of the chromium supplying composition based upon the weight of the treating solution will be employed, and while 0.1–0.3% of this material provides the preferred range, amounts greater than 2% may be employed. As amounts greater than this amount (2%) are utilized, little increase in benefits is observed, and therefore such procedure is considered wasteful. The activity of the chromium supplying element may be enhanced by the addition of a phosphate ion supplying acid or salt to the treating mixture thus permitting the use of smaller amounts of the chromate to obtain a desired result.

The alkylolamide condensation product of the treating composition is derived from the reaction between an alkylolamine and a composition containing a fatty acyl radical such as a fatty acid, fatty ester, fatty alcohol or fatty amide. The fatty acyl radical must also be substituted in an internal open chain portion of the molecule with an amine reactive group such as an oxirane group or halo and hydroxyl groups on contiguous carbons. The condensation product is prepared by heating and reacting a halohydroxy fatty acid, ester, amide or

alcohol having about 10–22 carbon atoms with a primary or secondary alkylolamine having 2–18 carbon atoms and having at least one free amino hydrogen. The reaction involves the substitution of at least one amino group along the alkyl chain of the fatty acyl radical in a non-terminal position. These compositions and the preparation thereof are more fully disclosed in the application of Thomas W. Findley et al., Serial No. 629,235, filed December 19, 1956.

Examples of halohydroxy substituted fatty acids, alcohols, amides, etc., which may be employed in preparing the alkylolamine hydroxy fatty condensation products include 9, 10 (10, 9) chlorohydroxy stearic acid, chlorohydroxylated soybean oil, bromohydroxy stearic acid, halohydroxylated oleyl alcohol, halohydroxylated tall oil, halohydroxylated rapeseed oil, and bromohydroxy undecylenic acid. Suitable oxirane containing compositions include methylepoxy stearate, exopidized soybean oil, epoxidized linseed oil, epoxidized rapeseed oil and any of the other epoxidized oils and derivatives thereof. These epoxidized fatty materials are prepared by the peracid epoxidation of fatty acid radicals containing unsaturation. The performic or peracetic acid epoxidation procedures involve the addition of an oxirane group across those portions of the straight chain in the molecule formerly occupied by unsaturated bonds. The oxirane containing fatty material and a molar excess of the alkylolamine are heated in the range 17–250° C. to prepare the alkylolamide.

Alkylolamines which may be employed in the formation of the condensation product include monoalkylolamines such as monoethanolamine, monopropanolamine, butanolamine, pentanolamine, hexanolamine and the intermediate monosubstituted alkylolamines up to and including laurylolamine. Generally alkylolamines having from 2–20 carbon atoms are satisfactory. Monoalkyl alkylolamines wherein the monoalkylolamines are substituted on the nitrogen atom with a short chain alkyl group having 1–10 carbon atoms are also suitable in preparing the condensation product. Examples of such compositions are ethyl ethanolamine, propyl ethanolamine, butyl butanolamine, hexyl ethanolamine, etc. Dialkylolamines are also contemplated as suitable alkylolamines in the preparation of the condensation product. Diethanolamine is a good example of a suitable dialkylolamine. Others include diisopropanolamine, dibutanolamine, dipentanolamine. In all cases whether the amine is a primary or secondary amine and whether substituted with two alkylolamino groups or one alkylolamine group and an alkyl group, there must be provided by the molecule at least one reactive amino hydrogen and at least one free hydroxyl group spaced from the amino nitrogen by at least two carbon atoms. Thus, when the alkylolamine is reacted with an oxirane-containing fatty acyl composition or halohydroxylated fatty acyl composition, an alkylolamino group or a substituted alkylolamino group will be attached to the fatty acyl radical along the chain thereof in a position next to or adjacent a hydroxyl group. It appears that the chain-substituted hydroxyl group in combination with a spaced hydroxyl group of the alkylolamine group has a considerable effect on the unexpected benefits provided by the condensation product in the method of this invention and also in the unexpected benefits derived from the mixture of this condensation product with the chromium supplying element in combating the development of wet storage stain.

The addition of phosphates to the treating solution enhances the activity of the treating agent. Phosphoric acid may be used in combination with the water-soluble chromate salts or water-soluble phosphate salts may be employed in combination with chromic acid or the water-soluble salts thereof. Water-soluble alkali metal phosphates and alkaline earth phosphates are particularly desirable for this purpose. Although phosphoric acid may be substituted for chromic acid in the treating solution with the alkylolamide condensate to obtain somewhat less satisfactory results than where chromic acid is employed, the combination of chromic acid and phosphoric acid is to be avoided since such a combination renders the treating solution too acidic. As the pH of the treating solution becomes more acid than about pH 4 the alkylolamide condensate if chromate ion is present is precipitated from the solution. Therefore, the treating solution must be maintained at a pH of around 5–9 for best results. This requirement of course precludes the use of strong acids such as mineral acids in an amount sufficient to render the pH below about pH 4. While the presence of the phosphate ion is beneficial, too great an amount of phosphoric acid should be avoided, particularly where amounts sufficient to increase the acidity to too great a degree are contemplated. Usually about 0.1–2% based on the weight of the treating solution of phosphoric acid or the water-soluble phosphate salt should be employed although amounts in the range 0.5–1.0% are preferred.

The following examples are included herein solely for purposes of illustration to show the treatment of galvanized steel plates and the results obtained.

Example I

Pieces of untreated galvanized steel plates four inches square were immersed in an aqueous solution containing 0.5% of the condensation product resulting from the condensation of diethanolamine and chlorohydroxy stearic acid, 0.1% potassium dichromate and 0.5% phosphoric acid. The treating solution was held at 100° F. and the galvanized plates were immersed in this solution for above five seconds. After removal of the plate from the solution the plate was dried and subjected to a 40-hour stack test in a high humidity chamber. At the end of 40 hours, less than 1% of the surface of the plate showed any indication of the development of wet storage stain.

Example II

Four-inch squares of untreated galvanized steel plate were immersed in an aqueous solution containing the same condensation product noted in Example I above in a concentration of 3%, 0.8% trisodium phosphate and 0.1% chromium trioxide (chromic acid). The solution was maintained at 120° F. The immersion time was 2.5 seconds. After the drying of the plates and subjecting the dried plates to the 40-hour stack test, there was less than 1% of the surface covered with the wet storage stain.

Example III

A treating solution was prepared by dissolving 0.1% chromic acid, 0.8% trisodium phosphate and 0.5% of the diethanolamine-chlorohydroxy stearic acid concentrate in water. This solution was held in a bath at about 130–135° F. in a continuous galvanizing line. As the steel plates emanating from the zinc coating step were received they were passed through the treating solution in a continuous fashion. The galvanized steel plate showed less than 2% wet storage strain development in the 40-hour stack test.

Another solution was preperad by dissolving 0.1% chromic acid, 0.8% trisodium phosphate, and 0.8% of the condensate prepared by reacting and condensing diethanolamine and methyl 9,10-epoxy stearate, in water. This solution was employed in substantially the same fashion as the diethanolamine-chlorohydroxystearic acid condensate solution. The preperation of the condensate requires a slightly longer reaction time inasmuch as the reaction between the halohydroxy material and the alkylolamine is somewhat more rapid than the reaction between the oxirane-containing material and the alkylol-

amine. However, the white rust inhibiting activity of both types of concentrate is substantial.

The 40-hour stack test involves spraying several 4-inch square plates with a mist of distilled water, stacking the plates horizontally under a one-pound weight, and holding these squares in a high humidity cabinet at 120° F. for 40 hours. Wet storage stain occurs on the surface of adjacent plates. While untreated galvanized plates show evidence of the white crumbly powder over most of the surface, the treated plates will exhibit almost no wet storage stain.

Example IV

The following example shows the use of the diethanolamine-chlorohydroxy stearic acid condensate along with phosphoric acid there being no chromic acid or chromate supplying composition present.

Pieces of untreated, galvanized steel plate 4 inches square were immersed in an aqueous solution containing 0.5% of the condensation product resulting from the condensation of diethanolamine and chlorohydroxy stearic acid and 0.5% phosphoric acid. The treating solution was held at 80° F. and the galvanized plates were immersed in this solution for about 5 seconds. After air-drying the plates were placed in the high humidity cabinet and subjected to the 40-hour stack test. Less than 2% of the surface of these treated plates showed any evidence of wet storage stain whereas a control sample not treated with the composition of the present invention exhibited wet storage stain over most of the surface.

Treatment time and treating solution temperature may vary considerably in plant operations. Solution temperatures varying from room temperature 65° F. to about 200° F. have been employed successfully although generally in a continuous operation in metal processing the temperature will range from about 100 to 200° F. In the interest of efficiency and saving of time the shortest effective treating time is the most desirable. It has been found that the minimum time is dependent only upon the period necessary to obtain a continuous coating of the treating solution on the surface being treated. In an efficient operation the treating solution may be sprayed on the surface being treated in a very short period of time. With the immersion technique treatment times as low as 2.5 seconds immersion of the plate in the treating solution have been successfully employed although it may be desirable to hold the galvanized surfaced material in thetrea ting solution for a longer period of time. Ordinarily no more than about 15 seconds' immersion is desirable in the immersion technique. Longer immersion times are not detrimental, but there is some evidence of the formation of a yellow "chromate stain" on the surface of the metal after long immersion periods.

Although the treating solution is most effective in combating wet storage stain both in alkaline and acidic media in the pH range 5–9, very acidic solutions (pH 4 and below) should be avoided since there is danger of precipitation of the treating solution of the treating ingredient from the solution. This application is a continuation in part of prior application Serial Number 785,332, filed January 7, 1959, now abandoned.

Obviously many modifications and variations of the invention hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A method of inhibiting the development of wet storage stain on zinciferous metals which normally tend to undergo degradation upon storage comprising: treating a zinciferous metal with a mixture of chromium ion supplying component and a condensation product of an alkylolamine of 2–20 carbon atoms and having at least 1 free amino hydrogen and a halohydroxy fatty acyl component.

2. A method for imparting an improved resistance to wet storage stain in a zinc-containing metallic surface which comprises: treating said surface with a mixture of a chromium-supplying element selected from the group consisting of chromic acid and alkali metal chromates and mixtures thereof and the condensation product resulting from the reaction between a halohydroxylated fatty material and an alkylolamine having 2–18 carbons and at least 1 available amino hydrogen.

3. A method for treating metal surfaces containing zinc as an essential ingredient to protect said metals against the development of wet storage stain comprising: treating said surface with a composition containing chromic acid and the condensation product of a halohydroxylated fatty material and an alkylolamine having from 2–20 carbon atoms.

4. A method for retarding the development of wet storage stain on zinciferous metal surfaces which comprises: treating said surface with an aqueous solution containing a chromium supplying element and an alkylolamine-halohydroxy fatty derivative, said chromium supplying element being selected from the group consisting of chromic acid and alkali metal salts of chromic acid and mixtures thereof, and said condensation product being prepared from a dialkylolamine of 2–20 carbon atoms and drying said surface to remove excess moisture therefrom.

5. A method of inhibiting the development of wet storage stain on galvanized metal surfaces which comprises: an object having a galvanized surface coating with an aqueous solution of chromic acid and the condensation product of chlorohydroxy stearic acid and diethanolamine maintained at a pH of 5–9 for a period of 1–15 seconds, removing said object from said solution and subjecting said object to a drying step.

6. A method of inhibiting the development of wet storage stain on galvanized metal surfaces which comprises: contacting and covering said surface with an aqueous solution of chromic acid and the condensation product of halohydroxy stearic acid and an alkylolamine of 2–20 carbon atoms, said solution having a pH around pH 5–pH 9 and drying said object to remove excess moisture therefrom.

7. A concentrate dilutable with water to provide a surface protector for zinc-containing metallic surfaces comprising: a mixture of a phosphate supplying element and chlorohydroxy stearic acid diethanolamine condensate in the ratio of about 1 part phosphate supplying element to about 5 parts of condensate, said mixture having a pH in the range 6–8.

8. A method of inhibiting the development of wet storage stain on a galvanized metal surface which comprises: contacting and covering said surface with an aqueous solution of chromic acid and the condensation product of halohydroxy stearic acid and an alkylolamine of 2–20 carbon atoms, said aqueous solution being maintained at a temperature of about 65° F. to about 200° F., and drying said surface to remove excess moisture therefrom.

9. A method of inhibiting the development of wet storage stain on zinciferous metals which normally tend to undergo degradation upon storage comprising: treating a zinciferous metal with a chromium ion supplying component and a condensation product of an alkylolamine of 2–20 carbon atoms and having at least one free amino hydrogen and a material selected from the group consisting of a halohydroxy fatty acyl component and an oxirane containing fatty acyl component.

10. A concentrate dilutable with water to provide a surface protector for zinc containing metallic surfaces comprising: a mixture of a phosphate supplying element and a condensation product of an alkylolamine of 2–20 carbon atoms and having at least one free amino hydrogen

and a material selected from the group consisting of a halohydroxy fatty acyl component and an oxirane containing fatty acyl component.

References Cited in the file of this patent

UNITED STATES PATENTS

2,277,016 Guest ..... Mar. 17, 1942
2,540,678 Kelly ..... Feb. 6, 1951
2,902,390 Bell ..... Sept. 1, 1959
2,918,390 Brown ..... Dec. 22, 1959
2,930,106 Wrotnowski ..... Mar. 29, 1960

OTHER REFERENCES

Brown: Iron Age, Nov. 8, 1956, pages 106–109.