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PROTECTIVELY COATED FERROUS METAL SURFACES AND METHOD OF PRODUCING SAME

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6 Claims. (Cl. 117-127)

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This invention relates to the formation of protective coatings, and has for its object the provision of an improved method of forming a hard protective coating, and, as a new article of commerce, the protectively-coated article. The invention is particularly applicable to the formation of protective and corrosion-resistant coatings for ferrous metal articles.

It has previously been proposed to employ mixtures containing soluble silicates and finely divided metals as cements, paints, and the like.

It has also been proposed to form protective and like coatings on metals by applying thereto a mixture containing a soluble silicate and finely divided aluminum or magnesium or alloys thereof, such coatings being alloyed to the base metal by a subsequent heat treatment.

The present invention broadly resides in the method of producing on the ferrous metal surface a silicated composition including the steps of preparing a mixture comprising finely divided metallic zinc (or alloy containing zinc) and an aqueous solution of an alkali-metal silicate, and converting the mixture to a substantially insoluble condition by reaction with carbon dioxide. Thus, the mixture, applied as a coating to the article to be protected, may be heated in an atmosphere of carbon dioxide (CO₂) in order to bring about the conversion thereof to a substantially insoluble condition. It is preferred, however, to incorporate a bicarbonate in the mixture whereby the carbon dioxide will be released when the heat is applied.

A salient form of the invention resides in a coating material containing zinc dust, sodium silicate and sodium bicarbonate.

For some purposes hereinafter referred to the coating material may advantageously contain basic oxides or hydroxides (e. g., magnesium oxide and calcium hydroxide) and/or zinc oxide in conjunction with a bicarbonate according to the nature of the surface to be treated.

Another feature of the invention, which is particularly applicable to the formation of firmly adherent coatings on ferrous metals, resides in the provision, in the coating mixture, of a borate, such as borax.

A modification of the invention resides in incorporating a finely divided reagent, such as graphite, in the coating to impart antifriction properties thereto.

The ingredients of the coating mixture may be mixed together and then applied to the surface to be protected by spraying, brushing or dipping, or alternatively, the metallic powder and an

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aqueous solution of silicate and bicarbonate may be applied separately to the surface or may be admixed in a spray immediately prior to being applied to the surface. The coating so applied is allowed to dry and set. Preferably it is heated to a temperature usually above 200° F. for a sufficient time to convert the coating to a substantially insoluble condition.

According to modified forms of the invention which hereinafter are fully described, a substantially insoluble coating is produced without the necessity of applying heat to the coating material.

Other objects and features of the invention are set forth in the ensuing detailed description of practical applications thereof.

Example 1

A vehicle suitable for applying coatings to iron and steel surfaces was prepared from the following ingredients:

	Parts by volume
Aqueous solution of sodium silicate (water glass) of about 1.4 specific gravity	100
Aqueous solution of sodium bicarbonate substantially saturated at 60° F.	12

These ingredients were intimately mixed at normal temperatures.

This liquid vehicle was then intimately mixed with an equal part by weight of commercial zinc dust and the mixture was then immediately brushed (in a like manner to paint) onto a lightly oxidised steel sheet.

The surface of the test piece was previously treated to remove any oil or grease therefrom as it has been found that the presence of such substances is detrimental to the formation of satisfactory coatings.

The coated specimen was then allowed to stand at normal temperature for a period of six hours during which time the coating became set. The coated specimen was then subjected to heat-treatment in an oven at a temperature of about 450° F. for about two hours. At the conclusion of the heat-treatment, the specimen was allowed to cool, and the coating thereon was washed with warm water to remove soluble alkali therefrom. The finished coating was insoluble or practically insoluble in both cold and boiling water, and the coating was firmly adherent and resistant to moderate heat. The coating moreover effectively protected the underlying surface of the steel sheet against corrosion. The character of the coating depends somewhat upon the temperature at which the heat-treatment is conducted, harder

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and firmer coatings being obtained at higher temperatures of heat treatment.

It may here be pointed out that various experiments have demonstrated that, in applying coatings to iron and steel surfaces, in accordance with the present invention, it is advantageous for such surfaces to be lightly oxidised or rusted, as in such cases a more firmly adherent coating is then formed thereon. If, however, a surface is heavily rusted, any loose scale should be removed prior to the application of the coating.

Experiments made with different varieties of zinc dust suggest that it is advantageous to expose some varieties to the atmosphere before mixing with the liquid vehicle.

It should also be pointed out that when zinc dust is mixed with the liquid vehicle as above described, a comparatively slow reaction takes place with evolution of hydrogen and it is accordingly necessary to use the mixture fairly promptly. This reaction may be retarded to some extent by incorporating in the mixture a small proportion of tung oil or a colloidal substance or a proportion of powdered zinc oxide.

Coatings produced as above described are suitable for a variety of uses including the protection of iron and steel sheets, ships' bottoms and iron and steel structures which are subject to corrosive influences. In the case of structures or parts which become heated to a sufficient temperature during normal use (e. g. boilers, stoves and exhaust manifolds of internal combustion engines), the aforesaid heat-treatment may, if desired, be effected by such normal use. Where the coated article is exposed to direct sunlight, the sun-rays often are sufficient to impart the necessary heat-treatment to the coating to dry and harden it.

The finished coatings, when produced as above described, are dull in appearance, but a metallic lustre may be imparted thereto by rubbing with a wire brush at the conclusion of the heat-treatment and before the coatings are allowed to become cool.

The proportion of zinc dust in the mixture may be varied considerably according to the nature of the coating desired. For general purposes, however, it is preferred to use from about 100% to 350% of such finely divided zinc by weight of the liquid vehicle.

In lieu of or in addition to zinc dust, one may employ finely divided alloys of zinc, e. g. magnesium-zinc, aluminum-zinc, calcium-zinc and cadmium-zinc.

In lieu of sodium silicate in the liquid vehicle, one may use other alkali silicates such as potassium silicate, or mixtures thereof. It should also be understood that sodium silicates of different specific gravities may be used. Thus, effective coating compositions may be made up with liquid vehicles containing from about 20% to 40% by weight of the alkali silicate, although particularly effective results have been obtained with alkali silicate solutions containing around 30% by weight of the silicate (i. e. having a specific gravity of approximately 1.3). The sodium silicate, for example, may be of any of the commonly marketed ratios of Na_2O to SiO_2 , which generally range from 1:1.1 to 1:3.9, but particularly satisfactory drying characteristics are obtained with an Na_2O to SiO_2 ratio between 1:2.4 and 1:2.6.

The amount of sodium bicarbonate added to the alkali silicate solution ranges from about 0.1 to about 0.8% by weight based on the weight of the alkali silicate solution. Amounts of sodium

bicarbonate within this range are sufficient to provide an amount of the bicarbonate available to liberate carbon dioxide upon heating of the coating composition over and above that amount of the bicarbonate consumed in neutralizing the free alkali in the silicate solution, the smallest amount of bicarbonate within the specified range being used when boric acid is used in its maximum amount and the largest amount of sodium bicarbonate being used in the absence of any added boric acid.

Potassium bicarbonate or other bicarbonate may be substituted for sodium bicarbonate. It is preferred, however, to employ sodium bicarbonate or potassium bicarbonate.

As mentioned hereinbefore, borax or boric acid may be included in the coating mixture, the presence of the borax or boric acid assisting in the formation of a more resistant and more tenacious coating. It is believed that borax acts in the nature of a flux. If desired, borax may be formed in situ by adding a proportion of boric acid in the aforesaid mixture in lieu of borax. When boric acid is used, it will react with some of the free alkali in the sodium silicate solution and to this extent permits a reduction in the required amount of sodium bicarbonate used within the aforementioned range. The amount of borax or boric acid added to the alkali silicate vehicle is generally of the order of about 0.2% (expressed as boric acid) by weight of the vehicle. Thus, a coating composition such as that described in Example 1 further containing 6 parts by volume of an aqueous solution of borax substantially saturated at 60° F. has been found to produce an exceptionally tenacious, abrasion resistant coating on a ferrous metal surface.

If the bicarbonate is omitted from the mixture described in the foregoing example, coatings formed with the mixture may be converted to a substantially insoluble condition by carrying out the heat-treatment in an atmosphere of CO_2 . The coatings so produced, however, are less firmly adherent and less homogeneous than those produced from a mixture containing bicarbonate.

Coatings suitable for some purposes may also be formed by substituting finely divided metal oxides (particularly zinc oxide and/or manganese dioxide) and/or metallic carbonates for some of the finely divided metal. In general, however, the coatings so formed do not present a metallic appearance and do not possess marked protective properties unless finely divided zinc is incorporated in the mixture.

Example 2

A liquid vehicle was prepared from the ingredients and in the manner described in Example 1. A film of the liquid vehicle was then sprayed onto the surface of a lightly oxidised steel sheet which was free of oil and grease. A coating of zinc dust was then sprayed onto the film of the liquid vehicle whereby a mixture thereof was formed in situ and the coated sheet was allowed to stand for a period of several hours until the coating had set.

The coated sheet was then heated in an oven for a period of 3 hours at a temperature of 450° F., and after removal from the oven, it was allowed to cool and was then washed with warm water.

The coating produced in this way was generally similar in appearance and properties to the coating formed on the steel sheet referred to in

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Example 1. Borax or boric acid may also be incorporated in the coating composition with attendant advantages.

This procedure has the advantage that it avoids the mixing of the zinc dust and the liquid vehicle before they are applied to the surface to be coated.

Alternatively, the zinc dust and the liquid vehicle may be simultaneously applied to the surface preferably by means of a spraying device in which separate streams of the vehicle and of the zinc dust are intimately mixed.

In general, it may be stated that the different ingredients of the coating mixtures described herein may be separately applied to a surface to form the requisite mixture in situ or said ingredients may be admixed in a spray immediately prior to their application to the surface.

Example 3

To a liquid vehicle prepared in the manner and from the ingredients described in Example 1, there was added about 10% by weight of a mixture of approximately equal parts of magnesium oxide and calcium hydroxide.

This vehicle was used as described in Example 1, that is to say, it was intimately mixed with an equal part by weight of zinc dust and was then brushed onto the surface of a steel sheet.

The coated sheet was allowed to stand at normal temperature for a period of 12 hours, at the conclusion of which it was found that the coating had been converted to the substantially insoluble condition. The inclusion in the mixture of the magnesium oxide and calcium hydroxide had obviated the formation of a significant proportion of soluble alkali in the coating and it was therefore unnecessary to wash it as in the foregoing examples.

This composition is therefore particularly useful in circumstances where it is inconvenient or impracticable to subject the coated article to a heat-treatment.

Furthermore, owing to the absence of substantial amounts of soluble alkali in the coating, it is particularly suitable as a base for a paint or other finish coat.

Whilst as above stated it is possible to dispense with the heat-treatment when magnesium oxide and calcium hydroxide are included in the mixture it is preferred, when practicable, to employ the heat-treatment in order to consolidate the coating.

It will be clear from the description following Example 1 that, if desired, borax or boric acid may also be included with advantage in the mixture described in Example 3.

The proportions of magnesium oxide and calcium hydroxide may be varied considerably and either may be used without the other. Other oxides (such as manganese dioxide) and hydroxides may also be employed in substitution for or in addition to magnesium oxide and calcium hydroxide.

Example 4

A mixture of liquid vehicle and zinc dust was prepared from the ingredients and in the manner specified in Example 1 and this mixture was brushed onto a lightly oxidised steel surface to form a coating.

The coating was allowed to stand at normal temperature until it had set after which a solution prepared by dissolving 10% of magnesium

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chloride in water was brushed thereon. It was found that a hard and substantially insoluble coating was rapidly produced in this way and without subjecting the material to a heat treatment.

It is believed that the magnesium chloride solution reacts with the silicate and the bicarbonate in the mixture to form silicated magnesium carbonates and magnesite.

This form of the invention therefore is particularly useful in circumstances where it is not practicable or convenient to subject the coated articles to a heat treatment, although if desired the coatings, after treatment with the magnesium chloride solution may be subjected to a heat treatment.

The strength of the solution may be varied within wide limits.

In lieu of magnesium chloride, a solution of calcium chloride or of a mixture of magnesium chloride and calcium chloride may be employed, in which case dolomite will be formed.

It should be understood that this treatment with magnesium chloride may also be usefully employed if borax or boric acid is also included in the coating mixture or if the latter is varied in any other manner described with reference to Example 1.

Example 5

A liquid vehicle was prepared in the manner and from the ingredients specified in Example 1.

A corresponding proportion by weight of zinc dust was then intimately mixed with the vehicle and in addition a proportion of commercial powdered graphite, equal to 4% by weight of the zinc, was incorporated therein.

The mixture was then brushed thickly onto the surface of a strip of spring steel and after being allowed to dry at normal temperature the coated strip was subjected to a heat-treatment at a temperature of 450° F. for a period of 12 hours.

The coatings so produced had antifriction and corrosion resisting properties.

This form of the invention, particularly when borax or boric acid is included in the composition, is particularly suitable for the formation of coatings on the leaves of automobile suspension springs. Such coatings may also be advantageously employed on other sliding parts and on shaft bearings.

The proportion of the graphite and the quality thereof may vary within fairly wide limits depending largely on the purpose for which the coating is required. In the case of leaf springs the proportion of graphite may advantageously be about 4% by weight of the zinc, as in the above described example, though 10% or more could be used if desired. In the case of a coating for a shaft bearing, the proportion of graphite may, in some cases, be as low as or even less than 0.5% by weight.

In lieu of mixing all of the ingredients before applying them to the articles to be treated, the graphite and/or zinc dust may be sprayed onto the articles either after the liquid vehicle has been applied thereto or simultaneously with the application of the liquid vehicle. Furthermore, the zinc dust and graphite may be admixed and may be applied to the surface without previous admixture with the liquid vehicle.

A further application of the invention resides in the formation of sound absorbent coatings for various purposes, such e. g. as on the interior

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surfaces of steel panels employed in the bodywork of closed motor vehicle.

In this application of the invention it is preferred to use a smaller proportion of the metallic coating agent and to incorporate in the mixture one or more ingredients such as cork dust, the presence of which will be conducive to the formation of a softer coating.

This application is a continuation-in-part of an application for Letters Patent of the United States filed March 17, 1938, Serial No. 196,562, by Victor Charles John Nightingall, now abandoned.

We claim:

1. The method of producing a hard protective coating on a ferrous metal surface which comprises applying to the surface a coating of a composition comprising finely divided metallic zinc incorporated in an aqueous solution of an alkali silicate, the aqueous solution containing about 20% to 40% by weight of the alkali silicate, the zinc being present in amount of about 100% to 350% by weight of said solution, and converting the coating to a substantially insoluble condition by reacting carbon dioxide therewith.

2. The method of producing a hard protective coating on a ferrous metal surface which comprises applying to the surface a coating of a composition comprising finely divided metallic zinc incorporated in an aqueous solution of an alkali silicate and an alkali bicarbonate, the aqueous solution containing about 20% to 40% by weight of the alkali silicate and about 0.1% to 0.8% by weight of the alkali bicarbonate, the zinc being present in amount of about 100% to 350% by weight of the aqueous solution, and drying the applied coating.

3. The method of claim 2, in which the applied

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coating is heated to a temperature of at least 200° F.

4. A ferrous metal article having on the surface thereof a hard protective coating resulting from the application thereto, and the reaction therewith of carbon dioxide, of a composition comprising finely divided metallic zinc incorporated in an aqueous solution of an alkali silicate, the aqueous solution containing from about 20% to 40% by weight of the alkali silicate and the zinc being present in amount of about 100% to 350% by weight of said solution.

5. A ferrous metal article having on the surface thereof a hard protective coating resulting from the application thereto and drying thereon of a composition comprising finely divided metallic zinc incorporated in an aqueous solution of an alkali silicate and an alkali bicarbonate, the aqueous solution containing from about 20% to 40% by weight of the alkali silicate and from about 0.1% to 0.8% by weight of the alkali bicarbonate, the zinc being present in amount of about 100% to 350% by weight of said solution.

6. A ferrous metal article according to claim 5, in which the composition applied to the surface of the article further contains about 0.2% of a compound of the group consisting of borax and boric acid by weight of the aqueous solution.

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