106-74 CROSS REFERENCE EXAM

Na silicate
Zn CrO_4 (5-40%) wt

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fe metal

UNITED STATES PATENT OFFICE

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PROCESS FOR INCREASING THE CORROSION RESISTANCE OF FERROUS ARTICLES

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6 Claims. (Cl. 117—62)65

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This invention is concerned with a method for improving the resistance of ferrous articles to corrosion. More particularly, the invention relates to a method for improving the corrosion resistance of ferrous articles which comprises (1) coating the said article with a thin adherent film composed of an alkali-metal silicate and (2) exposing the coated article to the vapors of a hydrocarbon-substituted halogenosilane.

The ferrous articles with which this invention is concerned comprise those made from iron or alloys of iron in which the iron is present, for instance, in amounts ranging from about 50 to 100 per cent and which are susceptible to corrosion by the action of moisture and oxygen. Examples of such ferrous metals are iron itself, substantially ferrous materials, the various corrosible steels, etc. This invention has particular application for rendering corrosion-resistant steel cartridges whose dimensions it is desired to maintain substantially unchanged, while at the same time coating the said cartridges by means of a process which is inexpensive and readily employed, and which yields a heat-resistant protective surface.

It has been suggested that the corrosion resistance of ferrous articles may be improved by exposing the surface of said articles, previously rendered moist, to vapors of a hydrocarbon-substituted halogenosilane and removing the hydrogen halide formed before it has had time to react appreciably with the ferrous surface. This process for improving the corrosion resistance is unsatisfactory even though the corrosion resistance is better than untreated articles. This fact becomes more evident as the treated article is subjected to continuing corrosive conditions.

We are aware that silicates in conjunction with other rust-proofing materials such as phosphates of iron and manganese or zinc (known as "bonderizing" or "phosphatizing"; see U. S. Patents 1,167,966 and 1,842,085) have heretofore been suggested as coatings over steel surfaces to improve the corrosion resistance of the article. Such a process is relatively unsatisfactory for any but the mildest sort of corrosive conditions; both the silicate coating and the phosphate coating are extremely porous and, therefore, articles coated with these materials are generally inadequately protected against corrosion, particularly when moisture condenses on the surface. Steel articles having phosphatized (i. e., bonderized) surfaces are subject to corrosion in spite of heat-treatment of the articles after exposure to the vapors of organohalogenosilanes.

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We have now discovered that bare surfaces of ferrous articles can be rendered corrosion-resistant by first coating the said ferrous surface with an adherent thin surface coating of an alkali-metal silicate, and thereafter subjecting the said coated surface (at least once, for instance, from 2 to 3 times) to the vapors of a hydrocarbon-substituted halogenosilane. Better corrosion resistance can be obtained by our claimed invention where the alkali-metal silicate is applied to a bare ferrous surface rather than a bonderized or phosphatized surface.

Among the alkali-metal silicates which may be employed are, e. g., potassium silicate, sodium silicate, lithium silicate, etc. Additional improvement in the resistance of the ferrous article to corrosion has been effected by incorporating in the alkali-metal silicate composition, preferably prior to coating the ferrous surface, from 10 to 90 per cent, preferably from 40 to 75 per cent, by weight, phosphoric acid (H_3PO_4), based on the weight of the alkali-metal silicate. The use in the alkali-metal silicate of zinc chromate ($ZnCrO_4$) or chromium oxide (CrO_3) in amounts of the order of 5 to 40 per cent, by weight, based on the weight of the alkali-metal silicate, either alone or with the phosphoric acid, has also given improved results.

The organohalogenosilanes, e. g., the hydrocarbon-substituted halogenosilanes, which may be employed in the vapor form for treatment of the silicate-coated ferrous article and methods of using same are more particularly disclosed and claimed in U. S. Patent 2,306,222—Patnode, and U. S. Patent 2,412,470—Norton, both of which patents are assigned to the same assignee as the present invention. The lower alkyl-substituted halogenosilanes are preferred, for example, the methyl and ethyl chlorosilanes, mixtures of such compounds, or mixtures of one or more of these compounds with silicon tetrachloride as disclosed more particularly in the aforementioned Norton patent.

The manner in which our claimed invention may be carried out may be varied within wide limits. Prior to coating the ferrous surface with the alkali-metal silicate, it is desirable that the surface be subjected to the action of a pickling bath and a caustic solution to remove any foreign matter present on the surface. After these treatments the article is washed and coated with the alkali-metal silicate.

The alkali-metal silicate (preferably containing a small amount of phosphoric acid and either zinc chromate or chromium oxide disclosed previously)

is advantageously applied in the form of an aqueous solution in any convenient concentration, e. g., a 3 to 15 per cent, by weight, aqueous solution. The method of application to the ferrous surface may be varied. For example, the ferrous article may be either dipped in the alkali-metal silicate solution or the solution may be sprayed upon the surface of the ferrous article. A short bake of the silicate-coated article for a period of from about 10 to 30 minutes at from 60° to 150° C. to remove any excess water is advantageously employed at this time. The alkali-metal silicate may also be applied to a ferrous article whose surface is at a temperature above 40° to 50° C. Such prior heating of the ferrous article decreases or eliminates the need for a subsequent bake.

Thereafter, the silicate-coated article may be subjected directly to the vapors of the hydrocarbon-substituted halogenosilane, or good results are also obtained if the silicate-coated article is passed into a chamber containing water vapor, and thereafter exposed to the vapors of the hydrocarbon-substituted halogenosilane or a mixture of a hydrocarbon-substituted halogenosilane and silicon tetrachloride as is more particularly disclosed and claimed in the aforementioned Patnode and Norton patents.

We have found that heating of the article after treatment with the hydrocarbon-substituted halogenosilane assists in effectively removing the hydrogen halide formed and in causing condensation of the reaction product resulting from the treatment of the silicate-coated surface with the hydrocarbon-substituted halogenosilane. Good results are obtained when this heating takes place within a relatively short time after treatment with the hydrocarbon-substituted halogenosilanes for a period of from 15 to 180 minutes at a temperature of from 60° to 125° C., preferably from 30 to 120 minutes at 75° to 100° C.

In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given by way of illustration and not by way of limitation.

Example 1

A steel cartridge case was placed in an acid pickling solution and thereafter in a concentrated caustic solution to remove any foreign matter. The steel case was washed and dried, and thereafter sprayed with a 7 per cent, by weight, aqueous sodium silicate solution containing 7 parts, by weight, sodium silicate, an analysis of which showed it to consist of 68.9 per cent H_2O, 24.7 per cent SiO_2 and 6.4 per cent Na_2O. The coated article was then heated at 100° C. for a short time to yield a thin adherent sodium silicate coating on the steel case. The case was placed in a humidifying chamber at 70° C. for 5 minutes, and thereafter subjected to the vapors of an atmosphere comprising a mixture of chlorosilanes consisting of, by volume, 1 part methyldichlorosilane and 2 parts of an azeotrope of silicon tetrachloride and trimethylchlorosilane. After about 2 minutes in the halogenosilane atmosphere, the shell casing was removed and baked in an oven at 100° C. for 2 hours. Tests of the porosity of the composite coating indicated enhancement of the corrosion resistance as a result of the aforementioned coating and treating procedures.

When another bare steel cartridge case was dipped in the aforementioned sodium silicate solution, baked 15 minutes at 100° C., humidified in a water vapor chamber for 1 minute, and thereafter subjected to the vapors of the above-described chlorosilane mixture, baked for 1 hour at 100° C., and again subjected to the vapors of the chlorosilane mixture, there was obtained a surface whose corrosion resistance was better than the bare surface.

Example 2

In this example, a cleaned steel cartridge case was heated to about 60° C. and sprayed with the same sodium silicate solution used in Example 1 except that about 4 per cent, by weight, phosphoric acid (H_3PO_4), based on the weight of the sodium silicate aqueous solution, was added to the said silicate solution prior to spraying the surface of the steel article. The case was exposed to the vapors of the chlorosilane mixture employed in Example 1 and thereafter baked for 1 hour at 100° C. Testing of this steel case rendered corrosion-resistant as described above showed that after 24 hours in the salt spray test the corrosion resistance of the bare steel surface was enhanced, and was even better than that obtained in Example 1.

Example 3

In another test, a steel cartridge case was cleaned and then treated with the same sodium silicate solution in the same manner as employed in Example 2 with the exception that 4 per cent, by weight, phosphoric acid and 1 per cent, by weight, zinc chromate, each ingredient based on the weight of the sodium silicate solution, were added to the sodium silicate solution prior to spraying of the surface of the steel cartridge. After spraying, the silicate-coated cartridge was subjected for one minute to the vapors of the same mixture of chlorosilanes as employed in Example 1. This steel case was more corrosion-resistant than any of the other treated cartridge cases.

It was surprising and unexpected to find that phosphatized (i. e., bonderized) steel surfaces treated with the organohalogenosilanes or phosphatized steel surfaces with an overcoating of sodium silicate and, thereafter, treated with the organohalogenosilanes similarly as was done in the foregoing examples, resulted in objects having poorer corrosion-resistance than the steel objects rendered corrosion-resistant in accordance with, for instance, the procedures outlined in Examples 2 and 3. Failure to use the organohalogenosilane treatment where a silicate coating was present on a phosphatized steel surface gave the poorest protection against corrosion.

Our method for improving the corrosion resistance of ferrous articles is inexpensive and is readily adaptable to a continuous process. Moreover, it is possible to render uniformly corrosion-resistant all sizes of articles whether they be large or small.

The fact that steel cartridge cases can be rendered corrosion-resistant to ordinary weathering conditions and to the effects of salt water spray without causing any material change in the dimensions of the case makes our process eminently suitable for that purpose.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A process for improving the corrosion resistance of steel articles which comprises (1) spraying a heated steel article with a dilute aqueous solution comprising sodium silicate and

CROSS REFERENCE EXAMINER

containing, by weight, from 10 to 90 per cent phosphoric acid and from 5 to 40 per cent zinc chromate, based on the weight of the sodium silicate, (2) removing the water from the aqueous silicate-phosphoric acid solution coating and subjecting the dried coated article to the vapors of a mixture comprising dimethylchlorosilane, silicon tetrachloride, and trimethylchlorosilane, and (3) thereafter heating the said treated article at from 75° to 100° C. for from 30 to 120 minutes.

2. A method for improving the corrosion resistance of a steel article which comprises (1) applying to the surface of said steel article a thin adherent coating of an aqueous solution comprising an alkali-metal silicate, said solution containing by weight, from 10 to 90% phosphoric acid, based on the weight of the alkali-metal silicate, (2) removing the water from the aqueous silicate-phosphoric acid solution coating and passing the dried coated article through an atmosphere containing water vapor, (3) subjecting the said water vapor-treated article to the vapors of a methyl chlorosilane, and (4) heating the article to a temperature of from 60° to 125° C. for from 15 to 180 minutes.

3. A process for improving the corrosion resistance of a steel article which comprises (1) applying to the surface of said steel article a thin adherent coating of an aqueous solution comprising sodium silicate, said solution containing by weight, from 10 to 90% phosphoric acid, based on the weight on the sodium silicate, (2) removing the water from the aqueous silicate-phosphoric acid solution coating and subjecting the dried coated article to the vapors of a mixture of halogenosilanes comprising silicon tetrachloride and trimethylchlorosilane, and (3) heating the said water vapor-treated article at from 60° to 125° C. for from 15 to 180 minutes to volatilize the hydrochloric acid formed.

4. A method for improving the corrosion resistance of the surface of a ferrous article which comprises (1) applying to the surface of the said ferrous article a thin adherent coating of an aqueous solution comprising an alkali-metal silicate, said solution containing, by weight, from 10 to 90% phosphoric acid, based on the weight of the alkali-metal silicate, (2) removing the water from the aqueous silicate-phosphoric acid solution coating and passing the dried coated article through an atmosphere

containing water vapor, (3) subjecting the said water vapor-treated article to the vapors of a hydrocarbon-substituted halogenosilane.

5. A method for improving the corrosion resistance of the surface of a ferrous article which comprises (1) applying to the surface of said ferrous article a thin adherent coating of an aqueous solution comprising sodium silicate, said solution containing, by weight, from 10 to 90% phosphoric acid, based on the weight of the sodium silicate, (2) removing the water from the aqueous silicate-phosphoric acid solution coating and passing the dried coated article through an atmosphere containing vapor, (3) subjecting the said water vapor-treated article to the vapors of a hydrocarbon-substituted halogenosilane.

6. A method for improving the corrosion resistance of the surface of a ferrous article which comprises (1) applying to the surface of said ferrous article a thin adherent coating of an aqueous solution comprising sodium silicate, said solution containing, by weight, from 10 to 90% phosphoric acid, based on the weight of the sodium silicate, (2) removing the water from the aqueous silicate-phosphoric acid solution coating and passing the dried coated article through an atmosphere containing water vapor, and (3) subjecting the said water vapor-treated article to the vapors of a methylchlorosiliane.

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