USE OF ALKYLAMINE BORATES AS CORROSION INHIBITOR FOR FERROUS METAL


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Claims priority, application Great Britain, June 19, 1963, Ser. No. 24,410/63
17 Claims. (Cl. 117—10)

ABSTRACT OF THE DISCLOSURE

Ferrous metals are protected from corrosion by use of alkylamine borates, especially the cycloalkylamine borates having 4 to 8 carbon atoms in the cycloalkyl group. The amine borates are preferably used as a dust to coat the metal article to be protected.

This invention relates to the reduction or prevention of corrosion of ferrous metals.

It is well known that when ferrous metals, such as steel sheets, strips and wire, are stored or transported, especially by sea, it is necessary to take precautions against rusting and other forms of corrosion, and that such precautions can be quite expensive and inconvenient. For example, a layer of grease is usually applied to steel sheet or strip coming from the mill, but this has the disadvantage that its subsequent complete removal is both necessary for many purposes and difficult; moreover, it is not easy to apply a protective grease layer to all parts of the surfaces of intricately shaped articles such as machinery.

The present invention provides a method whereby ferrous metal articles can be protected against atmospheric corrosion, in which these disadvantages are greatly mitigated or entirely eliminated.

According to this invention, there is provided the method of protecting ferrous metal articles from corrosion which comprises treating the surface of said articles with an alkylamine borate.

The alkylamine borates useful in this invention are those in which the alkyl groups contain at least 4, such as from 4 to about 18 carbon atoms, straight or branched chain, and especially the cycloalkylamine borates including alkyl-substituted derivatives thereof, in which the cycloalkyl groups contain from 4 to about 8 carbon atoms. Examples of such compounds are the borates of butylamine, bethylamine, 2-ethylhexylamine, dodecylamine, cyclohexylamine, cyclopentylamine, cyclooctylamine, and the like. The presently preferred borates are the cyclohexylamine borates, such as cyclohexylamine bborate, triborate, tetraborate, and mixtures thereof. Methods for preparing these compounds are described in copending applications Ser. No. 306,997 filed Sept. 6, 1963, now U.S. Patent No. 3,247,251 and Ser. No. 314,844 filed Oct. 9, 1963, now U.S. Patent No. 3,299,136, assigned to the assignee of the present invention.

In the preferred method of carrying out the invention, the alkylamine borate is in the form of a dust or powder which can be dusted onto the article to be protected, or applied to it in some other way as more fully described below. It has been found that a suitable dust or powder can be very easily produced by grinding the amine borate, such as in a ball mill, until at least a substantial proportion of the borate is capable of passing through a sieve of 52 mesh or smaller, such as down to 350 mesh (British Standard). For the sake of economy of material, it is desirable that the greater part or all of the amine borate is in the form of dust or powder particles, i.e., particles of diameter about 0.1 mm. and less; but the presence of a proportion of larger particles does not seriously affect the degree of protection conferred.

Not only such articles as sheets, strips and wire of ferrous metals, such as steels, can be protected by means of this invention, but also intricately shaped articles including machinery and pressed steel components. It has most surprisingly been found that the dusts or powders comprising the alkylamine borates are capable of penetrating into narrow spaces, and reaching parts of articles to which they have not been, and often cannot conveniently be applied directly, in a way of which conventional protective materials such as greases are quite incapable. For example, if the dust is blown against one side of an article, provided the article is not too large, it will be deposited in amount and with sufficient uniformity to confer the desired protection on the other side. Likewise, a coil of wire can be protected by blowing the alkylamine borate onto its outer layers. Also, rolled steel strip can be treated as it comes from the mill.

The amine borates can be used in association with other materials, whether solid, liquid or gaseous, which may act simply as carriers, or may themselves have some protective action. It is usually convenient to form a suspension of the dust or powder, with or without another finely divided solid which may itself have corrosion-inhibiting properties or may act solely as a diluent, in a current of air or other gas, and to cause the suspension to impinge on the surface, or part of the surface, to be treated. However, other methods of treating can be employed. For example, the dust or powder can be brushed or wiped onto the surface of the article, or small articles can be dipped under the surface of a body of the dust which, in such circumstances, behaves much as a liquid.

Another method is to apply to the surface to be treated a suspension of the dust in a suitable liquid, such as water or a lower alcohol or ketone such as methanol, ethanol, acetone, or methyl ethyl ketone, which is then evaporated. However, generally this is less advantageous.

"Treating" the ferrous articles with the alkylamine borate is also meant to include wrapping the articles in wrappings which have been impregnated or coated with the borate. Very useful anti-corrosion wrappings can be made by impregnating paper or other wrapping material with a solution of the alkylamine borate and evaporating off the solvent, leaving the amine borate in the material. A very small amount of the amine borate is sufficient to give a high degree of protection. Quantities down to 0.1 or 0.2 mg./sq. inch have been found to be effective, but somewhat larger amounts than this, especially from about 0.5 to about 50 mg./sq. inch are preferred. When the article is to be stored for a long period of time or under conditions which are especially prone to induce corrosion, the article can be immersed in a body of the amine borate dust or powder, or packed in drums otherwise filled with the amine borate, by itself or in admixture with a finely divided solid diluent.

It is remarkable that a very high degree of protection is obtained even though the dust does not provide a continuous protective layer over the surface to be protected as does a grease, for example. It appears that
each grain of amine borate exerts an effective protective action over an area extending considerably beyond its own dimensions, although the reason for this is not understood. It does not appear to be due to a continuous covering of vapor, since the effect is observed even when the article is not in an enclosed space; for example, steel sheet or other material on which the amine borate has been deposited can be stored in an open shed, it being merely necessary to ensure that the borate is not washed off, as by rain, or blown off, as by high winds. However, articles on which the amine borates have been deposited may be enclosed if desired, such as by wrapping in a suitable polymer film or sheet material which is impermeable to water vapor.

One great advantage possessed by the alkylamine borates over greases and like protective compositions is that for many purposes they do not need to be removed from the protected article before use, and even if in any case removal is desired, it can be easily done, such as by blowing with a jet of compressed air, by brushing, or by a simple wash with clean water. In some cases amine borate retained on the article may play a useful part in a later operation, as for example by acting as a flux in an enameling treatment, and it is frequently innocuous in circumstances in which the presence of a film of grease would be out of the question.

The invention is illustrated by the following examples, but is not to be limited to the specific examples given.

**EXAMPLE I**

Two small steel plates, 5 inches square, were carefully cleaned with emery paper and degreased with benzene. Half of each plate was then temporarily masked. The exposed portion of the first plate was lightly sprinkled with 4-5 mg. of finely divided cyclohexylamine tetraborate (less than 52 mesh), and that of the second plate with similarly finely divided borax. The test pieces were stored for three months (October to January) in a small unheated wooden building. At the end of this time the untreated areas were heavily corroded, and the borax-treated area of the second plate not much less so. The area of the first plate treated with the cyclohexylamine tetraborate was completely uncorroded.

This great superiority of the amine borate over borax was most unexpected, and appears to be due to the effect mentioned above whereby the protective effect of the former extends well beyond the individual grains, so that the protected areas overlap to form a continuous whole.

**EXAMPLE II**

Mild steel specimen plates 2 x 2 inches were cleaned with emery paper and then carefully degreased with acetone. Different plates were then evenly sprinkled with 4 mg. (1 mg./sq. inch) of 90 mesh cyclohexylamine diborate, triborate tetraborate, respectively. The specimens were protected from dust in such a way that the air could flow over them freely, and exposed in an unheated wooden building for 155 days (October to January). At the end of this time the powder was removed by gentle washing with warm water, followed by acetone, and dried in warm air. In all three cases corrosion was almost imperceptible.

Control experiments were carried out in which the known protective agents sodium benzoate, cyclohexylamine carbonate and dicyclohexylamine nitrate were used. All these are normally regarded as efficient corrosion-preventing agents, but all gave degrees of protection substantially less. Although the plates protected by dicyclohexylamine nitrate retained their luster, many isolated rust spots developed.

**EXAMPLE III**

A coil of mild steel wire of 10 gauge (S.W.G.) was subjected on both sides to a jet of air containing in suspension cyclohexylamine diborate powder, so as to de-

posit the powder on the wire at a loading estimated at about 1 mg./sq. inch. The wire coil was left in an unheated wooden building for 45 days, and at the end of this time was found to be practically free from visible signs of corrosion.

**EXAMPLE IV**

Several pallet loads of stacked steel pressings were treated by pneumatically spraying powdered cyclohexylamine borates on to the metal surfaces and other pallets were treated by electrostatically spraying the cyclohexylamine borates. The loadings obtained were between 0.5-8 mg./sq. inch. The treated pallets were stored in an unheated, well ventilated building. Good temporary protection was obtained for a period of several weeks, thus demonstrating efficient inter-process storage.

**EXAMPLE V**

Several 56 lb. cartons of nails were treated with quantities of cyclohexylamine diborate and triborate by (a) the powder being sprinkled throughout the body of the nails and (b) sachets being placed amongst the nails.

The quantities of cyclohexylamine borate used were between 3-6 oz. In all cases significant protection from corrosion was obtained, compared to the untreated nails, was obtained when the cartons of nails were stored for 30 days at 38° C. and 90% relative humidity.

**EXAMPLE VI**

Bins of chemically clean screws in the finished and part-finished state have a tendency to rust during storage before packaging. It has been found that a light dusting (1-4 mg./sq. inch) of cyclohexylamine tri-, tri- and tetraborate will prevent this for some time.

**EXAMPLE VII**

The polished internal bores of steel tubes have been protected from corrosion for several weeks by treating them with light coatings of cyclohexylamine diborate. It has been found that it is not necessary to close the ends of the tube for protection to be obtained (although closing the ends does enhance the length of storage time obtainable). The tubes threaded were tubes which had residues of honing oil present and tubes that had been thoroughly degreased.

The alkylamine borates employed in the present invention are prepared by reaction of an alkylamine with boracic acid or metaboracic acid, the ratio of reactants determining the specific borate obtained. The following examples illustrate the preparation of the diborate, triborate and tetraborate of cyclohexylamine.

**EXAMPLE VIII**

Cyclohexylamine (198.3 g.; 2.0 mole) and metaboric acid (87.44 g.; 2.0 mole) were mixed with light petroleum (150 ml.; B.P. 80°-100° C.) and the stirred reaction mixture was heated at 70° C. for 0.5 hour, after this time the mixture suddenly reacted and went solid. On the addition of a further 150 ml. light petroleum, the mixture again became stirrable and was heated under gentle reflux with stirring for a further 2.5 hours. The volatiles were removed under vacuum and the product was finally dried at 80° C. in an oven to give 176 grams (94.2%) of product having the following analysis:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percent</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexylamine</td>
<td>51.17</td>
<td>1.0</td>
</tr>
<tr>
<td>Br2</td>
<td>31.83</td>
<td>1.0</td>
</tr>
<tr>
<td>H2O</td>
<td>11.8</td>
<td>1.18</td>
</tr>
</tbody>
</table>

**EXAMPLE IX**

Cyclohexylamine triborate-heterogeneous system

Cyclohexylamine (50 g.; 0.504 mole) and boric acid (93.5 g.; 1.51 moles) were mixed in a ball-mill and milled
The mill and contents were then dried in an oven at 80° C. for 15 minutes, and the dry, lumpy product was finally ball-milled for a further 5 minutes to yield 120 g. (95.7%) of a fine powdery product having the following analysis:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percent</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexylamine</td>
<td>39.9</td>
<td>1.02</td>
</tr>
<tr>
<td>B2O3</td>
<td>42.6</td>
<td>2.48</td>
</tr>
<tr>
<td>H2O</td>
<td>17.6</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Formula: C6H6N2H2·3B2O3·2H2O.

**EXAMPLE X**

Cyclohexylamine tetraborate

Cyclohexylamine (100 g.; 1.08 mole) and boric acid (250 g.; 4.04 moles) were mixed with 250 ml. water and heated with stirring. A clear solution was obtained which yielded a white crystalline product on cooling. The solid was filtered and air dried. It then weighed 241 g. (yield 76.5%) having the following analysis:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percent</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexylamine</td>
<td>31.5</td>
<td>1.00</td>
</tr>
<tr>
<td>B2O3</td>
<td>44.7</td>
<td>2.02</td>
</tr>
<tr>
<td>H2O</td>
<td>23.8</td>
<td>4.15</td>
</tr>
</tbody>
</table>

Formula: C6H6N2H2·2B2O3·4H2O.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. The method of protecting ferrous metal articles from corrosion which comprises coating the surface of said articles with an alkylamine borate, in which the alkyl group contains 4 to about 18 carbon atoms.

2. The method of claim 1 in which said alkylamine borate is a cycloalkylamine borate, in which said cycloalkyl group contains from 4 to about 8 carbon atoms.

3. The method of claim 1 in which said alkylamine borate is cyclohexylamine borate.

4. The method of claim 1 in which said articles are treated by depositing on said articles about 0.1 to about 50 mg. of said alkylamine borate per square inch of the surface.

5. The method of claim 1 in which said alkylamine borate is a dust, the major portion of which has a particle diameter of not more than about 0.1 mm.

6. The method of protecting ferrous metal articles from corrosion which comprises depositing on the surface of said articles from about 0.5 to about 50 mg. of cyclohexylamine borate per square inch of said articles.

7. The method of claim 6 in which said cyclohexylamine borate is cyclohexylamine diborate.

8. The method of claim 6 in which said cyclohexylamine borate is cyclohexylamine triborate.

9. The method of claim 6 in which said cyclohexylamine borate is cyclohexylamine tetraborate.

10. The method of claim 6 in which said cyclohexylamine borate is a dust, the major portion of which has a particle diameter of not more than about 0.1 mm.

11. A corrosion resistant ferrous metal article, the surface of which is treated with an alkylamine borate in which the alkyl group contains from 4 to about 18 carbon atoms.

12. A corrosion resistant ferrous metal article, the surface of which is treated with a cycloalkylamine borate in which said cycloalkyl group contains from 4 to about 8 carbon atoms.

13. A corrosion resistant ferrous metal article, the surface of which is treated with cyclohexylamine borate.

14. A corrosion resistant ferrous metal article, the surface of which is coated with from about 0.5 to about 50 mg. of cyclohexylamine diborate per square inch.

15. A corrosion resistant ferrous metal article, the surface of which is coated with from about 0.5 to about 50 mg. of cyclohexylamine triborate per square inch.

16. A corrosion resistant ferrous metal article, the surface of which is coated with from about 0.5 to about 50 mg. of cyclohexylamine tetraborate per square inch.

17. The article according to claim 13 in which said cyclohexylamine borate is a dust, the major portion of which has a particle diameter of not more than about 0.1 mm.

**References Cited**

**UNITED STATES PATENTS**

3,203,971 8/1965 De Gray et al. ——— 252—389 X

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