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PROTECTION OF FERROUS METALS
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This invention relates to the protection of ferrous metals against corrosion, and more particularly to the use of long-chain aliphatic amines as anticorrosion agents for iron and steel surfaces, whether clean, rusty, chemically treated or plated with a relatively less corrodible metal.

Because of their susceptibility to corrosion, iron and steel are seldom used without some protection against the elements, and the art is quite extensive both on coatings designed for ultimate service and on materials for temporary protection during shipment and storage. Various "rust-proofing" processes are also employed, including the well known phosphate treatments based on phosphoric acid or acid phosphates of iron, manganese and zinc, and the chromate treatments using chromic acid or its salts. These processes are generally applied to clean metal surfaces, but phosphoric acid compositions also have been used for pretreatment of rusty metal before painting. Also in the case of ferrous metals that have been plated with a relatively non-corrodible metal, the continuity of the plate is often destroyed by the rusting or oxidation of the ferrous metal beneath the plate. This rusting is usually due to electrolysis and it has been difficult to prevent such rusting while not affecting the appearance of the plated surface.

This invention has as its object the treatment of ferrous metal surfaces to protect them from corrosion. A further object is the treatment of ferrous metal surfaces that have been plated with a non-corrodible metal in order to inhibit the pitting and oxidation brought about by electrolytic attack. Another object is to provide an improvement in the process of painting ferrous metal surfaces by providing a treatment for said surface that will render the surface rust-resistant over intervals between the usual phosphate and chromate rustproofing processes and the subsequent painting step. A still further object is to develop a satisfactory pretreatment for rusty surfaces in preparation for painting. A further object is to render metal surfaces water repellent and/or organophilic. A further object is to convert to the organophilic, hydrophobic condition hydrophilic, inorganic, massive structural surfaces normally having hydrophilic properties. Another object is to provide certain new and useful compositions of matter. Other objects will be apparent from the reading of the following description of the invention.

These objects are accomplished by applying to the surface to be treated an acyclic, aliphatic amine having at least one aliphatic group of a

chain length of at least 8 carbon atoms. Where outdoor weathering conditions are not involved, and it is not planned to apply a coating composition subsequently, the amine may be applied directly to the clean metal surface as a dilute solution in organic solvents.

Metal surfaces which are to be painted without removing the anticorrosion agent should, before applying the amine, be treated with an acid reagent from the class of phosphoric, chromic, molybdic, and oxalic acids and their acid salts. Such combination treatments may also be used in protecting surfaces plated with less corrodible metals such as copper, nickel, zinc, and tin, and also in preparing rusty metal surfaces for painting.

The following examples set forth certain well defined instances of the application of this invention. They are, however, not to be considered as limitations thereof, since many modifications may be made without departing from the spirit and scope of this invention.

Example 1

Cold-reduced 24-gauge steel sheet is prepared for storage by cleaning in a vapor degreaser, immersing briefly in a 2.5% solution of 9,10-octadecenylamine in toluol, draining and drying at room temperature. Steel sheet treated in this manner was subsequently subjected to the continuous condensation of moisture upon its surface. A 2 x 4" test specimen examined at the end of 170 hours' exposure was found to have only a single small rust spot on its surface while untreated steel sheet exposed in the same manner was covered with a scaly continuous film of rust. Steel sheet which was treated with 4% petrolatum in toluol and subjected to water condensation for 170 hours was found to be heavily rusted over about 70% of its area.

Example 2

Cold-rolled 20 gauge steel sheet is cleaned by scrubbing with an alkali silicate solution, rinsed with fresh water and dried in a current of hot air. The sheet, while still warm, is passed between cloth rolls saturated with a 3% solution in toluol acetone of a technical mixture of long-chain alkyl amines corresponding to the alkyl alcohols obtained by catalytic hydrogenation of sperm oil. The solvent evaporates readily during a short travel on belt conveyors and the sheets are then ready to be packaged for shipment. Steel sheet treated in this manner was free from corrosion after 250 hours' immersion in water

while untreated steel sheet similarly immersed was covered with a heavy deposit of rust in 24 hours. Steel sheet similarly treated with 10% petrolatum in toluene was severely rusted in 72 hours.

Example 3

Steel refrigerator panels are cleaned in a vapor degreaser, are dipped for two minutes in a boiling solution of ferrous dihydrogen phosphate and manganous dihydrogen phosphate, and are rinsed in cold water. They are then dipped for two minutes in a hot dilute solution of chromic acid, are removed from the solution and are allowed to dry. These panels are then dipped briefly in a 4% solution of n-octadecylamine in low-flash naphtha, and are then drained and dried at room temperature. Panels treated in this way may be stored for several months before application of oil-type coating compositions, and have been found to resist corrosion for three months or more when exposed outdoors. Panels processed similarly with the exception of the amine treatment lack rust resistance unless paint is applied soon after processing.

Example 4

White pickled sheets of steel are immersed briefly in a 2% solution of chromic acid in a 4/1 mixture of water and acetone. After draining and drying at room temperature the sheets are dipped in a 2% solution of tri-n-dodecylamine in toluol and dried in the open air. Steel sheets so treated are rust resistant when exposed to the weather for several weeks.

Example 5

Nickel-plated steel rods are immersed for fifteen minutes at room temperature in an aqueous solution containing 4% H_3PO_4 and 0.5% long-chain fatty alcohol sulfate. The solution is then washed with cold water and the rods are dried and dipped in a 4% solution in toluol of a technical mixture of long-chain alkyl amines corresponding to the alkyl alcohols obtained by the catalytic hydrogenation of coconut oil acids. The rods are dried in a current of warm air after removal from this solution. Rods so treated are resistant to rusting when exposed to continuous water condensation for several weeks.

Example 6

Galvanized iron corrugated sheathing is dipped in an aqueous solution comprising 2% chromic acid and 0.1% long-chain fatty alcohol sulfate. After drying at room temperature the metal is sprayed with a solution of dodecylamine in V. M. & P. naphtha and allowed to dry in the open air. Galvanized sheet treated in this way resists "white rusting" failure even in atmospheres where sulfur dioxide is present.

Example 7

Rusty steel which is to be painted is first wire brushed and a 10% solution of H_3PO_4 applied sparingly with a brush. When dry the surface is finally sprayed with a 4% solution of n-octadecylamine in toluol. The metal so treated may be exposed to continuous water condensation for a month without any tendency for rusting to be resumed.

In addition to having a high resistance to corrosion, rusted steel which had been so treated was highly receptive to oil-type coating compositions. Paint films applied to rusted metal treated only with 10% H_3PO_4 were, after 8 days' water im-

mersion, removed from the metal by an applied force of 16 lbs. per sq. in., whereas paint films applied to metal which had received both 10% H_3PO_4 and 4% octadecylamine solution treatment resisted removal (after 8 days' water immersion) until the applied force was 24 lbs. per sq. in.

Example 8

Structural steel columns carrying a tight coat of mill scale are sprayed with a solution of 1% molybdic acid and 3% chromic acid in hot water are allowed to dry and are then sprayed with 6% solution of tri-n-dodecylamine in mineral spirits. Columns treated in this manner may be shop-primed at some later date or shipped without further protection, and in either case corrosion difficulties are greatly reduced.

Example 9

Steam-blued sheet iron is dipped briefly in a 4% solution of n-hexadecylamine in xylol and allowed to dry in the open air. Such sheets are rust resistant even when exposed directly to the weather for several weeks.

Example 10

Steel sheet which was first phosphatized and then sprayed with 4% octadecylamine in toluene solution was exposed out-of-doors for 3 months. At the end of this period this treated steel was entirely rust-free, while steel sheet which had been similarly phosphatized but treated with light mineral oil was rusted heavily. Sheet which received no treatment subsequent to phosphatizing was covered with rust over its entire surface.

Example 11

A section of 1" angle iron bearing a tight covering of mill scale was dipped in a 2% solution of hexadecylamine in toluene and subsequently allowed to dry in the open air. This test specimen, a similar section of angle iron which had received no treatment, and a similar section of angle iron which had been treated with 2% petrolatum in toluene solution were all exposed out-of-doors during a season when precipitation was frequent. Within a week the untreated angle iron and the angle iron treated with petrolatum were rusted considerably while at the end of 4 weeks both of these test samples were rusted over 50% of their surfaces. The angle iron which had been treated with hexadecylamine resisted rusting during this period and when examined after 14 weeks' exposure was found to have only a very few minute spots of rust on its surface.

While certain specific compounds have been disclosed in the examples as operative for this process, other acyclic aliphatic amines having at least one aliphatic group of a chain length of at least 8 carbon atoms may be used to produce the improvements attributed to this invention. Long-chain amines other than those disclosed in the examples include didodecylamine, octylamine, dioctylamine, didecylamine, pentadecylamine, ethyldecylamine, dimethyldodecylamine, dioctadecylamine, tritetradecylamine, heptadecylamine, dimethyl-9,10-octadecenylamine, ethylmethyldodecylamine, diethyloctylamine, octyldodecylamine, methyloctadecylamine, as well as mixtures of two or more amines obtained by the catalytic reduction of mixtures of nitriles obtained from vegetable or animal oils or fats such as palm oil, beef tallow or peanut oil. From the point of view of value and cost, those monoamines having an aliphatic chain of 10 to 24

carbon atoms and especially those having an aliphatic chain of from 12 to 20 carbon atoms are particularly desirable.

Amines which are normally liquids and those which melt at moderate temperatures can be applied alone, but for most purposes dilute solutions in organic solvents are preferred. Such solutions will generally contain 2% to 8% amine, although in certain cases concentrations varying from 1% to 25% may be used. The solvent should generally boil under 150° C. to insure rapid evaporation, and usually will be an aromatic or aliphatic hydrocarbon. Alcohols, ketones, ethers and other solvents, however, may be used. The solutions may be applied by dipping, brushing, spraying or by any other convenient method such as passage between impregnated rolls. Time and temperature are not critical.

Although these compounds will usually be applied to metal surfaces by means of a solution using such well known processes as dipping, spraying, wiping, and brushing, it will be desirable at times to use other methods of application. A material which melts at reasonably low temperatures and which undergoes no decomposition in the region of its melting point may be applied in the liquid form without a diluent of any kind, provided that the application of the material is so regulated that the final protective film conforms to the desired thickness limits. These compounds may also be applied to the metal surface as a finely divided solid and the protective layer be formed by fusing the solid particles to a continuous coating at a suitable temperature. The protective agent may also be emulsified or dispersed in a liquid which is not a true solvent and applied to metal surfaces in this form, with the evaporation of the carrier occurring subsequently. It also may be preferred in certain cases to provide metal articles with a protective surface layer by permitting the condensation of vapor of a particular compound to occur on the metal surface.

When a paint film is subsequently to be applied to the metal surface it is preferred that the film or layer of anti-corrosive deposited on the metal surface be of such thickness that one pound will coat approximately 20,000 square feet of metal. A film of this thickness may readily be obtained by dipping the metal into a 4% solution of the protective agent. Films of a thickness such that one pound will coat approximately 10,000 square feet or of a thickness such that one pound will coat approximately 80,000 square feet may also, but less preferably, be used. These thicknesses may be obtained by dipping a sheet of steel into 8% and 1% solutions of the agents, respectively.

Long-chain amines are particularly effective as anti-corrodents when used following pretreatment with certain chemicals, including phosphoric, chromic, oxalic, and molybdic acids and their acid salts such as ferrous dihydrogen phosphate, manganous dihydrogen phosphate, zinc dihydrogen phosphate, potassium dichromate and sodium dimolybdate. These treatments in general follow the lines of well-known rustproofing processes.

Efficiency of the pretreatment is often increased by improving the wetting properties of the aqueous solutions used. This may be done by adding a water-miscible organic liquid such as ethanol or acetone, or by using small quantities of wetting agents such as the long-chain fatty alcohol sulfates.

The acidic reagent may be removed at the

proper time by rinsing or wiping off, or it may be allowed to dry in contact with the surface. In either case the surface should be essentially dry before application of the amine, as any moisture present interferes with the proper anchorage of these compounds to the metal.

As has been indicated previously, this invention is applicable not only to ferrous metals directly, but also to ferrous metal surfaces which have been plated with another metal or which carry oxide layers ranging from the thin films responsible for "temper colors," through mill scale to the heavy deposits which constitute ordinary rust. The use of acidic pretreatments with plated surfaces is limited to those which do not give excessive attack on the plating metal; for example, phosphoric acid cannot be used on zinc and cadmium without reduction or destruction of the luster associated with these metals.

This invention may be used to protect a wide variety of ferrous metal articles against corrosion during temporary or prolonged storage. The compounds used in this process are particularly well adapted to the protection of ferrous metal articles, such as bolts, nuts, nails, wire, sheets, tools, fine machinery parts, bearings, cutlery, gears, fire arms, metallic cases, etc., and to the treatment of ferrous metal articles which have been provided with a surface coating of some other metal or alloy, such as chromium, copper, nickel, cadmium, zinc, brass, aluminum, tin, lead, etc. In addition to such uses, these compounds may be applied to the surfaces of other metals and alloys, particularly those used for structural shapes and articles of commerce; for example, as sheets, rods, tubes, and the like. Among such metals are zinc, brass, bronze, aluminum, tin, copper, pewter, lead, magnesium, cadmium, Duralumin, nickel, etc.

Both steel and galvanized iron are often given a phosphate treatment in preparation for painting. This invention is likewise applicable to the preparation of such metals for industrial finishing, and can also be used on structural materials which are to be coated later in the field. Another important use is the field preparation of rusty iron and steel structures for painting.

Long-chain amines used directly on the metal are highly effective anticorrodents and possess a definite advantage in rust resistance over such commonly used materials as mineral oil and lanolin even when the latter are applied at three- or fourfold greater thickness. This is illustrated by the performance of steel sheet treated as in Example 2, which remained rust-free after several days' immersion in water while the surface of a corresponding sheet coated with four times as much petrolatum was completely rusted during this period.

When the amine is combined with an acidic pretreatment, still greater corrosion resistance is obtained and there is the further advantage of improved paint bonding and better protection from built-up paint films. Metal treated by a phosphatizing process must be painted immediately, as the treated surface is quite rust sensitive, and this makes it necessary that all "phosphatizing" be done in the plant where the finish is to be applied. Application of a long-chain amine to a "phosphatized" surface renders it quite rust resistant, thus permitting centralization of treating facilities and shipment of pretreated metal to the point of use. This method not only offers appreciable savings in cost for industrial uses, but also opens up an entirely new

outlet for such treated metal in field uses where chemical treatment on the job is out of the question.

Still another important advantage is in the pretreatment of rusted metal prior to painting. The rust-arresting power of phosphoric acid is well known and has led to several attempts to develop a practical method of using this product on rusty surfaces in the field as a preparation for painting. Traces of free acid remaining on the surface have an adverse effect on paint adhesion, and no satisfactory method of overcoming this difficulty has been found previously. Such treatments can now be used effectively by applying a solution of long-chain amine as the final step, which yields a surface of good paint-bonding characteristics as well as excellent corrosion resistance. Adhesion measurements carried out on painted rusty metal after extended water soaking have shown that the bond obtained with phosphoric acid-amine treated surfaces is 50% greater than that for the acid treatment used alone, and at least as good as that obtained when paint is applied without any pretreatment.

In addition to preventing corrosion, long chain amines also impart water repellence and organophilic character to surfaces to which they are applied. Such compounds are particularly useful in this respect when applied to the surface of massive inorganic structural bodies otherwise of an hydrophilic nature. A massive structural surface is defined as the surface of a structurally useful body capable of self-support and having one dimension of at least one-quarter inch, such bodies including massive objects constructed of glass, metal, porcelain, masonry, stone, asbestos cement board, and the like.

The many applications for treatment of such structural surfaces fall into two general classes. The first involves imparting a water repellent character to the surface for the purpose of preventing accumulation of water on the exterior and/or for protection of the underlying material. The second general class of applications involves the improvement in receptivity of structural surfaces to organic liquids.

In converting such massive inorganic structural surfaces from an hydrophilic to an hydrophobic, organophilic character, the long chain amine may be applied to the surface by any of the methods above mentioned in connection with reducing the corrosion of ferrous surfaces, such methods including application of a solution of the amine in a volatile solvent, and direct application at a temperature at which the amine is in the liquid form. In addition, such hydrophilic surfaces may be rendered hydrophobic and organophilic by the application of aqueous solutions of certain derivatives of the long chain amines that are, in contrast to the amines cited above, sufficiently soluble in water to permit their use in this manner without the use of the more expensive, more hazardous organic solvents. In some cases it may be desirable to evaporate the water after such treatment; whereas in other cases, this evaporation may be unnecessary. Thus many of the long chain amines above mentioned may be applied in the form of a dilute aqueous solution of a water soluble salt such as the chloride, sulfate, nitrate, acetate, sulfamate, formate or the like. Where desirable, either before, during, or after application to the surface, the long chain amine or water soluble salt may be reacted to form an electro-neutral water insoluble soap by reaction with ordinary long chain acids

including carboxylic, sulfonic, phthalic and the like, as well as with salts of such acids. Dilute solutions of dodecylammonium chloride, i. e., the salt of dodecyl amine and hydrochloric acid, have been especially useful in converting massive inorganic structural surfaces from an hydrophilic to an hydrophobic or water repellent character.

Whether applied directly, in the form of a solution in a volatile organic liquid, or as an aqueous solution, the long chain amine compound need be applied only in small quantities. Thus the change in surface characteristics of such smooth surfaces as glass and metal plate has been accomplished by using aqueous solutions of such amine derivatives having a concentration of $\frac{1}{4}\%$, $\frac{1}{10}\%$ and less; whereas rougher surfaces such as masonry and the like, often require a somewhat higher concentration due to the somewhat higher specific surface.

The water repellent property impartable to hydrophilic inorganic massive structural surfaces by use of long chain amine compounds is of considerable practical use. The ability to accomplish this effect by means of a water solution of such a long chain amine derivative is especially advantageous, in addition to the economic considerations involved, inasmuch as such hydrophilic surfaces are often covered by a film of water that makes impossible the direct application of an organic water-immiscible system. Thus a water-wet plate of glass such as a glass window or an automobile windshield can be made to shed water by application of a dilute aqueous solution such as one containing $\frac{1}{10}\%$ of dodecyl ammonium chloride, the solution being conveniently applied by means of a damp cloth. Whereas drops of water often tend to spread with a zero angle of contact on an untreated glass surface, application of the long chain amine derivative even in the form of its water solution tends to change the angle of contact of the excess water on the glass plate from 0° to 180° causing the water to collect as spherical drops that readily roll off of the surface. Prevention of adherence of water to glass surfaces in this manner is also useful in preventing the etching that often occurs on such surfaces, especially when the freshly prepared glass body comes in contact with moisture. This undesirable corrosive etching of surfaces of glass structures such as bottles, double windows, lenses, microscope slides, and the like is prevented by coating their surface with a long chain amine. Other massive inorganic structural surfaces than glass may be rendered water repellent. Among such are included masonry surfaces such as brick, concrete, mortar, plaster, stucco, stonework, and the like. Such masonry surfaces have in the past given considerable difficulty due to moisture penetration through walls constructed of these materials. Metal, polished marble and asbestos cement board represent other structural surfaces that may be rendered water repellent to advantage by such means. Although this process of rendering hydrophilic inorganic structural surfaces water-repellent has been found especially helpful in treatment of surfaces of relatively great extent, use has been made of this process for water-proofing inorganic fibrous materials such as glass wool, asbestos fibre, mineral wool, and the like where the fibrous material is of appreciable length (i. e., exceeding $\frac{1}{4}$ inch) and therefore has definite structural value. The advantage of such water repellent treated fibrous

material in insulation of structures is indicated.

In addition to the above enumerated uses of long chain amines and their derivatives in rendering massive inorganic structural surfaces water repellent, such compounds may be used to impart an organophilic character to such surfaces. Thus the above-mentioned surfaces such as glass, metal, masonry, and the like are more readily wetted by organic liquids after treatment of the surface with long chain amines or their derivatives by any of the methods above mentioned, the method of application as a water solution being preferred for this purpose. A few selected applications will serve to indicate the advantage of such a process. Thus any of the above-mentioned long chain amines and water soluble salts of the same are useful to the glazier. At times when atmospheric conditions are humid, it is ordinarily necessary to suspend glazing operations due to the fact that putty will not adhere to the glass surface with its layer of condensed moisture. However, use of long chain amine compounds permits continuation of glazing operations even under such adverse moisture conditions. The glass surface may be rendered organophilic by simply wiping the surface with a damp cloth containing a dilute solution of a water soluble amine derivative such as a salt thereof, thereby causing the putty to stick to the surface of the glass. If desired, the long chain amine derivative or the free amine itself may be incorporated in the putty prior to use, the agent then being applied to the glass surface by the putty itself during the normal glazing operation.

With this picture of the advantage of use of long chain amine compounds in rendering a glass surface preferentially wetted by an organic liquid binder such as putty even in the presence of water, other applications of this general process will be apparent. Thus it has been noted that, whereas laboratory glass ware and porcelain ware often resist being written upon by the ordinary "china marking" crayons because of a film of adsorbed moisture, long chain amine compounds applied either to the surface of the ware as a dilute aqueous solution or incorporated in the wax-like crayon permit writing to be accomplished in the usual manner without requiring removal of the adsorbed moisture film by heat. Other uses involving application of organic systems including paint and colored films to inorganic hydrophilic massive structural surfaces will be apparent. Thus, painting of masonry and metal surfaces by organic systems is improved by treatment of the surface of the same either by direct application of the compound to the surface according to the aforementioned methods or by application of the compound in the paint system itself. The process is especially helpful if the surface being painted is found to be already wetted by water or if it is to be later exposed to moisture conditions with danger of loss of adhesion. Other instances where this unique property of the long chain amines may be utilized include printing on tin plate under adverse moisture conditions, treatment of large stone pebbles for improving the bonding of gravel particles to the asphalt binder used in road making, and printing or marking designs on ceramic and porcelain ware.

Whereas the imparting of an organophilic character to such massive structural surfaces above mentioned is of prime importance, this invention has also been used for imparting an

organophilic character to fibrous materials such as glass wool, asbestos, mineral wool and the like, in which the average fibre length exceeds $\frac{1}{4}$ inch. With such an organophilic character the problem of coloring such fibrous material is simplified.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and therefore it is not intended to be limited except as indicated in the appended claims.

I claim:

1. The process for the protection from atmospheric corrosion of metallic surfaces susceptible to said corrosion which comprises applying to said surfaces a film of an acyclic aliphatic monoamine having an aliphatic group of a chain length of at least 8 carbon atoms, so as to provide a layer of amines having a thickness within the range corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

2. The process for the protection of iron against oxidation which comprises coating the iron surface with a film of an acyclic aliphatic monoamine, the aliphatic group of said amine having a chain length of 10 to 24 carbon atoms so as to produce a layer of amines having a thickness within the range corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

3. The process in accordance with claim 1 characterized in that the surface is a corrodible metal plated upon a ferrous metal.

4. The process in accordance with claim 1 characterized in that the metal surface is a continuous ferrous metal surface.

5. The process in accordance with claim 2 characterized in that a film is applied by treating the surface with a solution of the desired amine in volatile solvent.

6. As an article of manufacture a body having a metal surface susceptible to atmospheric corrosion, at least a part of which surface is coated with a film of an acyclic aliphatic monoamine having at least one aliphatic group of a chain length of at least 8 carbon atoms, said film having a thickness of amines corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

7. As an article of manufacture a body having an iron surface, at least a part of which surface is coated with a film of an acyclic aliphatic monoamine having at least one aliphatic group of a chain length of from 10 to 24 carbon atoms, said film having a thickness of amines corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

8. The product in accordance with claim 7 characterized in that it has a paint film superimposed on at least a part of said coated surface.

9. The process in accordance with claim 1 characterized in that the metallic surface is a phosphatized metallic surface.

10. The process in accordance with claim 1 characterized in that the metallic surface has been pretreated with an acid reagent selected from the class consisting of phosphoric, chromic, molybdic and oxalic acids and their acid salts prior to the applying of the amine.

11. The process in accordance with claim 1 characterized in that the metallic surface is a ferrous metal surface that has been oxidized, which oxidized ferrous metal surface has been pretreated with an acid reagent selected from the group consisting of phosphoric, chromic,

molybdic and oxalic acids and their acid salts prior to the applying of the amine.

12. The process in accordance with claim 1 characterized in that the metallic surface is the surface of a zinc-coated iron bearing body and that said metallic surface has been pretreated with an acid reagent selected from the group consisting of phosphoric, chromic, molybdic and oxalic acids and their acid salts prior to the applying of the amine.

13. The process for the protection from atmospheric corrosion of metallic surfaces susceptible to said corrosion which comprises applying to said surfaces a film of a mixture of long-chain alkyl amines, corresponding to the alkyl alcohols obtained by the catalytic hydrogenation of coconut oil acids, so as to provide a layer of amines having a thickness within the range corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

14. The process for the protection from atmospheric corrosion of metallic surfaces susceptible to said corrosion which comprises applying to said surfaces a film of dodecylamine, so as to provide a layer of dodecylamine having a thickness within the range corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of dodecylamine.

15. The process for the protection from atmospheric corrosion of metallic surfaces susceptible to said corrosion which comprises applying to said surfaces a film of n-octadecylamine, so as to provide a layer of n-octadecylamine having a thickness within the range corresponding to a

spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of n-octadecylamine.

16. As an article of manufacture, a body having a metal surface susceptible to atmospheric corrosion which has been pretreated with an acid reagent selected from the class consisting of phosphoric, chromic, molybdic and oxalic acids and their acid salts, at least a part of which pretreated surface is coated with a film of an acyclic aliphatic monoamine having at least one aliphatic group of a chain length of at least 8 carbon atoms, said film having a thickness of amines corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

17. As an article of manufacture, a body having a metal surface susceptible to atmospheric corrosion which has been phosphatized, at least a part of which surface is coated with a film of an acyclic aliphatic monoamine having at least one aliphatic group of a chain length of at least 8 carbon atoms, said film having a thickness of amines corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

18. As an article of manufacture, a body having a metal surface susceptible to atmospheric corrosion which surface is formed by a corrodible metal plated upon a ferrous metal, at least a part of which surface is coated with a film of an acyclic aliphatic monoamine having at least one aliphatic group of a chain length of at least 8 carbon atoms, said film having a thickness of amines corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

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