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[54] **METAL WARE HAVING WATERPROOF SURFACE AND PROCESS FOR MAKING**
9 Claims, 1 Drawing Fig.

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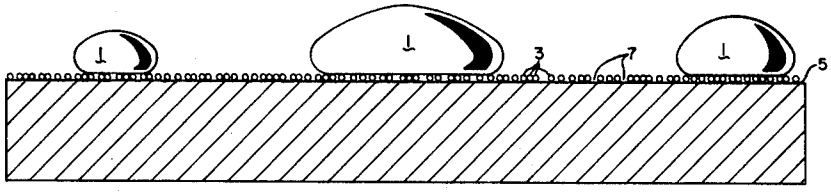
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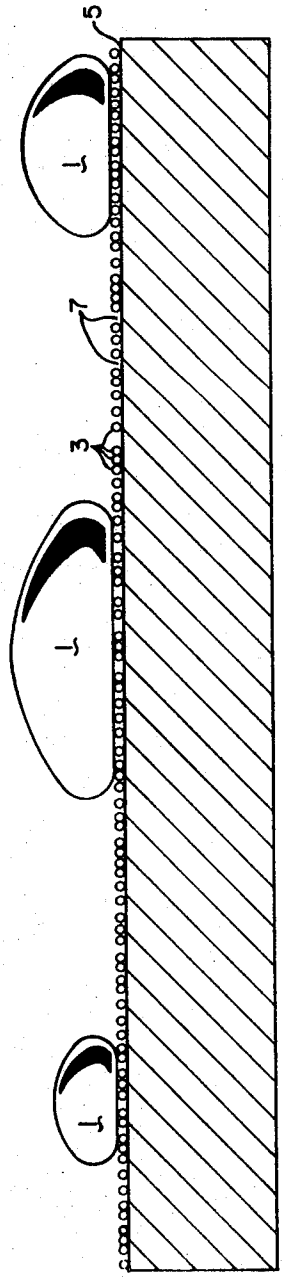
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ABSTRACT: A method is disclosed for waterproofing metallic surfaces by applying thereto the hydrophobic reaction product of a particulate metal oxide or metalloid oxide and an organosilicon compound.




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METAL WARE HAVING WATERPROOF SURFACE AND PROCESS FOR MAKING

THE PRIOR ART

Prior art methods for rendering metallic surfaces waterproof have generally involved the application of various film forming substances thereto. Accordingly, metallic surfaces are often coated with paints, oils, enamels, lacquers, polymers, waxes, etc. which thereafter function as moisture barriers between the metal surface and the atmosphere. Often, however, it is desirable or even imperative that metallic surfaces be rendered waterproof without coatings of the types described above. For instance, ferrous metals such as cold-rolled sheet are normally rustproofed upon manufacture by application of various oils or waxes thereto. However, when such sheet metal is to be formed, such as by drawing, into finished wares it is generally necessary that the metal be cleansed as thoroughly as possible of the rust preventive film both for purposes of forming and to prepare the end-item surfaces for the generally ultimately desired decorative and/or protective finishing thereof, e.g. painting or plating. Similarly, while such common metallic objects as nails are often rustproofed by applying oils thereto, the resulting treated nails are often rendered tacky and tend to collect substantial amounts of dust and grime on storage. Also, when a metallic object is to be exposed to an oxygen atmosphere it is imperative, for fire prevention purposes, that hydrocarbonaceous oils be assiduously stripped therefrom. In accordance with the present invention, however, the above and other problems normally relating to the above-mentioned prior art methods for rustproofing and/or waterproofing of metallic surfaces have been substantially completely overcome.

OBJECTS OF THE INVENTION

It is a principal object of the invention to provide a novel method for waterproofing metallic surfaces.

It is another object of the present invention to provide a novel method for rendering metallic surfaces resistant to water induced corrosion.

It is another object of the invention to provide a novel process for rustproofing ferrous metal surfaces.

Other objects and advantages of the present invention will in part be obvious and will in part appear hereinafter.

THE DRAWING

The drawing forming part hereof is a sectional, diagrammatic view of a typical metallic surface treated in accordance with the process of the invention and bearing thereon several water droplets.

GENERAL DESCRIPTION OF THE INVENTION

In accordance with the present invention it has been discovered that a metallic surface is substantially waterproofed when there is applied thereto a coating consisting of colloidal particulate metal oxides or metalloid oxides which, in turn, have been chemically reacted with organosilicon compounds so as to render said oxides hydrophobic.

DETAILED DESCRIPTION OF THE INVENTION

The colloidal oxides useful in the practice of the invention can generally be any metal or metalloid oxide having an average ultimate particle diameter of less than about 0.5 micron and preferably less than about 0.1 micron. In order that the particulate metal or metalloid oxide be rendered substantially permanently hydrophobic by a chemisorption reaction thereof with the organosilicon compound (which reaction will be discussed in detail below), it is further necessary that said starting oxide material bear on the surface thereof at least about 0.25 milliequivalent per gram and preferably above about 1.0 milliequivalent per gram of hydroxyl groups. Specific examples of suitable available starting materials are: pyrogenic and precipitated silicas, titania, alumina, zirconia, vanadia, chromia, iron oxide, silica/alumina, etc.

Additionally, it is desirable that the oxide be relatively nonporous, i.e. that the preponderance of the total surface area thereof be expressed as external rather than internal (pore volume). Generally speaking, the relative porosity of a colloidal particulate solid can be readily determined by (1) calculating the surface area thereof predicated upon the average particle diameter (such as visually determined by electron micrographic analysis) and assuming no porosity; (2) experimentally determining the actual total surface area by the well known BET-N_2 adsorption method. For the purposes of the present invention, those particulate colloidal solids having a difference between the calculated (electron micrographic) and BET-N_2 surface areas which represents less than about 10 percent of the BET-N_2 surface area are to be considered relatively nonporous. For convenience, the following equation may be utilized:

$$\frac{\text{BET-N}_2\text{ S.A.} - \text{E.M. S.A.}}{\text{BET-N}_2\text{ S.A.}} \times 100 = \%\text{ porosity}$$

Due principally to the above porosity consideration as well as their normally relatively high hydroxyl group population and availability, pyrogenic and precipitated silicas are starting materials of choice.

Pyrogenic silicas are generally defined as those silicas produced by the oxidation and/or hydrolysis at high temperature (above about 800° C.) of a silicon compound such as silicon tetrachloride, silicon disulfide and the like. Further details of pyrogenic silica producing processes can be had by references to U.S. Pat. Nos. 2,428,178; 2,990,249; 3,043,062; 3,203,759; 3,416,980; 3,130,008; 3,086,841 and 3,024,089.

The precipitated silicas are produced by the acidulation or neutralization of an aqueous alkali metal silicate solution. Said acidulation or neutralization results in precipitation of a silica hydrosol from solution which is then aged to a gel or semigel state, washed free of alkali metal salts, dried and ground to a colloidal impalpable powder. Further details relating to various permutations of the generalized precipitated silica process outlined above can be had by reference to U.S. Pat. Nos. 2,865,777; 2,900,348; 2,913,419; 2,995,422; 3,010,791; 3,034,913; 3,172,726; 3,250,594.

The art of treatment by reaction of metal oxides and metalloid oxides, particularly colloidal silicas, with various organosilicon compounds has been rather extensively developed. Accordingly, suffice it to say, that various organosilicon compounds bearing at least one functional moiety/molecule can be reacted through said functional moiety with hydroxyl groups existing on the surface of metal oxides or metalloid oxides. The resulting reaction product is characterized as a metal oxide or metalloid oxide having chemically bonded to the surfaces thereof organosilicon constituents or organosilicon groups represented generally by the formula:

$$\epsilon\text{—O—Si R}_a\text{X}_b$$

wherein ϵ represents the oxide surface; O is oxygen; Si is silicon; each R is any alkyl, aryl, arylalkyl, alkoxy, or aryloxy group; a is a number from 1 through 3; X is any halogen or hydroxyl group; b is a number from 0 through 2; and $a+b=3$. In the practice of the present invention it is much preferred that "a" in the above formula be at least 2 and that "b" be 1 or less. In any case, for the purposes of the instant invention, it is necessary that the metal oxide or metalloid oxide have chemically bound to the surface thereof at least about 0.5 and preferably above about 4 percent by weight thereof of such organosilicon constituents.

Specific examples of organosilicon compounds which can be reacted with the colloidal oxides useful in the invention are: organohalosilanes such as $(CH)_3$ SiCl, $(CH_3)_2SiBr_2$, $(CH_3)SiCl_3$, $C_4H_9SiCl_3$; organosilylamines such as $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2$, $(CH_3O)_2(CH_3)SiCH_2CH(CH_3)CH_2NH—CH_2CH_2NH_2$; organodisilazanes such as $(CH_3)_3—Si—NH—Si(CH_3)_3$ and $(C_4H_9)_3—Si—NH—Si(C_4H_9)_3$, etc. Organodisilazane treated oxides are particularly advantageous to

utilize in the present invention due to their generally superior hydrophobic properties and their normally total lack of occluded halogens thereon. Details concerning various specific processes for reacting colloidal metal and metalloid oxides with organosilicon compounds can be had by reference to the following U.S. Pat. Nos.: 2,510,661; 2,589,705; 2,705,206; 2,705,222 and 3,023,181.

Generally speaking the surfaces of any metal or alloys of metals of Groups Ib through VIII of the Mendeleev periodic table can be treated by the process of the invention. Thus, aluminum, titanium, molybdenum, copper, lead and the like can be substantially nonwettable by coating thereof with the hydrophobic colloidal oxides defined hereinabove. However, as will be demonstrated in the examples forming part hereof, ferrous metals or alloys normally subject to water induced rusting can be rendered substantially rust resistant by the process of the invention.

The method of application of the colloidal hydrophobic oxide treating agent to the metallic surface is generally not critical, provided, of course, that substantial contact of the treating agent with the metallic surface is achieved. Accordingly, the application step can be achieved, if desired, by simply applying the dry hydrophobic oxide, such as by dusting, to the surface to be treated. However, for purposes of ease and uniformity of application, particularly to vertical surfaces, we have further found that dispersion of the metal oxide in an inert volatile organic solvent provides an excellent system for subsequent application to the metallic surface. Such dispersions may be applied by spraying, printing, etc. or may be utilized as dip baths in which the metallic articles may be submersed. Light hydrocarbons such as mineral spirits or isopentane, alcohols such as methyl, isopropyl, propyl, butyl and pentyl alcohols and acetone have been found to generally constitute excellent solvent media which are usually inert both as to the hydrophobic oxides and the metal surfaces to be treated and which are further benefited by their volatility. The hydrophobic oxides may be dispersed in the inert liquid in any amount which does not result in substantial thickening of the resulting dispersion, e.g. up to about 15 weight percent of the total. Obviously, subsequent to the application step, the inert solvent medium is removed such as by air-drying, heating or other techniques known to the art.

The amount of metal oxide to be applied is subject to wide variation is not normally critical to the overall desired waterproofing effect. Generally speaking, it is desirable that the treated metallic surface be as uniformly coated as practicable such as to provide at least a monoparticulate layer of the metal oxide thereon. While heavier multilayer coatings may be utilized as a matter of choice, such coatings are generally only slightly, if any, more waterproof than the aforementioned monoparticulate layer of the metal oxide.

There follow a number of nonlimiting examples:

EXAMPLE 1

Ten 12*d* common nails were carefully washed with acetone. Five of these washed nails were utilized as controls while the remaining five were dipped for 5 seconds in an isopropyl alcohol bath containing dispersed therein about 2 weight percent of the total of a hydrophobic pyrogenic silica having an original BET-N_2 S.A. of about 200 M^2**200** M^2/gram, an original hydroxyl group concentration of about 1.5 meg./gram, an average ultimate particle diameter of about 0.015 micron and a surface area calculated from the average ultimate particle diameter of about 190 M^2/gram. Accordingly the porosity of this silica was about 5.0 percent. The hydrophobic properties of the base silica were imparted by reaction thereof with about 5 percent by weight of the silica of hexamethyldisilazane. Subsequent to the dipping step, the treated nails were air-dried. Next, all 10 nails were submerged in a saline water filled 5,000 ml. beaker. Within a few hours the untreated nails were observed to bear a rust coating which increased in severity over a 10-day period to such an extent that the nailheads were totally obscured by rust floc at the end of said period. The treated nails, however, remained bright and unrusted. Moreover, as viewed under the water surface from the moment of submersion, the silica treated nails were observed to have a silvery sheen over the entire surfaces thereof, suggesting the presence of an air layer formed between the metal surfaces and the water.

EXAMPLE 2

Clean test plates, each of 0.125×8×10 inch dimensions prepared from the following metals and metal alloys: type 403 stainless steel, S.A.E. 4130 chrome-molybdenum steel, 6061 aluminum, lead, titanium, zinc, and copper. Two plates were produced from each of said metals. The test plates were then placed in a panel fence at about a 45° angle from the horizontal. One of each type of the metal plates was left untreated. The remaining plates, however, were treated by spraying thereon an acetone dispersion containing, as the dispersed phase, about 2 wt. percent of the same type of treated silica as utilized in example 1. Said treated plates were then allowed to air dry. Next, water was sprayed on each of the panels simulating moderate rainfall for about one hour. During this period the untreated panels were observed to be wet out thoroughly by the sprays. However, the treated plates were substantially completely waterproofed by the hydrophobic metal oxide treatment thereof as evidenced by the immediate beading up and runoff of the water therefrom. Additionally, the water film formed over the untreated plates required substantial time to dry, the treated plates were substantially completely dry almost immediately subsequent to the cessation of the water sprays thereon.

Next, without further treatment of any kind, each of the plates, except for the aluminum and titanium plates were sprayed with a pigmented acrylic lacquer and dried under infrared lamps. The aluminum plates were sprayed with zinc chromate primer and air dried. The plates were then carefully examined for gloss, color, and film adhesion characteristics and no significant differences could be detected between the treated and untreated plates.

Referring now to the drawing, which, it is to be noted, is merely for illustrative purposes and is thus not to be considered as properly scaled. It is believed that the optical phenomenon experienced and described in example 1 when the nails were submerged beneath the water surface is due to the formation of an air layer between the water and the treated metallic surface. Accordingly, it is believed that the water repulsive properties of hydrophobic oxide particles 3 are sufficiently great to prevent the wetting thereof by water droplets 1. Thus, an effective water barrier is formed between metal surface 5 and water droplets 1 by the hydrophobic metal oxide or metalloid oxide coating even through discontinuities or spaces 7 between particles 3 are present. As a further advantage provided by the process of the invention, it has been noted that when a concave metallic surface is treated with a hydrophobic metal oxide or metalloid oxide, the concavity filled with water and thereafter the water is frozen, little or no adherence of the resulting ice cake to the metallic surface is encountered. Accordingly, the process of the invention can also be utilized to advantage for those applications wherein it is desired to render metallic surfaces resistant to the formation of adherent ice coating thereon. Accordingly, the treatment of exposed aircraft surfaces in accordance with the process of the present invention can provide marked benefits with respect to inflight icing problems.

What is claimed is:

1. A metal ware having a substantially uniform discontinuous surface coating thereon consisting essentially of the hydrophobic reaction product of a colloidal metal oxide or metalloid oxide having an average ultimate particle diameter of less than about 0.5 micron and at least about 0.5 percent by weight thereof of an organosilicon compound said reaction product having surface structures conforming to the formula:

$$\epsilon O-SiR_aX_b$$

wherein ϵ represents the metal oxide or metalloid oxide surface; O is an oxygen atom of said metal oxide or metalloid oxide surface; Si is a silicon atom; each R is any alkyl, aryl, arylalkyl, alkoxy or aryloxy group; a is a number from 1 through 3; X is any halogen or hydroxyl group; b is a number from 0 through 2; $a+b=3$; and wherein said silicon atom is bonded directly to said oxygen atom.

2. The metal ware of claim 1 wherein said metal comprises iron and is subject to water induced rusting.

3. The metal ware of claim 1 wherein said metal oxide or metalloid oxide has an average ultimate particle diameter of less than about 0.1 micron.

4. The metal ware of claim 1 wherein said metalloid oxide is pyrogenic or precipitated silica.

5. The metal ware of claim 1 wherein the concentration of said organosilicon surface structures represents at least about 4 percent by weight of the surface modified oxide.

6. The metal ware of claim 1 wherein, in the formula

$$\epsilon O-SiR_aX_b$$

a is 3 and b is 0.

7. The metal ware of claim 1 wherein said metal oxide or metalloid oxide has a percent porosity of less than about 10.

8. The metal ware of claim 1 wherein said metal oxide or

metalloid oxide is rendered hydrophobic by reaction thereof with an organodisilazane.

9. A process for rendering the surface of metals waterproof which comprises:

a. providing a dispersion consisting essentially of:

i. the hydrophobic reaction product of a particulate metal oxide or metalloid oxide having an average ultimate particle diameter of less than about 0.5 micron and at least about 0.5 percent by weight thereof of an organosilicon compound, said reaction product having surface structures conforming to the formula;

$$\epsilon O-SiR_aX_b$$

wherein ϵ represents the metal oxide or metalloid oxide surface, O is an oxygen atom of said metal oxide or metalloid oxide surface, Si is a silicon atom, each R is any alkyl, arylalkyl, alkoxy or aryloxy group, a is a number from 1 through 3, X is any halogen or hydroxyl group, b is a number from 0 through 2, $a+b=3$, and wherein said silicon atom is bonded directly to said oxygen atom and

ii. an inert organic volatile solvent;

b. applying said dispersion to the metal surface; and

c. removing the solvent portion of said dispersion from the metal surface.

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