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PROCESS OF RENDERING MASSIVE INORGANIC BODIES HYDROPHOBIC

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This invention relates to the rendering of massive inorganic structural surfaces hydrophobic and organophilic.

This application is a continuation-in-part of my copending applications Serial No. 273,578, filed May 13, 1939, now Patent No. 2,338,206, and Serial No. 477,453, filed February 27, 1943.

Surfaces of inorganic bodies, particularly those of massive form, are usually hydrophilic in their characteristics. Thus, such surfaces are easily wetted by water and conversely are difficult to wet by water-immiscible organic compounds such as oils, paints, putties, greases, and the like. This hydrophilic characteristic of such surfaces is often of considerable disadvantage. For example, certain structural surfaces, because of their porous nature, tend to transmit water due to this hydrophilic character of the materials. This difficulty is frequently encountered in connection with leaks in housing structures where brick, stone, and cement elements are involved. The hydrophilic characteristics of certain structural surfaces are also troublesome in that said surfaces usually have a film of moisture present thereon under prevailing atmospheric conditions of temperature and humidity. Because of this water film, these surfaces tend to resist wetting by water-immiscible organic liquid systems such as paints with which it is desired to coat the preferentially water-wetted surface.

In the past, attempts have been made to overcome the hydrophilic character of structural surfaces by coating them with water-immiscible organic systems such as oil paints and the like. A difficulty has been that the applied water-immiscible system, because of the adsorbed film of water already present on the surface, only superficially covers this surface without establishing intimate contact. As a result of this lack of intimate contact insufficient adhesion is developed and the organic film soon becomes detached from its support, thus ending its protective action. This type of failure in the protective film is particularly common in the painting of structural surfaces such as brick, plaster, and concrete. It is usually impractical to remove the film of adsorbed water by drying such surfaces under prevailing atmospheric conditions to insure intimate contact of the applied organic systems.

Other less porous massive inorganic structural surfaces, including glass, chinaware, marble, plain bright metal surfaces, and the like, also often resist the application of decorative and protective films because of the presence of an adsorbed moisture film thereon. The film of

adsorbed water on the hydrophilic surface can be removed by a heating process but this is for the most part impractical, particularly for structural materials, and as a result of the adsorbed film it is difficult to wet the surface with an organic system.

This invention has as its object the provision of a simple and practical process for changing the properties of the ordinarily hydrophilic surface of structural bodies so that said surface is hydrophobic. Another object is to accomplish this result under ordinary atmospheric conditions of temperature and humidity. Another object is to accomplish this result by use of an aqueous solution that renders the structural surface hydrophobic even in the presence of the water film present on such surface. A still further object is to render an inorganic structural surface having a film of condensed moisture thereon receptive to water-immiscible organic systems. Still another object is to render a glass surface hydrophobic and organophilic without changing its appearance. Other objects will be apparent from the following description of the invention.

The above and other objects may be accomplished in accordance with the following invention which comprises treating a massive inorganic structural hydrophilic surface with an acyclic, aliphatic amine having at least one aliphatic group of a chain length of at least 8 carbon atoms and salts of such amines.

The long-chain amines impart water repellence and organophilic character to the 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 struc-

tural surfaces from an hydrophilic to an hydrophobic, organophilic character, the long-chain amine may be applied to the surface by any of the methods, described in my copending application Serial No. 273,578, 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 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 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 $\frac{1}{4}\%$, $\frac{1}{16}\%$ and less; whereas, rougher surfaces such as masonry and the like, often require a somewhat higher concentration due to the somewhat higher specific surface.

In accordance with the preferred embodiment of my invention, the massive inorganic structural hydrophilic surface will be treated with a dilute aqueous solution of a water-soluble salt of a water-insoluble long-chain alkyl monoamine, having at least one alkyl group of a chain length of from 10 to 24 carbon atoms, thereby forming on such surface a thin, continuous, homogeneous coating of the water-soluble salt which is in the range of molecular dimensions. Coatings of this character are usually from 15 to 25 Angstroms in thickness and can usually be deposited from aqueous solutions of less than 1% in concentrations.

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

Example I

In the glazing of a window frame with 8" x 10" single thickness window glass carrying a condensed film of moisture, the edges of the outer surfaces of the glass where putty is to be applied are wiped with a cloth dampened with a 0.25% aqueous solution of dodecylammonium

chloride. The glazing operation is then completed in the normal manner by application of putty to make the seal between the glass and frame. If the treatment of the moisture-laden plate glass surface with the long-chain amine salt is omitted, great difficulty is experienced in making the putty stick to the wet glass surface.

Example II

In the course of the construction of a concrete highway after the usual finishing of the surface a few hours after pouring, the surface is then further treated by spraying with a 0.5% aqueous solution of octadecylammonium chloride to form a thin film of the amine salt on the surface. The solution can be brushed on with equally good results. By this treatment of the concrete surface the rate of passage of moisture from the interior of the concrete to the surface is materially diminished. The process of this invention can therefore be utilized to replace the costly laborious methods ordinarily practiced in curing of concrete, such as extended water spraying or covering with dirt, straw, or tarpaulin.

Example III

A concrete basement wall of a dwelling is sprayed with a 0.5% aqueous solution of hexadecylammonium chloride. By this treatment the particles at the cement surface are rendered hydrophobic so that the cement is not readily wetted by water and water cannot therefore readily permeate the surface. The water resistance of the surface can be further augmented by coating the treated surface with a water-immiscible organic liquid since this readily wets the treated surface even in the presence of moisture and aids in the subsequent exclusion of water.

A concrete water tank or a concrete barge can be similarly treated to provide water resistance at the surface.

Example IV

A 0.5% aqueous solution of octadecylammonium chloride is brushed on the exterior surface of a brick wall. The surface of the brick is rendered rainproof by this treatment.

Example V

A piece of laboratory glassware having on the surface thereof a layer of condensed moisture is rubbed with a cloth dampened with a 0.25% solution of dodecylammonium chloride. The surface of the glass is thereby rendered hydrophobic and organophilic and can be written on with a wax crayon. A similar piece of untreated glassware cannot successfully be marked with the wax crayon unless steps are taken to remove the film of moisture, for example, by heating or by friction.

The film of dodecylammonium chloride can be applied to the moist glassware directly from the wax crayon pencil by previously mixing 0.5% of dodecylammonium chloride with the wax of the crayon. The pencil thus prepared marks moist glassware very satisfactorily.

Example VI

The surface of plain chinaware is prepared for painting with an organic vehicle system by application of a film of octadecylammonium chloride applied by wiping the surface of the chinaware with a cloth dampened with a 0.25% aqueous solution of this compound. A glazing composition containing an organic solvent which is applied in the form of a design readily wets the

ceramic surface. With untreated chinaware, difficulty is frequently experienced in obtaining suitable wetting of the surface by the glazing composition in the organic solvent.

The long-chain amines, which may be employed in accordance with my invention, include decylamine, undecylamine, dodecylamine, tetradecylamine, pentadecylamine, hexadecylamine, octadecylamine, eicosylamine, tetracosylamine, octylamine, heptadecylamine, ethyldecylamine, dioctylamine, didodecylamine, methyl octadecylamine, dioctadecylamine, octyldodecylamine, dimethyl dodecylamine, dimethyl octadecylamine, tritradecylamine, ethylmethyl dodecylamine, diethyloctylamine, 9,10-octadecenyamine, dimethyl-9,10-octadecenyamine and the like. Also, included within the scope of my invention are mixtures of two or more of such amines, 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 coconut oil, palm oil, sheep tallow, 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.

When aqueous solutions are employed, I preferably employ in such solutions the water-soluble salts of water-insoluble long-chain alkyl monoamines having at least 1 alkyl group of a chain length of 10 to 24 carbon atoms. The long-chain amines which may be used in the form of their water-soluble salts in this process are the long-chain alkyl primary amines, for example, decylamine, undecylamine, dodecylamine, tetradecylamine, pentadecylamine, hexadecylamine, octadecylamine, eicosylamine, and tetracosylamine. Secondary long-chain alkylamines which can be used are ethyldecylamine, didodecylamine, methyl octadecylamine, and the like. Tertiary long-chain alkylamines that can be used are dimethyl dodecylamine, dimethyl octadecylamine, and the like. Unsaturated long-chain monoamines can also be used, for example, 9,10-octadecenyamine, dimethyl-9,10-octadecenyamine, and the like. Mixtures of the above amines, 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 coconut oil, palm oil, sheep tallow, or peanut oil can be used. The primary alkylamines having an alkyl chain of from 12 to 18 carbons are particularly desirable.

The water-soluble long-chain amine salts are those of inorganic and organic acids which salts are water-soluble at least to the extent of 0.1% at 20° C. For example, they are salts of acids such as hydrochloric, nitric, sulfamic, formic, acetic, propionic, and the like. Of this group, the monobasic inorganic acids are preferred, particularly hydrochloric acid.

Typical amine salts useful in this invention, in addition to those of the examples, are dodecylammonium nitrate, hexadecylammonium acetate, octadecylammonium sulfamate, dodecylammonium formate, 9,10-octadecenyammonium chloride, hexadecylammonium formate, and the like. These salts can be readily prepared from the amine and the acid by a neutralization procedure well known in the art.

In accordance with the preferred embodiment of my invention, the process may be carried out by applying the water-soluble long-chain amine

salts in the form of a dilute (usually less than 1%) aqueous solution. Only small proportions of the water-soluble salts are necessary since films formed on the surfaces are very thin. Generally, aqueous solutions of from 0.1% to 0.25% or 0.5% of the long-chain amine salts are adequate. By "very thin" is meant that the films are in the range of molecular dimensions or in the order of from 15 to 25 Angstroms in thickness. One gram of water-soluble amine salt of the type described herein can be used to cover from 200 to 600 square meters of surface of the material coated to change the character of the surface from hydrophilic to hydrophobic.

The solutions may be applied by dipping, brushing, spraying or by any other convenient method such as passage between impregnated rolls. Any excess of the water-soluble amine salt can be removed by draining, washing with water, or by wiping, and the like. The application may be made hot or cold since temperature of application is not a critical factor.

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 1% of dodecylammonium 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, stone-work, 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 the process of this invention in rendering hydrophilic massive inorganic structural surfaces hydrophobic or water repellent has been found especially advantageous in the treatment of surfaces of relatively great extent in one plane, use can also be made of this process for rendering water repellent inorganic fibrous materials such as glass wool, of asbestos fiber, mineral wool,

and the like where the fibrous material is of appreciable length (i. e., exceeding $\frac{1}{4}$ "'). The fibrous materials treated by the process of this invention can be more readily colored and their water repellent properties are of value when the materials are used as insulation in structures. This invention is useful for metal surfaces but is of particular importance for use on non-metallic inorganic massive structural surfaces, especially siliceous surfaces, e. g., glass and ceramics, and on calcareous surfaces, e. g., cement.

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 absorbed 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.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is understood that this invention is not to be limited to the specific embodiments shown and described.

I claim:

1. The process of rendering siliceous construction materials resistant to the passage of water therethrough which comprises treating such siliceous materials after formation thereof into their ultimate shape with amines chosen from the group consisting of aliphatic amines containing at least eight carbon atoms in an alkyl group thereof, and salts thereof.
2. The process of rendering siliceous construction materials resistant to the passage of water therethrough which comprises treating such siliceous materials after formation thereof into their ultimate shape with an aqueous solution of an aliphatic amine salt containing at least eight carbon atoms in an alkyl group thereof.
3. The process of rendering siliceous construction materials resistant to the passage of water therethrough which comprises treating the siliceous constructional material after formation into its ultimate shape with dodecylamine hydrochloride.
4. The process of rendering siliceous construction materials resistant to the passage of water therethrough which comprises treating the siliceous constructional material after formation into its ultimate shape with octadecylamine hydrochloride.
5. A preformed siliceous constructional material in ultimate shape containing an amino compound chosen from the group consisting of aliphatic amines having at least eight carbon atoms in an alkyl group thereof, and salts thereof.
6. A cast or molded set siliceous material containing a substance chosen from the group consisting of aliphatic amines having at least eight carbon atoms in an alkyl group thereof, and salts thereof.
7. Brick containing a substance chosen from the group consisting of aliphatic amines having at least eight carbon atoms in an alkyl group thereof, and salts thereof.
8. Cast concrete containing a substance chosen from the group consisting of aliphatic amines having at least eight carbon atoms in an alkyl group thereof, and salts thereof.
9. The process of rendering bricks water-repellent which comprises treating the brick with an amino compound chosen from the group consisting of aliphatic amines containing at least eight carbon atoms in an alkyl group thereof, and salts thereof.
10. The process of rendering cast concrete

structures water-repellent which comprises treating the concrete structure with an amino compound chosen from the group consisting of aliphatic amines containing at least eight carbon atoms in an alkyl group thereof, and salts thereof.

11. The process of rendering hydrophilic siliceous massive structural surfaces hydrophobic and organophilic which comprises bringing into contact with said surfaces a dilute aqueous solution of a water-soluble salt of a water-insoluble long-chain alkyl monoamine having at least one alkyl group of a chain length of from 10 to 24 carbon atoms, and removing any excess of said solution, so as to produce on said surface a coating of said salt in the range of molecular dimensions.

12. The process for rendering a hydrophilic

siliceous massive structural surface water repellent and organophilic which comprises bringing into contact with said surface a dilute aqueous solution of a water-soluble salt of a water-insoluble long-chain alkyl monoamine having at least one long-chain alkyl group of from 12 to 18 carbon atoms, and removing any excess of said solution, so as to produce on said surface a coating of a water-insoluble salt of said amine of molecular dimensions.

13. The process of claim 11 wherein the water-soluble salt is a hydrochloride of the amine.

14. The process of claim 12 wherein the water-soluble salt is dodecylamine hydrochloride.

15. The process of claim 12 wherein the massive structural inorganic surface is a glass surface.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 6, for the patent number "2,338,206" read --2,333,206--; page 4, first column, line 59, for "absorbed" read --adsorbed--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 10th day of October, A. D. 1944.

Henry Van Arsdale

Acting Commissioner of Patents.

(Seal)