

1

2,991,204
HYDROPHILIC SURFACE

Melvin J. Astle, Cleveland, Ohio, assignor to Harris-Intertype Corporation, a corporation of Delaware
No Drawing. Filed June 19, 1957, Ser. No. 666,787
17 Claims. (Cl. 148-6)

The present invention relates to a support member having a hydrophilic surface and to a process of making such an article.

This is a continuation-in-part of my application filed February 25, 1953, and assigned Serial No. 338,887.

In many industrial applications, it is desirable or necessary for a surface of an article to have an affinity or attractiveness for water. As exemplary of this, the usual "water fountain" of a lithographic press includes so-called intermediate roller which is continuously wetted by the water of the fountain and transfers the water to fabric covered dampening rollers which apply the water to a planographic plate for subsequent printing, as practiced in the lithographic art. Not only must such a roller continuously carry a film of water over its entire surface, but the roller must resist and reject any greasy ink which may be picked up by the dampening rollers from the image areas of the plate. Otherwise, even a gradual accumulation of ink renders the roller unfit for use and causes loss of press time while it is cleaned. It is, therefore, essential that such rollers possess and retain a hydrophilic and hence oleophobic character over extended periods of time.

In a like manner, additional articles such as plates, sheets, and other shaped objects often require an enhanced surficial effect which makes such articles available for applications where water-attractiveness provides a particular utility. The problem is peculiarly accentuated in that it has become increasingly popular to fabricate such articles from aluminum because of other desirable properties of aluminum, although aluminum is not readily wetted by water.

It is, therefore, a principal object of the present invention to provide a backing or support member having a hydrophilic surface and a process of producing it.

Another object is to provide a supporting surface with a hydrophilic coat which retains its hydrophilic character over extended periods of time.

A further object is to provide a coat for a metal surface having substantially dual layers, one of which chemically unites with the metal surface and the other of which chemically unites with the first layer and provides water-attractiveness.

A still further object is to provide an aluminum surface with a hydrophilic coat to enable the aluminum to be readily wetted by water.

Other objects will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features herein-after fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

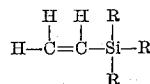
I have found that a hydrophilic character can be imparted to a supporting member or surface by a copolymer of a vinyl tri-substituted silane and an acrylic compound. Rollers or other articles provided with such a hydrophilic coat are readily wetted by water and retain their hydrophilic character over extended periods of time.

The type of backing or supporting member is not critical to the invention so long as the silane will adhere thereto. Ordinarily, a clean and dry metallic surface is preferred where there is a direct chemical union between

2

a polysilane or the silane portion of a copolymer, as hereinafter noted, and the surface of the metal such as zinc, copper, tin, lead, chromium, magnesium, aluminum, steel, and the like. However, other support members may be employed. For example, a paper sheet or plate suitably backed, or the paper sheet impregnated with a thermosetting resin such as phenolformaldehyde, can be employed. In these instances, the polysilane or copolymer are also bonded to the paper or its resin impregnant but adhere thereto in the manner of a paste and are not chemically united with this type of backing member. The heat-resistant resin is preferably used since it protects the paper during the heating steps which may be used in preparing a water-attractive article in accordance with the method disclosed herein. In the case of metallic surfaces, oxides may be present, either through exposure to air or through special treatment. For example, in the case of aluminum, the surface may if desired be chemically or electrolytically anodized, although this is not necessary.

For purposes of the invention, I have found that a vinyl tri-substituted silane having the following formula may be used:



wherein R is a monovalent substituent selected from the group consisting of alkoxy radicals, aryloxy radicals, and halogen atoms. For example, when an alkoxy radical is used, R may be methoxy, ethoxy, propoxy, butoxy, and pentoxy; when an aryloxy radical is used, R may be phenoxy, tolyloxy, and xylyloxy; and when a halogen atom is used, R may be chlorine, fluorine, iodine, and bromine. Partial polymers of the foregoing silanes may also be used. The vinyl trimethoxy and vinyl triethoxy silanes give the best results of the vinyl trialkoxy silanes, and vinyl trichloro and vinyl tribromo silanes are better than the other vinyl tri-halogenated silanes.

The acrylic compound with which the vinyl trisubstituted silane copolymerizes may be acrylic acid, methacrylic acid, the water soluble salts of such acids, such as, the ammonium, sodium, and potassium salts, acrylamide and methyl acrylamide.

The vinyl tri-substituted silane, hereinafter more simply referred to as the silane, and the acrylic compound may be simultaneously applied to the backing member as a mixture in a common solvent and then copolymerized. The silane portion chemically reacts with a metal surface, when this forms the backing member, and provides a strong bond therewith, while the acrylic portion provides the water attractiveness.

Ordinarily, however, it is preferred to form the copolymer directly on the backing member by reacting the ingredients in situ. Each ingredient is successively applied from a solvent. This provides a control on the layer of each reactant and, in particular, this technique has the advantage that only a part of the silane layer need react with the acrylic compound, so as to leave a covering of uncopolymerized silane immediately adjacent the backing member. This result is preferred, since a bond between uncopolymerized polysilane and the metal is stronger than a bond between the copolymer and the metal. Thus, in the preferred form of the invention, considering a direction away from a metal backing member, there is a metal-to-polysilane bond, a polysilane-to-copolymer bond, and a surficial water attractive effect due to the acrylic portion of the copolymer. Catalysts may be used to speed the copolymerization and reduce the time required for producing the copolymer.

More particularly, the silane is applied to a receiving

surface from a solvent. Any solvent may be used which satisfies these requirements:

- (1) Dissolves the silane.
- (2) Does not react with the silane.
- (3) Wets the supporting member.
- (4) Vaporizes at elevated temperatures.

The aromatic solvents such as toluene, benzene, and xylene have been found quite satisfactory as the solvent for the silane. However, the aliphatic solvents such as pentane, hexane, heptane, and octane, and the chlorinated aliphatics such as carbon tetrachloride and chloroform are also satisfactory. Any known method of coating suitable for providing a thin complete uniform coat may be used such as, for example, roller coating, blade coating, dipping, or spraying.

Following the silane application, heat is applied to remove the solvent and chemically unite the silane to the preferred metal backing surface. Temperatures of about 120° C. to about 200° C. are effective for so uniting the silane, though this range is not critical. There is also condensation of the silane with cross linking to form a polysilane, but the vinyl groups at this stage are unreacted.

From the foregoing, it will be appreciated that the concentration of the silane in its solvent is not critical. Ordinarily, a sufficient amount of silane is dissolved in the organic aromatic solvent to deposit a coat of desired area and thickness. However, repeated applications and dryings may also be used to obtain a desired silane coat. As an example, the silane may range from about 5 percent to 15 percent of the solvent. A sufficient amount of a catalyst such as ethanalamine may also be present to speed the reaction. A concentration of catalyst of one percent or less has been found to be satisfactory, although the range is not critical.

A solution of the acrylic compound is next applied over the silane film using any suitable technique, such as one of those described previously for applying the silane. The solvent for the acrylic compound must be compatible with the silane, that is, the solvent must be unreactive with the condensed polysilane and capable of penetrating or soaking into it. As used here and in the claims, the term "compatible" solvent is intended to have this definition.

By penetrating the silane film, the solvent facilitates the acrylic compound in reaching the vinyl groups of the silane for copolymerization therewith. Inasmuch as the silane film has been chemically anchored to the metal by the preceding treatment, the silane film can not be lifted from the metal surface by any solvent used for the acrylic compound. The amount of penetration and resulting stratification of the condensed polysilane and copolymerized silane-acrylic compound can be varied by the temperature and time of contact by the acrylic compound solvent with the polysilane coat. Indeed, there may be little or no penetration with only an interfacial copolymerization of the polysilane film and the acrylic compound.

The solvent for the acrylic compound is accordingly not critical and may be benzene, toluene, xylene, pyridine, petroleum ether, methanol, ethanol, butanol, monoalkyl ethers of ethylene glycol (Cellosolve) such as the methyl, ethyl, butyl, and isobutyl ethers of ethylene glycol, chloroform, carbon tetrachloride, and the like.

The alcohols are substantially insoluble with the condensed polysilane, and, their use results, accordingly, in little or no penetration of the silane coat. Benzene, toluene, and glycol are good solvents for both the silane and acrylic compound.

The concentration of the acrylic acid in its solvent is not critical. An amount sufficient to cover the condensed silane film to an extent desired may be initially incorporated in the solvent. As an example, the concentration may range from about 5 percent to 15 percent, although concentrations outside of this range may be em-

ployed. A sufficient amount of a catalyst may also be incorporated with the acrylic compound. The free radical-forming catalysts such as benzoyl peroxide, acetyl peroxide, urea peroxide, hydrogen peroxide, cumene hydroperoxide, potassium persulfate, and the like are useable. An exemplary proportional range which may be used for the catalyst is up to one per cent of the solution.

Following the application of the acrylic compound, the assembly is heated to produce a hydrophilic, water-insoluble copolymer. The rate of the copolymerization is affected by the temperature, catalyst, and concentration of catalyst employed. An operative but not exclusive range for so heating the silane and acrylic compound reactants is from about 120° C. to 300° C. for about 10 minutes to 12 hours. Higher temperatures, within limits imposed by the backing material, may be employed with corresponding reduction in time of heating. As an example, heating at 270° C. has produced satisfactory copolymerization in 10 minutes. As further evidencing the non-criticality of the concentration of the acrylic acid in its solvent, should any free acid remain after the copolymerization, the excess may be readily washed off by water.

Articles having their surfaces coated in the manner indicated have been found to acquire a hydrophilic character which persists over extended periods of time. This is also true in the case of an aluminum surface to which the silane strongly adheres, so that a difficultly wetted aluminum surface may now in accordance with the present invention be easily wetted by water.

Example I

An eight percent solution of vinyl triethoxy silane in toluene is applied to a clean and dry zinc plate and then dried between 125° C. and 200° C. for a sufficient time to drive off substantially all of the toluene and chemically bond the silane to the zinc plate. A ten percent solution of acrylic acid in xylene is then applied to the silane coat and the assembly heated from 135° C. to 160° C. in about 6 hours to produce a hydrophilic, water-insoluble copolymer over the zinc plate.

Example II

The surface of an aluminum roller is coated with a ten percent solution of vinyl trichloro silane in benzene having one percent of ethanalamine and then dried at about 150° C. until substantially all of the benzene is driven off and the silane is bonded to the aluminum roller. A 12 percent solution of methacrylic acid in methanol is applied as an overcoat, and the roller then heated at 150° C. for about eight hours. The roller is used as an intermediate roller in a water fountain of a lithographic press.

Example III

A seven percent solution of vinyl triphenoxy silane in heptane is prepared and about 0.8 percent of ethanalamine is added. The solution is then spread over a support member and the assembly dried at 180° C. until a coat of the silane is deposited. Another solution of seven percent sodium acrylate in xylene having about 0.6 percent of benzoyl peroxide as a catalyst is then applied over the silane coat and the two ingredients copolymerized in situ by heating at 175° C. for about seven hours.

Example IV

A 5 percent solution of vinyl tribromo silane in carbon tetrachloride containing about 0.5 percent ethanalamine as a catalyst is applied to a clean and dry copper plate and then dried between 125° C. and 200° C. for a sufficient time to drive off substantially all of the carbon tetrachloride and chemically unite the silane to the copper plate with accompanying condensation of the silane to produce a polysilane. Another solution of nine percent acrylamide in xylene is applied over the silane deposit for a sufficient time to penetrate only the outer portion of

the silane layer. The xylene solution contains about 0.7 percent of urea peroxide as a catalyst. The assembly is then heated from about 130° C. to 170° C. for about seven hours to produce a copolymer of the silane and acrylamide over and adhering to the polysilane.

Example V

A seven percent solution of vinyl triethoxy silane in toluene is applied to a clean and dry aluminum sheet and then dried between 125° C. and 200° C. for a sufficient time to drive off the toluene and chemically unite the silane to the aluminum sheet with attendant condensation to form a polysilane. A ten percent solution of acrylic acid in xylene is then applied to the silane coat and the assembly heated at 270° C. for 10 minutes to produce a hydrophilic water-insoluble copolymer over the polysilane coat.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the composition and method herein disclosed, provided the ingredients or steps stated by any of the following claims or the equivalent of such stated ingredients or steps be employed.

I therefore particularly point out and distinctly claim as my invention:

1. As an article of manufacture, a metal support having a coat of a polysilane chemically united therewith, said polysilane being formed from a vinyl tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine and bromine, and a hydrophilic film of a copolymer overlying and adhering to said coat consisting essentially of the reaction product of said vinyl tri-substituted silane with an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide.

2. As an article of manufacture, a backing support member provided with an aluminum surface and having chemically united over said aluminum surface a film of a condensed silane consisting essentially of vinyl trimethoxy silane, and a hydrophilic overcoat of a copolymer adhered to said film consisting essentially of the reaction product of said condensed silane with an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide.

3. As an article of manufacture, a backing support member provided with an aluminum surface and having chemically united over said aluminum surface a film of a condensed silane consisting essentially of vinyl triethoxy silane, and a hydrophilic overcoat of a copolymer adhered to said film consisting essentially of the reaction product of said condensed silane with an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide.

4. As an article of manufacture, a backing support member provided with an aluminum surface and having chemically united over said aluminum surface a film of a condensed silane consisting essentially of vinyl trichloro silane, and a hydrophilic overcoat of a copolymer adhered to said film consisting essentially of the reaction product of said condensed silane with an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide.

5. As an article of manufacture, a backing support member provided with an aluminum surface and having chemically united over said aluminum surface a film of a condensed silane consisting essentially of vinyl tribromo silane, and a hydrophilic overcoat of a copolymer adhered to said film consisting essentially of the reaction

product of said condensed silane with an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide.

6. A process of applying a hydrophilic surface to a member comprising applying to the member a solution of a vinyl tri-substituted silane having the general formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine, and bromine, drying to adhere the silane to the member, applying over the silane an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide in a solvent compatible with said silane, and copolymerizing the silane and acrylic compound.

7. A process of applying a hydrophilic surface to a metallic support member comprising applying to the member a solution of a vinyl tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine, and bromine, drying to chemically bond the silane to the metallic support member, applying over the silane a solution of an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide, the solvent forming the acrylic compound solution being compatible with said silane, and heating to copolymerize the silane and acrylic compound.

8. A process as claimed in claim 7 wherein the solvent for the acrylic compound is one selected from the group consisting of methanol, ethanol, butanol, the methyl, ethyl, butyl, isobutyl ethers of ethylene glycol, chloroform, pyridine, petroleum ether, benzene, toluene, and xylene.

9. A process of applying a hydrophilic surface to a metallic support member comprising applying to the member a solution of a vinyl tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine, and bromine, containing an ethanolamine catalyst, drying to drive off the solvent of said solution and chemically unite the silane to the metallic support member, applying over the silane a solution of an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide, the solvent forming the acrylic compound solution being compatible with said silane, and heating to copolymerize the silane and acrylic compound.

10. A process of applying a hydrophilic surface to a metallic support member comprising applying to the member a solution of a tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine, and bromine, drying to drive off the solvent of said solution and chemically unite the silane to the metallic support member with condensation to form a polysilane, applying over the silane an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide in a solvent containing an oxidizing catalyst, said solvent being compatible with the silane, and heating from about 120° C. to 300° C. for about 10 minutes to 12 hours to copolymerize the silane and acrylic compound.

11. A process as claimed in claim 10 wherein said

catalyst is one selected from the group consisting of benzoyl peroxide, acetyl peroxide, urea peroxide, hydrogen peroxide, cumene hydroperoxide, and potassium persulfate.

12. A process for forming a water-attractive surface on aluminum comprising applying to the aluminum a solution of a vinyl tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine, and bromine containing about one percent ethanolamine as a catalyst, drying to drive off the solvent of said solution and chemically unite the silane to the aluminum with condensation of the silane to form a polysilane, applying over the silane an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide in a solvent, said solvent containing a free radical-forming catalyst and being compatible with said polysilane, and heating about 120°C . to 300°C . for about 10 minutes to 12 hours to copolymerize the silane and acrylic compound.

13. A process of applying a hydrophilic surface on a metal backing member comprising applying to the member a solution of a vinyl tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine, and bromine, heating to drive off the solvent of said solution and chemically unite the silane to the metal backing member with condensation of the silane to form a polysilane, applying over the silane an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide in a solvent compatible with said silane, penetrating the outer portion of the silane with the acrylic compound solution, controlling the amount of penetration by the temperature and time of exposure of the acrylic compound solution with the silane, and heating to copolymerize the penetrated silane with the acrylic compound to form a copolymer coat over the condensed silane.

14. As an article of manufacture, a metal support having a coat of a polysilane chemically united therewith, said polysilane being formed from a vinyl tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine and bromine, and a hydrophilic film of a copolymer overlying and adhering to said coat consisting essentially of the reaction product of said vinyl tri-substituted silane with a water soluble salt of an acrylic acid.

15. A process of applying a hydrophilic surface to a metallic support member comprising applying to the member a solution of a tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine, and bromine, drying to drive off the solvent of said solution and chemically unite the silane to the metallic support member with condensation to form a polysilane, applying over the silane a water soluble salt of an acrylic acid in a solvent containing an oxidizing catalyst, said solvent being compatible with the silane, and heating to copolymerize the silane and acrylic compound.

16. As an article of manufacture, a support having a coat of a polysilane adhered thereto, said polysilane being formed from a vinyl tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine and bromine, and a hydrophilic film of a copolymer overlying and adhering to said coat consisting essentially of the reaction product of said vinyl tri-substituted silane with a water soluble salt of an acrylic acid.

17. As an article of manufacture, a support having a coat of a polysilane adhered thereto, said polysilane being formed from a vinyl tri-substituted silane having the formula $\text{CH}_2\text{CHSiR}_3$, wherein R is a monovalent substituent selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, phenoxy, tolyloxy, xylyloxy, chlorine, fluorine, iodine and bromine, and a hydrophilic film of a copolymer overlying and adhering to said coat consisting essentially of the reaction product of said vinyl tri-substituted silane with an acrylic compound selected from the group consisting of acrylic acid, methacrylic acid, the ammonium, sodium, and potassium salts of said acids, acrylamide, and methyl acrylamide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,258,221	Rochow	Oct. 7, 1941
2,397,287	Ostberg	Mar. 26, 1946
2,537,433	Waring	Jan. 9, 1951
2,601,337	Smith-Johannsen	June 24, 1952
2,645,628	Hurd	July 14, 1953
2,649,396	Witt et al.	Aug. 18, 1953
2,716,638	Cohen et al.	Aug. 30, 1955

OTHER REFERENCES

Post: Silicones and Other Organic Silicon Compounds, 1949, pp. 91, 107 and 108, Rheinhold Publ. Corp., 330 West Forty-second St., New York 18, New York.