

UNITED STATES PATENT OFFICE

2,680,073

METHOD OF SIZING PAPER

John B. Davidson and Thomas Robert Santelli,
Toledo, Ohio, assignors, by mesne assignments,
to Allied Chemical & Dye Corporation, New
York, N. Y., a corporation of New York

No Drawing. Application January 10, 1951,
Serial No. 205,430

6 Claims. (Cl. 92-21)

1

The invention relates to an improved method of producing sized paper, i. e., paper having reduced absorptivity to water.

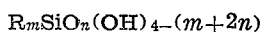
Silicones are known to have great potential value as low cost materials for imparting water repellency. One of the greatest impediments to the commercialization of silicones is that it has been difficult to use them in aqueous solution. For example, silicones have not been used successfully in aqueous solution as sizing agents in the manufacture of paper. An agent used in the manufacture of paper must be applied in very small quantities per square foot of paper in order to avoid prohibitive costs, so that the agent must be present in very dilute aqueous solution in the paper-making process.

For want of a better method of applying silicones in the manufacture of paper, persistent attempts have been made during the past ten years to commercialize methods of applying silicones by the use of a vapor, such as methyltrichlorosilane. However, such vapor treatment requires expensive equipment, and the treated paper must be given and after-treatment with another vapor such as ammonia.

The application of silicones in the form of aqueous emulsions also has been suggested. The disadvantage of this method is that a surface-active agent must be used in order to form an emulsion, and the presence of such an agent tends to cause a serious reduction in the water repellency of the paper that is produced.

The principal object of the invention is to provide a method of applying silicones as sizing agents in the manufacture of paper. More specific objects and advantages are apparent from the description, which illustrates and discloses but is not intended to limit the invention.

The present method of sizing paper comprises incorporating, at the wet end of the paper-making process, a silanol having an average unit structure corresponding to the formula



wherein m is a number from .05 to 3; n is a number from 0 to 1; and the radicals R are organic radicals having from one to twelve carbon atoms; the pH at the wet end of the paper-making process being brought between 3 and 8 not later than five minutes after the incorporation of the silanol.

In the sizing method that has been in common use heretofore a rosin soap is first thoroughly dispersed in a pulp suspension and alum is then added to set the size upon the paper fibers. If the alum is added before the rosin soap, setting and

2

formation of free rosin occurs upon the addition of the rosin soap and it is then impossible to disperse the rosin throughout the pulp suspension.

It has now been found that if in the procedure heretofore in common use a silanol is incorporated in the pulp suspension in place of a rosin soap, no effective sizing is obtained. The present invention is based upon the discovery that when a silanol is incorporated in the pulp suspension in place of the rosin soap, very effective sizing (or, if desired, strong water repellency) can be obtained by bringing the pH of the suspension between 3 and 8 not more than five minutes after the incorporation of the silanol in the pulp suspension. For example, if the agent that is added to make the adjustment of the pH comprises alum, the addition of the agent may be made prior to or substantially simultaneously with the incorporation of the silanol in the pulp suspension. Thus, in order to obtain effective sizing by the incorporation of a silanol in place of a rosin soap, it is necessary to use an order of addition of the alum and the sizing agent that cannot be used when the sizing agent is a rosin soap.

The fact that the pH at the wet end of the paper-making process must be brought between 3 and 8 not later than about five minutes after the incorporation of a silanol in order to obtain effective sizing of paper in accordance with the present method has been demonstrated as follows:

Kraft pulp (400 grams) was placed in a "Valley" beater (a standard beater designed for laboratory use), and water (23 liters) was added. To the resulting suspension was added an alkyl silicate (13 grams of a 32 per cent sodium ethyl silicate solution prepared as follows: ethyltriethoxysilane (1 mol) was mixed in a flask with water (220 grams) containing sodium hydroxide (1 mol) and ethanol (100 cc.), and the resulting mixture was distilled until about 250 grams of 87 per cent ethanol were recovered), and the mixture at a pH of 9.6 was beaten. At four time intervals during the beating (15 minutes, 45 minutes, 75 minutes and 210 minutes) samples were removed. Each sample of the beaten pulp suspension was mixed with alum (1 per cent based on the weight of dry pulp) and was diluted with water to a 0.3 per cent solids concentration. (The terms per cent and parts are used herein to mean per cent and parts by weight unless otherwise specified.) Each sample was then adjusted to a pH of 6.4, and handsheets of paper were made in accordance with the standard procedure employed in the art of making paper. The resulting

handsheets showed no sizing effect; i. e., no reduction in the absorptivity of the paper to water was observed.

The procedure described in the preceding paragraph was repeated except that alum (4 grams) was added to the paper pulp suspension to adjust the pH to about 6.7 before it was beaten (i. e., the alum was added immediately after the addition of the alkyl water glass to the beater). Handsheets of paper made from the beaten pulp suspension prepared in this manner were so effectively sized that they actually possessed strong water repellency (i. e., drops of water did not penetrate the paper but remained on the surface and could be readily shaken off).

Thus, it was demonstrated that upon incorporation of a silanol (derived from the alkyl silicate, as hereinafter discussed) at the wet end of the paper-making process, the time of adjustment of the pH (e. g., with alum) to within the range specified above is an essential factor if effective sizing of paper is to be obtained by the present method.

SILANOL

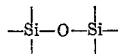
A silanol that may be employed in the present method of sizing paper has an average unit structure corresponding to the formula



wherein m is a number from .05 to 3; n is a number from 0 to 1; and the radicals R are organic radicals having from one to twelve carbon atoms. The term "monomeric silanol" is used herein to mean a substance whose molecule contains one silicon atom to which from one to three hydroxy radicals are attached (or two to three such silicon atoms which are connected by divalent organic radicals), the remaining free valences of the silicon atom(s) being attached by



linkages to monovalent organic radicals. A silanol employed in the present method may be partially condensed, i. e., may contain some polymeric molecules which can be considered to be derived by condensation between hydroxy groups attached to silicon atoms in two or more molecules of monomeric silanols, with the formation of



linkages. Thus, the letter " n " in the formula for the average unit structure of a silanol employed in the method of the invention represents the average degree of condensation in the silanol molecules. It is believed, however, that in at least part of the molecules of such a silanol n is 0, i. e., that at least part of the silanol molecules remain in monomeric form, since the fact that a silanol employed in the present method is capable of being dispersed in an aqueous medium, as hereinafter further discussed, indicates that the silanol molecules are of very low average molecular weight.

In the formula representing the average unit structure of a silanol employed in the practice of the invention the letter " R " is used to indicate the type of radical that may be attached to the silicon atoms in the silanol molecules. However, the use of a single letter is not intended to indicate that all the radicals of that type are the same. That is, in the molecule of a silanol in which more than one radical R is attached to a silicon atom (i. e., m is two or three), each radi-

cal R may be different. (Such a silanol may be prepared from, e. g., a mono-functional organosilane starting material in which all three organic radicals attached to the silicon atom are not the same, or from a mixture of tri-functional silanes in which the organic radicals attached to the silicon atoms are not all the same.) When the silanol contains, e. g., some dimeric molecules, each unit of a dimeric molecule may contain a different organic radical attached to the silicon atom. Thus in the structure of a silanol employed in the practice of the invention the organic radicals attached to silicon atoms in the silanol molecules are not limited to a single specific radical (i. e., R in the formula for the average unit structure of the silanol is not limited to a single specific radical but may be one or more of the various organic radicals hereinafter described).

In general the ratio of the total number of non-hydrolyzable radicals (i. e., organic radicals R) to the total number of silicon atoms in a silanol that may be used in the practice of the invention (i. e., the " R/Si ratio," in which R is the total number of non-hydrolyzable radicals attached to silicon atoms in the silanol and Si is the total number of silicon atoms therein, or m in the formula given above corresponding to the average unit structure of a silanol) is at least about .05 and is not higher than about 3. It is preferred that the R/Si ratio of a silanol employed in the practice of the invention be from about 1 to about 2.

An organic radical R , having from one to twelve carbon atoms, may be a monovalent organic radical, or a divalent organic radical connecting two silicon atoms. When R in the formula for the average unit structure of a silanol that may be used in the present method is a divalent organic radical, the silanol is hereinafter referred to as a "cross-linked silanol." Although the formula given above represents only one unit of a cross-linked silanol, a molecule of a cross-linked monomeric silanol used in the present method contains two silicon atoms connected by a divalent radical, or three silicon atoms connected by two or three divalent radicals. (The formula for the type of cross-linked silanol in which three silicon atoms are connected by three divalent radicals is, of course, cyclic.)

A monovalent organic radical having from one to twelve carbon atoms may be (1) a straight or branched chain primary, secondary or tertiary aliphatic hydrocarbon radical having saturated or unsaturated



bonds and having from one to twelve carbon atoms (i. e., a methyl, ethyl, 1-propyl, isopropyl, 1-butyl, isobutyl, 2-butyl or tertiary butyl radical, or any primary, secondary or tertiary alkyl radical having from five to twelve carbon atoms, or any alkenyl radical having from two to twelve carbon atoms); (2) an aryl radical which consists of from one to two benzene nuclei having not more than five side chains (which may be primary, secondary or tertiary alkyl radicals having from one to six carbon atoms, the total number of nuclear and side chain carbon atoms being not more than twelve), and having no substituents or having from one to three nuclear substituents each of which is a halogen atom of atomic weight less than 80 (i. e., chlorine, bromine or fluorine); (such aryl radicals include: phenyl, naphthyl, diphenyl, mono-, di- and tri-

chlorophenyls, tolyl, xyllys, ethylphenyl, n-propylphenyl, methylethylphenyls, isopropylphenyl, n-butylphenyl, isobutylphenyl, diethylphenyls, amylphenyl, butylmethylphenyls, propyldimethylphenyls, propylethylphenyls, diethylmethylphenyls, hexylphenyl, amylmethylphenyls, butylethylphenyls, butyldimethylphenyls, 2-bromo-p-xyl, 2-bromo-1-ethylphenyl, 2-bromo-4-ethyltolyl, 1-chloro-4-fluorophenyl, 1-chloro-4-ethylphenyl, 1-chloro-4-propylphenyl, 1,2-dichloro-4-ethylphenyl and 4-bromo-1,3-diethylphenyl); (3) an aralkyl radical which consists of any aliphatic hydrocarbon radical hereinbefore described, having from one to six carbon atoms, in which one hydrogen atom has been replaced by a phenyl radical or a substituted phenyl radical hereinbefore described, the total number of carbon atoms in the aralkyl radical being not more than twelve (such aralkyl radicals include: benzyl, beta-tolylbutyls, beta-tolylpropyls, beta-tolylisobutyls, beta-phenylethyl, beta-tolylethyls, beta-phenylpropyl, gamma-phenylpropyl, beta-(chlorophenyl)ethyls, beta-(trichlorophenyl)ethyls, beta-(dichlorophenyl)ethyls, beta-(dichlorophenyl)propyls, alpha-phenylethyl, alpha-tolylethyls, alpha-phenylpropyl, alpha-(chlorophenyl)ethyls, alpha-(trichlorophenyl)ethyls, alpha-(dichlorophenyl)ethyls and alpha-(dichlorophenyl)propyls); (4) any radical as described in (1) or (3) above in which from one to three hydrogen atoms attached to acyclic carbon atoms (other than a carbon atom connected to the carbon atom to which is connected the free valence) have been replaced by halogen atoms having an atomic weight less than 80 (such radicals include, e. g., alpha-halo- and gamma-halo-substituted propyl, alpha-halo-, gamma-halo- and delta-halo-substituted butyl, but not beta-halo-substituted propyl or butyl since such radicals, under the hydrolysis conditions hereinafter described, tend to decompose with the splitting off of an olefin from the silane molecule); or (5) a cycloaliphatic radical which consists of a single cycloaliphatic nucleus containing from five to six carbon atoms and having not more than three side chains containing a total of not more than six carbon atoms. (Such radicals include cyclopentyl, cyclohexyl, and alkyl-substituted cyclopentyl or cyclohexyl radicals in which the alkyl side chains, if any, are one, two or three in number, and not more than one side chain is bonded to any one nuclear carbon atom (each alkyl side chain may be a primary, secondary or tertiary alkyl radical having from one to six carbon atoms, as hereinbefore described.)

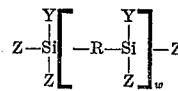
A divalent organic radical connecting two silicon atoms may be (A) a divalent aliphatic radical which can be considered to be derived by the removal of two hydrogen atoms from the molecule of (1) a straight or branched chain, saturated aliphatic hydrocarbon having from one to 12 carbon atoms (i. e., the divalent aliphatic radical may be methylene, ethylene, trimethylene, propylene, any butylene, or any alkylene radical having from 5 to 12 carbon atoms, e. g., any polymethylene radical from pentamethylene to dodecamethylene); or (2) a cycloalkane having from 5 to 12 carbon atoms (i. e., cyclopentane, cyclohexane, an alkylcyclopentane, an alkylcyclohexane or a substance in which two carbon atoms in the ring of cyclopentane or cyclohexane or an alkyl cyclopentane or cyclohexane are common to the ring of another such cycloalkane) in which the alkyl radicals, if any, attached to each ring, each have from one to six carbon atoms, have

straight or branched chains, and are from one to two in number (i. e., each alkyl radical is methyl ethyl, 1-propyl, isopropyl, 1-butyl, isobutyl, 2-butyl, tertiary butyl or a primary, secondary or tertiary alkyl radical having five or six carbon atoms); (B) a divalent hydrocarbon radical having from seven to twelve carbon atoms that can be considered to be derived by the replacement of a hydrogen atom in a divalent aliphatic radical having not more than six carbon atoms by an aromatic radical, the aromatic radical having not more than six nuclear carbon atoms; or (C) a radical as described in (A) or (B) in which from one to three hydrogen atoms have been replaced by halogen atoms having an atomic weight less than 80.

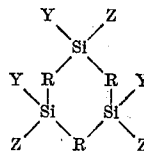
It is preferred that the monomeric molecule of a silanol employed in the present method contain only one silicon atom and that the monovalent organic radicals attached to silicon atoms in a silanol employed in the present method contain from one to six carbon atoms. It is preferred also that monovalent organic radicals that are aliphatic radicals consist of primary or secondary alkyl radicals having from one to six carbon atoms, and it is most desirable that they consist of primary or secondary alkyl radicals having from two to four carbon atoms.

SILANE STARTING MATERIALS

In the production of a silanol that may be used in the present method, a hydrolyzable organosilane composition, in which the organic radicals have from one to twelve carbon atoms, is subjected to hydrolysis, as hereinafter described. The term "hydrolyzable organosilane composition" is used herein to include not only a single hydrolyzable organo-substituted silane having the general formula $R_nSiY_{(4-x)}$ or having the general formula



or



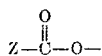
wherein R is an organic radical as hereinbefore defined, w is an integer from one to two, x is an integer from one to three, Y is a hydrolyzable radical and Z is a monovalent organic radical or a hydrolyzable radical, but also mixtures of two or more such hydrolyzable organo-substituted silanes, and mixtures of one or more such hydrolyzable organo-substituted silanes with one or more tetra-functional silanes having the general formula



wherein Y is a hydrolyzable radical. A hydrolyzable organosilane composition used in the practice of the invention may comprise from 5 to 100 mol per cent of a hydrolyzable organo-substituted silane or mixture of such silanes and from 0 to 95 mol per cent of a tetra-functional silane or mixture of tetra-functional silanes. (The terms "per cent" and "parts" are used herein to mean per cent and parts by weight unless otherwise specified.)

"Hydrolyzable radical" is used herein to include halo, alkoxy, amino, aroxy and acyloxy. The halo radical is any one having an atomic

weight less than 80. The alkoxy radical is any primary or secondary alkoxy radical having from one to four carbon atoms (i. e., methoxy, ethoxy, 1-propoxy, isopropoxy, 1-butoxy, isobutoxy or 2-butoxy). Amino is simply the —NH_2 group. Aroxy radicals are any in which the aryl group is phenyl, or a mono-, di- or tri-substituted phenyl radical, each substituent being a primary, secondary or tertiary alkyl radical having from one to five carbon atoms, the total number of carbon atoms in the side chains being not more than five (i. e., the aryl radical is phenyl, or ortho-, meta- or para-methyl phenyl, any di- or tri-methyl phenyl, or any substituted phenyl in which the substituents are: one ethyl; one ethyl and one methyl; two ethyls; two methyls and one ethyl; two ethyls and one methyl; either propyl radical; either propyl radical and methyl; either propyl radical and two methyls; either propyl radical and ethyl; any butyl radical; any butyl radical and methyl; or any pentyl radical). The acyloxy radical has the general formula



in which Z is a saturated or unsaturated straight, branched or closed chain hydrocarbon radical having from one to eighteen carbon atoms, or phenyl or substituted phenyl, the substituents, if any, consisting of from one to three alkyl radicals each having from one to five carbon atoms, and all having a total of not more than five carbon atoms, as hereinbefore described.

Examples of hydrolyzable organo-substituted silanes that may be used as starting materials for the preparation of silanols to be employed in the practice of the present invention include: alkylsilanes such as methyltrichlorosilane, methyltribromosilane, methyltrifluorosilane, ethyltrifluorosilane, diethyldifluorosilane, ethyltrichlorosilane, diethyldichlorosilane, diethyldiethoxysilane, diethylchloroethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, ethylchlorodiethoxysilane, ethyltripropoxysilane, ethyltri-1-butoxysilane, ethyltriisopropoxysilane, 1-propyltrichlorosilane, 1-propyltrifluorosilane, 1-propyltriethoxysilane, dipropyldiethoxysilane, dipropyldichlorosilane, 1-butyltrichlorosilane, isobutyltrichlorosilane, 1-butyltriethoxysilane, isobutyltriethoxysilane, dibutyldifluorosilane, 1-butyltributoxysilane, 1-pentyltrichlorosilane, isoamyltrichlorosilane, 1-pentyltrifluorosilane, 1-pentyltriethoxysilane, di-1-pentyl-difluorosilane, 1-hexyltrichlorosilane, 1-hexyltriethoxysilane, 1-heptyltrichlorosilane, 1-octyltrichlorosilane, 1-decyltrichlorosilane, 1-dodecyltrichlorosilane, alpha-chloroethyltrichlorosilane, alpha-chloropropyltrichlorosilane, gamma-chloropropyltrichlorosilane, alpha-chlorobutyltrichlorosilane, isopropyltrichlorosilane, tertiary hexyltrichlorosilanes, secondary butyltrichlorosilane, secondary amyltrichlorosilanes, secondary hexyltrichlorosilanes, secondary octyltrichlorosilanes, and secondary nonyltrichlorosilanes; alkenylsilanes such as vinyltrichlorosilane, allyltrichlorosilane and allylmethyl-dichlorosilane; arylsilanes such as phenyltrichlorosilane, α -naphthyltrichlorosilane, α -naphthyltriethoxysilane, phenyltriethoxysilane, phenyltrifluorosilane, diphenyldichlorosilane, p-chlorophenyltrichlorosilane, p-tolyltrichlorosilane, p-totyltriethoxysilane and phenylmethyl-dichlorosilane; aralkylsilanes such as beta-tolylbutyltrichlorosilanes, beta-tolylpropyltrichlorosilanes, beta-tolylisobutyltrichlorosil-

anes, benzyltrichlorosilane, beta-phenylethyltrichlorosilane, beta-tolyethyltrichlorosilanes, beta-phenylethyltrichlorosilane, beta-tolyethyltrichlorosilanes, beta-phenylpropyltrichlorosilane, gamma-phenylpropyltrichlorosilane, beta-(chlorophenyl)ethyltrichlorosilanes, beta-(trichlorophenyl)ethyltrichlorosilanes, beta-(dichlorophenyl)ethyldichlorosilanes, beta-(dichlorophenyl)propyltrichlorosilanes, alpha-phenylethyltrichlorosilane, alpha-tolyethyltrichlorosilanes and alpha-(chlorophenyl)ethyltrichlorosilanes; cycloaliphaticsilanes such as cyclohexyltrichlorosilane, cyclohexylmethyl-dichlorosilane, trimethylcyclohexyltrichlorosilanes and p-tertiaryamylcyclohexyltrichlorosilane.

Examples of tetra-functional silanes that may be used as starting materials in the present method include: ethyl orthosilicate, propylorthosilicate, phenyl orthosilicate, silicon tetrachloride, silicon tetrafluoride and silicon tetrabromide.

Examples of cross-linked organosilanes that may be used as starting materials in the present method include: bis(trichlorosilyl)isobutanes, tri(dichlorosilylmethylene), trichlorosilylmethyltrichlorosilane, 1,2-bis(trichlorosilyl)ethane, trichlorosilylethylcyclohexyltrichlorosilane, 1,6-bis(trichlorosilyl)hexane, 1,6-bis(trichlorosilyl)-2,5-dimethylhexane and 1,3-bis-(trichlorosilyl)propane.

If desired, silane starting materials may be used in the present method which can be considered to be derived by replacing with a hydrogen atom a hydrolyzable radical in an organosilane whose molecule contains more than one hydrolyzable radical attached to a silicon atom. Such starting materials include, for example, diethylchlorosilane, methylchlorosilane, trichlorosilylmethyl-dichlorosilane and ethyldichlorosilane. It is to be understood, of course, that when the hydrolyzable organosilane composition used in the production of a silanol employed in the present method comprises such a silane, hydrogen atoms may be present in place of some of the hydroxy groups in the formula for the average unit structure of the silanol. No substantial difference in the properties of the resulting silanol can be detected, however, when hydrogen atoms are thus present in place of some of the hydroxy groups.

The preferred hydrolyzable organo-substituted silane starting materials for use in the practice of the invention are monorgano- and diorgano-substituted silanes in which the organic radicals contain from one to six carbon atoms. When the organic radicals consist of alkyl radicals, it is preferred that they be primary or secondary alkyl radicals, and it is desirable that they be primary or secondary alkyl radicals having from two to four carbon atoms. It is most desirable, however, that the organic radicals be phenyl radicals.

Because the hydrolyzable radicals are removed from the silane starting materials in the hydrolysis procedure by which silanols are produced, it does not matter which hydrolyzable radical or radicals are present in the silane starting materials. The significant radical for the purposes of the present invention is —OH , and any radical that is replaced upon hydrolysis by —OH can be used in the practice of the invention. For this reason economic considerations govern the choice of hydrolyzable radicals. The least expensive and most readily available are preferred, but the by-products formed in the reaction may also govern the choice

of hydrolyzable radicals. (For example, since vapors from methoxysilanes are highly toxic, it is usually not desirable to hydrolyze silane mixtures in which the hydrolyzable radicals are methoxy radicals.) It is preferred that the hydrolyzable radicals in any one mixture of silanes used in the production of a silanol employed in the method of the invention be chloro or ethoxy radicals. Although the hydrolyzable radicals in any one mixture of silanes which is hydrolyzed in the production of a silanol may be different, it is preferred that they be the same, since the hydrolysis is more readily controlled when all the hydrolyzable radicals are the same.

Alkyltriethoxysilanes or alkyltrichlorosilanes in which the alkyl radicals have from two to four carbon atoms are readily available and economical to use as starting materials in the present method. (Silanols produced from such silanes also cure very rapidly when used in the present method of sizing paper.) It is most desirable that the hydrolyzable organo-substituted silane starting materials comprise phenyltriethoxysilane or phenyltrichlorosilane since such silanes are also readily available and since such silanes can be used to produce paper having extremely strong water repellency.

PRODUCTION OF SILANOL

As hereinbefore stated, the present method of sizing paper comprises incorporating a silanol (as hereinbefore defined) at the wet end of the paper-making process. This is known as "wet end addition," the term referring not only to addition in the beater, but also to addition in the machine chest, head box, fan pump or any other desired point at the wet end of the paper-making process. Wet end addition is a more convenient and less expensive method of applying a resin for sizing paper than other methods such as tub sizing. When a silanol is incorporated in the beater in the present method, it may be incorporated before or after the paper pulp is beaten.

A silanol that is used in sizing paper by the present method, in which " n " is from 0 to 1, is capable of dispersing throughout the paper pulp suspension at the wet end of the paper-making process before the paper is made. (When the silanol is dried after being applied to paper as a sizing agent in accordance with the present method, condensation of the silanol takes place to form an insoluble silicone which reduces the absorptivity of the paper to water.) Thus, the paper pulp at the wet end of the paper-making process is actually treated with an aqueous dispersion of a silanol. The term "aqueous dispersion of a silanol" is used herein to indicate that the particles of the silanol are submicroscopic in size and may be in true solution in the aqueous dispersing medium or may be in a colloidal state in the aqueous dispersing medium. In the practice of the present method, the aqueous dispersing medium is, of course, the water employed at the wet end of the paper-making process. Although the present method comprises incorporating a silanol at the wet end of the paper-making process, it is not actually necessary to produce a silanol by hydrolysis of a hydrolyzable organosilane composition and then to add this silanol at the wet end of the paper-making process. That is, a hydrolyzable organosilane composition may be added at the wet end of the paper-making process under such conditions that a silanol dispersion is formed, i. e., the silanol may be incorporated by producing it

directly at the point of addition of the hydrolyzable organosilane composition at the wet end of the paper-making process. In the following discussion of the production of a silanol that may be used in the present method, it is to be understood, of course, that the same conditions apply whether the water used for hydrolyzing the organosilane is actually the water present at the wet end of the paper-making process so that a silanol is produced directly at the point of addition of a hydrolyzable organosilane, or whether the silanol is produced in a separate aqueous solution and is then added to the wet end of the paper-making process. Whatever the method of incorporation, the term "silanol dispersion" is used hereinafter to mean the silanol as it exists when it is incorporated at the wet end of the paper-making process.

In the production of an aqueous silanol dispersion, a hydrolyzable organosilane composition, as hereinbefore defined, is subjected to hydrolysis, the pH being maintained at not less than 3 during the hydrolysis reaction, and the pH of the resulting aqueous dispersion being brought between 3 and 8. The procedure that is preferred for the hydrolysis may vary somewhat in accordance with the particular hydrolyzable organosilane composition used, but whatever procedure is employed, the conditions are such that the resulting product comprises essentially a silanol (in which n is from 0 to 1) and not a highly condensed polymeric siloxane.

In general, for any of the silane starting materials hereinbefore described (in which the organic radicals connected to silicon atoms by $-C-Si-$ linkages have from one to twelve carbon atoms) the procedure employed for hydrolysis conducted at a pH not less than 3 may consist in simply adding the hydrolyzable organosilane composition (preferably an organochlorosilane composition) dropwise to water containing a buffer (or the buffer may be added to the water simultaneously with the silane, as hereinafter further discussed). The rate of addition of the silane may be as rapid as is consistent with temperature control. It is desirable to use a large excess of water over that which is theoretically required to hydrolyze the organosilane composition, in order to avoid gelation. Such a large volume of water need not be present during the hydrolysis (it is present, of course, when the hydrolysis is conducted at the wet end of the paper-making process), but may be added after the hydrolysis to dilute the silanol dispersion to the desired concentration. However, the amount of water used for the hydrolysis should be great enough so that the aqueous medium in the resulting aqueous silanol dispersion, before further dilution, is at least from about 50 to about 70 per cent of the dispersion. The water used for the hydrolysis may be at ordinary temperatures, but it is preferable that it be maintained at about 5 to 10 degrees C. during the hydrolysis.

In the hydrolysis of an organosilane composition in which the hydrolyzable radicals consist of chloro radicals, a buffer may be used to prevent the dropping of the pH below 3 which normally occurs during the hydrolysis of chlorosilanes because of the formation of hydrogen chloride as chlorine atoms attached to silicon atoms are replaced by hydroxy groups. At such a low pH the silanol formed by hydrolysis of a chlorosilane would condense rapidly to a silicone resin of high molecular weight, so that an

ordinary hydrolysis procedure (without a buffer) cannot be used to prepare a silanol for use in the present method, i. e., a silanol in which n is from 0 to 1, which is capable of being dispersed in aqueous solution. The buffer used may consist of the hydroxide of any metal which is capable of forming a chloride (i. e., capable of taking up the liberated chlorine atoms to form a chloride), or a salt of such a metal base with any weak acid. The salt must be a salt of a weak acid so that the formation of the free acid in solution during the hydrolysis will not have the effect of the formation of a strong acid such as hydrochloric acid, namely, the dropping of the pH below 3, which must, of course, be avoided in the preparation of a silanol for use in the present invention.

A buffer employed in the present method, in the hydrolysis of chlorosilanes, may consist of an alkali metal base in which the alkali metal has an atomic weight between 22 and 40 (i. e., sodium or potassium hydroxide), or an alkaline earth metal base (i. e., barium, strontium, or calcium hydroxide), or any metal base which is capable of forming a chloride and which it is economically feasible to use in the present method (e. g., lead hydroxide, zinc hydroxide, or magnesium hydroxide). It is preferable that a buffer which consists of a metal base be sodium or potassium hydroxide. When the buffer used in the practice of the invention comprises a metal hydroxide, it is preferable to add the buffer dropwise to the water simultaneously with the dropwise addition of the silane, using, for example, two separate dropping funnels. Two indicators should be used so that the rates of addition can be controlled to prevent the pH during the hydrolysis from going below 3 or above 8. Ordinarily, a buffer such as sodium hydroxide is employed in an amount sufficient to take up all the chlorine atoms as they are removed from the silane molecules, and the pH is usually maintained at about 7 during the hydrolysis.

A buffer which is a salt of any metal base hereinbefore described and a weak acid may be present initially in the water used for the hydrolysis. The more common buffers such as sodium carbonate, sodium bicarbonate, sodium acetate, sodium citrate, sodium phosphate, etc., are preferred in the practice of the invention from the standpoint of economy.

Usually it is preferable that the proportion of a buffer salt in a hydrolyzing solution employed in the present method be sufficient to take up the chlorine atoms as they are removed from the silicon atoms during the hydrolysis. Thus, if the buffer employed is, for example, sodium acetate, the resulting aqueous dispersion of a silanol contains sodium chloride. In addition, it also contains some acetic acid. Thus, the pH of the silanol dispersion may not be approximately 7.5 (i. e., approximately neutral) but may be lower because of the presence of the weak acid. The use of such a silanol dispersion is within the scope of the invention since the pH of an aqueous silanol dispersion employed in the invention is brought within the range between 3 and 8 as hereinafter further discussed. Such a range is considered substantially neutral, since it permits the silanol dispersion to be used for sizing paper without the harmful effect that a more strongly acid solution might have on the paper and without the decrease in the sizing effect that might result if the silanol dispersion were more alkaline. It is preferable in the prac-

tice of the invention to bring the pH of the silanol dispersions within a range from about 4 to about 7.4 and it is most desirable that the pH be brought between about 5 and about 6.8 for reasons hereinafter explained.

Various silanols which may be employed in the present method for imparting water repellency to paper may be produced by the following procedures.

(a) A buffer (10.14 grams of sodium bicarbonate) is mixed with water (500 grams) and the solution is placed in a 2,000 ml. three-necked round bottom flask equipped with a stirrer and a dropping funnel. An organosilane (6 grams of methyltrichlorosilane) is placed in the dropping funnel and is added to the flask dropwise with stirring over a period of about two minutes. When the addition is complete, the mixture in the flask is poured into water (1,000 grams).

(b) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 7.56 grams, and the organosilane used is dimethyldichlorosilane (6 grams).

(c) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 4.62 grams, and the organosilane used is trimethylchlorosilane (6 grams).

(d) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 9.07 grams, and the organosilane used is ethyltrichlorosilane (6 grams).

(e) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 6.38 grams, and the organosilane used is dimethylechlorosilane (6 grams).

(f) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 4.12 grams, and the organosilane used is diethylchlorosilane (6 grams).

(g) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 8.32 grams, and the organosilane used is propyltrichlorosilane (6 grams).

(h) The procedure described in (a) is repeated except that the amount of sodium bicarbonate used is 7.31 grams, and the organosilane used is a sec.-amyltrichlorosilane (6 grams), prepared as follows: A mixture of pentenes (1.19 mols, comprising a high percentage of 2-pentene) and silicochloroform (1 mol) is pumped into an opening at the bottom of a reactor which consists of a vertical tube approximately twenty inches in length, having an internal diameter of about five inches. The length of the reactor is surrounded by electrically heated coils, covered with asbestos packing, which maintain the temperature in the reactor at approximately 370° C. The reactants are permitted to remain in the reactor for approximately one hour, during which time the pressure inside the reactor is about 1,000 pounds per square inch gauge. The reactor is cooled to room temperature, and the products formed are removed and fractionally distilled through a jacketed column four feet in length packed with glass helices. The products recovered include a 48 per cent yield (based on pentene) of a sec.-amyltrichlorosilane, B. P. 165-170° C. at atmospheric pressure, as well as unreacted silicochloroform and pentenes.)

(i) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 6.80 grams, and the organosilane used is 1-hexyltrichlorosilane (6 grams).

(j) The procedure described in (a) is repeated except that the amount of sodium bicarbonate

used is 6.05 grams, and the organosilane used is 1-octyltrichlorosilane (6 grams).

(k) The procedure described in (a) is repeated except that the amount of sodium bicarbonate used is 5.54 grams, and the organosilane used is a mixture of nonyltrichlorosilane (6 grams, comprising mainly secondary nonyltrichlorosilanes).

(l) The procedure described in (a) is repeated except that the amount of sodium bicarbonate used is 4.79 grams, and the organosilane used is 1-dodecyltrichlorosilane (6 grams).

(m) The procedure described in (a) is repeated except that the amount of sodium bicarbonate used is 7.05 grams, and the organosilane used is phenyltrichlorosilane (6 grams).

(n) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 6.8 grams, and the organosilane used is cyclohexyltrichlorosilane (6 grams).

(o) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 9.32 grams, and the organosilane used is vinyltrichlorosilane (6 grams).

(p) The procedure described in (a) is repeated, except that the amount of sodium bicarbonate used is 6.8 grams, and the organosilane used is a tert.-hexyltrichlorosilane (6 grams).

(q) The procedure described in (a) is repeated except that the amount of sodium bicarbonate used is 7.81 grams and the organosilane used is 1-butyltrichlorosilane (6 grams).

(r) A silanol dispersion is prepared by the procedure described in (q) except that the buffer used is sodium carbonate (4.98 grams).

(s) A silanol dispersion is prepared by the procedure described in (q) except that the buffer used is sodium acetate (7.63 grams).

(t) The procedure described in (a) is repeated, except that the organosilane used consists of a mixture of 1-butyltrichlorosilane (3.99 grams) and silicon tetrachloride (2.01 grams), and the amount of sodium bicarbonate used is 9.32 grams.

(u) The procedure described in (a) is repeated, except that the organosilane used consists of a mixture of 1-butyltrichlorosilane (3 grams), and silicon tetrachloride (3 grams), and the amount of sodium bicarbonate used is 9.49 grams.

(v) The procedure described in (a) is repeated, except that the organosilane used consists of a mixture of 1-butyltrichlorosilane (0.3 gram) and silicon tetrachloride (5.7 grams), and the amount of sodium bicarbonate used is 11.8 grams.

A cross-linked silanol dispersion may be prepared as follows:

(w) A cross-linked silane (a bis(trichlorosilyl)isobutane) is prepared according to the following procedure:

A carbon steel reactor consisting of a vertical tube approximately twenty inches in length, having an internal diameter of five inches, is heated to a temperature of approximately 340 degrees C. by means of electrical heating coils which surround the length of the tube. A mixture of silicochloroform (3340 grams) and commercial diisobutylene (1910 grams of a mixture comprising 80 weight per cent of 2,4,4-trimethylpentene-1 and 20 per cent of 2,4,4-trimethylpentene-2) is pumped into the heated reactor through an opening in the bottom. When the addition, which requires a period of about one hour, is complete, the opening is sealed and the mixture is allowed to remain in the reactor for four hours longer. During this period the mixture is heated by means of the heating coils at temperatures ranging between 320 and 340 degrees C., while the pressure

inside the reactor ranges from 1000 to 1200 pounds per square inch gauge. The heating is then discontinued, and the product is removed.

The product recovered (4350 grams) is fractionally distilled through an electrically heated, jacketed glass column four feet in length, packed with single-turn glass helices and having a variable reflux head. The forerun (i. e., material boiling in a range up to about 135 degrees C. at 740 mm. Hg.) comprises low boiling hydrocarbon gases (which are primarily saturated hydrocarbons having three or four carbon atoms), silicochloroform (200 grams) and a mixture of the diisobutylene starting materials (10 grams). The following materials are recovered after collecting the forerun: methyltrichlorosilane (740 grams); a fraction (370 grams) boiling within a range of 148 to 200 degrees C. at 740 mm. Hg., which comprises a mixture of pentyl-, hexyl- and heptyltrichlorosilanes; a fraction (1075 grams) which is a mixture of octyltrichlorosilanes comprising 2,4,4-trimethyl-1-pentyltrichlorosilane and 2,4,4-trimethyl-3-pentyltrichlorosilane; and a bis(trichlorosilyl)isobutane, which is believed to be 1,3-bis-(trichlorosilyl)isobutane (1260 grams, B. P. 225 to 236 degrees C., density at 28 degrees C. compared with that of water at 4 degrees C. (d_4) 1.377, index of refraction at 27 degrees C. (n_D^{27}) 1.472). A residue (60 grams) remains after the distillation.

A bis(trichlorosilyl)isobutane prepared as described above (6 grams) is added to a solution of sodium bicarbonate (9.32 grams) in water (500 grams) by the procedure described in (a) above. When the addition is complete, the mixture in the flask is poured into water (1,000 grams).

(x) The procedure described in the preceding paragraph is repeated except that a mixture of ethyltrichlorosilane (5.4 grams) and the bis(trichlorosilyl)isobutane (0.6 gram) is used, and the amount of sodium bicarbonate used is 9.25 grams.

(y) The procedure described in the last paragraph of (w) above is repeated except that the bis(trichlorosilyl)isobutane is first chlorinated to form a bis(trichlorosilyl)-2-chloroisobutane (believed to be 1,3-bis(trichlorosilyl)-2-chloroisobutane). The amount of sodium bicarbonate used is 8.57 grams.

A silanol dispersion for use in the practice of the invention may be prepared as follows from a hydrolyzable organosilane composition in which the hydrolyzable radicals consist of alkoxy radicals:

(z₁) Ethyltriethoxysilane (20 grams) is placed in a 2,000 ml. round bottom flask equipped with a stirrer and containing water (500 ml.). Sulfuric acid (a sufficient amount of a 0.6 N solution to give a pH of 4) is then added and the mixture is refluxed until a clear solution is obtained.

(z₂) Butyltributoxysilane (20 grams) is refluxed for one hour in water (500 ml.) after addition of a sufficient amount of a .6 N sulfuric acid solution to give a pH of 4).

The pH of the dilute silanol dispersions produced by the procedures described above is already within the range (i. e., between 3 and 8) required at the wet end of the paper-making process in accordance with the present method. It is preferable to adjust the pH of such dilute silanol dispersions between about 4 and about 7 and preferably between about 5 and about 6, for such compositions are relatively stable in such pH ranges, i. e., as evidenced by a lack of gel particles in the dilute dispersions when they are permitted to stand before incorporation at the wet

end of the papermaking process. (For example, the stability of these dispersions may be from several days to two weeks depending on the particular silanol, concentration of silanol, pH, temperature, etc.) These preferred ranges are preferably used also at the wet end of the paper-making process, as is hereinafter further discussed.

Thus, if desired, such silanol dispersions may be produced beforehand and then incorporated when required at the wet end of a paper-making process in accordance with the present method, without further adjustment of the pH at the wet end. Of course, the volume of water in such dilute dispersions is taken into consideration in adjusting the dilution at the wet end of the paper-making process to the desired value. (For example, the paper pulp in a beater is ordinarily diluted with water to about a three to four per cent concentration of pulp. Thus, if a silanol dispersion, prepared as hereinbefore described, is incorporated in the beater before the pulp is beaten, at least part of the water for preparing the beaten pulp suspension is supplied by the silanol dispersion.) Ordinarily, it is more convenient to prepare a silanol by hydrolysis of a hydrolyzable organosilane composition directly at the desired point of incorporation of the silanol at the wet end of the paper-making process, the pH at the wet end of the process being brought between 3 and 8 not later than five minutes after the incorporation of the silanol, as hereinafter discussed. However, when the organic radicals attached to silicon atoms by



linkages in a hydrolyzable organosilane composition are alkyl radicals containing from one to four carbon atoms, or phenyl radicals, a most desirable procedure for incorporating a silanol at the wet end of the paper-making process is by the addition of a water-soluble silicate. Such a water-soluble silicate is an alkaline solution of a highly stable water glass-type of composition. Upon incorporation of such a silicate at the wet end of the paper-making process and upon neutralization, a silanol dispersion for sizing paper by the present method is produced.

A water-soluble silicate (i. e., an alkaline water glass type of composition) may be prepared by simply mixing a hydrolyzable organosilane composition in which the organic radicals are alkyl radicals containing from one to four carbon atoms or phenyl radicals, and in which the hydrolyzable radicals consist of alkoxy groups (preferably, of course, ethoxy groups) with an aqueous solution of an alkali metal base such as sodium or potassium hydroxide. (Although other metal hydroxides such as the alkaline earth metal hydroxides may be employed, the solubility of a water glass type of composition tends to be less when the composition is a salt of a metal of higher molecular weight.) It is preferable to use about one mol of sodium or potassium hydroxide per mol of the organoalkoxysilane composition so that a hydrogen atom from only one of the hydroxy groups attached to a silicon atom in the molecule of the silanol resulting from the hydrolysis is replaced by an atom of the metal derived from the metal hydroxide. The water-soluble silicate so produced resembles ordinary water glass except that it is a solution of a mono-metal salt of an organosilicic acid rather than a solution of a salt of silicic acid. The mono-metal salt is preferred from the standpoint of economy

since the salt must be neutralized in the preparation of a silanol dispersion at the wet end of the paper-making process and the use of a larger proportion of the metal base would simply require the use of more acid to obtain the proper pH for sizing paper by the present method.

When the hydrolyzable groups in a hydrolyzable organosilane composition which is hydrolyzed in the preparation of a water-soluble silicate are alkoxy groups (e. g., ethoxy groups) they are released during the hydrolysis of the silanes as an alcohol (e. g., ethyl alcohol). Usually it is preferable to add a small amount of alcohol (e. g., about 100 cc. per mol of hydrolyzable organosilane) when the reactants are mixed, since the presence of the alcohol, which acts as a mutual solvent for the silane and the water, makes the reaction proceed at a more even rate. This proportion of alcohol along with the alcohol that is formed during the hydrolysis may be recovered from the water glass type of solution by distillation.

When the hydrolyzable groups in an organosilane composition which is hydrolyzed in the preparation of a water-soluble silicate are halo radicals, it is necessary to add the silane to the aqueous solution of sodium or potassium hydroxide dropwise and to maintain the temperature of the hydrolyzing solution at not more than about 10 degrees C. in order to obtain a soluble water glass rather than a solution containing gel particles. Furthermore, the proportion of sodium or potassium hydroxide in the aqueous solution must be great enough not only to form a mono-metal salt of the resulting silanol but also to neutralize the hydrohalic acid produced during the hydrolysis. Thus, it is usually more practical to convert halosilane starting materials to the corresponding alkoxy silane starting materials (recovering, of course, the hydrohalic acid that is produced) and then to hydrolyze the alkoxy silane starting materials to produce a water-soluble silicate.

It is preferable that the proportion of water in the solution of sodium or potassium hydroxide which is used in the preparation of a water-soluble silicate be such that the resulting silicate solution comprises at least about 50 to 70 per cent of water. Although the proportion of water in the silicate solution may be considerably higher, it is usually preferable to minimize the volume of solution to be handled by keeping the dilution of the silicate solution at a minimum until the silicate is converted to a silanol by adjusting the pH between 3 and 8. Thus, the acid used to adjust the pH may be added at the wet end of the paper-making process, the silanol resulting from the neutralization of the silicate being in the desired concentration in the paper pulp suspension. It is preferred that the water-soluble silicate be a sodium silicate.

Any acid may be used to neutralize a water-soluble silicate in the production of a silanol dispersion at the wet end of the paper-making process. Strong acids such as sulfuric, phosphoric and hydrochloric acids are most conveniently employed.

In the practice of the invention the pH of a silanol dispersion at the wet end of the paper-making process should be not higher than about 8 and not lower than about 3, and is preferably between 4 and 7.4 in order to avoid the formation of gel particles in the dispersion. Furthermore, in order to obtain a sizing effect on paper it is necessary to bring the pH at the wet end of the paper-making process between 3 and 8 and

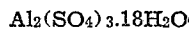
preferably between 4 and 7.4 not later than five minutes after the incorporation of the silanol. Thus, when a silanol is incorporated at the wet end of the paper-making process by addition of a water-soluble siliconate (which is a highly alkaline solution) and then neutralizing the siliconate to form a silanol, the neutralization must be accomplished not later than five minutes after the addition of the siliconate to the wet end of the paper-making process, and the pH upon neutralization preferably is not higher than about 7.4. It is desirable, therefore, in incorporating a silanol at the wet end of the paper-making process by adding a water-soluble siliconate, to add the acid for neutralizing the siliconate to produce a silanol either before or simultaneously with the addition of the water-soluble siliconate. It is preferable to avoid lowering the pH too far beyond the neutral point on the acid side, since the greatest stability of the silanol (i. e., as evidenced by the lack of gel particles) occurs just beyond the neutral point on the acid side. Thus, it is preferred that the pH at the wet end of the paper-making process be approximately 4 to 7.4 and most desirably about 5 to 6.8, not only because a silanol dispersion within such ranges at the wet end of the paper-making process has the greatest stability but also because it has the greatest sizing effect on most types of paper. It is to be understood, of course, that the pH of a water-soluble siliconate may be adjusted before it is incorporated at the wet end of the paper-making process, i. e., that the silanol may be formed by neutralizing the siliconate outside the paper-making process, so that when the actual silanol is incorporated at the wet end of the process, the pH at the point of incorporation will already be within the range required for obtaining effective sizing of paper by the present method.

The methods of incorporating a silanol at the wet end of the paper-making process in the practice of the invention may be summarized as follows: (1) A hydrolyzable organosilane composition may be hydrolyzed by dropwise addition to the aqueous pulp suspension at the wet end of the paper-making process, so that a silanol is formed at the point of addition of the hydrolyzable silane. (Ordinarily, a buffer is employed at the wet end, particularly with organochlorosilanes, so that the pH at the wet end of the paper-making process is within the range required for effective sizing as the silanol is incorporated); (2) A water-soluble siliconate may be added slowly to the aqueous pulp suspension at the wet end of the paper-making process and neutralized (i. e., adjusted to a pH between about 4 and about 7.4), either by adding the siliconate after the suspension has been adjusted to a pH such that the siliconate is neutralized as it is added, or, preferably, by adding a neutralizing agent along with the siliconate, or by adding a neutralizing agent not later than about five minutes after the siliconate has been added; or (3) A silanol may be produced by adding either a hydrolyzable organosilane composition or a water-soluble siliconate to a hydrolyzing solution that is separate from the paper-making process and then incorporating the resulting silanol dispersion at the wet end of the paper making process, the pH of the silanol dispersion ordinarily being already within the range required at the wet end of the paper-making process in order to obtain effective sizing of paper.

ALUMINUM-CONTAINING SALT

In the present method of sizing paper it is preferable to incorporate at the wet end of the paper-making process a water-soluble aluminum-containing salt. The incorporation of such a salt appears to permit greater retention of silanol on the paper since it greatly decreases the proportion of silanol required in the pulp suspension to obtain effective sizing. In fact, when a water-soluble aluminum-containing salt is employed in the present method, such a high degree of water repellency may be imparted to paper as to be completely disproportionate to the small amount of silanol used.

A water-soluble aluminum-containing salt that is incorporated at the wet end of the paper-making process in the present method may be any aluminate, or any salt of aluminum (or of a complex of aluminum and one or more other metals, e. g., an alkali metal such as sodium or potassium) with an inorganic acid (e. g., nitric, sulfuric or hydrochloric acid), that is soluble in the water employed at the wet end of a paper-making process. Such salts include: aluminum chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; sodium aluminum chloride, $\text{AlCl}_3 \cdot \text{NaCl}$; aluminum sulfate,



aluminum potassium sulfate,



sodium aluminate, NaAlO_2 ; and aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Aluminum sulfate (referred to as "alum" in the art of making paper) is preferred in the practice of the invention.

A water-soluble aluminum-containing salt employed in the present method should be used at the wet end of the paper making process in an amount that is at least about 20 per cent of the weight of silanol (calculated as hereinafter described) deposited on the paper, and most desirably about 40 per cent of the weight of silanol deposited on the paper, if a substantial improvement (i. e., actual water repellency) is desired over the sizing effect obtained when no such salt is employed. Although the use of about 70 to 100 per cent of a water-soluble aluminum-containing salt (based on the weight of silanol deposited on the paper) ordinarily gives a high degree of water repellency when as little as about 1 per cent of silanol is deposited (based on the weight of dry paper pulp), a larger proportion of an aluminum-containing salt may be used if greater retention of the silicone on the paper is required. (However, since the addition of an acid salt such as alum lowers the pH at the wet end of the paper-making process, the maximum proportion of an acid salt that can be used may be limited by the minimum pH that is permissible at the wet end of the paper-making process after the incorporation of the silanol, as hereinbefore discussed.) If desired, the aluminum-containing salt may be used to bring the pH at the wet end of the paper-making process after incorporation of the silanol between 3 and 8 (preferably between 4 and 7.4). However, if the silanol is incorporated by the addition of a water-soluble siliconate, which is highly alkaline, it may be desirable to neutralize the mixture at the wet end of the paper-making process with an acid first and then to bring it within the range at which the most effective sizing of paper is obtained (i. e., 5 to 6.8) by the addition of a water-soluble aluminum-containing salt. Similarly, when a buffer is present at the

wet end of the paper-making process so that a silanol formed by dropwise addition of a hydrolyzable organosilane at the wet end is substantially neutral or is approximately within the most desirable pH range, it may be desirable to incorporate only a small amount of an aluminum-containing salt, not to change the pH substantially but to cause greater retention of the silicone on the paper, i. e., a greater sizing effect, or a strong degree of water repellency. Care should be taken in neutralizing a water-soluble silicate with an acid before the addition of an acidic water-soluble aluminum-containing salt that the pH is not lowered too far beyond the neutral point on the acid side, so that upon addition of the acidic aluminum-containing salt the pH at the wet end of the paper-making process is below the range hereinbefore specified. That is, the pH of the silanol dispersion should be high enough at the time of addition of such a salt so that a portion of the salt that is at least the minimum hereinbefore described can be added without reducing the pH below 3.

The aluminum-containing salt may be added to the paper pulp at the wet end of the paper-making process before or simultaneously with the incorporation of the silanol, or after the incorporation of the silanol. If the salt is used alone to adjust the pH at the wet end of the paper-making process to within the range at which the present sizing effect is obtained, and if the pH of the silanol dispersion at the wet end of the paper-making process before the addition of the salt is higher than about 7 to 8, it is necessary to add the salt within about five minutes after the incorporation of the silanol to prevent the silanol from precipitating out. However, if an acid has been added to adjust the pH so that it is not higher than about 7 to 8, the salt may be added at any time after the incorporation of the silanol. Of course, if the silanol is prepared by addition of a hydrolyzable organosilane composition at the wet end of the paper-making process, and a buffer is employed so that the resulting silanol is approximately neutral, the aluminum-containing salt may be added whenever desired after the incorporation of the silanol. If the silanol is prepared outside of the paper-making process it can be mixed with the water-soluble aluminum-containing salt before it is incorporated at the wet end of the paper-making process.

In general, the minimum proportion of silanol used in the present method is that which imparts an appreciable sizing effect, i. e., reduction in the absorptivity of the paper to water. The maximum proportion of silanol used in the present method is that above which any increase in sizing effect is not sufficiently great to make a larger proportion of silanol economically feasible, or above which the sizing effect obtained is greater than is desired (e. g., a high degree of water repellency in paper may not be desirable for some purposes). The proportion of silanol that is necessary to impart a given degree of sizing effect to paper may depend, of course, upon the pH conditions employed in the production of the paper, upon the specific silanol employed, and upon the method of obtaining the proper pH conditions at the wet end of the paper-making process (i. e., upon whether or not a water-soluble aluminum-containing salt is used, etc.). When a water-soluble aluminum-containing salt is not incorporated at the wet end of the paper-making process, the proportion of silanol used

(calculated as hereinafter described) should be at least about 1 per cent of the weight of dry pulp in order to obtain an appreciable sizing effect, increased proportions being required to produce an increased degree of sizing effect. When a water-soluble aluminum-containing salt is employed in the present method, the proportion of silanol used may be from about 0.5 per cent to about 3 per cent of the weight of dry pulp, but in some applications the concentration may be lower or higher, depending upon the degree of sizing or water-repellency that is desired. Ordinarily, when a water-soluble aluminum-containing salt is employed, a concentration of silanol in the pulp suspension that is about 1 per cent of the weight of dry pulp imparts strong water repellency economically and efficiently.

The proportion of silanol, expressed as "per cent of the weight of dry pulp," means the weight of the silanol divided by the weight of the dry pulp times 100. The weight of the silanol is calculated herein as though all OH groups attached to silicon atoms in the silanol molecules were completely condensed during the reaction by which the silanol dispersion is obtained. (It is believed, of course, that actually in the preparation of the dispersion very little condensation of the OH groups attached to the silicon atoms in the silanol molecules takes place, and this method of calculation is used only for convenience in determining the concentration of silanol in a silanol dispersion.) Thus, for example, a butylsilanol in a dispersion derived from a butyltrichlorosilane is assumed to have the formula $\text{BuSiO}_{1.5}$ in calculating the per cent of butylsilanol in the dispersion.

As an example of the marked effect that the use of a water-soluble aluminum-containing salt in the practice of the invention has upon the proportion of a silanol required to obtain a given sizing effect (for example, strong water repellency), it has been found that about 1 per cent of an ethylsilanol used in conjunction with 1 per cent of alum (based on the weight of dry pulp) imparts at least as high a degree of water repellency to kraft paper as approximately 10 to 15 per cent of the ethylsilanol used without a water-soluble aluminum-containing salt.

As hereinbefore indicated, in the present method the purpose of bringing the pH at the wet end of the paper-making process between 3 and 8 not later than five minutes after the incorporation of the silanol is to permit the silanol to be dispersed throughout the paper pulp suspension, i. e., to prevent the silanol from condensing to a polymeric siloxanol which would precipitate out of a dilute pulp suspension. However, once the silanol has been thoroughly dispersed throughout the pulp suspension at the wet end of the paper-making process and is "set" on the paper fibers, the pH may be raised above 8, for example, as high as 10, if desired, although raising the pH above 8 reduces the water repellency of the paper. Thus, the silanol may be incorporated, e. g., in the beater (either before or after the pulp suspension is beaten) and the pH adjusted to within the range between 3 and 8 within five minutes after the incorporation of the silanol. Then, after the silanol has been thoroughly dispersed throughout the suspension, for example, just before the suspension is transferred from the beater to the headbox to make the paper, the pH may be raised as high as 10. Ordinarily, however, it is preferable that the pH be adjusted to from about 5 to about 7 after the

silanol is dispersed throughout the paper pulp suspension, in order to obtain more effective sizing, and it is most desirable that the pH be from about 5 to about 6, because the maximum sizing effect may be obtained in this pH range. Thus, the pH range for obtaining the maximum sizing effect after the silanol is dispersed throughout the pulp suspension, e. g., at the time the paper is made, may be the same as that which is employed during the time that the silanol is being dispersed throughout the paper pulp suspension.

In the present method of sizing paper, which comprises incorporating a silanol at the wet end of the paper-making process, the silanol may be used in conjunction with other sizing agents commonly employed in the art of making paper, e. g., rosin, paraffin wax, etc. to obtain the properties required of paper for specific uses. The present method can be used for sizing paper of any types, e. g., kraft, sulfite, hemp, etc.

The following examples illustrate the practice of the invention:

Example 1

The present method of sizing paper may be carried out by the following procedures:

(a) Pulp (400 grams of kraft pulp) is placed in a "Valley" beater (a standard beater designed for laboratory use) and water (23 liters) is added. The beater is run for five minutes (slush period) before a load (4500 grams) is placed on the lever arm which applies a force to the beater roll. Samples are withdrawn at various intervals during the beating to measure the rate at which water passes through the pulp (freeness) as Schopper freeness. The beating is continued until a freeness of 500 is reached. A buffer (26 grams of sodium bicarbonate) is then added to the beaten pulp suspension. An organosilane (16 grams of 1-butytrichlorosilane) is then added dropwise to the suspension over a period of about ten minutes. Handsheets of paper made from the beaten pulp suspension (adjusted to a pH of 6) in accordance with the standard procedure employed in the art of making paper show a distinct reduction in absorptivity to water.

(b) When the procedure described in (a) is repeated except that a small amount of a water-soluble aluminum-containing salt (2 grams of alum) is added as soon as the addition of the organosilane is complete, the handsheets of paper show strong water repellency, i. e., drops of water placed on the paper can be shaken off with substantially no wetting of the surface of the paper.

(c) The procedure described in (a) is repeated except that the organosilane used is ethyltrichlorosilane. Handsheets made from the beaten pulp suspension adjusted to a pH of 7.3 show a similar sizing effect.

(d) The procedure described in (a) is repeated except that the organosilane used is the sec.-amyltrichlorosilane prepared as hereinbefore described. Handsheets made from the beaten pulp suspension adjusted to a pH of 5.8 show a similar sizing effect.

(e) The procedure described in (d) is repeated except that the organosilane used is phenyltrichlorosilane. Similar results are obtained.

(f) The procedure described in (d) is repeated except that the organosilane used is a mixture of nonyltrichlorosilanes (comprising mainly secondary nonyltrichlorosilanes). Similar results are obtained.

(g) The procedure described in (d) is repeated except that the organosilane used is 16 grams of a mixture consisting of 60 mol per cent of a

sec.-amyltrichlorosilane, 20 mol per cent of ethyltrichlorosilane and 20 mol per cent of silicon tetrachloride. Similar results are obtained.

(h) The procedure described in (d) is repeated except that the organosilane used is 1-hexyltrichlorosilane. The handsheets of paper show very good water repellency.

(i) When the procedure described in (b) is repeated except that the amount of kraft pulp used is 150 grams, the amount of water added to the beater is 7 liters and a silanol (any of the dilute aqueous silanol dispersions prepared as hereinbefore described) is poured into the beaten pulp suspension instead of adding (dropwise) a chlorosilane, a similar sizing effect (i. e., strong water repellency) is obtained.

Example 2

Ethyltriethoxysilane (5 grams) is mixed with water (500 grams). The solution is then mixed with 200 grams of a beaten pulp suspension containing 3.4 grams of kraft pulp, and sodium hydroxide is added to adjust the pH to 8. After the suspension has stood at room temperature for 12 hours, the pH is adjusted to about 5.8 with alum. Handsheets of paper made from this suspension show very good water repellency.

The following examples illustrate a preferred procedure for sizing paper by the present method.

Example 3

(a) A beaten pulp suspension is prepared by the procedure described in Example 1. A water-soluble silicate (8.5 grams of a 47 per cent ethyl water glass solution prepared as follows: Ethyltriethoxysilane (192 grams) is mixed in a flask with water (168 grams) containing sodium hydroxide (40 grams) and ethanol (100 cc.), and the resulting mixture is distilled until 148 grams of 90 per cent ethanol have been recovered) is added to the beaten pulp suspension. Immediately thereafter, the pH is adjusted with sulfuric acid to about 6.4 to 6.8 and a water-soluble aluminum-containing salt (4 grams of alum) is added. Handsheets of paper made at a pH between 5.8 and 7.6 from this suspension show strong water repellency.

(b) The procedure described in (a) is repeated except that no sulfuric acid is added and the amount of alum added is 24 grams. Handsheets of paper made at a pH of 5.8 show strong water repellency.

(c) The procedure described in (a) is repeated except that the aluminum-containing salt used is sodium aluminate, NaAlO_2 . Sheets of paper made at a pH between 5.8 and 6.4 show strong water repellency.

(d) The procedure described in (c) is repeated except that the aluminum-containing salt used is aluminum potassium sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$. The resulting sheets of paper show strong water repellency.

(e) The procedure described in (c) is repeated except that the aluminum-containing salt used is aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The resulting sheets of paper show strong water repellency.

Similar good results are obtained when pulp consisting of 20 per cent rayon and 80 per cent G-hemp is used in place of the kraft pulp in the procedures described in (a) through (e) of this example.

Example 4

(a) A 33 per cent solution of a propyl water glass is prepared by mixing propyltriethoxysilane (206 grams) in a flask with water (168 grams)

containing sodium hydroxide (40 grams) and ethanol (100 cc.), and distilling the resulting mixture until 228 grams of 90 per cent ethanol have been recovered. This silicate solution (12 grams) may be used in place of the ethyl water glass in the procedure described in Example 3 (a) to obtain paper having strong water repellency.

(b) A 32 per cent solution of a butyl water glass is prepared by mixing butyltriethoxysilane (220 grams) in a flask with water (168 grams) containing sodium hydroxide (40 grams) and ethanol (100 cc.), and distilling the resulting mixture until 190 grams of 90 per cent ethanol have been recovered. This silicate solution (12.8 grams) may be used in place of the ethyl water glass in the procedure described in Example 3 (a) to obtain paper having strong water repellency.

(c) The procedure described in (b) is repeated except that a 32 per cent phenyl water glass prepared from phenyltriethoxysilane by the procedure hereinbefore described for the preparation of a 32 per cent ethyl water glass is used. The water repellency of the paper produced from this phenyl water glass solution is even greater than the strong repellency produced by the alkyl water glasses hereinbefore described.

Having described the invention we claim:

1. The method of sizing paper that comprises treating an aqueous pulp suspension by steps in the following order: (1) adding a water-soluble aluminum compound to said suspension, (2) adding an aqueous solution of a water-soluble salt of an organosilicic acid and a metal selected from the class consisting of alkali metals and alkaline earth metals, and (3) preparing paper from said suspension, said aluminum salt being present in amount sufficient to neutralize the organosilicic acid salt and to completely precipitate and fix the organosilicic acid generated thereby on the pulp fibers and said organosilicic acid having an average of 0.05 to 3 organic groups containing from 1 to 12 carbon atoms attached to each silicon atom by carbon-silicon bonds.

2. The method of sizing paper comprising treating an aqueous pulp suspension by steps in the following order: (1) adding aluminum sulphate to a uniform, dilute suspension of paper pulp of

the type used in the making of paper, (2) adding an aqueous solution of a water-soluble alkali metal salt of an organosilicic acid to said aluminum sulphate treated pulp suspension, and (3) forming paper from said aluminum sulphate and organosilicic acid salt-treated suspension, said aluminum sulphate being added in amount sufficient to completely neutralize said alkali metal salt present and to precipitate and fix the organosilicic acid generated thereby to the pulp fibers and said organosilicic acid having an average of 0.05 to 3 non-hydrolyzable organic groups containing from 1 to 12 carbon atoms attached to each silicon atom by carbon-silicon bonds.

3. The method of sizing paper comprising the steps of treating an aqueous pulp suspension in the following order: (1) adding aluminum sulphate to said suspension, (2) adding an aqueous solution of an alkali-metal silicate containing from 1 to 12 carbon atoms to said aluminum sulphate-treated suspension, agitating said suspension, and (3) forming paper from said aluminum sulphate and silicate-treated suspension, said aluminum sulphate being added in amount sufficient to completely neutralize the amount of alkali-metal silicate added and to precipitate and fix the silicic acid generated thereby to the pulp fibers.

4. The method of claim 3 in which the silicate utilized is butyl silicate.

5. The method of claim 3 in which the silicate utilized is ethyl silicate.

6. The method of claim 3 in which the silicate utilized is phenyl silicate.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,507,200	Elliot et al. -----	May 9, 1950
2,528,554	Rust -----	Nov. 7, 1950

OTHER REFERENCES

Bergendahl et al., Paper Trade Journal, vol. 125, No. 10, Sept. 4, 1947, pp. 40-48 (p. 44 pertinent).

Bass, et al., Modern Plastics, Nov. 1944, p. 124.