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AQUEOUS DISPERSIONS OF CARBOXY-FUNCTIONAL SILICONES

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U.S. Cl. 260—29.2 M 1 Claim

ABSTRACT OF THE DISCLOSURE

A sizing agent for paper is disclosed which is a siloxane copolymer containing about 0.1 to 50 mole percent of carboxy-functional siloxane units. Paper sized with this siloxane has enhanced resistance to wetting. Sizing can be accomplished by either internal sizing processes (wet end) or surface sizing processes (dry end).

This application is a division of application Ser. No. 847,742, filed Aug. 5, 1969 now U.S. 3,729,444.

This invention relates to a sizing agent for paper, the paper which has been sized with this agent, and two methods for sizing the paper.

It is well known that cellulosic fibers constitute the bulk of finished paper. In addition thereto, however, finished paper usually has a wide variety of internally contained or surface carried ingredients employed to impart particular desired properties to the paper. These ingredients include, for example, fillers such as clay, chalk and other oxides and salts of metals, dyes and colorant materials, mordants, retention aids, wet-strength agents, sizing agents, and the like.

Paper is sized in order to increase its resistance to penetration by liquids, particularly water, and to improve its printability. The most common sizing system is rosin soap (sodium rosinate) and papermakers' alum (aluminum sulfate). In addition to these sizes, hydrocarbon and natural waxes, starch, sodium silicate, glues, casein, synthetic resins, latices, and various silicones have been employed as sizing agents.

A variety of mechanisms by which sizing takes place have been proposed. There has been, however, little agreement among those skilled in the art as to the mechanisms involved. The actual mechanism involved probably varies with the particular sizing agent being employed and it is likely that the various sizing agents perform their function by varying mechanisms.

It is an object of this invention to provide a new sizing agent for paper. It is another object to provide a high quality sized paper. A further object of this invention is to provide new methods for sizing paper. Another object is to provide a treatment for paper, particularly newsprint, whereby linting of the paper during printing is substantially reduced. These and other objects of the invention will become readily apparent to those skilled in the art from the following description and the claims.

More specifically, this invention relates to a size for paper which is a siloxane copolymer consisting essentially of about 50 to 99.9 mole percent of

$$R_nSiO_{\frac{4-n}{2}}$$

units wherein R is a hydrocarbon or a substituted hydrocarbon radical and n has a value of from 0 to 3, and about 0.1 to 50 mole percent of

$$HOOC{-}R'{-}\overset{R_m}{\overset{|}{Si}}O_{\frac{3-m}{2}}$$

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units wherein R is as defined above, R' is a divalent linking group attached to the silicon atom via a silicon-carbon bond and m has a value of from 0 to 2, at least 90 mole percent of all the siloxane units in the copolymer containing an R radical being ones wherein at least one of the R radicals is a methyl radical, at least 90 mole percent of all the siloxane units in the copolymer having a degree of substitution of 2, and said siloxane copolymer having an overall degree of substitution in the range of about 1.8 to 2.1.

This invention also relates to an aqueous dispersion of the siloxane copolymer as defined above.

This invention still further relates to a paper sized with a siloxane copolymer as defined above.

This invention also relates to a process of internally sizing paper which includes the step of adding the size to the paper pulp at the wet end before the formation of the web, wherein the improvement comprises employing as the size a siloxane copolymer as defined above.

Finally, this invention relates to a process of surface sizing paper which includes the step of applying the size to the paper after the web has been formed, the improvement comprising employing as the size the siloxane copolymer as defined above.

As stated above, the R group in the siloxane copolymer can be any monovalent, hydrocarbon or substituted hydrocarbon radical, with the provision that at least 90 mole percent of all the siloxane units in the copolymer containing an R radical being ones wherein at least one of the R radicals is a methyl radical. Illustrative of the other R radicals that can be present are alkyl radicals such as the methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl, dodecyl, octadecyl and myricyl radicals; alkenyl radicals such as the vinyl, allyl and hexenyl radicals; cycloalkyl radicals such as the cyclobutyl and cyclohexyl radicals; aryl radicals such as the phenyl, xenyl and naphthyl radicals; aralkyl radicals such as the benzyl and 2-phenylethyl radicals; alkaryl radicals such as the tolyl, xylyl and mesityl radicals; the corresponding halohydrocarbon radicals such as 3-chloropropyl, 4-bromobutyl, 3,3,3-trifluoropropyl, chlorocyclohexyl, bromophenyl, chlorophenyl, alpha,alpha,alpha-trifluorotolyl and the dichloroxenyl radicals; the corresponding cyanohydrocarbon radicals such as 2-cyanoethyl, 3-cyanopropyl and cyanophenyl radicals; the corresponding isocyanohydrocarbon radicals such as the 3-isocyanopropyl and 6-isocyano hexyl radicals; the corresponding hydroxyhydrocarbon radicals such as the 3-hydroxypropyl, 5-hydroxypentyl, hydroxyphenyl and hydroxynaphthyl radicals; the corresponding mercaptohydrocarbon radicals such as mercaptoethyl, mercaptopropyl, mercaptohexyl and mercaptophenyl; ether and ester hydrocarbon radicals such as

$—(CH_2)_3OC_2H_5$, $—(CH_2)_3OCH_3$, $—(CH_2)_3COOC_2H_5$ and $—(CH_2)_3COOCH_3$; the corresponding thioether and thioester hydrocarbon radicals such as

$$—(CH_2)_3SC_2H_5 \text{ and } —(CH_2)_3COSCH_3;$$

and nitrohydrocarbon radicals such as the nitrophenyl and 3-nitropropyl radicals. It is preferred that the R radical contain from 1 to 18 carbon atoms.

In the carboxy-functional siloxane unit, R' which links the carboxy group to the silicon atom can be any divalent linking group attached to the silicon atom via a silicon to carbon (Si—C) bond. This by way of illustration, R' can be a divalent linking group such as a divalent hydrocarbon radical, divalent radicals consisting of carbon, hydrogen and oxygen atoms and divalent radicals consisting of carbon, hydrogen and sulfur atoms. Specific examples of R' include the methylene, ethylene, propylene, hexamethylene, decamethylene, $—CH_2CH(CH_3)CH_2—$, phenylene, naphthylene, $—C_6H_4—CH_2—C_6H_4—$

$$-CH_2-C_6H_4-C_6H_4-CH_2-,$$

$$-C_6H_4-O-C_6H_4-,\ -CH_2CH_2SCH_2CH_2-,$$

$$-CH_2CH_2OCH_2-,\ -C_6H_4-S-C_6H_4-,$$

$$-CH_2CH(CH_3)\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-$$

$$-(CH_2)_3\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-$$

and the

$$-(CH_2)_3\overset{O}{\overset{\|}{C}}-S-CH_2CH_2$$

radical. It is preferred that the R′ radical contain from 2 to 10 carbon atoms.

As set out above, the siloxane copolymer of this invention consists of 50 to 99.9 mole percent, preferably 90 to 99 mole percent, of the

$$R_nSiO_{\frac{4-n}{2}}$$

units and 0.1 to 50 mole percent, preferably 1 to 10 mole percent, of the

$$HOOC-R'-\overset{R_m}{\overset{|}{Si}}O_{\frac{3-m}{2}}$$

units. In the first siloxane unit *n* can have a value of 0, 1, 2 or 3 and in the second siloxane unit *m* can have a value of 0, 1 or 2. However, it should be noted that these values of *n* and *m* are subject to the limitation that at least 90 mol percent of all the siloxane units in the copolymer have a degree of substitution of 2 and that the siloxane copolymer must have an overall degree of substitution in the range of about 1.8 to 2.1. Thus while the siloxane copolymer can contain some small amounts of unsubstituted silicon atoms or mono- and tri-substituted silicon atoms as well as di-substituted silicon atoms, the amounts of these units other than the di-substituted units is limited in order to obtain the results desired according to this invention.

So far as is known at this time, the method of preparation of the siloxane copolymer of this invention is not critical. However, the emulsion polymerized copolymers are preferred in that they tend to give somewhat better results than the corresponding solvent or bulk polymerized copolymers and in that it is preferably to employ the copolymer in the form of an aqueous dispersion and therefore the resulting copolymer does not have to be emulsified or dispersed after preparation when the copolymer is prepared by the emulsion polymerization technique. The details of the various techniques by which these copolymers can be prepared will be obvious to those skilled in the art from the instant disclosure.

In accordance with this invention, it is preferred that the paper be sized by a wet end technique; that is it is preferred that the paper be internally sized by a process which includes the step of adding a size to the paper pulp at the wet end before the formation of the web. Thus, for example, an aqueous dispersion of the siloxane copolymer size as defined heretofore can be added to the paper pulp at the beater, at the head box, at the fan pump, or in the stock chest. Thus, when the web is laid down it will have mixed with it the size of this invention. The use of the size of this invention, however, is not limited to a wet end sizing process. It is also very useful for surface sizing paper in a process which includes the step of applying the size to the paper after the web has been formed. Thus, any conventional technique of application, such as a water box on a calender, tub sizing, size press, transfer rolls, spraying and the like can also be employed for sizing the paper. After application of the size of this invention, the paper is handled in the same manner that it would be as if the size hadn't been applied; that is to say, it is simply dried by a conventional technique such as standing at room temperature, passing it through a hot air oven, exposing to infrared, microwaves, or dielectric heating, or by passing it over hot dryer cans.

The amount of the siloxane copolymer size of this invention employed should be at least sufficient to enhance the resistance of the paper to wetting by an aqueous medium. The amount of the size of this invention present in and/or on the final product will obviously depend to some extent on the intended end use of the product. As soon as some increase in resistance to wetting is discernible, as compared to the untreated state, the treated paper can be deemed sized. Generally speaking, when the size is added to the wet end an amount in the range of 0.2 to 50 pounds of siloxane solids per ton (2000 lbs.) of dry paper pulp solids will be employed. Preferably the amount used in the wet end will be in the range of 0.5 to 4 pounds. This is roughly equivalent to depositing an amount of 0.01 to 2.5 percent by weight of silicone solids on the finished paper with a preferred range of 0.025 to 0.2 percent by weight of silicone solids being deposited. As far as the concentration of the siloxane copolymer in the aqueous dispersion used in a dry end process, this is not critical and only the amount deposited is actually significant.

Now that those skilled in the art may better understand how the instant invention can be practiced, the following examples are given by way of illustration and not by way of limitation. All parts and percents referred to herein are on a weight basis unless otherwise specified.

EXAMPLE 1

A mixture of 917.3 g. of water and 2.5 g. of dodecylbenzenesulfonic acid were combined in a 2000 ml. three-necked flask fitted with a condenser, air stirrer and addition funnel. The solution was stirred and heated to 60° C. at which time a mixture of 73.7 g. (0.61 mole) of dimethyldimethoxysilane and 6.5 g. (0.032 mole) of $CH_3OOC(CH_2)_3Si(CH_3)(OCH_3)_2$ were added from the addition funnel over a one and one half hour period. A stable, bluish-white emulsion resulted. The emulsion was then heated for an additional 6 hours at 60° C., then cooled to room temperature and stirred for 18 hours. Evaporation of a 10 g. sample of the acidic emulsion afforded 3.91 percent solids. The deposited polymer was a clear, viscous fluid. An additional sample of polymer isolated via isopropanol precipitation of the colloid by mixing 3 volumes of isopropanol per volume of colloid was analyzed by infrared spectroscopy and found to contain an ester to acid ratio of 2.7:1.0 showing that part of the ester functionality had been converted to the carboxy functionality.

The above prepared siloxane copolymer was evaluated by immersing a 12.5 cm. Whatman No. 1 filter paper in 20 ml. of the acidic colloid for 5 minutes then air-drying it at 60° C. for 3 hours. For purposes of comparison, an identical piece of filter paper was immersed in 20 ml. of acidic dimethylsiloxane colloid prepared by the emulsion polymerization of hexamethylcyclotrisiloxane employing dodecylbenzenesulfonic acid as the surfactant-catalyst. A drop of water was placed on the treated filter papers and the time noted for it to be absorbed into the paper. At this point, treatment with the carboxy-functional containing siloxane copolymer was slightly better than with the dimethylsiloxane polymer treatment. Each treatment filter paper was then placed in an eight ounce bottle of toluene, shaken for 1 hour, and then rinsed with fresh toluene and dried for 30 minutes at 60° C. Upon retesting the filter paper treated with the carboxy-functional siloxane copolymer of this invention, still exhibited good water resistance whereas the filter paper treated with the dimethylsiloxane polymer was no longer hydrophobic. The weights of the filter paper at intervals throughout this experiment indicated that the amount of treatment imparted to each filter paper was approximately the same

and that the carboxy-functional siloxane polymer was retained on the paper during the toluene extraction.

EXAMPLE 2

A mixture of 90.5 g. of water, 0.5 g. of dodecyl benzene sulfonic acid and 9.1 g. (0.041 mole) of dimethylcyclotrisiloxane were added to a 250 ml. three-necked flask fitted with a condenser, air stirrer and addition funnel. After stirring for 24 hours at room temperature, a white opaque emulsion was obtained. Then 1.3 g. (0.006 mole) of $CH_3OOC(CH_2)_3Si(CH_3)(OCH_3)_2$ was added to the emulsion from the addition funnel over a 40 minute period and then stirred for 18 hours at room temperature. The appearance of the emulsion remained essentially unchanged. Evaporation of a 10 g. sample of the emulsion at 60° C. and 1 mm. of mercury pressure afforded 5.9 percent solids. Analysis of the polymer (obtained via isopropanol coagulation) by infrared indicated an ester to acid ratio of 2.6:1.0.

When the above prepared carboxy-functional siloxane copolymer is used to size paper in the same manner as Example 1, substantially identical results are obtained.

EXAMPLE 3

To a 500 ml. three-necked flask equipped with condenser, stirrer and addition funnel, there was added 50 g. of isopropanol and 143 g. (0.794 mol) of mercaptopropylmethyldimethoxysilane and then the system purged with nitrogen. Then 1 g. of azobisisobutyronitrile was added to the flask and the contents heated to 76° C. Then a mixture of 50 g. of isopropanol and 59 g. (0.820 mol) of acrylic acid was added via the addition funnel over a period of 53 minutes. After the addition was complete, the solution was stirred for an additional 7 minutes, then cooled and filtered to obtain a clear, slightly yellow solution of $HOOCCH_2CH_2S(CH_2)_3Si(CH_3)(OCH_3)_2$. Infrared analysis of the product showed only a trace of C=C remaining from the acrylic acid.

2320 g. of water and 80 g. of dodecylbenzenesulfonic acid were mixed and then 1600 g. of dimethylsiloxane cyclics were stirred into the previously prepared solution. This mixture was then homogenized by passing it three times at 4000 p.s.i. through a homogenizer. This mixture was then allowed to polymerize at room temperature to obtain an emulsion of a hydroxyl endblocked polydimethylsiloxane polymer.

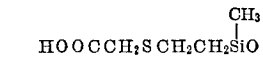
There was mixed together 250.65 g. of the above prepared hydroxyl endblocked polydimethylsiloxane polymer emulsion, 200.95 g. of water and 25 g. of a 20 percent aqueous solution of dodecylbenzenesulfonic acid and the resulting mixture heated to between 85 and 90° C. Then there was added to this mixture 23.40 g. of the above prepared carboxy-functional silane. The resulting mixture was then heated for 4 hours at 85 to 90° C. The reaction was carried out in a flask that was equipped with a reflux condenser, stirrer, thermometer and Pyr-O-Vane heat well regulator. The resulting product contained about 95 mole percent of dimethylsiloxane units and about 5 mole percent of the carboxy-functional siloxane units.

A 10 g. sample of the above prepared siloxane copolymer emulsion containing about 0.004 g. of silicone solids was evaluated as a paper size by spraying the solution onto a 9 inch by 12 inch commercial newsprint sheet weighing about 3.7 g. After application, the paper was dried in a conventional dryer. About 0.11 percent by weight of the silicone solids based on the dry weight of the paper was added on. The resistance of the paper thus sized to penetration by water was tested by placing a drop of water on the sheet with an eyedropper and observing the number of minutes required for the water to soak in. In this test, the time for the water to soak in was greater than 30 minutes, the maximum time for which this test is run.

A second-carboxy-functional siloxane copolymer identical to the one above was prepared in the same manner and also evaluated as a paper size. The same paper was used for this test, however, the size was applied from a 0.2 percent solution and padded onto the paper. This resulted in a pickup of about 0.2 percent silicone solids on the paper. This paper was also evaluated using the above described water drop test. Penetration time, or time for total absorption of the water drop, was 29 minutes on the paper sized with the copolymer whereas a control sample containing no treatment required only 3 minutes for the water to be completely absorbed.

EXAMPLE 4

To a 500 ml. three-necked flask equipped with condenser, stirrer and addition funnel there was added 66.6 g. (98 percent) of thioglycolic acid and 1 g. of azobisisobutyronitrile. The flask was purged with nitrogen and the contents then heated to 80° C. Then there was added over about a 30 minute period, at 80 to 86° C., 133.4 g. of a copolymer composed of about 50 mole percent dimethylsiloxane units and 50 mole percent of methylvinylsiloxane units, said copolymer containing about 12 percent (16 g.) of residual toluene from the preparation of the copolymer by cohydrolysis. After the addition was complete heating was continued for an additional 30 minutes at 82 to 84° C. The resulting siloxane copolymer contained about 50 mole percent of dimethylsiloxane units and 50 mole percent of



units.

To a flask there was added 136.2 g. of the hydroxyl endblocked polydimethylsiloxane emulsion prepared in the preceding example, 138 g. of water and 15.9 of a 20 percent aqueous solution of dodecylbenzenesulfonic acid. This mixture was heated to 85 to 90° C. and then 9.9 g. of the above prepared carboxy-functional siloxane copolymer was added and the resulting mixture heated at 85 to 90° C. over night. The resulting product contained about 95.5 mole percent of dimethylsiloxane units and about 4.5 mole percent of the carboxy-functional siloxane units.

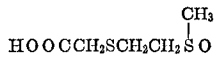
The above prepared carboxy-functional siloxane copolymer was evaluated as a paper size by applying it in the form of a 0.2 percent silicone solids aqueous dispersion to a commercial newsprint by padding it onto the paper. This resulted in about a 100 percent wet pickup of the aqueous dispersion of the size, or the depositing of 0.2 percent of silicone solids based on the weight of the dry paper onto the newsprint. The water resistance of the sized paper was evaluated employing the water drop test of the preceding example. The sized paper required 26 minutes before the drop of water was completely absorbed whereas the control containing no sized treatment required only 3 minutes for complete absorption of the water drop.

EXAMPLE 5

There was mixed together 942 g. of a hydroxyl endblocked dimethylsiloxane polymer, 58 g. of methylvinylcyclosiloxane, 10 g. of water and 10 g. of an acid-clay catalyst and then the mixture heated with stirring under a condenser at 80° C. overnight (about 18 hours), then cooled to room temperature and filtered to obtain a clear fluid.

There was mixed together in a quartz vessel 134 g. of the above prepared dimethyl-methylvinyl siloxane copolymer, 7 g. (98 percent) of thioglycolic acid and about 60 g. of hexane. The vessel was then thoroughly purged with nitrogen and then a small quantity of azobisisobutyronitrile added and the mixture radiated with ultraviolet light. The temperature was allowed to rise to 50° C. and then held at between 40 and 50° C. for 1 hour. The hexane and other light volatile materials were stripped off by heating to 40° C. at about 5 mm. of

mercury pressure to obtain a white liquid product which was a copolymer containing about 95 mole percent dimethylsiloxane units and about 5 mole percent of

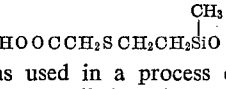


units. Titration of the product with 0.1 N potassium hydroxide showed 51.2 milliequivalents of acid per one hundred grams of product as compared to a theoretical value of 52.8 milliequivalents of acid.

20 g. of the above prepared carboxy-functional siloxane copolymer was stirred into a solution of 78 g. of water and 2 g. of the sodium salt of dodecylbenzenesulfonic acid to obtain a fairly stable emulsion. This emulsion was applied to paper as a size and then the paper evaluated by the above described water drop test. The sized paper showed a water resistance time of 25 minutes and 30 seconds as compared to a time of 2 minutes and 40 seconds for an untreated paper.

EXAMPLE 6

A printing grade paper was made using a 12 inch Fourdrinier paper making machine. The pulp used in making this paper was composed of about 70 percent hardwood kraft and about 30 percent of softwood kraft. When alum was present in the paper, it was present in the amount of 1½ percent based on the dry weight of the pulp solids. Varying amounts of a siloxane copolymer size consisting essentially of about 95 mole percent of dimethylsiloxane units and about 5 mole percent of



siloxane units was used in a process of surface sizing paper wherein it was applied to the paper after the web had been formed via a press sizer. The amount of siloxane employed is set out in the table and is given in pounds of siloxane solids per ton of dry pulp solids. The papers thus produced were evaluated for water resistance employing a drop test wherein 15 microliters of an aqueous dye solution at a pH of about 1 was placed on the paper and the time for total absorption of the test drop was measured. These papers were also evaluated for Mullen burst strengths on a Mullen tester using water in the chamber. The tensile strengths of the paper were also measured on a Model J Scott Tester, the samples being pulled at the rate of 12 inches per minute. Tensile strengths were measured in both the length (machine) and width (cross-machine) directions of the sample. The results of the tensile strengths are reported in terms pounds per linear inch. The treatments of the various paper and the results of the testing are set forth in the table below.

Paper	Alum	Siloxane (lbs./ton)	Water resistance (min.)	Mullen burst strength (lbs.)	Tensile strength (lbs./in.)	
					Length	Width
A [1]	No	0	1	28	26.8	13.2
B	No	1	¾	19	18.8	10.8
C [1]	Yes	0	2	31	27.4	16.0
D	Yes	0.5	5	30	24.8	13.0
E	Yes	1	25	29	26.1	12.5
F	Yes	2	12	27	22.5	13.0
G	Yes	4	21	29	22.8	14.4

[1] Included for comparison.

EXAMPLE 7

Papers were made as in the preceding example, except that a process of internally sizing the paper involving the addition of the size to the paper pulp at the wet end before the formation of the web was employed. Also in this example a conventional retention aid was used in making papers A–E, 0.08 pound of retention aid per ton of dry pulp solids was used in making paper A, 0.16 pound in making papers B–E, and none in making paper F. In the table below, papers A, B and C were sized by metering the siloxane copolymer into the pulp. In papers

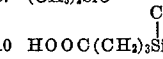
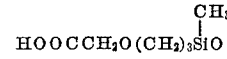
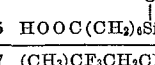
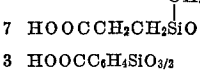
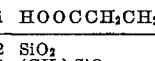
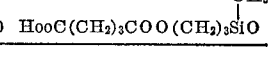
D and E, the size was stirred with the pulp about an hour before formation of the paper. The carboxy-functional siloxane copolymer size employed in this example was identical to the one used in the preceding example. The treatment of the paper and the results of the tests are set forth in the table below.

Paper	Alum	Siloxane (lbs./ton)	Water resistance (min.)	Mullen burst strength (lbs.)	Tensile strength (lbs./in.)	
					Length	Width
A	Yes	2	30	27	26.2	13.1
B	Yes	4	30	23	24.5	10.8
C	No	4	1	36	29.6	15.8
D	No	4	¾	35	31.8	16.1
E	Yes	4	30	28	26.9	13.5
F [1]	Yes	0	2			

[1] Included for comparison.

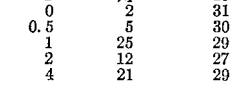
EXAMPLE 8

When the following siloxane copolymers are substituted for those of the preceding examples as sizing agents for paper, substantially equivalent results are obtained.

Copolymer	Mole percent	Siloxane units
(A)	3	$(CH_3)_3SiO_{1/2}$
	87	$(CH_3)_2SiO$
	10	
(B)	5	$C_5H_{11}SiO_{3/2}$
	92	$(CH_3)_2SiO$
	3	
(C)	10	$(CH_3)C_6H_4SiO$
	85	$(CH_3)_2SiO$
	5	
(D)	7	$(CH_3)CF_3CH_2CH_2SiO$
	83	$(CH_3)_2SiO$
	7	
	3	$HOOCC_6H_4SiO_{3/2}$
(E)	1	$NC(CH_2)_3SiO_{3/2}$
	98	$(CH_3)_2SiO$
	1	
(F)	2	SiO_2
	48	$(CH_3)_2SiO$
	50	

That which is claimed is:

1. An aqueous dispersion of a siloxane copolymer consisting essentially of about 90 to 99 mole percent of $(CH_3)_2SiO$ units, and about 1 to 10 mole percent of



units wherein R′ is composed of carbon, hydrogen and sulfur atoms, the sulfur atoms being present in the form of thioether linkages, said R′ containing from 2 to 10 carbon atoms.

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MURRAY TILLMAN, Primary Examiner

A. H. KOECKERT, Assistant Examiner

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

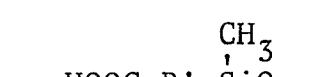
PATENT NO. : 3,763,069

DATED : October 2, 1973

INVENTOR(S) : Alvin E. Bey, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 60, the formula should read,



Signed and Sealed this

Eighth Day of February 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks