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Payne et al.

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[54] **SYNTHETIC BULK FABRIC TREATED WITH ORGANICALLY MODIFIED SiO_2 AQUASOL**

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[52] **U.S. Cl.** **428/96;** 427/427; 428/241; 428/331

[51] **Int. Cl.²**... **B32B 3/02;** B32B 5/16; B32B 33/00

[58] **Field of Search**..... 117/139.5 CF, 138.8 N, 117/141, 169 A, 169 R; 161/66; 427/427; 428/96, 241, 331

[56] **References Cited**

UNITED STATES PATENTS

2,734,834	2/1956	Rainard et al.	117/139.5 CF
2,734,835	2/1956	Florio et al.	117/139.5 CF
2,877,142	3/1956	Rusher et al.	117/169 R
2,928,754	3/1960	Schappel	117/139.5 CF
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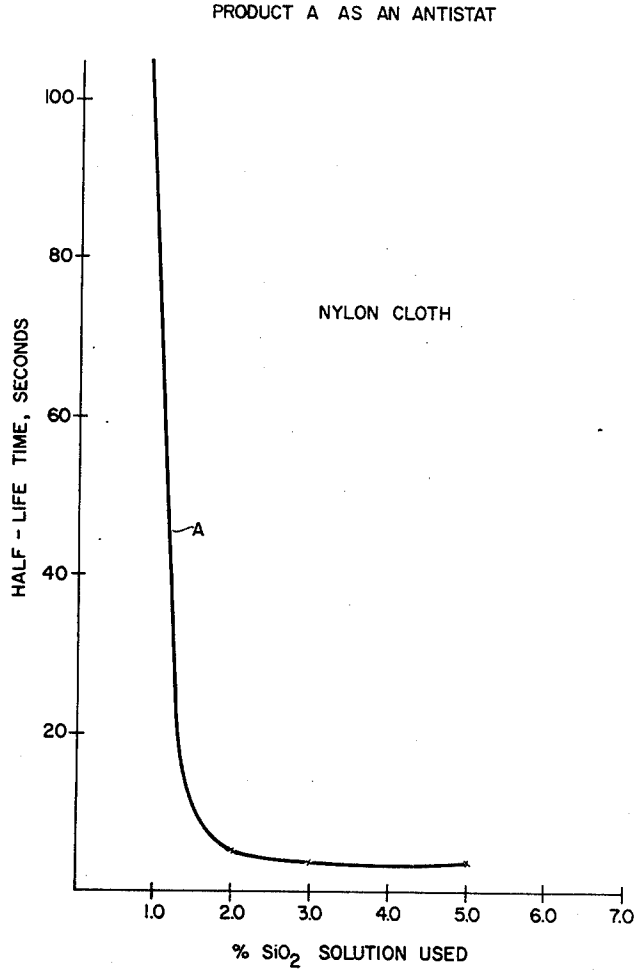
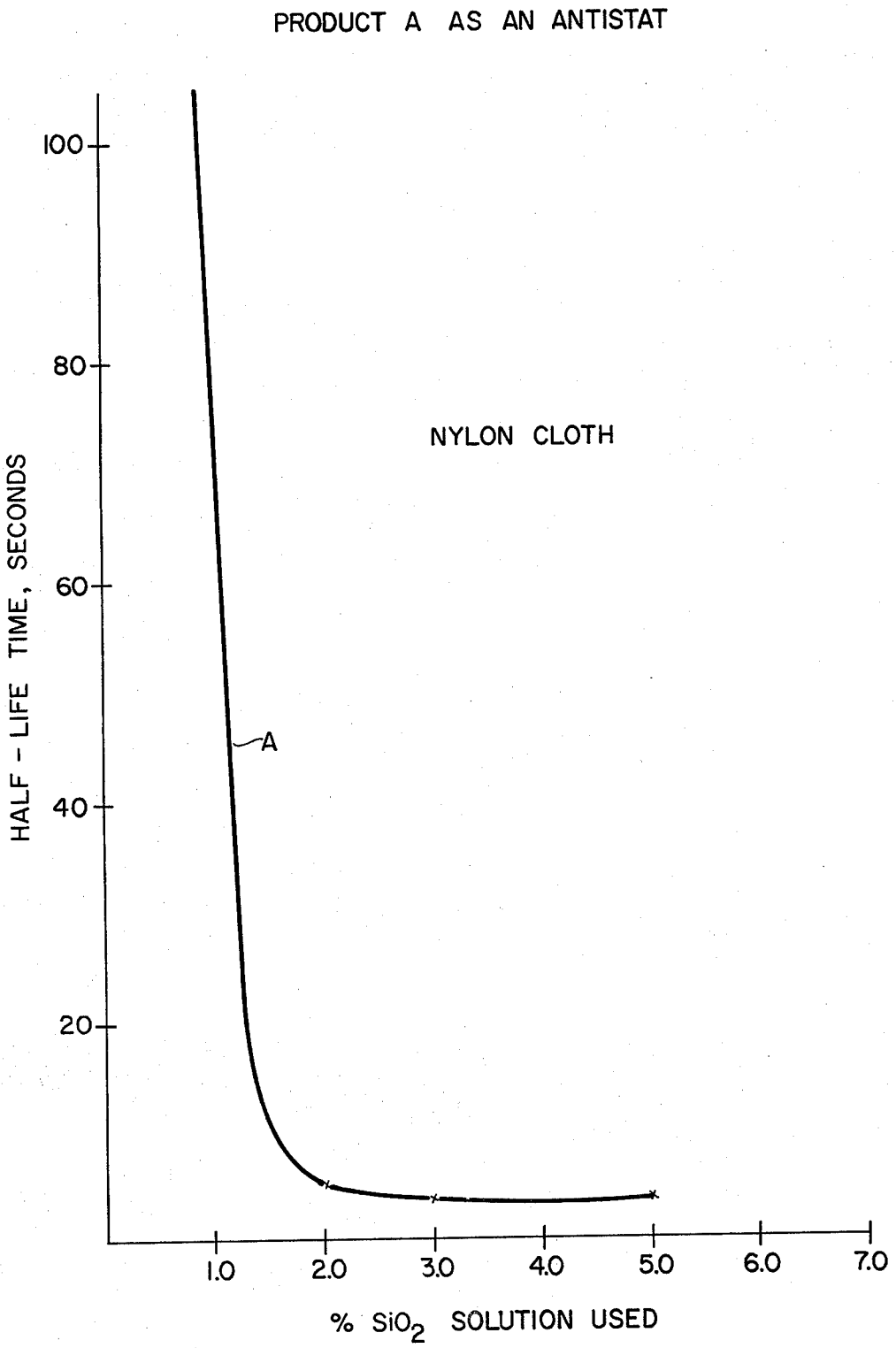
[57] **ABSTRACT**

A synthetic fabric bulk pile carpet and like soft material having both improved antistatic and antisoil characteristics obtained by applying from about 0.5 to 4% SiO_2 based upon the dry weight of the pile of an organically modified silica aquasol wherein generally there exists a double layer of an organic quaternary salt or hydroxide on each silica particle. Preferred quaternaries are dicoco dimethyl ammonium chloride, di(hydrogenated tallow)dimethyl ammonium chloride, tallow trimethyl ammonium chloride, and lauryl trimethyl ammonium chloride and methods of treating carpets and fabrics are disclosed.

5 Claims, 1 Drawing Figure




PRODUCT A AS AN ANTISTAT
NYLON CLOTH
HALF - LIFE TIME, SECONDS
100
80
60
40
20
A
1.0
2.0
3.0
4.0
5.0
6.0
7.0
% SiO2 SOLUTION USED

SYNTHETIC BULK FABRIC TREATED WITH ORGANICALLY MODIFIED SiO_2 AQUASOL

The present invention is concerned with the utilization of a modified aquasol on pile fabric of carpets and on other soft material and this application contains subject matter related to Peter H. Vossos, Ser. No. 373,217, filed June 25, 1973. The modified aquasol is coated with a double layer of a quaternary ammonium salt or hydroxide. The pertinent prior patent art is noted below and deals with related compounds and methods of treating textiles wherein the treating agent is an organosol modified with a quaternary ammonium compound:

U.S. Pat. No. 2,601,291 Horning et al. (duPont)
U.S. Pat. No. 2,692,863 Iler (duPont)
U.S. Pat. No. 3,629,139 Vossos (Nalco)
U.S. Pat. No. 3,652,329 Vossos (Nalco)
U.S. Pat. No. 3,660,301 Kovarik et al. (Nalco)

With respect to treating pile fabric, U.S. Pat. No. 2,622,307 Cogovan et al. (Mohawk Carpet) is of interest.

U.S. Pat. No. 3,033,699 Aarons et al. (duPont) is specially of interest with respect to pile fabric and carpets by treatment with a combination of silica and clay which functions as a combined antistatic and antisoil treatment.

In the literature E. Matijevic, *Surface and Colloid Science*, Volume 6, John Wiley and Sons, 1973, pages 74, 84–86, teaches the effect of adding organic bases to aqueous silica sol and the resultant antisoil and antistatic or conductive properties added thereto.

Additionally, R. K. Iler, *The Colloid Chemistry of Silica and Silicates*, Cornell Press, 1955, pages 100–112, relates to the types and effects of counter-ion concentration of additives to reverse the charge on the silica.

In the present description the term "soft materials" embraces fabrics consisting of carpets, wall coverings, draperies, car interiors, etc.

THE STARTING AQUEOUS SILICA SOLS

Generally, any aqueous silica sol can be used for this invention. These are well known to the art. The starting aqueous silica sol can range from 10 to 60 percent by weight of discrete, dense colloidal particles of amorphous silica. The average particle diameter can range from 3 to 150 millimicrons and can have an average surface area from 20 M^2/g. to 1,000 M^2/g. It is preferred that the starting aqueous silica sol be from 30 to 50 percent by weight of discrete, dense colloidal particles of amorphous silica. The preferred particle diameter should range from 16 to 22 millimicrons and have an average surface area from 135 to 190 M^2/g.

The following is a table of commercially available aqueous silica sols. These are sold by Nalco Chemical Company under the Trademark Nalcoags.

It is preferred that the starting aqueous silica sols used in this procedure be double deionized by any of the well-known techniques. If the sol is not double deionized, it will be necessary to dilute the starting aqueous silica sol to approximately 35% silica.

A preferred starting silica sol for purposes of the present invention is that denoted as Nalcoag 1034A, a double deionized sol, containing 34% colloidal silica calculated as SiO_2. Typically Nalcoag 1034A contains less than 600 ppm of sodium, Na^+, calculated as Na_2O, and 180 ppm of chloride, Cl^-, as combined chloride and sulfate.

TABLE I

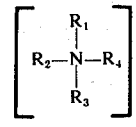
Nalcoag	1030	1034A	1035	1050	1060	1130	1140
Percent colloidal silica, as SiO_2	30	34	35	50	50	30	40
pH	10.2	3.1	8.6	9.0	8.5	10	10
Average particle size, millimicrons	11–16	16–22	16–22	17–25	40–60	8	15
Average surface area, $M^2/gram$	190–270	135–190	135–190	120–176	50–75	375	200
Specific gravity at 68°F	1.205	1.230	1.255	1.385	1.390	1.214	1.296
Viscosity at 77°F c.p.s.	5*	5*	5	70*	5–10	7	8
Na_2O, percent	0.40	0.06*	0.10	0.30	0.10	0.65	0.40

*Less than

In utilizing commercial silica sols, effort was made to start with a relative concentration of SiO_2:Na_2O of greater than about 200/1.

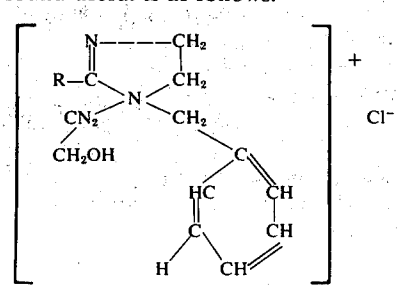
THE QUATERNARY AMMONIUM COATING

The quaternary ammonium compound has the formula:



wherein R_1, R_2 are methyl
R_3 is methyl or a C_8—C_{20} long hydrocarbon chain;
R_4 is a C_8—C_{20} long hydrocarbon chain;
X^- is an anion selected from the group consisting of chloride, bromide, iodide, and hydroxide.

Another quaternary ammonium compound that has been found useful is as follows:



wherein
R is alkyl hydrocarbon chain having 2–6 carbon atoms.

In the formulae above the nitrogen substituent groups are chosen with the viewpoint of providing water solubility or having some degree of water dispersibility provided by 2 or 3 methyl coupled with 1 or 2 long hydrocarbon chain groups to provide the necessary fatty residue for the coating. Thus, operable compounds are those where R_4 or $R_3 + R_4$ are lauryl, plamityl, stearyl, oleyl, octyl, caprylyl, etc., and these may be similar or dissimilar. Preferred substituents for R_3 and R_4 are quaternary amines derived from mixtures of

fatty acids that occur in various fats and oils such as coconut oil, hydrogenated tallow, hydrogenated castor oil, etc. Specific examples of preferred quaternary compounds include:

Lauryl trimethyl ammonium chloride
Dicocodimethyl ammonium chloride
Di(hydrogenated tallow) dimethyl ammonium chloride
Tallow trimethyl ammonium chloride

An additional operable compound not consonant with the formulae supra, is tricaprylmethyl ammonium chloride. Additionally operable are the alkyl trimethyl ammonium salts with anions consonant with the first formula above which are listed in Table 39, *Encyclopedia of Chemical Technology* II, Volume 19, Wiley Interscience, 1968, page 564, and incorporated herewith by reference.

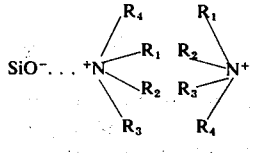
Experimental data indicated that the coating on the silica particles by the quaternary is a double coating of molecular nature which, as an end result, reverses the negative charge on the silica with a positive charge on the outward nitrogen, which is part of the second coating of quaternary.

SOLVENT

The starting silica aquasols are preferably double deionized sols, and it has been found highly advantageous to add a hydrophilic bridging solvent such as a lower alkanol and a preferred alkanol is isopropanol. The amount of isopropanol utilized is preferably about 3–10% by weight of the water in the aquasol. The lower alkanol, e.g., isopropanol, conveniently is added during the preparation of the aquasol at the point of addition of the quaternary. The addition of the alkanol helps stabilize the quaternary and to lessen gelation and precipitation tendencies. Generally, the mixture is stirred from about 1–60 minutes.

METHOD OF MANUFACTURE.

In the present process, two discrete layers of the organic quaternary material are coated onto each silica particle. As the first layer goes on, it neutralizes any charge (negative) on the silica particle and imparts an organophilic surface. At this point, the sol becomes less stable and there is a tendency for gelation or precipitation to occur. There is a decided thickening visually noticeable. The lower alkanol solvent which is a requisite acts to solubilize or disperse the coated sol in water. As the second coat becomes a layer, a different charge (positive) is imparted to the particle and the sol is restabilized. The second layer is oriented with its organophilic portion toward the surface and its ionic portion toward the solvent.



A preferred manufacturing process which enables the manufacture of the present double coated layer is as follows. In step one, the lower alkanol solvent is added to the quaternary amine in excess. As step two, the colloidal silica is added with sustained mixing into the amine solution. A preferred sol to use is a double deionized sol with the properties like Nalco 1034A (see Table I). A silica sol of this type has little charge on its surface and tends to be more stable in the critical period during the application of the first coating or in the intermediate stage of manufacture. Alternative commercial sols may be used, but optimum results are obtained by utilization of sols having 135–190 M^2/gram average surface area. In the initial contact between the silica particle and the amine, the system may thicken, but the alcohol prevents gelation or precipitation until the system thins out when additional silica sol is added. By the procedure of adding the sol to the amine solution, there is always an excess of amine and the two layers can go onto the silica sequentially. Further the simultaneous existence of both positive and negative sols is avoided.

The above is the preferred method for production of the double layered sols. Other less preferred methods are by utilization of high shear mixing and in certain favored cases the elimination of the alcohol stabilizer.

THE AMOUNT OF QUATERNARY COATING ON SiO_2

The amount of the quaternary in relation to the silica depends upon the particle size of the colloidal silica. The smaller the particle size, the more quaternary will be required. In general, the ratio of SiO_2 to quaternary will be from 25 to 1 to 2 to 1, and more often will be from 3:1 to 10:1. For an average particle diameter of 20 millimicrons a ratio of about 3 to 1 is typical.

The above percentage or concentration additions of quaternary have been found optimum in using the combination of Nalcoag 1034A and the quaternary dicoco dimethyl ammonium chloride. However, additional variations over the range depending especially on the quaternary selected are necessary as the length of the long carbon chain or chains varies. The size of the silica particle also affects the amount of quaternary necessary. The purpose of the present invention is to produce a molecular double layer of quaternary and generally reversal of charge.

The present formulation uniformly requires a layer of quaternary which is physically sorbed and contains a molecular double layer. In the case of a charged silica sol, layer one, the innermost layer around the silica, neutralizes the negative charge on the silica particle, and the second or outermost layer disposed with its organophilic portion toward the SiO_2 surface reverses the charge so that the coated particle is now significantly positively charged. Thus, both the variables as to the silica particle size and as to the fatty chain length influence the amount of quaternary necessary to produce the double layer.

The present invention uniquely combines a silica fraction acting as an antisoil agent and a quaternary fraction acting as an antistatic agent. The application of the quaternary silica compounds of the present invention to pile fabric and carpets is usually in the nature of 1–4% by added weight based upon the percent of silica as SiO_2 added to the dry weight of the pile. Less than about 1% or in some cases, 0.5% gives lack of treating effect and above 4% produces a white carpet or pile fabric.

In the past it has been found that commercial quaternary compounds used as antistatic agents present a very bad soiling problem and in fact are prosoil agents. However, in the present compounds, when combined

with silica, these carpet-treating preparations can be viewed as both antistatic and antisoil. The amount of coating or treating agent is similar to the prior art, for example, U.S. Pat. No. 2,622,307 Cogovan (Mohawk) at column 4, lines 33–49, when referring to the coating of colloidal silica on pile yarns. The combination of antistatic and soil-resistant components is also noted in the prior art in U.S. Pat. No. 3,033,699 Aarons et al. (duPont) which utilizes a combination of clay and colloidal silica sol and in that patent also is utilized the soil testing using Sanders and Lambert's synthetic soil at Example 1 and column 4.

FIG. 1 represents results from antistat tests at different percentages of silica where the half-life time expressed in seconds was measured according to the procedure of Example III-A.

In the followinng experimental procedures the antistatic effect is due to the quaternary component and is measured and observed on fabric samples treated by dip methods. The antisoil effect is due to the silica component and is measured on fabric samples treated by spraying.

EXAMPLE I

Preparation of Quaternary Coated Silica Aquasols

A 34% SiO_2 sol in H_2O was coated with a fatty quaternary amine. To 11.2 parts of Arquad 2C-75 (dicoco dimethyl ammonium chloride) was added 3.5 parts of isopropanol followed by 85.3 parts of Nalcoag 1034A deionized silica sol. The preparation was repeated several times and it was noted that the results improved where slow addition was followed with good mixing in the preparation to avoid the formation of gel particles. It was further noted that the product went through a very thick stage as the 1034A silica sol was added, but the sol thinned out when it was all added. The product was found to be stable over a one-year period.

An additional run which doubled the amount of isopropanol was advantageous in the speed of solubility of the quaternary. The silica sol utilized, Nalcoag 1034A, has a pH of 3.4. In separate runs, this pH was varied from 3.4 to 3.8 without adversely affecting the product. However, where the pH was lowered to about 2.9, difficulties were experienced with a cloudy product which did not exhibit a sol-like appearance.

Additional experiments or runs were made with Nalcoag 1050, a 50% colloidal SiO_2, which had been diluted to about 35% and the results were quite similar to those obtained utilizing the 34% SiO_2 or Nalcoag 1034A above as shown in Example II.

EXAMPLE II

Preparation of Double Coated Silica Sol

To 33.6 grams of Arquad 2C-75 was added 10.5 grams isopropanol followed by 150 ml of Nalcoag 1050 silica sol diluted with 90 grams of water. The preparation was made with good mixing throughout the addition steps. The product became very thick during the Nalcoag 1050 addition but thinned out again after a period of a few minutes. The product is stable over a one-year period.

EXAMPLE III-A

Antistatic Properties

Static electricity tests were done on pieces of nylon cloth pre-prepared by washing with detergent for 1 cycle and then washing without detergent for 1 cycle before drying. The nylon cloth was then cut into 5 inches × 5 inches squares and immersed in the test solution, wrung out to 100% wet retention, thus giving a carry-over of 2.15% silica based on dry weight of the cloth, and dried at 120°C for 5 minutes. Statis electricity tests were performed using the Stati-Tester, Model 169, from Most Associates, Inc., Marblehead, Massachusetts. A voltage of from 50–300 volts at 100 milliamps was applied to the nylon cloth. The initial voltage was measured and then the current shut off.The time required for the voltage to drop to half its initial value with no current applied was recorded as the half-life time. The shorter the time, the faster the charge dissipated from the cloth.

In the above, the quaternary utilized was dicoco dimethyl ammonium chloride and the original silica sol was 1034-A.

Results of the tests are shown below.

Treating Solution	Initial Voltage	Half-Life Time
Water	215	> 10 min.
0.87% Quat-2.15% Silica Sol	197	1.5 sec.
2.15% Silica Sol	200	> 10 min.

The results show that the quaternary modified silica sol functions as an effective antistatic agent and that the silica sol alone does not.

EXAMPLE III-B

Additional experiments were made utilizing the procedure of Example III-A but substituting di(hydrogenated tallow)dimethyl ammonium chloride, tallow trimethyl ammonium chloride, or lauryl trimethyl ammonium chloride for the dicoco dimethyl ammonium chloride utilized in Example III-A.

EXAMPLE III-C

Utilizing the procedure of Example III-A, additional tests were made with different silica sols at a 1% solid silica level. Table II shows the results of the tests.

TABLE II

Antistat Tests of Various Silica Sols

Silica Sol Used	Initial Voltage	Half Life Time	Temp RH	26°C 8%
Control (Chicago Tap Water)	210	10 min.		
1% 1030	195	10 min.		
1% 1034A	175	10 min.		
1% Product A*	190	30 sec.		

*Prepared by producing an organic double coating on a silica sol, 1034A, which double coating is dimethyl dicoco ammonium chloride, in such a manner that the product contains 30% SiO_2 and 8% quaternary.

TABLE III

Comparison of Product A vs Other Commercial Antistat Formulations

Sample	Dilution	Initial Voltage	Half Life Time	emp RH	26°C 8%
Control (Chicago Tap Water)	—	205	10 min.		
Product A	1:8	180	1 sec.		
Statico+	1:4	210	1 sec.		
Bonds EHP	1:26	80	0.5 sec.		

TABLE III-Continued

Comparison of Product A vs Other Commercial Antistat Formulations

Sample	Dilution	Initial Voltage	Half Life Time	emp RH	26°C 8%
26-12**					

+Statico manufactured by Walter Legge Company, Chicago.
**Bonds EHP26-12 manufactured by Bond Chemical Products, Chicago.
Both of the above compounds are fatty quaternary compounds.

EXAMPLE III-D

Utilizing the test procedures of Examples III-A, B, and C, certain antistatic properties were ascertained as follows. The components of Product A were checked individually for their antisoiling characteristics. This was done at several concentration levels corresponding to the following dilution ratios of the product:

1. 1:8 dilution of Product A
2. 1:15 dilution of Product A

A 1:8 dilution of Product A contains 3.9% silica and 1:6% quaternary (dicoco dimethyl ammonium chloride). A 1:15 dilution of Product A contains 2.5% silica and 0.87% quaternary. Tests were run on the individual components of each dilution for antistat values and the results are reported below in Table IV.

TABLE IV

Antistat Values for Components of Product A

Sample	Initial Voltage	Half Life Time	emp RH	26°C 22%
Control (Chicago Tap Water)	215	10 min.		
1:8-Product A	220	0.5 sec.		
3.9%-1034A	230	8 min.		
1.6%-dicoco dimethyl ammonium chloride	120	0.5 sec.		
1:15-Product A	190	1.5 sec.		
2.15%-1034A	200	10 min.		
0.87%-dicoco dimethyl ammonium chloride	150	0.5 sec.		

The results show that the silica needs the quaternary double coating to give antistat properties to the product.

EXAMPLE IV-A

Antisoil Properties

Testing of Product A for antisoiling properties required formulating a synthetic dirt which would soil carpeting evenly. Following the recommendation of U.S. Pat. No. 3,033,699 Aarons et al. (duPont), a bulked Sanders & Lambert synthetic dirt was prepared. This dirt mixture is the "standard dirt" mixture used for antisoiling tests by industry and gives fairly reproducible results with even soilings.

90% nylon-10% wool carpet samples were sprayed with test solutions to give a coverage of about 2% silica based on the weight of the pile of the rug. After drying, the test samples were placed along the wall of a quart metal can. About 800⅛ inch steel balls and 2.0g synthetic dirt were added to the can. The can was rotated on a set of rollers for ½ hour at 120 rpm. The carpet samples were then vacuumed and the brightness measured on a brightness meter made by Martin Sweets Co., Louisville, Ky.

The quaternary dicoco dimethyl ammonium chloride and the original silica sol was 1034-A.

Results of the tests are shown below.

Treating Solution	Brightness Before Soiling	Brightness After Soiling and Vacuuming	% of Original Brightness
Water	24.4	15.0	61.5
0.8% Quat-	24.4	16.4	67.2
2.15% Silica Sol			
0.87% Quat	24.4	12.7	52.0

The results show that the quaternary modified silica sol functions as an effective antisoilant and that the quaternary alone actually behaves as a prosoilant.

EXAMPLE IV-B

Additional experiments were made utilizing the procedure of Example IV-A but substituting di(hydrogenated tallow) dimethyl ammonium chloride, tallow trimethyl ammonium chloride, or lauryl trimethyl ammonium chloride for the dicoco dimethyl ammonium chloride utilized in Example IV-A.

EXAMPLE IV-C

Soiling characteristics of textile pile treated with Product A versus some selected commercial products are shown below in Table V.

TABLE V

Soiling Tests of Product A Versus Selected Commercial Products

Sample	Dilution	Brightness	% of Original Brightness
Original	—	24.9	100.0
Untreated & Soiled	—	14.2	57.0
Product A	1:8	15.0	60.2
Statico+	1:4	11.9	47.8
Bonds EHP26-12*	1:26	10.5	42.2

+Statico manufactured by Walter Legge Co., Chicago.
*Bonds EHP26-12 manufactured by Bond Chemical Products, Chicago.
Both of the above compounds are fatty quaternary compounds.

EXAMPLE V

Static and soiling characteristics of fabric treated with a composition similar to Product A except that the silica sol was an alkaline sol, Nalcoag 1050, rather than Nalcoag 1034A. Results are shown below.

TABLE VI

Antistat Values for Quat-1050 Products Versus Product A

Sample	Dilution	Initial Voltage	Half Life Time	emp RH	26°C 17%
Control (Chicago Tap Water)	—	210	5 min.		
Product A	1:8	170	0.5 sec.		
Quat-1050*	1:8	170	0.5 sec.		
Product A	1:15	220	6 sec.		

*The aqueous silica sol sold by Nalco Chemical Co., Chicago, under the name Nalcoag 1050.

TABLE VII

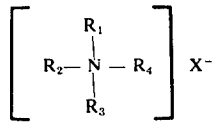
Antisoil Values for Quat-1050 Product Versus Product A

Sample	Dilution	Brightness	% of Original Brightness
Original	—	20.5	100.0
Untreated & Soiled	—	13.1	63.9
Product A	1:8	16.8	82.0
Quat-1050	1:8	17.3	84.4
Product A	1:15	16.1	78.5

The results indicate that the Quat-1050 product from alkaline stabilized values gave both antistat and antisoil values comparable with the acid stabilized sol of Product A.

We claim:

1. Synthetic bulk fabric having improved antistatic and antisoil properties, said fabric having been treated with an aquasol containing a minor amount of an aqueous polar solvent selected from lower alkanols having uniformly dispersed therein discrete dense colloidal particles of amorphous silica having an average particle diameter of 3–150 millimicrons and average surface area of from about 20 M^2/g to 1000 M^2/g, said silica particles having absorbed on their surfaces a quaternary ammonium salt or hydroxide, with the weight ratio silica, expressed as SiO_2, to the quaternary ammonium being at least 2:1 wherein the quaternary ammonium has the formula:



wherein

R_1, R_2 are methyl;

R_3 is methyl or a C_8—C_{20} long hydrocarbon chain;

R_4 is a C_8—C_{20} long hydrocarbon chain;

X^- is an anion selected from the group consisting of chloride, bromide, iodide, and hydroxide.

2. The synthetic bulk pile carpet fabric according to claim **1** wherein the quaternary ammonium salt or hydroxide is dicoco dimethyl ammonium chloride.

3. The synthetic bulk pile carpet fabric according to claim **1** wherein the quaternary ammonium salt or hydroxide is di(hydrogenated tallow)dimethyl ammonium chloride.

4. The synthetic bulk pile carpet fabric according to claim **1** wherein the quaternary ammonium salt or hydroxide is tallow trimethyl ammonium chloride.

5. The synthetic bulk pile carpet fabric according to claim **1** wherein the quaternary ammonium salt or hydroxide is lauryl trimethyl ammonium chloride.

* * * * *