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COATED OLEOPHOBIC FABRICS

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This invention relates to oleophobic finishes for fibrous materials. This application is a continuation-in-part of applicant's copending application Serial No. 85,469, filed January 30, 1961, and now abandoned.

The staining of fabrics with liquid born stains has long been a problem with respect to household and industrial fabrics. The degree to which the stain spreads and penetrates the fabric depends upon the degree to which the liquid carrier wets the fabric. If the liquid carrier spreads rapidly and widely into the fabric, it carries the stain with it, thereby producing a large spot which is difficult to remove unless the entire fabric is immersed in a solvent for the stain. Whereas, this is feasible for most garments, it is not feasible for upholstery or for many other decorative fabrics.

The advent of organosiloxane finishes was a major step forward in the elimination of water born stains, since the fabrics treated with heretofore employed organosiloxanes are highly water repellent. This means that a water born stain would not wet the fabric and hence the stain did not soak in. Thus, for example, water-based ink spilled on a commercial siloxane treated fabric can be easily removed without leaving a spot.

However, such was not the case with oil born stains. This was true because with heretofore employed siloxane finishes oil readily wet the surface and hence the stain was rapidly carried into the fabric. Furthermore, attempts to remove spots with a dry-cleaning solvent often resulted in ringing due to the fact that the solvents spread rapidly into the fabric and caused migration of the stain to the outer edges of the wet area. Thus, although siloxane treated fabrics heretofore available are easier to clean than fabrics which are untreated, they still leave much to be desired from the standpoint of resistance to oil stains.

In recent years oleophobic finishes have been developed for fabrics. The term, oleophobic, means that the fabric is not wet by the oil and acts toward oil just as a water repellent fabric acts toward water. However, heretofore oleophobic finishes were comprised principally of polyfluorinated organic or organosilicon compounds. Thus, for example, certain fluorinated sulfonamides containing 10 or more fluorine atoms per molecule give excellent oleophobicity. The same is true of highly fluorinated polyorganosiloxanes in which the silicon atoms are substituted with fluoroalkyl radicals and in which the fluorine content of the molecule is at least 48 percent by weight and preferably higher. Such materials make fabrics highly oleophobic.

However, highly fluorinated materials, whether organic or organosilicon are very expensive. Furthermore, the highly fluorinated organic compounds often give fabrics a harsh hand. This is undesirable for many applications.

It was known prior to this invention as shown in U.S. Patent 2,728,692, that dimethylpolysiloxane gums could be applied to wool and cured thereon to reduce the shrinkage of the wool during laundering. It was also known from U.S. Patent 2,940,875 that "devolatilized" dimethylpolysiloxane gums could be applied to fibrous materials for the purpose of improving the "abhesiveness" of the fibrous material. These gums were devolatilized by mixing with a small amount of finely divided silica and then heated to remove volatiles.

However, the gums described in the aforesaid patents do not give oleophobic finishes when applied to fabrics and cured. Applicant has found, however, most unexpectedly that certain dimethylpolysiloxane gums when applied to fabric and completely cured, do give olephobic finishes as described hereinafter.

It is the primary object of this invention to provide an oleophobic finish for fabrics at a lower cost than is possible with the oleophobic finishes previously known. Another object is to provide a finish which combines water repellency, oil repellency and excellent hand. Another object is to produce a finish having greater abrasion resistance than heretofore used oleophobic finishes. Other objects and advantages will be apparent from the following description.

This invention relates to an oleophobic article comprising a fabric coated with a cured polysiloxane consisting essentially of polydimethylsiloxane, which polysiloxane when applied to the base member had a viscosity of at least 1,000,000 cs. at 25° C., said coated fabric having an oil rating of at least 50.

The term "oil rating of at least 50" as employed in the specification means that the material is not wet by a drop of U.S.P. heavy mineral oil for a period of at least 2 minutes after a drop is placed on the coated base member. It is simple to determine when the drop has wet the base member since the area under the drop turns dark when wetting has taken place. It has been found that when a fabric is sufficiently oleophobic to pass the above tests, that it is sufficiently oleophobic to make substantially easier the removal of oil born stains thereform and also is substantially resistant to such stains.

It should be understood that the above test is the minimum required for the materials of this invention. It is possible employing the dimethylpolysiloxane gums hereinafter described to obtain oil ratings far in excess of this minimum. In other words, such materials are even more resistant to staining and even easier to clean than those having the minimum rating.

The term "consisting essentially of" polydimethylsiloxane means that the polymer is composed principally of dimethylsiloxane units but can contain other copolymerized siloxane units such as methylvinylsiloxane units, ethylmethylsiloxane units, monomethylsiloxane units and other siloxane units in amounts which do not interfere with the essential oleophobic nature of the polydimethylsiloxane.

For the purpose of this invention the polysiloxane must have a viscosity of at least 1,000,000 cs. at 25° C. Such siloxanes, are hereinafter referred to as "gums." It is essential that the polymer molecules be of such size that the viscosity of the polymer is at least this minimum figure. There is no critical upper limit to the viscosity provided of course, that the polymer is in such a state that it can be dispersed in a liquid and applied to the fabric. It appears that the higher the polymer the better oleophobicity one obtains.

Furthermore, the polysiloxanes which are employed in this invention must be essentially free of polymer molecules which are not capable of curing and which have very low molecular weights. When such molecules are present in the polydimethylsiloxane gum the latter is inherently incapable of producing an oleophobic finish even when cured.

In the commercial production of dimethylpolysiloxane gums, cyclic siloxanes are generally polymerized with alkaline catalysts. The resulting polymer may or may not be devolatilized by heating to remove unpolymerized cyclics. In any event when either the undevolatilized or heat devolatilized gum is applied to fabric and cured, the resulting fabric is readily wet with oil. As a matter of

fact, it is as readily wet with oil as if no siloxane were present.

The low molecular weight materials which ruin the oil repellency of polydimethylsiloxane gums, are not restricted to volatile components, but also include nonvolatile low molecular weight components. As a matter of fact a very volatile cyclic such as octamethylcyclotetrasiloxane is not detrimental if present in gum in normal amounts since it will evaporate during the curing of the gum coating. Precisely what the detrimental components are, applicant has not been able to determine. However, it is apparent that they must include nonvolatile cyclic molecules and nonvolatile linear molecules. Such materials are not removed by heat alone.

High molecular weight polydimethylsiloxanes suitable for use in this invention can be prepared in at least two ways. The best method is to extract the low molecular weight components from a dimethylpolysiloxane gum by the use of suitable solvents. Thus, one can dissolve the polysiloxane in toluene and then add sufficient methanol to precipitate the gum. This causes the high molecular weight components to precipitate while the low molecular weight components remain in solution.

The best solvent system is isopropanol. This is true because hot isopropanol dissolves both high and low molecular weight dimethylsiloxanes. However, when the solution is cooled to room temperature only the high molecular weight components precipitate. Thus, one can decant the solution of the low molecular weight components and the precipitated polymer is suitable for use in this invention.

During the solvent fractionation it is essential that any bond rearranging polymerization catalysts be removed or neutralized so that it does not degrade the polymer during fractionation. This can be done by any convenient method, such as by washing the catalyst from the polymer with water or by neutralizing any alkaline catalyst with an acid and an acid catalyst with a base.

A second way of producing polymers suitable for use in this invention is by the careful condensation of cyclic free hydroxyl endblocked polydimethylsiloxanes with a non-bond-rearranging catalyst such as calcium oxide. This produces polymers in which essentially all of the molecules are of high molecular weight. In general, the process involves heating a hydroxylated polysiloxane of say 1,000 cs. viscosity under reduced pressure to remove cyclic molecules and thereafter adding about a 20 mol excess of calcium oxide per mol of hydroxyl group in the polysiloxane. The mixture is then heated to a temperature of about 140° C. or above, whereupon the condensation of the SiOH groups takes place to form a high molecular weight gum which is free of nonvolatile low molecular weight material. This gum can be used without solvent extraction.

It should be understood that this invention is not limited to the above described theory as to why the gums prepared by the method of this invention are operative.

It is essential that the cure of the siloxane be sufficiently complete to produce the desired oleophobicity. The polysiloxane gums can be cured by conventional techniques. For example, the gum can be mixed with a SiH containing siloxane and the conventional metal catalysts such as heavy metal salts of carboxylic acids, or the gum can be cured by mixing with alkylpolysilicates or alkylorthosilicates and the conventional heavy metal carboxylic acid catalyst. In addition the gums can be cured by mixing with alkyl titanates.

In general, it is preferable to heat the coated fabric in order to enhance the cure of the gum. This is particularly true for commercial operation in a textile mill where fast curing is needed in order to maintain the proper speed in the production line. However, heating is not essential if the proper curing system is selected.

The gums can be applied to the fabric in any convenient manner such as by padding, dipping or spraying. They

can also be applied to the fabric either in the form of aqueous emulsions or solutions in organic solvents. The concentration of the siloxane gum in the treating medium is not critical nor is the pickup on the fabric critical, provided sufficient siloxane is applied to the fabric so that when cured it will give an oil rating within the specified range. Normally, the use of a 2 percent by weight solution or a 2 percent by weight emulsion gives a satisfactory treatment. Higher or lower concentrations can be used if desired.

In general, the amount of siloxane pickup is not more than 25 percent by weight based on the weight of 25 percent by the fabric. More than 25 percent is wasteful and approaches closed-pore coating. A preferred range of pickup is up to 5 percent by weight and a most preferred range is up to 2 percent.

The gum can be applied to any fabric, woven or knitted, organic or inorganic. Such fabrics include those made from, for instance, cotton, rayon, linen, wool, silk, synthetic fabrics such as nylon, Orlon, Dacron and Dynel, glass, metals and asbestos. Thus it can be seen that the compositions of this invention can be applied to fabrics made from cellulosic fibers, proteinaceous fiber, polyamide fibers, polyester fibers, glass fibers, vinylic fibers, asbestos fibers and metal fibers.

It should be understood that the fabrics of this invention are not only oleophobic, but they are also hydrophobic, thus they are resistant to a wide variety of liquid born stains and such as those produced by lubricating greases, lubricating oils, gravy, butter, lard, catsup, mustard, bacon grease, French dressing and mayonnaise. Also fabrics treated according to this invention do not give ringing when wet with dry-cleaning solvents such as carbon tetrachloride, perchloroethylene, petroleum ether and like.

The oil rating of the fabrics shown below has reference to the concentration of n-heptane in the U.S.P. heavy mineral oil employed. In each case, a drop of the oil with or without dissolved heptane was placed on the fabric and the behavior was observed for 2 minutes. If the drop did not wet the fabric within 2 minutes, the fabric was considered to be oleophobic and given a rating as follows: If the fabric was not wet by pure mineral oil but was wet with mineral oil containing 10 percent by volume heptane, the oil rating was 50. If the fabric was not wet by oil-containing 10 percent by volume n-heptane, but was wet by oil-containing 20 percent by volume n-heptane, the oil rating was 60. The oil rating was thus checked by adding increments of 10 percent by volume n-heptane until a dilution was found which wet the fabric. The fabric was then assigned an oil rating of the dilution next below that which wet the fabric. Thus, the oil rating could vary from 50 to 100. The latter indicating that the fabric was oleophobic to a solution of 50 percent mineral oil and 50 percent by volume n-heptane.

The test for solvent ringing comprises wetting a portion of the fabric with from 2.5 to 3 ml. of perchloroethylene and allowing the solvent to spread and then dry. The fabric was observed to determine whether a ring remained after the solvent had evaporated.

The spray ratings shown below are a measure of the water repellency of the fabric. The spray ratings were determined in accordance with test ASTM D583–54.

The following examples are illustrative only and should not be construed as limiting the invention which is properly delineated in the appended claims.

EXAMPLE 1

A potassium hydroxide polymerized polydimethylsiloxane gum was dissolved in toluene to give a 10 percent by weight solution of the gum. Acetic acid was then added immediately in an amount sufficient to neutralize the potassium. The toluene solution was then diluted with 400 ml. of methanol per liter of toluene

solution. The mixture was stirred during the addition of the methanol and warmed to 50° to 60° C. It was then cooled and the high molecular weight polymer precipitated. The solvent was then decanted and the precipitate was washed 3 times with methanol. The resulting fractionated gum was heated at 60° C. overnight and then at 100° C. for 2 hours to remove remaining solvent.

This extracted polymer was dissolved in toluene and 5 percent by weight tetrapropyltitanate based on the weight of the polysiloxane was added. Wool flannel fabric was dipped into the solution, air dried and then heated 15 minutes at 125° C. The resulting wool was coated with 2 percent by weight of the cured dimethylpolysiloxane. The resulting wool fabric had an oil rating of 80 and a spray rating to water of 90. This shows excellent oleophobicity and hydrophobicity.

EXAMPLE 2

An alkaline polymerized dimethylpolysiloxane gum was dissolved in hot isopropanol and the solution was cooled. The high polymer precipitated. The solution was decanted. The precipitate was heated in a steam oven to remove the remaining isopropanol.

231 g. of 20.25 percent by weight toluene solution of this polymer was mixed with 80 g. of a 10 percent by weight aqueous solution of polyvinyl alcohol, 8.6 g. of a fluid trimethylsilyl endblocked methyl hydrogen polysiloxane and 80 g. of water, on a Colloid mill. The resulting emulsion (1) was employed as follows:

14.4 g. of (1) was mixed with (2) 2.9 g. of an aqueous emulsion containing 4 percent by weight dibutyltin diacetate and 18.2 percent by weight zinc octoate, both based on the weight of (2). The resulting mixture was then diluted with water to give 100 g. of diluted emulsion.

Wool gabardine was padded with this emulsion, air dried and then heated 5 minutes at 275° F. to cure the polysiloxane. The resulting fabric was coated with 1.2 weight percent polydimethylsiloxane. This fabric had an oil rating of 60 and a spray rating of 70.

EXAMPLE 3

The polydimethylsiloxane gum employed in this example was fractionated from isopropanol as described in Example 2.

The fractionated gum together with a fluid trimethylsilyl endblocked methylhydrogen polysiloxane and dibutyltin dilaurate were dissolved in an aliphatic hydrocarbon sold under the name Stoddard Solvent in amount such that the solution contained 1.7 percent polydimethylsiloxane gum, 0.3 percent methylhydrogensiloxane, .3 percent dibutyltin dilaurate and 97.7 percent solvent. Samples of the following fabrics were each immersed in this solution, air dried and then heated for the times and temperatures shown in the table below. The oil rating and spray rating of each sample was then determined and the results are shown in said table.

Table

Fabric	Spray Rating			Oil Rating		
	5 min. at 225° F.	5 min. at 275° F.	3 min. at 325° F.	5 min. at 225° F.	5 min. at 275° F.	3 min. at 325° F.
Wool Gabardine	80	80	--------	60	60	--------
Wool Flannel	80	80	--------	60	60	--------
Cotton (80 thread per inch)	70	70	70	60	60	60
Cotton (red poplin)	60	60	60	60	60	60
Spun acetate	80	80	--------	60	60	--------
100% Viscose	70	70	70	50	50	50
Nylon	70	70	70	60	60	60
Cotton Dacron	70	70	70	70	60	60
Wool Dacron	80	80	--------	60	50	--------

EXAMPLE 4

Polydimethylsiloxane gum free of low molecular weight material was dissolved in toluene and to the solution was added 18 percent ethylpolysilicate and 2 percent dibutyltin dilaurate both based on the weight of the polydimethylsiloxane gum. Wool flannel was impregnated with this solution and air dried. The fabric was then heated 15 minutes at 125° C. to cure the siloxane. The percent by weight pickup on the wool was 2 percent dimethylpolysiloxane. The resulting fabric had an oil rating of 70 and a spray rating of 80.

EXAMPLE 5

Equivalent results are obtained when the following fabrics are employed in the process of Example 3: glass, copolymers of acrylonitrile and vinylidene chloride and polyacrylonitrile.

EXAMPLE 6

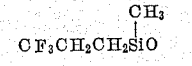
A copolymer gum consisting of .568 mol percent methylvinylsiloxane units and 99.432 mol percent dimethylsiloxane units was fractionated as shown in Example 1. The precipitated gum was heated to remove the solvent. A solution of the resulting gum was dissolved in Stoddard Solvent and mixed with methylhydrogenpolysiloxane and dibutyltin dilaurate in amount to give a solution of 1.7 percent by weight gum, .3 percent by weight methylhydrogensiloxane, .3 percent by weight dilaurate and 97.7 percent by weight solvent.

The solution was applied to wool flannel and the fabric heated as shown below. The spray and oil ratings were then determined.

	Cured 5 min. at 225° F.	Cured 5 min. at 275° F.
Spray rating	80	80
Oil rating	50	60

EXAMPLE 7

A copolymer gum consisting of 7.5 mol percent



units and 92.5 mol percent dimethylsiloxane units was fractionated in accordance with the procedure of Example 2. The resulting gum was made into a formulation of 1.7 percent by weight gum, .3 percent by weight methylhydrogensiloxane, .3 percent by weight dibutyltin dilaurate and 97.7 percent by weight Stoddard Solvent.

Wool samples were immersed in this solution and each was heated as shown below with the following results:

	Spray Rating	Oil Rating
5 min. at 225° F	80	60
5 min. at 275° F	80	60

EXAMPLE 8

An aqueous emulsion (1) was prepared of the following composition in parts by weight:

	Parts
Dimethylpolysiloxane gum free of low molecular weight material	120
Trimethylsilyl end blocked methylhydrogenpolysiloxane fluid	21.3
Aromatic solvent having a boiling range of 184 to 213° C. and a flash point (tag closed cup) of 150° F.	252
Perchloroethylene	86.7
Acetic acid	0.8
Polyvinyl alcohol	12.0
Water	307.2

An aqueous emulsion (2) was prepared containing 4 percent by weight of dibutytin diacetate and 18.2 percent by weight of zinc octoate.

The following mixtures were made from these two emulsions, shown in parts by weight:

Mixture	Parts of (1)	Parts of (2)	Parts of water
1	10.20	4.25	35.55
2	20.40	8.50	21.10
3	59.75	24.90	

Samples of wool gabardine were treated by three times dipping and padding in the mixtures as shown below, after which they were allowed to air dry overnight and then cured 10 minutes at 250° F. To insure a large pick-up of siloxane, sample number 4 was hand wrung after the third dip rather than padded, with all operations otherwise as above. Oil ratings were determined on each of the samples and are shown below. The percent siloxane pickup was determined by weighing the fabric sample before and after treatment:

Sample	Mixture Used	Percent Pickup	Oil Rating
1	1	2.57	60
2	2	4.85	60
3	3	8.63	60
4	3	22.5	60

That which is claimed is:

1. A coated fabric having open pores, said fabric being coated with up to 25% by weight of a cured methylpolysiloxane consisting essentially of polydimethylsiloxane, which siloxane when applied to the fabric had a viscosity of at least 1,000,000 cs. at 25° C. and said coated fabric being oleophobic to such an extent that a drop of U.S.P. heavy mineral oil will not wet the surface thereof for a period of at least two minutes.

2. An article in accordance with claim 1 wherein the fabric is wool.

3. An article in accordance with claim 1 wherein the fabric is made of cellulosic fibers.

4. An article in accordance with claim 1 wherein the fabric is made of glass fibers.

5. A coated fabric having open pores, said fabric being coated with up to 5% by weight of a cured methylpolysiloxane consisting essentially of polydimethylsiloxane, which siloxane when applied to the fabric had a viscosity of at least 1,000,000 cs. at 25° C. and said coated fabric being oleophobic to such an extent that a drop of U.S.P. heavy mineral oil will not wet the surface thereof for a period of at least two minutes.

6. An article in accordance with claim 5 wherein the fabric is wool.

7. An article in accordance with claim 5 wherein the fabric is made of cellulosic fibers.

8. An article in accordance with claim 5 wherein the fabric is made of glass fibers.

9. A coated fabric having open pores, said fabric being coated with up to 2% by weight of a cured methylpolysiloxane consisting essentially of polydimethylsiloxane, which siloxane when applied to the fabric had a viscosity of at least 1,000,000 cs. at 25° C. and said coated fabric being oleophobic to such an extent that a drop of U.S.P. heavy mineral oil will not wet the surface thereof for a period of at least two minutes.

10. An article in accordance with claim 9 wherein the fabric is wool.

11. An article in accordance with claim 9 wherein the fabric is made of cellulosic fibers.

12. An article in accordance with claim 9 wherein the fabric is made of glass fibers.

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