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SOIL RESISTANT FABRIC AND METHOD OF MAKING THE SAME

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This invention relates to the treatment of surfaces to reduce the adherence or attraction of particles thereto and more particularly to the treatment of fabrics, paper and paper-like materials, paint films and other materials to reduce their color change due to pick-up and retention of particles on their exposed surfaces.

A more specific object is to reduce color change or greying of fabrics (flat or pile), covering or wrapping material such as paper, and films such as paint or varnish, due to the pick-up and retention of particles during use.

Another object is to reduce the particle adherence of surfaces without introducing an undesirable discoloration or whitening or otherwise harmfully altering the appearance or feel of the treated material.

Another object is to reduce the adherence of soil particles to surfaces.

Other objects and advantages will be apparent as the nature of the invention is more fully disclosed.

This application is a continuation-in-part of copending application Serial No. 289,670, filed May 23, 1952, and now abandoned.

In order to obtain comparative results and to determine the suitability of a selected composition for the above purpose a series of tests have been developed for measuring the particle adherence and the color change of a surface treated as described herein, called the adherence index and whitening index respectively. The adherence index is determined by comparing the color changes produced on treated and untreated samples by the standard soiling test procedure outlined below, using the same instrument for both tests. The whitening index is the color change produced by the treating composition, as measured in a colorimeter. The adherence and whitening indices define the characteristics of the coating and are a measure of the nature of the composition which is applied to the material to form the coating. The composition used as a source of particles for measuring the adherence index is a synthetic soil composition which is described hereinafter. It is chosen because the treatments described herein have practical value in altering what are commonly termed the soil-resistance characteristics of fabrics or surfaces.

The standard test procedure is as follows:

ADHERENCE INDEX

The adherence index test is made in a cylindrical ball mill, constructed of heavy gage metal 12″ in diameter and 6″ high. On the circumference are placed 3 equidistant openings 4″ x 4″. Three removable doors overlap these openings and are held to the mill by means of wing bolts. A 1″ O. D. x 8″ long steel perforated pipe is welded through the axis of the mill and contains a removable cap on one end and a sealed cap on the other. A perforated fiber tube is placed in this pipe and serves as the soil holder. Three radial steel baffles ¾″ x 6″ are located on the inside wall of the mill, equidistant between the openings. Thirty steel balls ¼″ in size are placed in the mill.

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In operation samples of the material to be tested, such as a rug cut 5″ x 5″ are placed over the openings in the mill so that ½″ laps over on all sides. The removable doors are then clamped over the samples and the wing bolts tightened. A charge of synthetic soil particles is placed in the fiber tube and this in turn is placed in the steel pipe. The pipe is then capped and the mill rotated for 20 minutes at 60 R. P. M.

The synthetic soil is based on a composition set forth in an article in the Journal of American Oil Chemical Society, May 1950, pages 153–9, by H. L. Sanders and J. M. Lambert, on a survey of the street dirt of six cities across the nation. A modification has been made to make it more applicable to this testing procedure. The synthetic soil composition is as follows:

Composition:	Percent
Peat moss	37
Cement	17
Kaolin clay	17
Silica (200 mesh)	17
Molacco furnace black	1.75
Iron oxide	.5
Mineral oil	8.75

The degree of pick-up of soil particles, or adherence index is calculated from measurements on a "color eye" (an electronic colorimeter made by the Instrument Development Labs.). The instrument measures the tristimulus values X, Y and Z which give an indication of the redness, greenness and blueness respectively reflected from objects. Five places on each sample are measured before and after soiling in the ball mill using the "daylight" illuminant, specular reflectance setting, with a white vitrolite block as standard. For measuring a pile rug the sample is placed in the holder of the instrument and the average of five readings is computed for X, Y and Z. The adherence index is defined as the ratio of the color difference of the treated sample, before and after ball milling to the color difference of the untreated sample before and after ball milling, computed according to the following equation:

$$\text{A. I.}=\frac{\sqrt{\Delta X_T^2+\Delta Y_T^2+\Delta Z_T^2}}{\sqrt{\Delta X_U^2+\Delta Y_U^2+\Delta Z_U^2}}$$

where X_T, Y_T and Z_T are the redness, greenness and blueness of the treated samples as measured on the "color eye"; X_U, Y_U and Z_U are the same characteristics of the untreated samples; ΔX, etc. is the color change due to ball milling and A. I. is the adherence index.

An adherence index of 1 would indicate equal particle adherence of the treated and untreated samples. An index above 1 indicates that the treated sample has greater adherence than the untreated sample, and an index of less than 1 indicates that the treated sample has less adherence than the untreated sample.

WHITENING INDEX

The whitening index is measured as the color difference between the treated sample and the untreated sample (prior to ball milling) measured on the "color eye" as above and computed according to the following equation:

$$\text{W. I.}=\sqrt{(X_T-X_U)^2+(Y_T-Y_U)^2+(Z_T-Z_U)^2}$$

Treatment which produces an adherence index of less than .85 and a whitening index of 10.6 or below, as determined by the above procedure has been found satisfactory for improving the soil resistance of surfaces of the type specified.

The treatment in accordance with this invention consists of depositing on the surface to be protected a composition containing a mixture of two or more metal oxides having characteristics which make them effective for the purpose as illustrated by the specific examples.

The oxides are applied to the specimens from a dispersion in water under conditions to leave a coating of hydrous oxides of the desired weight and composition after the vehicle has been removed. The coating may or may or may not be continuous.

The material can be treated in various ways depending upon its type and the results desired. In the case of pile fabrics, such as rugs or carpets, the dispersion may be sprayed over the pile surface in an amount to produce the desired particle pick-up, or the dispersion may be applied by means of a carpet cleaning brush, and then dried, or the fabric may be inverted and the pile only dipped into the dispersion. When used as a part of a standard rug-making process the dispersion may be sprayed onto the pile (face up) or the pile dipped (face down) after sizing and the treated rug then passed through a standard drier for removing the vehicle. If the treatment is applied to a carpet on the floor it may be dried at room temperature by allowing it to stand for a sufficient period of time.

After drying the coating has the property of adhering strongly to the surface. If eventually removed as a result of repeated cleaning or use it can be easily renewed.

The treatment is effective on various textiles such as wool, cotton, jute, viscose rayon, acetate rayon, nylon, acrylics, polyesters, and other synthetic and regenerated fibers and/or blends thereof.

Rugs having pile composed of wool yarn or a synthetic yarn or of blends thereof, such as wool and rayon or wool and nylon may be treated by spraying the dispersion, preferably in the form of a fine mist and then drying.

Cotton pile rugs may be immersed in the dispersion until the desired pick-up has taken place on the fibers. The fabric is then passed between squeeze rollers and dried to leave the desired oxide coating on the pile.

It has also been found that the treatment above described in many cases improves the resistance to moths and other insects and enhances the fire resistance of the treated materials.

In accordance with the invention the oxides should be hydrous, that is contain water of hydration or adsorbed or absorbed water so as to increase their adherence to the treated surface. The oxides should have a surface area of 15 to 200 square meters per gram and should have an average working particle size of not over .6 micron, an average ultimate or primary particle size of 5 to 50 millimicrons, should be non-hydroscopic and inert to the atmosphere and to the treated material. Preferably the oxides should have a surface area of 35 to 130 square meters per gram. Certain aerogels and certain oxides produced as set forth in the following examples have been found to have the characteristics required for the purpose of this invention.

Example 1

Pyrolytic alumina may be prepared as a reaction product resulting from the hydrolysis and dehydration of a volatile aluminum halide or from the thermal decomposition of aluminum sulfate in a high temperature gaseous environment. This finely divided product is an essentially crystalling form of aluminum oxide whose X-ray diffraction lines correspond most closely with those of the so-called gamma modification of alumina. The particle size of the aluminum oxide may be produced over the range of 5–50 millimicrons diameter and a surface area range of 15–200 square meters per gram as measured by the Brunauer-Emmett-Teller method of low temperature nitrogen adsorption. The hydrous aluminum oxide produced by this process contains a minimum of 90% Al_2O_3, the remaining 10% consisting of physically adsorbed moisture, chemically combined water (removable by heating to 1000° C.) and residual non-metallic elements resulting from the incomplete decomposition of the original aluminum-bearing raw material salts.

An example is a pyrolytic alumina sold under the trade name of Alon by Godfrey L. Cabot, Inc., which has a hardness of 9 (MHO scale) and a packed density of 4 to 5 lbs. per cubic foot. It is mildly acidic and is unreactive with the atmosphere and with the materials treated.

Pyrolytic hydrous silica may be made from silicon tetrachloride by the above procedure. Such a silica is sold by Godfrey L Cabot, Inc., under the trade name of Aerosil. When made into a dispersion it is designated by the trade name Soltex. Oxides produced as above described are herein defined as pyrolytic oxides.

A stable depersion having a pH of 8.5 is prepared by mixing ½ part of Alon with ¼ part of trisodium phosphate in 100 parts of water. To this is added ½ part of Soltex (solids basis) while stirring. The average working particle size of the dispersion is below .6 micron. The average ultimate or primary particle size is between 5 and 50 millimicrons.

This dispersion is sprayed as a fine mist onto the pile surface of an Axminster pile carpet having a backing composed of cotton chain and filler yarns, jute stuffer yarns and one-half inch pile having a weight of 23.2 ounces per square yard composed of a blend of 50% wool and 50% rayon. The pH of the pile was 4 to 4.5. The spray was controlled so that the weight of the dispersion taken up by the pile was about 100% of the pile weight and was concentrated on the pile with the backing remaining substantially dry. The carpet was then passed through a drier at a temperature of about 175° F. to remove the water and leave a coating of hydrous alumina and silica on the pile of about 1% by weight of the pile, corresponding to about .011 ounce per square yard of exposed fiber surface (as distinguished from carpet surface). The coating was most concentrated at the free ends of the pile although some of the coating may extend down to the portion of the pile anchored in the backing.

A sample of carpet so treated, when given the adherence and whitening tests described above, was found to have an adherence index of .60 and a whitening index of 1.9.

Other phosphates which do not have a harmful effect on the dispersion or on the materials being treated may be used in place of the trisodium phosphate, for example, sodium hexametaphosphate. The quantity may be varied to give a pH of 7.5 to 13.0. The phosphates also act as dispersing agents.

A floor test in which the carpet was placed in a corridor adjacent an untreated sample where both samples were walked on equally by several thousand persons showed that this sample soiled more slowly than the same carpet untreated and was more easily cleaned by a standard vacuum cleaner.

A pile carpet may be inverted and the pile only dipped into the dispersion to obtain the same pick up if desired.

Other stable white or colorless crystalline hydrous oxides produced pyrolytically that may be used in combination with each other or with alumina or silica or both as in Example 1 are:

Oxides of—
- Titanium
- Zirconium
- Magnesium
- Zinc

Example 2

A stable dispersion having a pH of 4.1 may be made by mixing one-half part of Alon with ⅛ part of sulfuric acid (66° Bé.) with 100 parts of water. While stirring ½ part of Soltex (solids basis) is added. This dispersion was applied to the rugs, dried and tested in accordance with the procedure outlined in Example 1. An adherence index of .72 and a whitening index of 3.2 was obtained.

Other acids and acid salts that do not have a harmful effect on the dispersion or on the material to be treated may be used for pH control in place of the sulfuric acid. For example:

Phosphoric acid
Oxalic acid
Acetic acid

Example 3

Aerogels may be produced by the process disclosed in the Kistler Patent No. 2,093,454 in which the metal chloride is treated with ethylene oxide to form the metal oxide and ethylene chloride, the ethylene chloride being removed by repeated washings with ethyl alcohol and the oxide dried in an autoclave under pressure. The product comprises fine cellular particles of metal oxide in which air spaces or cells replace the electrolytes. The particles are inert to the atmosphere and to the materials treated, are essentially free from electrolytes and hygroscopic salts. When made into a dispersion, the cellular structure breaks up into particles of hydrous oxide of extremely small particle size extending in range down to a few thousandths of a micron.

Dispersions containing equal parts of hydrous alumina aerogel and Soltex (solids basis) so produced are particularly useful for the present purpose and when used for treating pile carpets as in Example 1 to form a coating of alumina and silica 2% by weight of the pile, showed an adherence index of .58 and a whitening index of 2.0.

Other examples of aerogel dispersions that can be used are those made from aerogels of oxides of:

Silicon
Titanium
Magnesium
Thorium
Zinc

These oxides can be used in combination with each other or with one or more of the oxides of the previous examples.

Example 4

Aluminum hydroxide precipitate was prepared by addition of excess ammonium hydroxide to 300 ml. of 24% basic aluminum acetate. The aluminum hydroxide was carefully washed and dispersed in 700 ml. of water. To this, 64.5 ml. of 1 normal hydrochloric acid was added dropwise with stirring. The mixture was heated to a boil for 30 minutes. This resulted in peptizing action and produced a dispersion containing 5.8% hydrous aluminum oxide. A mixture of this dispersion with Soltex (equal parts on a solids oxide basis) diluted to 1% total solids and applied to a pile carpet as in Example 1 gave an adherence index of .61 and a whitening index of 4.0.

Other essentially salt-free hydrous oxides prepared by standard methods in stable white or transparent crystalline form which are useful for the present purpose are oxides of the following:

Silica	Germanium
Titanium	Magnesium
Beryllium	Thorium
Cerium	Zinc
Columbium	Zirconium

These oxides can be used in combination with each other or with any of the oxides of the preceding examples.

Example 5

A stable dispersion may be used by using a pyrolytic or aerogel oxide and another oxide of a different type. For example, a dispersion may be made by mixing ½ part of Alon and ½ part of Ludox (solids basis), a hydrous silica (sold by Du Pont) with ¼ part of tri-

sodium phosphate, and ⅛ part of 2% Carbowax dissolved in 100 parts of water. This material was used to treat pile fabric in accordance with the procedure outlined in Example 1. An adherence index of .60 and a whitening index of 1.9 were obtained.

The effect of surface area of the oxide on reducing the soil adherence is shown by the following table:

TABLE 1

Surface Area (m.²/gram)	Index	
	Adherence	Whitening
49	.71	11.4
64	.66	7.5
68	.73	5.8
90	.74	5.8
94	.71	6.0
115	.71	7.0
122	.84	8.0
150	.87	8.0
225	.90	8.3
375	.96	13.6

Similar results are obtained by treating upholstery pile fabric as in the above example.

Example 6

Other examples of suitable combinations of oxides follow:

TABLE 2

Composition	Weight of Deposit on Weight of Pile, Percent	Index	
		Adherence	Whitening
Alon	.5	.60	1.9
Syton [1]	.5		
Soltex	.5	.60	7.0
Titanium oxide	.5		
Alon (pyrolytic)	.5	.72	6.5
Titanium oxide (pyrolytic)	.5		
Soltex (pyrolytic)	.5	.65	4.3
Titanium oxide (pyrolytic)	.5		
Soltex (pyrolytic)	.5	.68	5.1
Aluminum aerogel	.25		
Alon (pyrolytic)	.5	.77	7.3
Silica (precipitated)	.5		
Soltex (pyrolytic)	.5	.78	9.8
Alumina (precipitated)	.5		
Soltex (pyrolytic)	.5	.72	6.3
Titanium oxide (precipitated)	.25		
Aluminum aerogel	.25	.74	7.6
Ludox (precipitated)	.5		
Aluminum aerogel	.25	.70	9.0
Magnesium oxide (precipitated)	.5		
Alumina (precipitated)	.5	.78	9.8
Ludox (precipitated)	.5		
Ludox (precipitated)	.5	.83	10.0
Zirconium oxide (precipitated)	.5		
Thorium oxide (precipitated)	.5	.79	10.0
Alumina (precipitated)	.5		

[1] SiO_2 made by Monsanto Chemical Co.

TABLE 3.—EXAMPLES OF THREE-COMPONENT SYSTEMS

Composition	Weight of Deposit on Weight of Pile, Percent	Index	
		Adherence	Whitening
Alon (pyrolytic)	.25	.78	7.0
Titanium oxide (precipitated)	.50		
Ludox (precipitated)	.25		
Alon (pyrolytic)	.25	.72	8.0
Magnesium oxide (precipitated)	.5		
Ludox (precipitated)	.25		
Alon (pyrolytic)	.25	.77	7.3
Titanium (precipitated)	.50		
Silica (precipitated)	.25		

About .125% Carbowax or other high molecular weight wax-like solid which is water dispersible and non-tacky at room temperature may be added to any of the above mixtures to improve the hand of the material treated and to decrease the dusting.

The pH of the water dispersion of the compositions of the above tables may be adjusted to the desired value by adding from ⅛% to ½% of trisodium phosphate as required. About .25% usually produces satisfactory results.

Example 7

A dispersion in an organic vehicle may be made by adding ½ part Alon and ½ part Aerosil to 100 parts of isopropanol or of ethyl alcohol containing from 1% to 10% water. This dispersion can be used as in any of the previous examples.

Other volatile organic vehicles that can be used are:

Methanol
Acetone
Ethylene glycol
Carbon tetrachloride

Example 8

A mixture containing ½ part Alon, ½ part Ludox, ¼ part trisodium phosphate, ⅛ part Carbowax (a polyethylene glycol high molecular weight wax made by Carbide and Carbon Chemical Corporation), ¼ part sodium lauryl sulfate, and 98⅜ parts of water was used in standard on location cleaning of a soiled pile carpet in an amount to leave a coating of about 1¼% of a dry basis of oxides on the pile surface after drying. This resulted in cleaning the carpet and reducing the adherence of subsequent soil thereto.

A coating of .5% to 1.5% dry solids based on the weight of the pile has been found most effective for many types of pile materials although the coating may be varied from .25% to 5% for some purposes. An excess of the composition may be used but usually does not further decrease the adherence index and may increase the whitening index. In addition it may result in excessive dusting and may become noticeable in the feel of the material.

The surface area of fiber coated was calculated by the following equation:

$$A_s = W \times \frac{1}{D} \times \frac{4}{d_f} \times F$$

Where W equals the total weight of fiber per square yard; A_s equals the effective exposed fiber surface area (in square yards) per square yard of fabric; D equals average density of the fiber in pounds per cubic yard calculated by (specific gravity) × 1685; d_f equals average diameter of the fiber in yards calculated by (fiber diameter in microns) × 1.095 × 10^{-6}; and F equals a factor showing the average degree of penetration of the treating dispersion expressed as a fraction of the total fiber area which is coated.

F values of from one-third to one-twelfth may be used, depending upon yarn construction, coating technique, fiber diameter, and fabric construction.

While in general the weight of coating varies from 0.25 per cent. to 5.0 per cent. of the fabric weight, the amount of material applied per square yard of exposed fiber surface may vary from .003 to .054 ounce per square yard of exposed fiber surface area computed as above. A range of .0063 to .024 ounce per square yard of exposed surface usually produces satisfactory results.

If pile surfaces are treated by spraying or dipping the major part of the coating is deposited on the exposed pile tufts toward the free ends thereof although some of the composition may migrate to the bound portions of the pile and to the backing.

Standard detergents, wetting and dispersing agents may be used with the above dispersions if desired. These are particularly useful to effect a combination of cleaning and treating.

Although certain specific examples have been given for purposes of illustration other hydrous metal oxides having similar properties and producing a similar effect may be used, particularly other pyrolytic oxides and aerogels having properties similar to pyrolytic alumina and alumina aerogel as set forth above. The invention may be adapted to various uses as will be apparent to a person skilled in the art.

What is claimed is:

1. The method of reducing the particle adherence characteristics of a fabric having a surface exposed to such particles without producing an undesirable color change therein, which method comprises applying to said surface while in a substantially unsoiled condition a dilute dispersion comprising a liquid vehicle containing particles of a mixture containing substantial proportions of at least two hydrous stable metal oxides having a surface area of 15 to 200 square meters per gram and an average working particle size of not over .6 micron, said oxides being selected from the group consisting of aluminum, silica, titanium, beryllium, cerium, columbium, germanium, magnesium, thorium, zinc and zirconium, and removing the liquid vehicle to leave on said surface a coating of said particles having a weight of .003 ounce to .054 ounce per square yard of exposed surface area.

2. The method set forth in claim 1 in which one of said oxides comprises pyrolytic alumina.

3. The method set forth in claim 2 in which the second oxide comprises silica.

4. The method set forth in claim 1 in which the dispersion contains trisodium phosphate.

5. The method set forth in claim 1 in which one of said oxides comprises alumina aerogel.

6. The method set forth in claim 1 in which said oxides comprise alumina and silica.

7. A fabric having an exposed surface and a coating comprising a mixture containing substantial proportions of at least two hydrous metal oxides on said surface in an amount of about .003 ounce to .054 ounce per square yard of exposed surface area, said metal oxides being selected from the group consisting of aluminum, silica, titanium, beryllium, cerium, columbium, germanium, magnesium, thorium, zinc and zirconium, said oxides having prior to drying a surface area of 15 to 200 $m.^2/g.$ and an average particle size of not over .6 micron, being non-hygroscopic, inert to the atmosphere and to such material, said coated surface having adherence and whitening characteristics corresponding to an adherence index of not over .85 and a whitening index of not over 10.6 determined as defined herein.

8. A fabric as set forth in claim 7 in which one of said oxides is a pyrolytic oxide.

9. A fabric as set forth in claim 7 in which one of said oxides is an aerogel.

10. A fabric as set forth in claim 7 in which one of said oxides is a pyrolytic alumina.

11. A fabric as set forth in claim 7 in which one of said oxides is an alumina aerogel.

12. A fabric as set forth in claim 7 in which said oxides are alumina and silica.

13. A pile fabric having a backing and pile tufts anchored therein and extending upwardly therefrom, said pile tufts having a surface coating in an amount of .25% to 5% by weight of the pile of a substance containing a major portion of a mixture containing substantial proportions of at least two hydrous metal oxides selected from the group consisting of aluminum, silica, titanium, beryllium, cerium, columbium, germanium, magnesium, thorium, zinc and zirconium, said oxides having a surface area of 15 to 200 $m.^2/g.$, an average working particle size of not over .6 micron, being non-hygroscopic, inert to the atmosphere and inert to the material of the pile fabric, said coated surface having the adherence and whitening characteristics corresponding to an adherence index of not over .85 and a whitening index of not over 10.6 determined as defined herein.

14. A pile fabric as set forth in claim 13, in which one of said oxides is a pyrolytic oxide.

15. A pile fabric as set forth in claim 13, in which one of said oxides is an aerogel oxide.

16. A pile fabric as set forth in claim 13, in which one of said oxides is a pyrolytic alumina.

17. A pile fabric as set forth in claim 13, in which one of said oxides is an alumina aerogel.

18. A pile fabric as set forth in claim 13, in which said oxides are alumina and silica.

19. The method of making a pile fabric having improved particle adherence characteristics and composed of a backing having pile tufts anchored therein and extending upwardly therefrom which comprises applying to the surface of said pile tufts while in a substantially unsoiled condition a dilute dispersion comprising a liquid vehicle containing particles of a mixture containing substantial proportions of at least two hydrous stable metal oxides having a surface area of 15 to 200 square meters per gram and an average working particle size of not over .6 micron, said oxides being selected from the group consisting of aluminum, silica, titanium, beryllium, cerium, columbium, germanium, magnesium, thorium, zinc and zirconium, and removing the liquid vehicle to leave on said tufts a coating of said particles having a weight of .003 ounce to .054 ounce per square yard of exposed surface area.

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