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METHOD OF DRY CLEANING AND RENDERING FABRICS WATER REPELLENT

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This invention relates to the treatment of fabrics for the purpose of making them water repellent.

The dry cleaning industry which must often provide, in addition to cleaning, a fabric treatment designed to impart water repellency to the cleaned article, has found that this is most conveniently done by immersing the article in dry cleaning solvent which contains the water proofing impregnant in solution. There are, however, only a limited number of dry cleaning solvents suitable for use, for reasons principally of fire hazard and cost, and difficulty has arisen in finding impregnants which are sufficiently soluble in commercial dry cleaning solvents at room temperature and which at the same time provide adequate water repellency. Thus, although many types of water repellent formulations are available, prior to the present invention, none have shown to an outstanding degree the characteristics of high solubility in dry cleaning solvents combined with the ability to impart a high degree of water repellency.

For example, many relatively high melting point waxes such as carnauba, candelilla, beeswax, Gersthafer, and microcrystalline petroleum waxes will in many cases impart good water repellency when applied to fabrics in solution, but lack sufficient solubility in dry cleaning solvents at room temperature to permit their application to the fabric as a solution in such solvents. Accordingly, this and other relatively high melting point waxes must be dissolved in special solvents or dissolved in dry cleaning solvents heated above room temperature in order to permit their application. Either of these alternatives is obviously undesirable from the standpoint of convenience, safety and economy.

Other materials which show satisfactory solubility in commercial dry cleaning solvents such as low melting point waxes, e.g., petroleum scale waxes melting for example at 130° F. have been found to impart inadequate water repellency to treated fabrics even when applied in prohibitive concentrations.

In addition to possessing the desirable properties of good solubility in commercial dry cleaning solvents and the ability to impart good water repellency to the treated fabrics, the ideal water proofing impregnant suitable for use in dry cleaning operations should also be light in color so that undesired darkening of light garments is avoided and should also be essentially neutral in character, that is having neither basic nor acid character. Acidity in such a composition is particularly undesirable since the common method for determining the exhaustion point of a dry cleaning solvent is to titrate the acid concentration in the solvent (ordinarily originating from body acids removed from garments). Obviously, acidity contributed to the solution from extraneously added material such as an impregnant would introduce errors into this standard method of determining the exhaustion point of the dry cleaning solvent.

Another desideratum of an ideal water repellency composition for use with dry cleaning solvents is its ability to form concentrated solutions with relatively volatile, relatively odorless and at the same time inexpensive solvents. As will be explained hereafter in more detail, this property is important with respect to the ability of the composition to be made up in the form of a satisfactory

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"concentrate" that is, a highly concentrated solution which will dissolve easily and quickly in the dry cleaning solution itself.

It has now been found that water repellency compositions suitable for use in dry cleaning solutions, and having all of the desirable properties discussed above, may be provided by the combination of a relatively low melting point wax and a thermoplastic, solvent soluble terpene resin. Such a composition not only has good solubility in all dry cleaning solvents in commercial use but also imparts excellent water repellency to the fabric immersed in the impregnant-containing solvent. Such a composition furthermore is light in color, is substantially neutral, and in addition can be made up into convenient-to-use concentrates using inexpensive, relatively volatile solvents.

The superior water repellency imparted by the combination of relatively low melting point wax and a terpene resin is quite surprising since neither of these materials when used alone to impregnate the fabric is capable of imparting satisfactory water repellency when used in acceptable concentrations. Yet in combination these two apparently inferior components give in practical concentrations a water repellency rating as good as or higher than some of the most effective and more commercial expensive water repellency compositions now on the market.

The relatively low melting point wax employed should be a paraffin wax having a melting point within the range of 105 to 155° F. and preferably 125 to 145° F. By paraffin wax is meant a wax composed essentially of solid hydrocarbons chiefly of the methane series C_nH_{n+2} .

The terpene resins which are used in the compositions of the invention are thermoplastic hydrocarbon resins having the general formula $(C_{10}H_{16})_n$. They are produced by the catalytic polymerization of terpenes of the general formula $C_{10}H_{16}$ such as alpha pinene, beta pinene, dipentene, limonene, alpha terpinene, myrcene, allo-cimene and ocimene. The preferred terpene resins are those derived predominantly from alpha and beta pinene, while the most desirable are those derived primarily from the catalytic polymerization of beta pinene.

The resins are prepared by treating the monomer, preferably in an inert diluent solvent such as toluene, xylene, or naphtha, with a Friedel Crafts catalysts, such as aluminum chloride, stannic chloride, antimony trichloride, ferric chloride, aluminum bromide, aluminum iodide, boron fluoride, or beryllium chloride, aluminum chloride being a preferred catalyst. The polymerization reaction is highly exothermic and provision is made for agitation and heat exchange so as to control the temperature conditions during the addition of the catalyst, which is added gradually, within close limits, usually in the range of from 20° to 60° C. After the polymerization, the polymer is thoroughly washed to remove the halide catalyst. The catalyst-free polymer solution is distilled with steam at reduced pressures to remove solvent, unreacted terpenes, and if desired low terpene polymers.

Depending upon the polymerization conditions and the various cuts into which the polymerization product is distilled, these terpene resins may range from viscous liquids to hard brittle solids at room temperature. Those suitable for use in the compositions of the invention have softening points (measured by the A.S.T.M. ring-and-ball method E28) ranging from 40° C. to 140° C. and preferably from 75° C. to 125° C.

The ratio of resin:wax (on a weight basis) should be in the range of from 1:20 to 3:1, and preferably within the range of 1:4 to 2:1.

Generally speaking, the higher the melting point of the wax within the range defined above, the lower will be the amount of wax required to give satisfactory water

proofing properties and thus in general, the higher the resin:wax ratio in the water-repellent composition. Conversely, a less highly refined, lower melting wax should be used in greater quantity than a more highly refined higher melting wax to give equivalent water proofing properties to the treated fabric.

An excellent way to introduce the wax-resin water repellent composition of the invention into the dry cleaning solution is in the form of a highly concentrated solution or "concentrate." Such a concentrate has the advantage that it disperses and dissolves easily and quickly in the dry cleaning solution, in contrast to the solid form of the wax-resin blend which will generally require more time and agitation to dissolve. An important advantage of the compositions of the invention is their ability to form concentrated solutions, or concentrates with inexpensive petroleum solvents particularly odorless mineral spirits which have relatively good volatility and thus do not tend to leave non-volatile residues in the fabric. Particularly preferred are petroleum solvents which have been treated to remove odor producing constituents such as aromatic compounds and sulfur compounds. Odorless mineral spirits is an example of a solvent which has been thus treated. Odorless mineral spirits and similar solvents, although of lower solvating power than other petroleum solvents satisfactorily dissolve the wax-resin mixtures of the invention to produce gels or soft solids which are readily soluble in dry cleaning solvents.

The preferred solvents for preparing the water repellent "concentrates" of the invention are deodorized hydrocarbon petroleum solvents, particularly those known as odorless mineral spirits having flash points of from 100° F. to 160° F. and preferably from 120° to 140° F. (by A.S.T.M. tag closed cup method).

To make up the concentrate the resin and wax are allowed to stand in a small amount of the solvent for several days with occasional agitation. By gently heating the solids in the solvent the concentrate can be formed more rapidly. The concentrate should normally contain only enough solvent to substantially solvate the resin:wax mixture, this amount generally being about 30% to 80% by weight of solvent.

Although the use of a concentrate as described above is generally more convenient and desirable, if desired, the wax-resin impregnated composition may be added to the dry cleaning solution in a solid form. A mixture of the wax and resin in solid form may be obtained by blending the resin and wax together at temperatures of from about 125° to 300° F. until substantially homogeneous and then solidifying. If used in solid form, the wax-resin impregnant is preferably reduced to a flake or chip form to facilitate more rapid solution of the impregnant composition in the dry cleaning solution.

The resin-wax compositions of the invention, either in solid form, or predissolved to form convenient concentrates as described above, are compatible with and have good solubility in all dry cleaning solvents in commercial use. These include perchloroethylene, which, though relatively expensive, has the highly desirable properties of non-flammability and relatively low toxicity; Stoddard solvent and other relatively high flash point (above 100° F.) petroleum distillates which, though flammable, are desirable for their low cost; and others such as carbon tetrachloride, trichloroethylene, etc. The composition of the invention is sufficiently soluble in these commonly used dry cleaning solvents, and is, in general, sufficiently soluble in liquid hydrocarbon and halogenated hydrocarbon solvents to permit the composition to be dissolved in sufficient concentration to impart excellent water repellency characteristics, and at the same time provide a solution having a cloud point sufficiently low (preferably 60° F. or below) such that the water repellent materials remain in solution at the temperatures normally encountered in dry cleaning operations.

The resin-wax impregnant should be dissolved in the

dry cleaning solvent to provide a solution containing at least 3% by weight of the resin-wax combination to obtain a minimal water proofing effect. When the impregnation is carried out at room temperature (70° F.) the resin-wax concentration in the solvent should generally not exceed 8% by weight, since greater concentrations than these are generally not required to give the desired water repellency, and higher concentrations will tend to precipitate out should the ambient temperature drop appreciably below a normal operating temperature of for example 70° F. This might happen for example, when the solution is stored in an unheated room overnight. For good-to-optimum water repellency and maximum economy, the resin-wax combination should be present in the dry cleaning solution in amounts ranging from about 4 to 7% by weight.

In ordinary dry cleaning practice it is customary to employ a detergent in the solvent to assist in the removal of certain types of soil. Generally speaking, satisfactory water repellency is not obtained in the presence of a detergent and accordingly in most cases it will be desirable to conduct the water repellency treatment in the absence of a detergent, such as by subjecting the garments, after detergent cleaning to a solution which is free from detergent and contains the water repellency impregnant.

The following examples serve to illustrate the practice of the present invention and the advantages obtained.

Example 1

40 parts of a white paraffin petroleum wax having a melting point of 130° F. and 16 parts of a terpene resin are mixed with 44 parts by weight of odorless mineral spirits (a deodorized petroleum solvent having an American Petroleum Institute gravity at 60° F. of 55.5; a flash point of 128° F. (as determined by A.S.T.M. tag closed cup method) and a boiling range of from 352° F. (initial B.P.) to 398° F. (A.S.T.M. end point). The terpene resin employed having the general formula $(C_{10}H_{16})_n$ was prepared by the catalytic polymerization of a mixture of pinenes consisting predominantly of beta pinene, with some alpha pinene, in the presence of an aluminum chloride catalyst. It has a softening point of 115° C. (as determined by A.S.T.M. ring-and-ball method E28). The mixture is allowed to stand for several days with occasional agitation, after which a solvated homogeneous mass was obtained of jelly like consistency.

This concentrate has a flash point of 135° F. tag closed cup, and at a dilution of 1:9 in Stoddard solvent has a cloud point of less than 60° F. The cloud point of the dry cleaning solution is defined as the temperature at which turbidity appears in the solution due to the precipitation of the impregnant.

This impregnant, in relatively low dilutions e.g. 1:7 to 1:10 produces excellent water repellency on the treated fabrics as will be illustrated in the comparative tests of Example 3.

Example 2

A water repellent concentrate, containing a smaller amount of a somewhat higher melting point paraffin wax, is prepared as follows: 20 parts of a petroleum paraffin wax of the crystalline type having a melting point of 134° F. and 20 parts of the terpene resin employed in Example 1 are mixed with 60 parts of the solvent of Example 1 and the mixture allowed to stand with occasional agitation until solvated and an essentially homogeneous concentrate obtained.

This composition has a cloud point of less than 60° F. when used in a dilution of 1:9 in Stoddard solvent and a flash point of 130° F. tag closed cup. This composition likewise provides excellent water repellency at relatively low dilutions as illustrated in the comparative tests of Example 3.

Example 3

The following water repellency tests show the ad-

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vantages obtained by using the terpene resin-paraffin wax combination of the invention in contrast to the use of either of these components alone. The water repellency tests were connected in accordance with the standard spray rating tests of the American Association of Textile Chemists and Colorists (test No. 22-52). A spray rating of 90 or above is considered to represent entirely satisfactory water repellency, while a spray rating of 100 represents total water repellency. The tests were conducted using Stoddard solvent as the dry cleaning solvent and the respective concentrations of the wax and resin are shown in the table below.

Test No.	Composition of Impregnation Solution— Percent of weight			Spray Rating
	Wax	Resin	Stoddard Solvent	
1. (Composition of Ex. 1 diluted 1:7 by volume in Stoddard Solvent)-----	5	2	93	100
2. (Composition of Ex. 2 diluted 1:9 by volume in Stoddard Solvent)-----	2	2	96	100
3. (Control)-----		8	100	50
4.-----			92	50
5.-----	5		95	70
6.-----	7		93	70
7.-----	10		90	70

From the above tests it can be seen that the combination of the terpene resin and paraffin wax in Examples 1 and 2 produced excellent water repellancies at a total solids content of 7% and 4% respectively. The terpene resin alone even in a concentration of 8% produces no improvement in water repellency over the control where no impregnant of any kind was employed. The wax alone, even in concentrations ranging up to 10% by weight, provides water repellency below acceptable standards.

Example 4

Twenty parts by weight of the paraffin wax employed in Example 2 and 20 parts by weight of a terpene resin prepared by polymerizing terpenes consisting predominantly of beta pinene (and containing minor amounts of alpha-pinene) in the presence of an aluminum chloride catalyst and having a softening point (by A.S.T.M. ring-and-ball method E28) of 125° C., are solvated in 40 parts by weight of the odorless mineral spirits of Example 1 to form a concentrate. This concentrate has a flash point of 130° F. (tag closed cup), and at a dilution of 1:9 in Stoddard solvent has a cloud point of less than 60° F.

This product used at a dilution of 1:9 in Stoddard solvent or perchloroethylene gives water repellency spray ratings of 100 in fabrics tested in accordance with the standard spray rating tests referred to above.

Example 5

Twenty parts by weight of the paraffin wax of Example 2 and 20 parts by weight of a terpene resin obtained

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by polymerizing terpenes consisting predominantly of beta pinene in the presence of an aluminum chloride catalyst and having a softening point (by A.S.T.M. ring-and-ball method E28) of 40° C. are solvated in 40 parts by weight of the odorless mineral spirits of Example 1 to form a concentrate. This product has a flash point and cloud point substantially the same as the concentrate of Example 4. Used in a dilution of 1:9 in Stoddard solvent or perchloroethylene it gives water repellency rating of slightly under 100 in accordance with the standard spray rating tests referred to above.

The water repellency compositions of the foregoing examples are all light in color and impart no noticeable discoloration even to the lightest fabrics. Furthermore, they are neutral in character and thus impart no undesirable acidity to the dry cleaning solvent in which they are used. Furthermore, although they provide excellent water repellency to the treated fabrics, they are readily removed by normal dry cleaning procedures, and thus do not build up on the fabric in the course of repeated water proofing treatments.

A still further advantage of the paraffin wax-resin compositions of the invention is that they provide desirable sizing action, and thus may be employed as a combination water proofing and sizing impregnant. Such sizing action is not provided by the use of waxes alone.

We claim:

1. A method for imparting water repellency to fabrics in the course of a dry cleaning operation comprising the steps of immersing the fabrics in a dry cleaning solvent selected from the class consisting of hydrocarbon and halogenated hydrocarbon solvents containing from 3% to 8% by weight of a water repellency composition consisting essentially of a mixture of a paraffin wax having a melting point of from 105° to 155° F. and a thermoplastic terpene resin having a softening point by the ball-ring method of from 40° to 140° C. and prepared by the polymerization of terpenes of the general formula $C_{10}H_{16}$, the weight ratio of resin:wax in said composition being in the range of from 1:4 to 2:1.

2. A method in accordance with claim 1 in which said paraffin wax has a melting point of from 125° to 145° F. and in which said terpene resin has a softening point by the ball-ring method of from 75° to 125° C.

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