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DURABLE WATER AND OIL REPELLENCY

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The present invention relates to durable water and oil repellency, and it particularly relates to methods and compositions for imparting durable water and oil repellency to textiles, leather, paper, Fiberglas, non-woven sheet materials and other woven, knitted or matted fibrous materials.

Although not limited thereto, the present invention will be particularly described in its application to methods and compositions for imparting durable water and oil repellent finishes to woven and other textile materials.

It is among the objects of the present invention to provide a durable water and oil repellent finish particularly applicable to textiles and other materials which will be highly resistant to laundering and dry cleaning and which will enhance the texture and hand of materials.

Another object is to provide a durable, novel oil and water repellent finish to textiles and other materials without interfering with the tensile strength and without undesirably affecting the color or other characteristics of the textile material and with enhancement of the body and hand of the textile materials.

A further object is to impart a durable water and oil repellent finish to woven textiles composed of either natural or synthetic fibers or combinations thereof which will enhance and greatly improve the softness and hand without undesirably affecting other desirable properties such as lack of gas-fading, brilliancy of the dyed materials, crease resistant properties and the like.

Still futher objects and advantages will appear in the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

The present invention will be particularly described in connection with its application to combined dispersions with water or organic solvents of fluorocarbons alkylene imine compounds, such as ethylene and propylene imine or carbon compounds derived therefrom containing a

grouping.

It has ben found that when fluorocarbon latices have been used in small percentages in either aqueous or organic solvent baths, they are not particularly effective and cannot be uniformly applied to or deposited upon fibrous sheet material whether woven, knitted or matted, and that they tend to separate out and form gummy or large particles which not only decrease the quality of the textile material but disadvantageously affect its appearance, thus making continuous application impossible.

These difficulties are particularly increased in the presence of other textile finishing adjuvants used for hand modification, including urea formaldehyde resin, other thermo-setting resins, pyridinium water repellents and various methylol stearamide types of water repellents and silicone water repellents.

With padding arrangements in which the textiles are passed over and under a series of rollers either to give a single or double nip effect, the agitation of the liquid and

the roller arrangement apparently increases this undesirable agglomeration gum formation and large particle deposit. The fluorocarbons used have very poor resistance to shearing action unless properly stabilized.

It is, therefore, among the particular objects of the present invention to provide a method of enabling application of fluorocarbons in water or organic solvent dispersion so that there will be an elimination of such gum formation caused by poor stability to shearing and tendency to deposit upon the application rolls which prevents application in padding systems either of the double or single nip type.

It has been surprising that these operations may be carried on without difficulty and high effectiveness and efficiency, by the inclusion of emulsified ethylene and propylene imine derivatives with the fluorocarbons, either in equal proportions or in a proportion of 1.5 parts to 2.0 parts of the emulsified ethylene and propylene imine derivatives to 3.0 parts of the fluorocarbon derivative.

The preferred proportion results in a treating bath or padding system having an aqueous emulsified dispersion of 2 to 5% of a fluorocarbon and 2 to 5% of an imine compound.

Although the fluorocarbon derivatives may widely vary, some of the compounds which have been found to be most effective are the following:

Generally these compounds are of the general formula

$$R—Z$$

where R is a saturated fluorocarbon cyclic or non-cyclic radical containing 3 to 8 carbon atoms and Z is a monocarboxylic acid radical or derivative, such as an anhydride, halide, amide, nitrile, ester or salt.

Compounds having the formula

$$CH_2{:}CHCOOCH_2(CF_2)_nCF_3$$

may also be used where n may be between 2 and 18.

Compounds containing the radical

$$(CF_2)_n.SO_2$$

where n is between 2 and 12 may also be employed.

As a typical form of these compounds, the following may be utilized.

(a) n-Heptafluorobutyric acid and its esters and salts.

(b) Nonadecafluoro capric acid and its esters and salts.

(c) 1, 1-dihydro perfluoroalkylacrylate and polymers of fluoroalkyl esters of acrylic acid having the formula

$$CH_2{:}CHCOOCH_2R$$

where R is a perfluoro alkyl group having 1 to 4 carbon atoms and 1 to 3 fluorine atoms per carbon atom.

(d) Polyvinyl 1,1-dehydroperfluoroalkyl ethers.

(e) Perfluoroalkyl alkanol sulfonyl fluorides.

(f) Acrylate esters of N-alkyl, N-alkanol perfluoroalkane sulfonamides.

(g) Saturated perfluoromonocarboxylic acids, their esters, salts and metal complexes, particularly chromium complexes.

(h) Perfluorobutyryl and perfluorooctanoyl chloride and compounds in which chlorine is replaced by bromine, hydroxy, carboxy or amino groups.

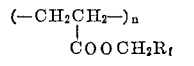
The preferred fluorocarbons are acrylate compounds as set forth in (c) and (f). These compounds are generally described in U.S. Patents 2,803,615, 2,642,416, 2,826,564 and 2,839,513. The preferred compound set forth in (f) is specifically described in Patent No. 2,803,615.

The preferred fluorocarbon finishes are desirably of the following types:

(a) Chromium complexes of saturated perfluoromonocarboxylic acids.

$$(CF_3(CF_2)_nCO_2Cr_2OH)^{4+}$$

(b) Polymers of fluoroalkyl esters of acrylic acid.



where R_f is any perfluorinated alkyl group.

(c) A combination of fluorocarbon and pyridinium-type water-repellent finish.

(d) A product of perfluorobutyryl and perfluorooctanoyl chloride with cellulose.

These compounds are generally commercially sold by Minnesota Mining and Manufacturing Company under the tradenames of Scotchgard FC–154, FC–201, FC–203, FC–205 and FC–208.

Desirably, the fluorocarbons are used in an emulsion with a nonionic surface active agent.

These compounds are desirably incorporated in an aqueous solution of 30% concentration, such as Scotchgard FC–208 and in a 15% organic solvent solution, such as Scotchgard FC–203.

Among the ethylene and proplene imine derivatives that may be utilized are:

(A) Octadecylethylene urea
(B) Octadecylpropylene urea
(C) Stearamido ethylene imine
(D) Lauramido ethylene imine
(E) Stearamido propylene imine
(F) Lauramide propylene imine
(G) 2-stearlyamino-4:6-propylene imine-1:3:5-triazine
(H) 2-stearylamino-4:6-ethylene imine-1:3:5-triazine

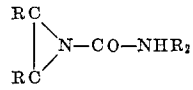
The preferred derivatives are those tabulated as (a) and (b) above.

The ring structure

present in the additive compound gives the synergistic effect (where R is hydrogen or an alkyl group containing 1 to 5 carbon atoms).

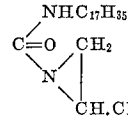
Desirably, the ring should have a straight chain attached to the nitrogen atom containing 12 to 22 carbon atoms and desirably including a carboxyl group and high molecular weight alkyl primary amine.

Such a preferred compound will have the formula:



where R is hydrogen or an alkyl group containing 1 to 3 carbon atoms and R_2 is an alkyl group containing 16 to 18 carbon atoms.

The preferred compound is octadecyl propylene urea:

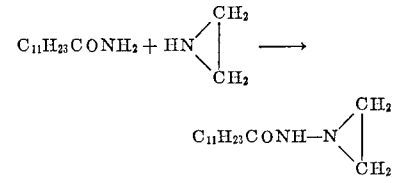


It has been found that with the emulsified ethylene and propylene derivatives, the water emulsion of the fluorocarbons is highly stable, and these emulsified ethylene and propylene derivatives will stabilize the bath resulting in a uniform deposit of the finishing composition and will prevent pad roll build up.

The addition of emulsified ethylene and propylene greatly increases the bath life and results in a stable aqueous padding bath, and it has great resistance to mechanical shearing and which will be stable even with vigorous stirring, continuous rolling of fabrics through pad at great speeds, with resultant agitation and with repeated pumping operations.

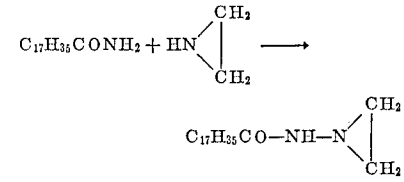
In respect to the imine derivatives whether ethylene or propylene imine, these are generally prepared in the following manner.

(I)



lauramido ethylene imine

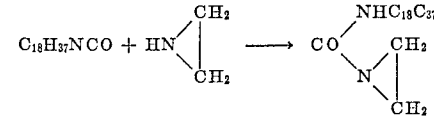
(II)



stearamido ethylene imine

Octadecylethylene urea is prepared as follows:

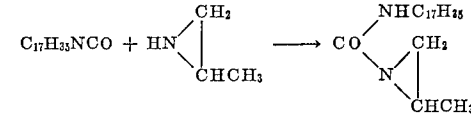
(III)



The alkyl group which is indicated as being $C_{18}H_{37}$ may vary in its number of carbon atoms from 8 to 22.

Octadecylpropylene urea may be prepared as follows:

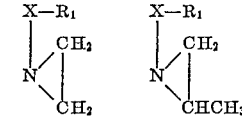
(IV)



octadecyl propylene urea

In general, these compounds all contain the following grouping:

(V)

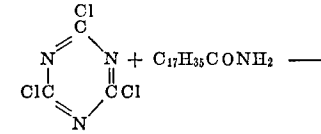


where R_1 is an alkyl group having from 8 to 22 carbon atoms and X is a —NH— linkage or a —CO— linkage and in some instances includes —NH— and —CO— linkages.

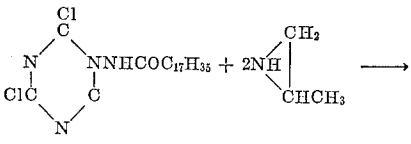
In one type of compound, the X linkage will also contain as part thereof five or six membered saturated or unsaturated alicyclic, aromatic or heterocyclic ring compounds, such as morpholine, triazine, oxazoline, imidazoline, piperidine, piperazine, pyrazoline and pyrrolidine which ring groups may have alkyl, hydrogen or other groups attached to nitrogen and carbon atoms in the ring. Desirably, these ring compounds or groups have one to three nitrogen atoms, or one oxygen atom or one sulfur atom as part of the ring structure.

A particularly satisfactory compound is a triazine which may be prepared according to the following equations:

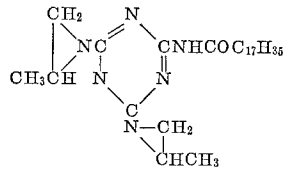
(VI)



(VII)



(VIII)



Example 1

In aqueous padding in double nip padding roll arrangement, a woven cotton fabric may be passed through a bath containing ½ to 3% of solids which bath will have 2 to 4% of a 30% aqueous solution of alkylene urea of one of the above alkylene ureas and from 2 to 4% of a 30% aqueous emulsion of one or two of the above fluorocarbons.

Such a bath with a pickup of ½ to 2½% solids will give a very high oil and water repellency and will greatly increase the spray ratings.

Example 2

With a non-aqueous solution, it is possible to use in a chlorinated solvent having a boiling point of 72° to 88° C., 2%–3% of a 30% solvent mixture of one of the above imine derivatives and 2%–3% of one of the above fluorocarbons (for example, Scotchgard FC–203) in 15% solution. In general the proportions used in the bath should be 2 to 5% of each of the fluorocarbon and imine compounds. In general, in the bath the proportion of imine compound to fluorocarbon compound ranging from equal parts by weight to 1.5 parts by weight of the former and 3 parts by weight of the latter.

Preferably a pH of 6 to 8 is employed with the water systems, and a temperature of 70° to 100° F. is also desirably employed.

Instead of hydrocarbon solvents, it is also possible to use chlorinated solvents such as trichloroethane as the principal liquid bath constituent.

The various baths will have an indefinite bath life without formation of gummy substances on the pad rollers, and the fabrics will have greater water and oil repellency which will not be possible with the imine derivatives by themselves nor with the fluorocarbons by themselves.

The imine derivatives and the fluorocarbons by themselves produce low water repellency, but in combination, they produce unusually high water repellency.

The preferred water and oil repellent surfacing on the fabric should have a weight of 2 to 10% of the fabric, with the imine and fluorocarbon being present in about equal proportions or one being present in proportions of at least 30 to 70% of the other.

Example 3

In preparing one bath product, it is possible to use the following proportions of the imine derivatives and the fluorocarbons.

59% octadecyl-propylene urea (30% concentration)
43% emulsified fluorocarbon (Scotchgard FC–208)—30% concentration

This is a most effective aqueous bath when used in 2 to 5% solid concentration.

Although padding is the preferred form of application, dipping, spraying or other methods of liquid treatment may be employed.

In these aqueous baths, it is possible to use various types of thermo-setting and non-thermo-setting resins

such as polyvinyl acetate, acrylic resins, urea formaldehyde resin, melamine formaldehyde resins, dimethyl ethylene resins and urea triazone resins in amounts ranging from 10% to 20% without breaking the bath and without disadvantageously affecting the water or oil repellent properties.

As catalysts, it is possible to use zinc nitrate and magnesium chloride, however, amine hydrochloride types are preferable as catalysts for the resin systems.

Example 4

With a solvent phase composition, it is possible to utilize the following in making a one piece product.

40% imine derivative (30% concentration)
60% fluorocarbon-15% (Scotchgard FC–203) in chlorinated solvent

The concentration of the bath may be from 2 to 5% solids with a pick up of 60 to 70% on the woven textile fabric.

This composition may be applied by padding, dipping or spraying.

Desirably, applications are made at room temperature, and the drying followed by curing is carried out at 240° to 320° F. for a period of 3 to 10 minutes.

The oil repellent and water repellent treating baths for textile materials disclosed above contain 2 to 5% of a fluorocarbon and 2 to 5% of an alkylene imine.

As many changes could be made in the above durable water and oil repellency, and many widely different embodiments of this invention could be made without departing from the scope of the claims, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Having now particularly described and ascertained the nature of the invention, and in what manner the same is to be performed, what is claimed is:

1. A process of imparting water and oil repellency to material, which comprises finishing them with a combination of an alkylene imine compound and a fluorocarbon, said imine being selected from the group consisting of ethylene imine and propylene imine and said fluorocarbon being selected from the group consisting of acrylate esters of perfluoro alkyl compounds, the proportion of imine compound to fluorocarbon compound ranging from equal parts by weight to 1.5 parts by weight of the former and 3 parts by weight of the latter.

2. A process of imparting water and oil repellency to material, which comprises finishing them with a combination of an alkylene imine compound and a fluorocarbon, in an aqueous emulsion, said imine being selected from the group consisting of ethylene imine and propylene imine and said fluorocarbon being selected from the group consisting of acrylate esters of perfluoro alkyl compounds, the proportion of imine compound to fluorocarbon compound ranging from equal parts by weight to 1.5 parts by weight of the former and 3 parts by weight of the latter.

3. A process of imparting water and oil repellency to material, which comprises finishing them with a combination of an alkylene imine compound and a fluorocarbon in an organic solvent, said imine being selected from the group consisting of ethylene imine and propylene imine and said fluorocarbon being selected from the group consisting of acrylate esters of perfluoro alkyl compounds, the proportion of imine compound to fluorocarbon compound ranging from equal parts by weight to 1.5 parts by weight of the former and 3 parts by weight of the latter.

4. An oil repellent and water repellent treating bath for textile materials consisting essentially of a dispersion from 2 to 5% of a fluorocarbon and 2 to 5% of an alkylene imine compound, said imine being selected from the group consisting of ethylene imine and propylene imine and said fluorocarbon being selected from the group

consisting of acrylate esters of perfluoro alkyl compounds, the proportion of imine compound to fluorocarbon compound ranging from equal parts by weight to 1.5 parts by weight of the former and 3 parts by weight of the latter.

5. An oil repellent and water repellent treating bath for textile materials consisting essentially of a dispersion of an alkylene imine compound and a fluorocarbon, said imine being selected from the group consisting of ethylene imine and propylene imine and said fluorocarbon being selected from the group consisting of acrylate esters of perfluoro alkyl compounds, the proportion of imine compound to fluorocarbon compound ranging from equal parts by weight to 1.5 parts by weight of the former and 3 parts by weight of the latter.

6. A fabric having an oil and water repellent surfacing composed of a fluorocarbon and an alkylene imine compound, said imine being selected from the group consisting of ethylene imine and propylene imine and said fluorocarbon being selected from the group consisting of acrylate esters of perfluoro alkyl compounds, the proportion of imine compound to fluorocarbon compound ranging from equal parts by weight to 1.5 parts by weight of the former and 3 parts by weight of the latter.

7. A process of imparting water and oil repellency to textile materials which comprises treating the textile materials with an aqueous bath containing ½ to 3% of solids which will have 2 to 4% of a 30% aqueous solution of octadecylethyleneurea and from 2 to 4% of a 30% aqueous emulsion of a perfluoro alkyl acrylate ester to give a pickup of ½ to 2½% solids, said bath having a pH of 6 to 8 and a temperature of 70 to 100° F.

8. A process of imparting water and oil repellency to textile materials which comprises treating the textile materials with an aqueous bath containing ½ to 3% of solids which will have 2 to 4% of a 30% aqueous solution of octadecylpropyleneurea and from 2 to 4% of a 30% aqueous emulsion of a perfluoro alkyl acrylate ester to give a pickup of ½ to 2½% solids, said bath having a pH of 6 to 8 and a temperature of 70 to 100° F.

9. A process of imparting oil and water repellency to textile materials which comprises treating the fabric with a chlorinated hydrocarbon solvent having a boiling point of 72 to 88° C. with 2 to 3% of a 30% solution of octadecylethyleneurea and 2 to 3% of a 15% solution of a perfluoro alkyl acrylate.

10. A process of imparting oil and water repellency to textile materials which comprises treating the fabric with a chlorinated hydrocarbon solvent having a boiling point of 72 to 88° C. with 2 to 3% of a 30% solution of octadecylpropyleneurea and 2 to 3% of a 15% solution of a perfluoro alkyl acrylate.

11. An oil and waterproofing combination consisting essentially of a combination of an imine compound selected from the group consisting of octadecylethyleneurea and octadecylpropyleneurea and a perfluoro alkyl acrylate, the proportion of imine compound to acrylate ranging from equal parts by weight to 1.5 parts by weight of the former and 3 parts by weight of the latter.

12. A water and oilproofing agent consisting essentially of a combination of octadecylalkyleneurea and $CH_2{:}CHCOOCH_2(CF_2)_nCF_3$, wherein n is between 2 and 12, the proportion of the former to the latter being in the order of from equal parts by weight to ½ part by weight of the former to 1 part by weight of the latter.

13. A textile fabric having a water and oil repellent surfacing composed of 2 to 10% by weight of a surfacing composed of an octadecylalkyleneurea and a perfluoro alkyl acrylate ester present in the proportions varying from 30% of one to 70% of the other.

14. An oil and water bath for processing textile fabrics consisting essentially of 2 to 5% solid concentration of a mixture of 59% octadecylpropyleneurea of 30% concentration and 43% of emulsified perfluoro alkyl acrylate.

15. An oil and water bath for processing textile fabrics consisting essentially of 2 to 5% solid concentration of a mixture of 59% octadecylpropyleneurea of 30% concentration and 43% of emulsified perfluoro alkyl acrylate and also containing 10 to 20% of a thermosetting resin of the melamine formaldehyde type and magnesium chloride as a catalyst.

16. An organic solvent composition for treating textile fabrics consisting essentially of 2 to 5% solid concentration of a solution of 40% octadecylalkyleneurea of 30% concentration and 60% of a 15% concentration of perfluoro alkyl acrylate, all being dissolved in a chlorinated hydrocarbon solvent.

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MORRIS LIEBMAN, *Primary Examiner.*