

[54] **FLUORINATED OILY SOIL RELEASE AGENTS**

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[58] **Field of Search**..... 260/849, 67.6 R, 249.6

[56] **References Cited**

UNITED STATES PATENTS

3,128,272	4/1964	Wear et al.	260/249.6
3,296,264	1/1967	Gagliardi	260/249.6

3,503,915	3/1970	Peterson	260/849
3,510,455	5/1970	Olson	260/67.6 R

FOREIGN PATENTS OR APPLICATIONS

1,233,970	6/1971	United Kingdom
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Primary Examiner—John C. Bleutge

[57] ABSTRACT

An adduct is prepared by heating together, in the presence of an acid catalyst, (1) a perfluoroalkyl alcohol of formula $R_f(CH_2)_n-OH$ such as perfluoroalkylethyl alcohol; (2) a polyalkylene glycol such as polyethylene glycol having a molecular weight of about 1000; and (3) a poly(alkoxymethyl)melamine such as hexa(methoxymethyl)melamine. These adducts are effective in promoting oil and water repellency and oily soil release from textiles.

7 Claims, No Drawings

FLUORINATED OILY SOIL RELEASE AGENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to new compositions which when applied to textile substrates confer oil and water repellency and improved washability to said substrates, enhancing the removal therefrom of oily stains. More particularly this invention is directed to the adducts formed by the reaction of a perfluoroalkyl alcohol, a polyalkylene glycol and a poly(alkoxymethyl)melamine and the use of such adducts as oily soil release agents for textiles.

2. Prior Art

Textiles are routinely treated to enhance desirable properties and minimize undesirable properties. Synthetic fabrics and fabrics composed of blends of natural and synthetic fibers have good strength and resistance to abrasion, and also sufficient resilience to allow shape retention when worn or otherwise distorted in use. Such fabrics are often treated with finishing agents to give them a softer "hand" or feel. Cotton fabrics normally have a good "hand" but are often treated to increase fiber resilience and crease resistance.

Fabrics, particularly cotton containing fabrics, are often treated with thermosetting organic resins to give them permanent press characteristics. In addition to the thermosetting resin, catalysts and various modifying additives or finishing agents such as softeners, anti-static agents, etc. are also used to provide suitable commercial fabrics. Many of such treated fabrics have good wearing characteristics but the tendency of the fiber to accept oily stains is increased, and the ability of the material to release such stains upon laundering is usually reduced. "Wicking" or diffusion of the stain into the bulk of the fabric makes the stain even more difficult to remove. An improvement in the resistance of the fabric to staining can be provided through treatment with agents which impart oil and water repellency. However, oily stains can still occur despite these treatments, when oil or oily materials are forced into the fabric, such as may result from pressure or prolonged contact. The ability of the material to release this sort of stain is inhibited by the fluorochemical treating agents. The most serious problem with wash and wear and permanent press fabrics is the permanent kind of stain which cannot be removed by conventional home laundering.

Thus the prior art treatments for promoting oily soil release suffer from various shortcomings. Some treatments are effective for a while but do not retain their effectiveness through repeated launderings. The cost of any such treatment must, of course, be weighed against the value of improvement attained.

An object of this invention is to provide a composition for treating fabrics to endow said fabrics with greater oily stain release on laundering. A further object of the invention is to provide textile treating agents which confer oil and water repellency in normal wear, are durable and stable to repeated launderings, and which release oily stains and soil during laundering of the treated fabric. Other objects will become evident from our disclosure.

SUMMARY

In summary, this invention is directed to an adduct prepared by condensing in the presence of an acid catalyst

A. an alcohol of the formula

1. $R_f(CH_2)_n-OH$

wherein

R_f is perfluoroalkyl of from 4 through 16 carbon atoms;

n is an integer from 1 through about 16;

B. a polyalkylene glycol of the formula

2. $HO(CH_2-CHR-O)_mH$

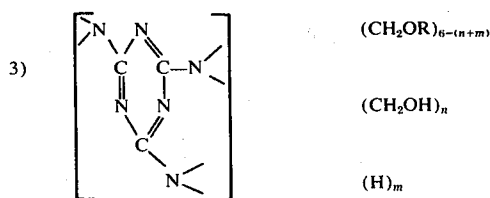
wherein

R is hydrogen or methyl, and

m is 8 to 450;

and having a molecular weight between about 400 and about 20,000; and

C. a poly(alkoxymethyl)melamine of the formula



wherein

R is alkyl of one to 5 carbon atoms;

n has a value of 0 to 2; and

m has a value of 0 to 3 with the limitation that $n + m$ cannot exceed a value of 3;

wherein the equivalents ratio of A to B is from about 20/1 to 1/20, and the equivalents ratio of A + B to C is from about .5/1 to 1.5/1.

These adducts provide a durable, launderable treatment employing reasonably low add-on for effectiveness with an economical, easily manufactured new adduct.

DESCRIPTION OF THE INVENTION

Components

The adducts of this invention are derived from the three classes of functional compounds referred to above. The reactivity of alkoxymethylmelamines is well known. These compounds react readily with compounds containing active hydrogens to produce the alcohol corresponding to the alkoxy group and a condensate incorporating the melamine residue. The adducts of this invention are produced by reacting, under conditions promoting the removal of the alcohol product, an (alkoxymethyl)melamine, a polyfluoroalkyl alcohol and a polyalkylene glycol. The adducts produced contain segments terminating in perfluoroalkyl groups. Polyether groups are believed to link some melamine residues. The adducts possess, therefore, qualities of oil and water repellency due to the pendant oleophobic perfluoroalkyl groups, and also hydrophilic properties associated with the polyalkylene oxide chains. When applied to a substrate, as for example a synthetic textile such as a polyester garment or cloth in conjunction with a crease resistant resin, the adducts of this invention improve not only oil and water repellency but also the easy removal by normal laundering procedures of oily stains which are present.

Among the useful alkoxymethylmelamines are the alkyl ethers of trimethylol melamine and hexamethylol melamine. Alkyl groups of from 1 to about 5 carbon atoms can be conveniently employed, a practical consideration being the ease or difficulty with which the corresponding alcohol can be removed from the reaction in which the adduct is formed. The preferred melamine derivatives are the hexa(alkoxymethyl)melamines where the alkyl groups have from 1 to 4 carbon atoms, and most preferred is hexa(methoxymethyl)melamine, which is commercially available.

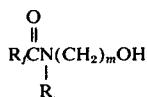
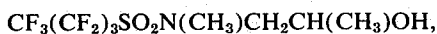
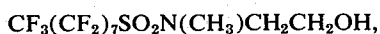
The polyalkylene glycols are also commercially available in a variety of molecular weights. Both polyethylene glycols and polypropylene glycols are commercially available and can be employed in the adducts of the invention in molecular weights of from about 400 to about 20,000. Polyethylene glycols of molecular weight from 400 to 4,000 are preferred, while polyethylene glycol of molecular weight about 1,000 is most preferred.

As polyfluoroalcohols, there may be used compounds containing perfluorinated alkyl groups of 4 to 16 carbon atoms. A general formula for useful alcohols is shown above as formula (1). Preferred alcohols are those where n is about 1 to 4, most preferably 2, and the perfluoroalkyl groups are straight or branched chain alkyls of 4 to 14 carbons. The most preferred polyfluoroalcohol is $R_f-CH_2CH_2-OH$ where R_f is a mixture of perfluorinated straight chain alkyl groups of 6-14 carbon atoms with an average molecular weight of 470. These alcohols are produced as described in U.S. Pat. Nos. 2,965,659, 3,145,222, 3,171,861 and 3,283,012.

Additionally polyfluoroalcohols where inert groups are present between R_f and $(CH_2)_n$ can be employed. Examples of these are



where m is 1 to 8,



where

R_f is perfluorinated C_4 to C_{16} alkyl,

R is C_1 to C_4 alkyl and m is 1 to 3.

Reaction

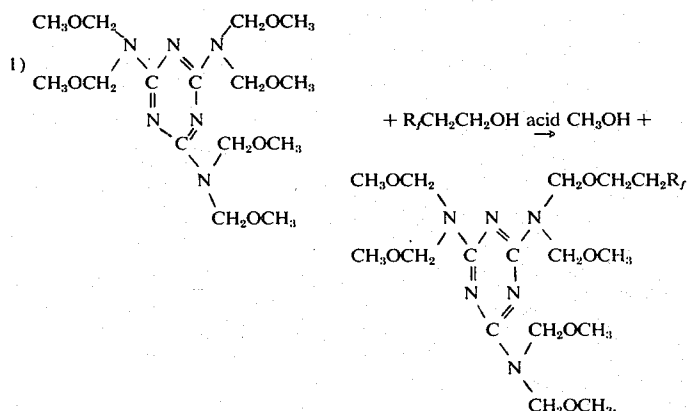
When an alkoxymethylmelamine is heated with an alcohol in the presence of an acid catalyst, an ether interchange reaction occurs with the elimination of the alcohol corresponding to the alkyl group. The reaction is disclosed in U.S. Pat. No. 3,296,264 where hexa(methoxymethyl)melamine and pentadecafluorooctyl alcohol are heated in equimolar proportions with a little orthophosphoric acid as catalyst to yield pentadecafluoromethyl penta(methoxymethyl)melamine and methanol. The polyalkylene glycols react with alkoxymethylmelamines in the same way, except that each glycol molecule can react with 2 alkoxymethylmelamine molecules instead of one.

Useful products are obtained with a wide variation in the amounts of the three primary ingredients employed. It is preferred to use a slight excess of the alkoxymethylmelamine compound in terms of its reactivity with active hydrogens available in the polyfluoroalcohol and the polyalkylene glycol. In these reactions, a hexa(alkoxymethyl)melamine molecule can react stoichiometrically with 6 equivalents of an active hydrogen containing molecule. A polyalkylene glycol molecule can react with 2 equivalents of a compound susceptible to reacting with an active hydrogen, while a polyfluoroalcohol is monoequivalent, offering only one active hydrogen for reaction. Thus for example, 1 mole (6 equivalents) of hexa(methoxymethyl)melamine can react with 2 moles of a polyethylene glycol (4 equivalents) plus 2 moles of polyfluoroalcohol (2 equivalents). It is preferred to employ the alkoxymethyl melamine reactant in an approximately stoichiometrically equivalent amount, plus or minus about 10%, most preferably with a stoichiometric excess of about 5%.

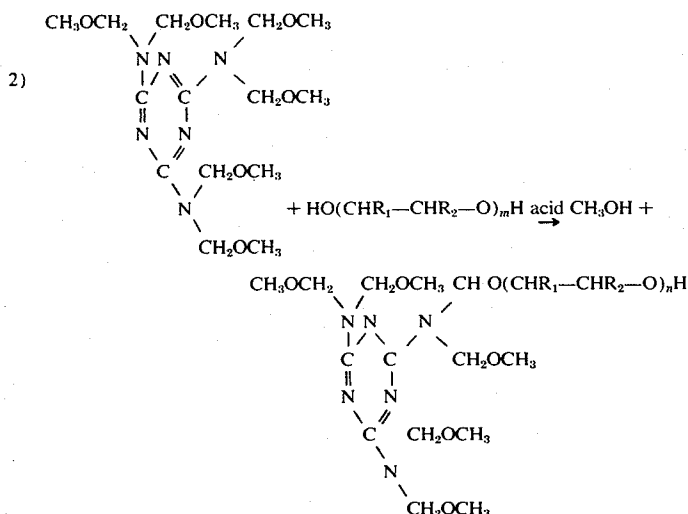
While a very wide range of proportions of polyfluoroalcohol to polyalkylene glycol can be used, it is preferred to employ about 1 to 20 equivalents of the polyfluoroalcohol to 1 equivalent of polyalkylene glycol. The most preferred mixture for producing an adduct of the invention contains about 5 equivalents of perfluoroalcohol, about 2 equivalents of polyalkylene glycol and about 7.5 equivalents of poly(alkoxymethyl)melamine.

Polyalkylene glycols in large measure confer functional performance (as hydrophilic or hydrophobic) in proportion to the weight employed whether the molecular weight is high or low. The weight proportion of polyfluoroalcohol to polyalkylene glycol is therefore of significance also, and a favored ratio is about 70 parts of polyfluoroalcohol to about 30 parts of polyethylene glycol.

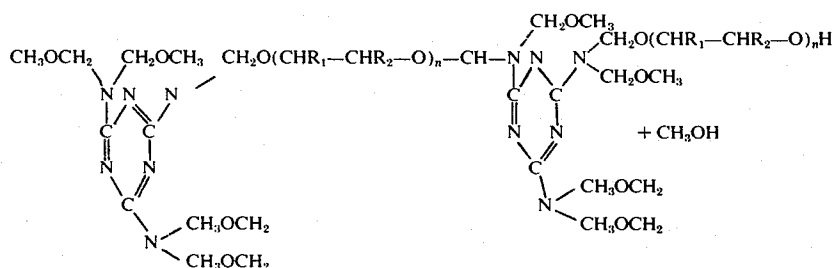
Reactions which occur produce the following types of linkage



The perfluoroethyl alcohol can, of course, react at more than one of the methoxy group linkages.



The product of (2) can condense to form



In the adducts of the invention most, if not all of the alkoxy groups of the hexa(alkoxymethyl)melamine have reacted so that nearly all have been converted to linkages of the type illustrated in (1), (2), or (3) above.

As stated above, the polyalkylene glycol can react at more than one of the methoxy group linkages. Thus linking of the segments as shown in (3) can occur through reaction of the hydroxy group at the other end of the already linked polyalkylene oxide unit. The products of the reaction include, therefore, a number of molecular species with different proportions of polyfluoroalcohol and polyalkylene glycol substitution on the melamine rings, and varying degrees of linking of the rings through the polyalkylene oxide chains. The polyfluoroalcohol and polyalkylene glycol units do not link with each other under the conditions employed.

In preparing the products, the dry reactants are charged to a vessel equipped with an agitator and fitted for fractional distillation. Also charged to the vessel is an acidic material serving as a catalyst and optionally a reaction solvent or diluent which maintains fluidity in

the mixture but takes no part in the reaction. The inert solvent or diluent can be a mixture of compounds and

is chosen not only for its fluidization properties but also

for its boiling point, which is preferably from about 50°C. to 150°C. so that it can be distilled or partially distilled from the mixtures after the desired reaction is finished. Most preferred are diluents which form azeotropes with the alcohol by-product of the reaction and can thereby facilitate its removal.

The mixture is stirred at reflux temperature and the distillate containing alcohol of reaction removed. When the desired amount of alcohol has been removed, the acidity conferred by the catalyst is neutralized with a base such as sodium bicarbonate or ammonia, and water is gradually added as distillation is continued until all of the solvent or diluent has been removed by steam distillation. Distillation can be carried out at atmospheric pressure or under vacuum. Sufficient water is added to maintain a stirrable viscosity in the reaction mixture. The solid content of the final mixture will preferably be about 20-25%. The cooled mixture is stirred, optionally in a high-shear mixer, to prepare a stable dispersion. The dispersion is best diluted to 10 to 15% solids for maximum stability, while a small

amount of isopropanol, such as 5–10% of total dispersion weight also improves the stability of the dispersion. Too much isopropanol, such as 20% or more, may completely dissolve the solid material.

Among materials suitable for use as inert diluents are hydrocarbons such as benzene, toluene and xylene; halogenated hydrocarbons such as monochlorobenzene, 1,1,2,2-tetrachloro-1,2-difluoroethane and carbon tetrachloride; and ketones and ethers of suitable boiling point.

Compounds suitable for use as reaction catalysts are acidic materials such as p-toluenesulfonic acid, phosphoric acid and even sulfuric or hydrochloric acid if a very small amount is used.

Use

For treating textiles, it is unnecessary to isolate the solid products of the reaction. Because of the aqueous solubility of the adducts of this invention, the improved properties they confer on textile substrates do not have the desired durability unless the adducts are coapplied with a permanent press or crease resistant resin. The adduct and resin can be conveniently coapplied from an aqueous emulsion by dipping the textile material into a bath, by spraying or calendar coating. The permanent press or crease resistant resin is accompanied by the usual resin catalyst, usually an acidic material such as zinc nitrate, magnesium chloride, an amine hydrochloride or an organic acid. The treated material is dried at about 120°C., then cured at the prescribed resin curing temperature and time, usually about 165°C. for about 3 to 5 minutes. The resin and adduct are thus fixed to the fabric, and the functional attributes of the adduct persist through a number of launderings.

Permanent press and crease resistant resins are well known in the textile art. As an example of a permanent press resin, there may be mentioned 1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone. Crease resistant resins are exemplified by compounds such as tetramethylolacetylenediurea, dimethylol [cyclic]ethylene urea, melamine-uron compositions, hexamethylol melamine and the dimethyl ether of trimethylol melamine.

All of these products are useful as textile treating resins and when properly applied and cured are fixed durably to textile material. They are broadly described as aminoplast resins. Their use has been largely on textiles composed of polyester-cotton blends and on cotton itself. The adducts of the invention are useful on polyester-cotton blends and on polyester textiles, especially knitted goods.

The oil and water repellency and soil release properties obtained by coapplication of the adducts of this invention along with permanent press or crease resistant resins are not shown by textiles treated with the resins only.

The amount of the adduct of the invention usefully deposited on textile material can range from about 0.1 to 5.0% based on weight of dry fiber. Preferably the amount will be from about 0.2 to 2.0%. The amount of aminoplast resin coapplied can range from about 0.1 to 10.0% of the resin based on weight of dry fiber. Since these products are normally sold in a diluted form, usually at 50% concentration, the amount of commercial resin formulation used can be much higher. Preferably the amount of actual aminoplast resin codeposited will

be from about 0.1 to 1.0%, as this amount will ordinarily serve to durabilize the properties conferred by the adduct of the invention. Where a crease-proofing treatment is being applied, much larger amounts of crease-proofing resin can be coapplied with the adduct of the invention. Treatment baths can also include other textile treating agents such as softeners, static eliminators, snag resistant agents and the like.

As mentioned before, the adducts of this invention can be conveniently applied by dipping, or by spraying an aqueous emulsion of the adducts onto the textile. Solutions of the adducts and resins in organic solvents can also be used.

The following examples illustrate this invention. Parts and percentages referred to therein are by weight unless otherwise indicated.

EXAMPLE 1

Into a suitable vessel were charged 140.1 parts of $R_f\text{---CH}_2\text{CH}_2\text{OH}$ where R_f is a mixed perfluoroalkyl of 4 to 14 carbon atoms, the average molecular weight being 470, 60.0 parts of $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{H}$ ("Carbowax", 1000, Union Carbide Co.), 28.7 parts of hexa(methoxymethyl)melamine ("Cymel" 300, American Cyanamid Co.), 129.9 parts of toluene, 120.1 parts of methylisobutyl ketone and 0.15 parts of p-toluenesulfonic acid monohydrate. This ratio of reactants corresponds to 0.3 equivalent of polyfluoroalcohol, 0.12 equivalent of polyethylene glycol and 0.441 equivalent of hexa(methoxymethyl)melamine. The vessel was fitted with an agitator, a thermometer and a fractionating column with refluxing distillation head.

The reaction mass was stirred and heated at reflux, removing the methanol product as an azeotropic distillate; 15.4 parts of methanol were collected, slightly more than theorized, probably due to presence of a little methanol in the hexa(methoxymethyl)melamine. When the mass became rather viscous at the end of the reaction, about 0.48 part of 10% ammonium hydroxide solution was added to neutralize the catalyst. All of the solvent material was then removed by distillation as water was added at a rate sufficient to keep the mass stirrable. The solids content when all solvent material had been removed was 20–25%. The mass was removed from the reaction vessel and vigorously agitated in a high shear blender to give a stable dispersion of the solid product in water. Isopropanol was added to aid the dispersion, the final composition containing 11.4% solids and 8% isopropanol. The 11.4% polymer suspension can be applied to polyester and polyester-cotton textiles as described hereinafter.

The composition was applied to 100% polyester double knit fabric from an aqueous bath at a treatment level of 0.31% dry adduct on the textile material along with 1.0% melamineuron crease resistant resin composition ("Aerotex" 23 Special of American Cyanamid Co.) and 0.2% resin catalyst ("Accelerator" MX, MgCl_2 solution of American Cyanamid Co.) The treated fabric samples were dried 4 minutes at 250°F. and cured for 3 minutes at 320°F. Results of tests applied initially to fabrics as treated and also to treated fabrics after 5 home washes are shown in Table I below.

TABLE I

	Treated Sample	Untreated Sample
Initial Soil Release	15	180
Initial Oil Repellency	6	0
Initial Water Repellency	70	70
After 5 Home Washes -		
Soil Release	17	53
Oil Repellency	5	0
Water Repellency	70	0

Explanation of the tests is given in the next examples.

EXAMPLES 2-7

A series of preparations were made employing the general procedure of Example 1, but varying the mol ratio of the three primary constituents as used in that example and also using 1,1,2,2-tetrachloro-1,2-difluoroethane in place of the toluene and methylisobutylketone used in Example 1. The amounts of the various reactants used, the amount of product obtained, and the equivalents ratio of the polyfluoro reactant (A) to polyalkylene glycol reactant (B) are shown below in Table II.

TABLE II

Example No.			2	3	4	5	6	7
A)	Fluoroalcohol	moles	.1	.1	.1	.1	.1	.1
		equiv.	.1	.1	.1	.1	.1	.1
		parts	46.7	46.7	46.7	46.7	46.7	46.7
B)	"Carbowax" 1000	moles	.031	.031	.02	.02	.011	.011
		equiv.	.062	.062	.04	.04	.022	.022
		parts	31.1	31.1	20.0	20.0	10.7	10.7
C)	Hexa(methoxymethyl)-melamine	moles	.027	.021	.023	.019	.020	.016
		equiv.	.162	.126	.138	.114	.120	.096
		parts	10.5	8.4	9.1	7.6	7.9	6.3
			1.6	1.6	2.5	2.5	4.5	4.5
Equivalent ratio A/B			1.0	1.0	1.0	1.0	1	1
p-Toluenesulfonic acid monohydrate, parts			.05	.05	.05	.05	.05	.05
1,1,2,2-Tetrachloro-1,2-difluoroethane, parts			163.7	163.7	163.7	163.7	163.7	163.7
Solid product, parts			56.6	56.5	54.5	44.7	46.7	41

Each of the above products was applied to polyester-cotton fabric samples (designated 224R-2) along with "Aerotex" 23 Special, a commercial crease resistant resin (melamine-uron composition), dried and cured. The treated fabric was tested for oil repellency, water repellency and soil release.

The Oil Repellency Test is the American Association of Textile Chemists and Colourists Standard Test Method 118-1966. The Water Repellency Test is the American Association of Textile Chemists and Colourists Standard Test Method 22-1952 (ASTM D-58363). The Soil Release Test is that described in

"Textile Chemist and Colourist" 3 No. 10, October (1971). The soil release values given herein are expressed as $1000 \times W$, the "soiling value" of the washed fabric of the reference article. The lower the number, the more easily the soil is removed in the wash test.

The soil release numbers have no absolute value but are compared, in every case, with an untreated blank subjected to the same soiling treatment.

To prepare a bath for applying the textile treating agents it was first determined how much of the liquid dispersion was retained on a standard size cloth sample when it was dipped and wrung twice. The bath was then prepared by adding weighed amounts of the reaction product "Aerotex" 23 Special and "Aerotex" catalyst, "Accelerator" MX $MgCl_2$ solution, to water, mixing and diluting to a standard volume. Weight was adjusted so that each treated and dried cloth sample had taken up, based on its dry weight, a known amount of the solid reaction product, 1.0% of the commercial "Aerotex" 23 Special Product and 0.2% of the commercial catalyst. In the present examples the bath contained also 2.0% of its weight of isopropanol.

After dipping and wringing, the test cloths each were dried for 4 minutes at 250°F., then cured for 3 minutes

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at 320°F. The treated cloth pieces were tested as treated, and again after 5 home washes.

A standard wash consisted of a complete wash and spin dry cycle in a conventional automatic washing machine (Sears-Roebuck Kenmore Model 600) using about 18 gallons of water, 90.0 g. AATCC detergent number 124 and a 4 lb. load of textile material. Temperature of washing was 140°F. The load was tumble dried at up to 180°F. in the companion clothes drying machine (Kenmore 600).

Results of the tests for Examples 2-7 are listed below in Table III.

TABLE III

Example	Reaction Product % on wt. of cloth	Oil Repellency		Water Repellency		Soil Release	
		Initial	After 5 Washes	Initial	After 5 Washes	Initial	After 5 Washes
2	.31	6	3	70	70	6	10
3	.31	5	3	50	70	7	13
4	.286	6	4	70	80	9	5
5	.286	5	3	70	80	23	14
6	.265	2	2	70	80	40	45
7	.265	6	5	70	70	11	31
Untreated		0	0	70	0	530	524

In this series of examples, preparation of the composition of the invention was carried out in the manner described for Examples 2-7. The equivalents ratio of the polyfluoro reactant (A) to the polyethylene glycol (B) was varied from

$$\frac{1.6}{1.0} \text{ to } \frac{5.0}{1.0}$$

Materials used for each preparation are shown in Table IV.

TABLE IV

		8	9	10
A) Fluoroalcohol	moles	.1	.1	.1
	equivalents	.1	.1	.1
	parts	46.7	46.7	46.7
B) "Carbowax" 1000	moles	.031	.02	.01
	equivalents	.062	.04	.02
	parts	31.1	20.0	10.7
C) Hexa(methoxymethyl)melamine	moles	.032	.028	.024
	equivalents	.195	.168	.146
	parts	12.6	10.9	9.5
Equivalent ratio A/B		1.6	2.5	5.0
		1.0	1.0	1.0
p-Toluenesulfonic acid monohydrate, parts		.05	.05	.05
1,1,2,2-Tetrachloro-1,2-difluoroethane, parts		163.7	163.7	163.7
Solid product, parts		84	59.4	58.4

Treatment baths were prepared for each of the three samples and the compositions were applied to 100% polyester double knit fabric designated Chem. 224R2. Each test cloth took up, in addition to the polyfluoro adduct as % of dry fabric weight, 1.0% melamine-uron permanent press resin composition ("Aerotex" 23 Special of American Cyanamid Co.) and 0.2% resin catalyst ("Accelerator" MX - MgCl₂ solution of American Cyanamid Co.). The treated test cloths were dried 4 minutes at 250°F., then cured for 3 minutes at 320°F. and tested as described for examples 2-7.

Test results are shown in Table V below.

TABLE V

Example	Reaction Product % on wt. of cloth	Oil Repellency		Water Repellency		Soil Release	
		Initial	After 5 Washes	Initial	After 5 Washes	Initial	After 5 Washes
8	.31	2-3	0	70	70	48	64
9	.285	5	2	70	70	17	29
10	.265	7	1	70	70	6	27
Untreated		0	0	70	70	128	165

TABLE VI

Example No.		11	12	13
A) Fluoroalcohol	moles	.1	.1	.1
	equivalents	.1	.1	.1
	parts	46.7	46.7	46.7
B) "Carbowax" 1540	moles	.02	.013	.007
	equivalents	.04	.026	.014
	parts	31.1	20.0	10.7
C) Hexa(methoxymethyl)melamine	moles	.028	.025	.023
	equivalents	.168	.15	.137
	parts	10.9	9.8	8.9
Equivalent ratio A/B		2.5	3.8	7.1
		1	1	1
p-Toluenesulfonic acid monohydrate, parts		0.05	0.05	0.05
1,1,2,2-Tetrachloro-1,2-difluoroethane, parts		163.7	163.7	163.7
Solid product, parts		68	68.8	53.0

EXAMPLES 11-13

In this series of examples preparation of the composition of the invention was carried out as in the previous examples. These three examples employed polyethylene glycol having a molecular weight of 1540. Materials used for each preparation are shown in Table VI.

The products were applied and tested as described for Examples 8-10. Results of the tests are shown in Table VII.

TABLE VII

Example	Reaction Product % on wt. of cloth	Oil Repellency		Water Repellency		Soil Release	
		Initial	After 5 Washes	Initial	After 5 Washes	Initial	After 5 Washes
11	.31	7	2	70	70	11	19
12	.285	6	1	70	70	9	70
13	.265	6	0	70	70	15	30
Untreated		0	0	70	70	128	165

EXAMPLES 14-16

Preparation of the compositions in these examples was again carried out as in the previous examples. These three examples employed polyethylene glycol having a molecular weight of 4000. Materials used for each preparation are shown in Table VIII.

The products were applied and tested as described for the previous six examples. Results of the tests are shown in Table IX.

TABLE VIII

Example No.		14	15	16
A) Fluoroalcohol	moles	.1	.1	.1
	equivalents	.1	.1	.1
	parts	46.7	46.7	46.7
B) "Carbowax" 4000	moles	.0078	.005	.00265
	equivalents	.0156	.01	.0053
	parts	31.1	20.0	10.6
C) Hexa(methoxymethyl)melamine	moles	.0231	.022	.021
	equivalents	.1387	.132	.126
	parts	9.0	8.6	8.2
Equivalents ratio A/B		6.4	10	18.8
p-Toluenesulfonic acid monohydrate, parts		1	1	1
1,1,2,2-Tetrachloro-1,2-difluoroethane, parts		.05	.05	.05
Solid product, parts		163.7	163.7	163.7
		79	68.7	59.5

TABLE IX

Example	Reaction Product % on wt. of cloth	Oil Repellency		Water Repellency		Soil Release	
		Initial	After 5 Washes	Initial	After 5 Washes	Initial	After 5 Washes
14	.308	4	1	50	70	21	26
15	.280	4	0	70	70	27	9
16	.265	3	0	70	70	17	20
Untreated		0	0	70	70	128	165

TABLE X

Example No.		17	18	19
A) Fluoroalcohol	moles	.1	.1	.1
	equivalents	.1	.1	.1
	parts	46.7	46.7	47.7
B) "Carbowax" 200	moles	0.1	.058	.026
	equivalents	.2	.117	.052
	parts	20.0	11.7	5.2
C) Hexa(methoxymethyl)melamine	moles	.074	.064	.038
	equivalents	.45	.325	.228
	parts	29.2	21.1	14.8
Equivalents ratio A/B		0.50	0.86	1.9
p-Toluenesulfonic acid monohydrate, grams		1	1	1
1,1,2,2-Tetrachloro-1,2-difluoroethane, grams		.05	.05	.05
Solid product, grams		163.7	163.7	163.7
		84.2	66.7	61.8

TABLE XI

Example	Reaction Product % on wt. of cloth	Oil Repellency		Water Repellency		Soil Release	
		Initial	After 5 Washes	Initial	After 5 Washes	Initial	After 5 Washes
17	.27	0	0	70	70	54	104
18	.245	0	0	70	70	113	114
19	.229	0	0	70	70	217	174
Untreated		0	0	0	0	226	449

TABLE XII

Example No.		20	21	22
A) Fluoroalcohol	moles	.1	.1	.1
	equivalents	.1	.1	.1
	parts	46.7	46.7	46.7
B) "Carbowax" 600	moles	.033	.0195	0.0085
	equivalents	.067	.0389	.017
	parts	20.0	11.7	5.2
C) Hexa(methoxymethyl)melamine	moles	.041	.034	.029
	equivalents	.25	.208	.176
	parts	16.3	13.6	11.4
Equivalents ratio A/B		1.5	2.6	5.9
		1	1	1
p-Toluenesulfonic acid monohydrate, parts		.05	.05	.05
1,1,2,2-Tetrachloro-1,2-difluoroethane, parts		163.7	163.7	163.7
Solid product, parts		63.0	67.4	59.0

TABLE XIII

Example	Reaction Product % on wt. of cloth	Oil Repellency		Water Repellency		Soil Release	
		Initial	After 5 Washes	Initial	After 5 Washes	Initial	After 5 Washes
20	.252	4	2	70	70	18	2
21	.235	3	1	70	70	9	65
22	.220	2	1	70	70	36	282
Untreated		0	0	0	0	226	449

EXAMPLES 17-19

Preparation of the compositions was again carried out as in the previous examples. The three comparative examples employed polyethylene glycol having a molecular weight of 200, which is below the lower limits of this invention. Materials used for the preparation are shown in Table X.

The products were applied and tested as for the previous 9 examples. Results of the tests are shown in Table XI.

EXAMPLES 20-22

Preparation of the composition was carried out as in the previous examples. These three examples employed polyethylene glycol having a molecular weight of 600. Materials used for the preparation are shown in Table XII.

The products were applied and tested as described for the previous 12 examples. Results of the tests are shown in Table XIII.

EXAMPLES 23-28

Into a suitable vessel, equipped with a column for fractional distillation, there was charged 63 parts of the polyfluoroalcohol $R_f\text{CH}_2\text{CH}_2\text{OH}$ where R_f is a mixed perfluoroalkyl of 4 to 14 carbon atoms where average molecular weight of the alcohol was 470, 27 parts of polyethylene glycol of 1000 molecular weight, 0.069 parts of p-toluenesulfonic acid monohydrate and 300 parts of 1,1,2,2-tetrachloro-1,2-difluoroethane. The mixture was heated to reflux and a distillate of water and halogenated diluent removed until no more water appeared in the distillate. The diluent was separated from the water and returned to the reaction vessel. In a separate vessel 12.8 parts of hexa(methoxymethyl) melamine was similarly dried, and was then charged to

the first vessel with the other reactants. The entire charge was then heated to reflux and the methanol reaction product was removed by fractionation. At the end of the reaction the temperature at the top of the fractionating column reached 93°C., the boiling point of the diluent. The mass was cooled at 50°-60°C. and a solution of 63 parts of sodium bicarbonate, 1720 parts of water was added. Sufficient additional water was added to provide a 25% solids mixture on a diluent free basis. The temperature of the mass was again raised and the halogenated diluent removed by distillation under reduced pressure. Temperature in the reaction vessel was not allowed to go above 75°C. When all of the diluent had been removed, the charge was cooled to 25°-30°C. About 315 parts of isopropanol were then added for each 454 parts of solids in the charge, and sufficient water was added to bring the solids content to 17.0%. The mass was homogenized in a high shear mixer. A stable dispersion resulted which was water extendable, and finally water was added to bring the solids content to 11.4%.

The adduct was coapplied to 100% polyester double knit textile samples with 6 representative commercial crease resistant resins shown below in Table XIV. Aqueous baths were prepared to contain the adduct, the commercial resin and a 2 part catalyst, one-half zinc nitrate and one-half aluminum glycollate - glycolic acid mixture. The amount of each commercial product used was 0.5% of the product as sold on the weight of dry textile. In each test there was deposited on the fabric 0.456% of its weight of the solid adduct prepared above.

TABLE XIV

Example	Commercial Resin	Chemical Type
23	"Aerotex" Cream 450	methylol urea carbamate
24	"Karaset" 1452	

TABLE XIV-Continued

Example	Commercial Resin	Chemical Type
25	"Cymel" 300	hexa(methoxymethyl)-melamine
26	"Aerotex" Reactant 23 Special	melamine-uron
27	"Permafresh" 183	dihydroxydimethylol-ethylene urea
28	"Permafresh" 168	dihydroxydimethylol-ethylene urea

In each test there was also deposited on the fabric 0.1% of a resin catalyst,

"Sunkem" Catalyst X4 (zinc nitrate solution) 15

After dipping the test fabric pieces and wringing to the proper wet pick-up, the pieces were dried at 250°F. for 4 minutes then cured at 320°F. for 3 minutes.

The pieces were tested for oil and water repellency and for soil release both initially and after 5 home washes as already described herein. Results obtained are shown in Table XV below. 20

TABLE XV

Example	Oil Repellency		Water Repellency		Soil Release	
	Initial	After 5 Washes	Initial	After 5 Washes	Initial	After 5 Washes
23	6	3	70	70	21	209
24	6	3	70	70	9	36
25	5	4	70	70	40	156
26	5	3-4	70	70	7	145
27	6	4	70	70	13	67
28	6	4	70	70	2	50
Untreated	0	0	70	70	700	1072

EXAMPLE 29

Preparation of the adduct was carried out as in the previous examples using polypropylene glycol in place of polyethylene glycol. Materials used for the preparation are shown in Table XVI below.

TABLE XVI

Materials	
A) Fluoroalcohol	moles equivalents parts 0.30 0.30 140.1
B) Polypropylene glycol (mol. wt. 1025)	moles equivalents parts 0.0535 0.107 60.0
C) Hexa(methoxymethyl)-melamine	moles equivalents parts 0.071 0.426 27.7
Equivalent ratio A/B	5.6
p-Toluenesulfonic acid	0.3 parts
1,1,2,2-Tetrachloro-1,2-difluoroethane	491 parts
Solid product	214.5 parts

EXAMPLE 30

Materials used are shown in Table XVII below. Preparation of this adduct was carried out as described in example 29.

TABLE XVII

Materials	
5 A) Fluoroalcohol	moles equivalents parts 0.30 0.30 140.1
B) Polypropylene glycol (mol. wt. 2025)	moles equivalents parts 0.0296 0.059 60.0
10 C) Hexa(methoxymethyl)-melamine	moles equivalents parts 0.0628 0.377 24.5
p-Toluenesulfonic acid	0.3 parts
1,1,2,2-Tetrachloro-1,2-difluoroethane	491 parts
Solid product	190.8 parts

EXAMPLE 31

The preparation of this adduct was carried out as in example 29. Materials are shown in Table XVIII below.

TABLE XVIII

Materials	
40 A) Fluoroalcohol	moles equivalents parts 0.30 0.30 140.1
B) Polyethylene glycol (mol. wt. 20,000)	moles equivalents parts 0.003 0.006 60.0
45 C) Hexa(methoxymethyl)-melamine	moles equivalents parts 0.0536 0.323 20.8
p-Toluenesulfonic acid	0.3
1,1,2,2-Tetrachloro-1,2-difluoroethane	491 parts
Solid product	212.7 parts

EXAMPLE 32

Preparation of this adduct was carried out as in example 29, but using hexa(butoxymethyl)melamine in place of hexa(methoxymethyl)melamine. Materials are shown in Table XIX below.

TABLE XIX

Materials	
60 A) Fluoroalcohol	moles equivalents parts 0.30 0.30 140.1
B) Polyethylene glycol (mol. wt. 1000)	moles equivalents parts 0.06 0.12 60.0
65 C) Hexa(butoxymethyl)-melamine	moles equivalents parts 0.0748 0.447 48.0
p-Toluenesulfonic acid	0.3 parts
1,1,2,2-Tetrachloro-1,2-difluoroethane	491 parts
Solid product	215 parts

Samples from the previous four examples, 29-32, were tested for oil and water repellency and soil release

quality on 100% polyester double knit fabric. In each instance an emulsion was prepared to contain 11.4 parts of the solid adduct, 8.0 parts of isopropyl alcohol, 11.4 parts of 1,1,2,2-tetrachloro-1,2-difluoroethane, 50.0 parts of water and 1.14 parts of octadecyltrimethyl ammonium chloride. The mixture for each emulsion was agitated in a high shear mixer and pH adjusted to 8.0 ± 0.2 with sodium bicarbonate. Sufficient water was finally added to bring the total weight of each emulsion to 100 parts except for the product of example 31 which required more water to achieve a reasonably low viscosity. The emulsion from example 31 contained 9.75% of the prepared adduct.

Aqueous baths were prepared to contain sufficient adduct in each case to deposit 1.425% of the adduct on the dry weight of test fabrics. From the same bath was deposited in each case 1.0% of "Aerotex" 23 Special crease resistant resin and 0.2% of "Accelerator" MX catalyst as previously described. The wet treated test pieces were dried at 250°F. for 4 minutes, then cured for 3 minutes at 325°F.

Test results are shown in Table XX below.

TABLE XX

Example	Oil Repellency		Water Repellency		Soil Release	
	Initial	After 5 Washes	Initial	After 5 Washes	Initial	After 5 Washes
29	1	0-1	70	70	12	82
30	0	1	70	70	8	50
31	5	1	70	70	16	19
32	2	1	0	0	8	11
Untreated	0	0	0	0	195	81

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An adduct prepared by the condensation, in the presence of an acid catalyst and under temperature and pressure conditions that result in the removal of alcohol formed by the condensation, of

A. an alcohol of the formula

1. $R_f(CH_2)_nOH$ wherein R_f is perfluoroalkyl of from 4 through 16 carbon atoms; and n is an integer from 1 through about 16.

B. a polyalkylene glycol of the formula

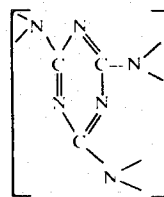
2. $HO(CH_2-CHR-O)_mH$

wherein R is hydrogen or methyl; and m is an integer from about 8 through about 450;

and having a molecular weight between about 400 and about 20,000; and

C. a poly(alkoxymethyl)melamine of the formula

(3)

 $(CH_2OR)_{n+m}$ $(CH_2OH)_n$ $(H)_m$

wherein

R is alkyl of one to 5 carbon atoms;

n has a value of 0 to 2; and

m has a value of 0 to 3 with the limitation that $n + m$ cannot exceed a value of 3;

wherein the equivalents ratio of A to B is from about 1/20 to 20/1 and the equivalents ratio of A + B to C is from about 0.5/1 to 1.5/1.

2. An adduct of claim 1 wherein the poly(alkoxymethyl)melamine is hexa(methoxymethyl)melamine.

3. An adduct of claim 2 wherein the alcohol has the formula $R_f-CH_2CH_2-OH$ and R_f is perfluoroalkyl of 4 through 14 carbon atoms.

4. An adduct of claim 3 wherein the polyalkylene glycol is a polyethylene glycol having a molecular weight of from 400 to 4000

5. An adduct of claim 4 wherein the alcohol has an average molecular weight of about 470 and the formula $R_f-CH_2CH_2-OH$ wherein R_f is a mixture of perfluorinated straight chain alkyl groups of 6 through 14 carbon atoms

6. An adduct of claim 5 wherein the polyethylene glycol has a molecular weight of about 1000.

7. An adduct of claim 1 prepared by condensing in the presence of an acid catalyst

A. about 5 equivalents of the alcohol;

B. About 2 equivalents of the polyalkylene glycol; and

C. about 7.5 equivalents of the poly(alkoxymethyl)melamine poly(alkoxymethyl)melamine.

* * * * *