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3,232,790

## METHOD FOR TREATING TEXTILE WITH PER- FLUOROALKYL COMPOUNDS AND THE TREATED TEXTILE

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This invention relates to textile finishing methods, and more particularly to a method of making textiles oil and water repellent.

It is known to treat textiles and other fibrous materials with aqueous solutions or dispersions of compounds which contain a plurality of perfluoroalkyl radicals having at least 4 carbon atoms in each alkyl radical in order to make them oil repellent. The oil repellency produced in this manner does not satisfactorily resist laundering of the textile materials at relatively high temperatures. The known treatments provide a measure of water repellency, but such water repellency does not meet commercial requirements. It is an added disadvantage of the afore-described treating method that aqueous solutions or dispersions of the perfluoroalkyl compounds tend to form coatings on the rolls of a padding machine or the like during treatment of the textiles, and thus render continuous operation of the machines difficult, or even impossible.

It is the primary object of the invention to provide a treatment for making textile materials oil and water repellent which avoids the drawbacks of the known method described above while retaining its well known advantages.

A more specific object of the invention is the provision of a method for treating textile materials with perfluoroalkyl compounds of the type described to obtain a finish which resists laundering at relatively high temperatures.

Another object is the provision of such a method which can be continuously carried out on conventional equipment of the padding machine type without requiring interruption of the process because of the formation of coatings on the machine rolls.

An additional object of the invention is the provision of a finishing method which provides a good, soft hand to the material treated. A further object is the provision of a method which is well suited for the treatment of synthetic fiber materials.

Yet another object is the provision of a textile finishing method which is applicable to cotton and rayon fabrics, and may be employed on such fabrics in conjunction with conventional procedures for making the fabrics wrinkle resistant.

We have found that the shortcomings inherent in known textile treating methods employing perfluoroalkyl compounds can be overcome by adding to the treating bath dispersions of an N-alkyl-N',N'-alkylene urea the alkyl radical of which has more than 10, and preferably 11 to 22 carbon atoms, and the alkylene radicals of which have 2 to 3 carbon atoms.

Quite surprisingly it has been found that even very small amounts of these alkyl-alkylene ureas not only

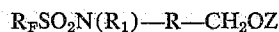
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greatly improve the water repellency effects of the treating bath, but that they also completely prevent the formation of coatings on the rolls of the padding machines during the treatment of the textile materials. Extended continuous runs are possible. Moreover, the oil repellency of the treated fabrics is not only not reduced but the laundry resistance of the water repellent finish is greatly increased.

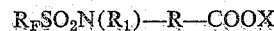
It is an additional advantage of the method according to the invention that the alkyl-alkylene ureas of the invention impart to the textile material a pleasant, soft hand and agreeable drape.

The method of the invention is particularly well suited for the treatment of woollens and of materials consisting partly or entirely of synthetic fibers, such as polyester fibers, nylons, polyacrylonitrile. Very good effects are also produced on other fabrics of fibrous materials of natural or synthetic origin. It is particularly advantageous to combine the treatment according to the invention with the conventional wrinkle proofing treatment of cellulosic fiber materials such as native cotton or rayon. For this purpose, the fibrous materials are treated with a finishing solution which, in addition to finishing agents of the invention, contains a suitable synthetic resin forming agent, such as methylol urea, or its ethers, methylol melamine or its ethers, or reactive resins such as methylol-ethylene urea, methyloltriazone derivatives, and the catalysts which are necessary for curing the precondensates jointly employed with these resins. Suitable catalysts include the ammonium salts of strong inorganic acids, which may be used jointly with ammonium salts of weak acids if so desired and salts of multivalent metals such as magnesium, zinc, and the like with strong inorganic acids.

Examples of suitable compounds containing a plurality of perfluoroalkyl radicals each radical having at least 4 carbon atoms include the water soluble chromium coordination complexes of saturated perfluoro-monocarboxylic acids or substituted carboxylic acids having at least one perfluoro radical with at least 4 carbon atoms as disclosed in U.S. Patent No. 2,662,835; aqueous dispersions of basic salts of aluminum with perfluoro-monocarboxylic alkanolic acids or substituted carboxylic acids having at least one perfluoro alkyl radical of at least 4 carbon atoms; aqueous dispersions of polymers or copolymers of esters of 1,1-dihydro-perfluoroalkanols with acrylic acid as disclosed in U.S. Patent No. 2,642,416; aqueous dispersions of polymers or copolymers, the monomer units having the formula:



wherein  $R_F$  is a perfluoroalkyl radical having at least 4 carbon atoms;  $R_1$  is hydrogen or an alkyl radical having 1 to 6 carbon atoms;  $R$  is a divalent alkylene radical having 1 to 12 carbon atoms, and  $Z$  is the residue of acrylic or methacrylic acid; or aqueous dispersions of polymers or copolymers, the monomer units having the formula



wherein  $R_F$ ,  $R_1$  and  $R$  represent the same radicals as mentioned above, and  $X$  is a polymerizable radical selected from the group consisting of allyl, methallyl, and vinyl radicals.

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Among the N-alkyl-N',N'-alkylene ureas having an alkyl radical of more than 10, and preferably 11 to 22 carbon atoms, it is preferred to employ those having an alkyl radical of 15 to 19 carbon atoms. The dispersions of these compounds are prepared in a basically known manner by reacting an aliphatic isocyanate having a carbon chain of preferably 11 to 22 carbon atoms with an alkylene imine, the alkylene radical of which has 2 to 3 carbon atoms.

The dispersions may be stabilized by the addition of non-volatile, strongly basic compounds, or of volatile bases in conjunction with quaternary nitrogen compounds of the formula



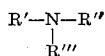
wherein  $R_a$  is an alkyl radical having more than 10 carbon atoms,  $R_b$  is a pyridin, or oxyethylmorpholine radical, and  $Z'$  is the residue of a monobasic acid.

The N-alkyl-N',N'-alkylene ureas are added to the textile treating baths according to the invention in preferred amounts of 1 to 15 grams per liter.

The amount of the compounds which contain a plurality of perfluoroalkyl radicals is preferably 2 to 15 grams, and more specifically 6 to 10 grams per liter.

The textile material is impregnated, and preferably saturated with the treating baths of the invention which is facilitated by the addition to the baths of a monohydric alkanol having 3 to 4 carbon atoms, or of mixtures of such alcohols. The fibrous material is extracted after impregnation to a desired pick-up, dried at temperatures between 100 and 120° C., and finally cured at temperatures between 130 and 160° C. for periods of 10 to 3 minutes. If synthetic resins and the corresponding curing catalysts are jointly employed with the textile treating agents of the invention, it may be desirable to wash the fibrous material after curing in order to remove residual catalysts.

For the highest oil and water repellency, for a finish which permanently resists laundering and dry cleaning, and for best operating characteristics on the padding machine, that is, for complete avoidance of the formation of coatings on the padding machine rolls, we prefer additionally to mix with the treating solutions certain water insoluble precondensates which are soluble in monocarboxylic lower alkanolic acids. These products are obtained by condensing an aminotriazine having at least 2 amino radicals on each triazine ring with formaldehyde and a monohydric alkanol having 1 to 5 carbon atoms. The precondensate contains for each triazine ring at least 1 aliphatic radical having more than 10, and preferably 11 to 22 carbon atoms, and at least 0.2 mol equivalents of the basic amino radicals of an alkanolamine of the general formula



wherein  $R'$  is hydrogen, and alkyl radical of 1 to 4 carbon atoms, a hydroxyalkyl radical having 2 to 4 carbon atoms, or one of the radicals  $-CH_2-CH_2-NR''R'''$ , and  $-CH_2-CH_2-CH_2-NR''R'''$ ;  $R''$  is a hydroxyalkyl radical having 2 to 4 carbon atoms; and  $R'''$  is hydrogen, or a hydroxyalkyl radical having 2 to 4 carbon atoms.

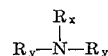
The monocarboxylic lower alkanolic acids in which the precondensates of the invention are soluble include formic acid and acetic acid.

The water insoluble precondensates which are soluble in dilute aqueous lower monocarboxylic alkanolic acids may be prepared according to various methods.

They are obtained by heating 1 mol of an aminotriazine, and particularly of melamine, with 1 to 2 mols of an aliphatic monocarboxylic acid having more than 10 carbon atoms and particularly 15 to 19 carbon atoms; 16 to 18 mols, and particularly 9 to 15 mols of paraformalde-

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hyde; and 0.2 to 1.2 mols, and preferably 0.5 to 1.0 mol of an alkanolamine which preferably is of the formula

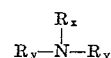


wherein  $R_x$  is hydrogen or a hydroxyalkyl radical having 2 to 3 carbon atoms; and  $R_y$  is a hydroxyalkyl radical having 2 to 3 carbon atoms; in the presence of a monohydric alkanol having 1 to 5 carbon atoms to a temperature of 110° to 140° C. while volatile constituents are permitted to distill from the reaction mixture until the residue is soluble in a dilute monocarboxylic acid, more particularly in hot, 5 to 10% acetic acid.

The aliphatic monocarboxylic acid having more than 10 carbon atoms may be replaced in the above synthesis method by 0.5 to 1 mol of the corresponding acid anhydride.

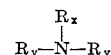
Precondensates of the same type are arrived at when the aminotriazine and the aliphatic monocarboxylic acid having more than 10 carbon atoms or its anhydride are replaced by 1 mol of a melamine derivative in which 1 to 3 hydrogen atoms of the amino radicals are replaced by aliphatic acyl radicals having more than 10 carbon atoms and particularly 15 to 19 carbon atoms.

Yet another method of preparing the precondensates of the invention employs as starting materials methylol-aminotriazines, and particularly methylol melamines which are etherified with lower monohydric alkanols having 1 to 4 carbon atoms. 1 mol of the etherified methylol melamine is heated with 1 to 2 mols of an aliphatic monocarboxylic acid having more than 10 carbon atoms, and preferably 15 to 19 carbon atoms to a temperature of 130-200° C., and preferably until almost the entire amount of fatty acid is present in the combined forms. This reaction may be performed at ambient pressure or in a vacuum. The intermediate product obtained is then reacted with 0.2 to 1.2 mols, preferably 0.5 to 1.0 mol of an alkanolamine which preferably has the formula



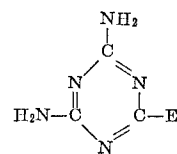
wherein  $R_x$  and  $R_y$  are the radicals mentioned above, by heating to a temperature of 100-130° C. until a sample of the condensation product is soluble in a dilute, aqueous monocarboxylic acid such as formic acid or acetic acid. The last mentioned condensation reaction also may be performed in a vacuum.

According to yet another method, one mol of a 2,4-diamino-6-alkyl-1,3,5-triazine, the alkyl group is containing at least 10, preferably 15 to 22 carbon atoms, is heated with paraformaldehyde preferably in amounts of 5 to 8 mols, with 0.2 to 1.2 mols, and preferably with 0.4 to 1.0 mol of an alkanolamine which is preferably of the formula



wherein  $R_x$  and  $R_y$  have the same meaning, and with a lower monohydric alkanol having one to five carbon atoms. The volatile constituents are permitted to distil from the reaction mixture, and heating is continued until the product is soluble in a dilute monocarboxylic acid, and particularly in hot five to ten percent aqueous acetic acid.

A further method of synthesizing the pre-condensates of the invention starts with an aminotriazine derivative which is obtained by reacting one mol of a compound of the formula



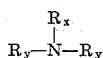
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wherein E is hydrogen, amino radical, alkyl radical with 1 to 22 carbon atoms; with at least 1 mol of an alkyl isocyanate per mol of said aminotriazine derivative and at most one mol of said alkyl isocyanate per equivalent amino radicals. Especially used are derivatives obtained by heating one mol of melamine with 1.2 to 2 mols of said alkylisocyanate.

The alkyl radical of said alkyl isocyanate has more than ten, and preferably fifteen to nineteen carbon atoms.

The reaction is performed at 200 to 260° C. until a clear liquid is obtained.

One mol of this intermediate aminotriazine derivative obtained is heated to 130 to 160° C. with six to eighteen (preferably nine to fifteen) mols paraformaldehyde, 0.2 to 2.0 (preferably 0.7 to 1.5) mols of an alkanolamine, preferably of the formula



wherein  $R_x$  and  $R_y$  have the same meaning, and a lower monohydric alkanol having at most five carbon atoms and preferably four carbon atoms. The volatile constituents are permitted to evaporate from the solution, and heating is continued until the product is soluble in dilute monocarboxylic acids, such as hot five to ten percent aqueous acetic acid.

It will be understood that the nature of the monocarboxylic acid employed in the solubility test is not critical, and that a 5 to 10% acetic acid solution is employed because of its convenience and ready availability. Actually any concentration of acetic or formic acid in the range of 5 to 30% will be found equally satisfactory. The solubility test is performed either by adding the precondensate to a hot aqueous solution of the acid, or by adding the precondensate to the cold acid solution, and jointly heating the precondensate with the acid.

The amount of the water insoluble, acid soluble precondensate which is added to the treating solution is preferably of the order of 1 to 10 grams per liter. These limits however are not critical, and very good results may be obtained with amounts of the acid soluble precondensate which are as low as 0.2% of the alkyl-alkylene urea employed. The acid soluble precondensates are preferably added to the treating baths as a 50% mixture with an organic solvent which is non-miscible with water, and particularly with a hydrocarbon or a halogenated hydrocarbon, or in the form of the 50% mixture with a material which itself imparts water repellent properties to the fabric, such as paraffin, a wax, or mixtures of both.

The water insoluble precondensates which are soluble in dilute organic acids have an emulsifying effect on the other constituents of the treating baths. Upon drying, and particularly at the temperature of the conventional curing treatment, they become insoluble and water repellent. The precondensates are employed in the form of aqueous emulsions which are prepared by dissolving mixtures of the precondensates with paraffin, wax or solvents in the presence of dilute organic acids. It is also possible to premix dispersions of the N-alkyl-N',N'-alkylene ureas with a 50% solution of a precondensate in a solvent which is not miscible with water and free of hydroxyl groups, and to add the premixed dispersions to the treating bath.

When this procedure is followed, the treating bath is prepared by the addition of only one material instead of 2 materials, and only one weighing or measuring operation is involved. Only one concentrated dispersion needs to be diluted in the treating plant. The addition of the precondensate to the alkyl-alkylene urea dispersion also enhances the stability of the latter as more fully disclosed in our Patent No. 3,148,164.

The term "textiles and other fibrous materials" as used herein will be understood to cover all types of fibrous materials, whether natural or man-made, and all forms which such fabric may assume, such as woven or knitted fabrics, non-woven fabrics such as felts, sheet material

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such as paper, yarns, threads, slubbings, rovings, and other intermediate products of the textile industry.

The textiles and other fibrous materials treated according to the method of the invention are not only oil and water repellent but they also resist staining. Wine, even red wine, and other alcoholic beverages, coffee, fatty meat sauces, butter, oils, tar, and like contaminants can be simply wiped off with a rag containing a suitable solvent, without the formation of sightly rings on the cleaned fabrics. While conventional oil and water repellency treatments impart some resistance to staining, the last traces of staining material can usually only be removed by saturating the material with a suitable solvent which after evaporation leaves annular areas of discoloration.

Water absorption as reported in the examples which will now follow is measured on the Bundesmann spray apparatus. The rating "excellent water repellency" is applied to fibrous material which after ten minutes testing on the spray apparatus does not show any sign of wetting. "Good water repellency" is a rating given to materials showing first traces of wetting after ten minutes. "No water repellency" is reported where the fibrous material is wetted after 10 minutes testing.

Oil repellency is reported as tested by the well known method of Minnesota Mining and Manufacturing Co. The fibrous material is positioned to provide a horizontal surface, and drops of mixtures of purified mineral oil ("Nujol") and n-heptane are placed on the surface. The mixture containing the highest percentage of n-heptane which does not wet the fabric or the fibrous material under the drop determines the rating. The mixtures of paraffin and heptane are assigned arbitrary rating numbers of 0 to 100 according to the following table:

TABLE 1

Percent n-heptane in mixture (by volume):	Oil repellency rating
70 -----	100++
60 -----	100+
50 -----	100
40 -----	90
30 -----	80
20 -----	70
0 -----	50
No resistance to mineral oil -----	0

The following examples are further illustrative of the method of the invention, and it will be understood that the invention is not limited thereto. All parts and percentages are by weight unless otherwise specifically stated. All temperatures are in degrees C.

#### Example 1

Several lengths of a polyester fabric weighing 50 grams per square meter, having a linen weave of 47 warp thread per centimeter and 40 filling threads per centimeter (both Nm. 200), are respectively saturated with the treating baths described below, extracted between squeeze rolls to a pick-up of 50%, dried at 120°, and cured 5 minutes at 150°.

**Bath A.**—The bath is prepared by stirring 10 grams of the emulsion of an alkyl-alkylene urea prepared as described hereinafter in small consecutive portions into a five-fold amount of water, and by adding the dispersion formed to a mixture of 30 ml. of isobutanol and 700 ml. water whereupon 25 grams of a 30% aqueous dispersion of a polymer are carefully stirred into the mixture. The polymer is obtained by polymerizing a compound of the formula



The liquid obtained is diluted with cold water to one liter.

**Bath B.**—25 grams of the above described polymer dispersion are added to a mixture of 30 ml. isobutanol and 700 ml. water, and the liquid obtained is diluted with water to one liter.

The oil and water repellency of fabric samples treated in baths A and B is determined immediately after completion of the finishing treatment, and again after 3 laundry cycles in which a fatty alcohol sulfonate is employed as a detergent at a temperature of 40°. The results obtained are shown in Table 2.

TABLE 2

Bath.....	Oil Repellency		Water Absorption, percent		Water Repellency	
	A	B	A	B	A	B
Initial.....	100++	100+	2.5	18	Excellent	None.
After 3 laundry cycles.....	100+	80	14	25	Good.....	None.

The above mentioned dispersion of the N-alkyl-N',N'-alkylene urea is prepared according to the following method:

28.5 grams ethylene imine are diluted with 125 grams distilled water, and mixed at 20° with a solution consisting of 126.5 grams distilled water, 15 grams of aqueous ammonia (d. 0.90), and 45 grams of glycerol triricinoleate which has been etherified with 30 mols of ethylene oxide. 200 grams octadecyl isocyanate are slowly added drop by drop to the solution obtained with stirring and cooling. After the reaction has gone to completion, 450 grams distilled water and 10 grams aqueous ammonia solution are added, and the mixture is mechanically homogenized by means of high speed stirrer. It is diluted to 1,000 grams by means of a solution of 66 grams octadecyl - oxymethylene-hydroxyethylmorpholinium chloride in 134 grams distilled water.

#### Example 2

A cotton popeline weighing 160 grams per square meter and having 58 warp threads (Nm. 77) per centimeter and 24 filling threads (Nm. 65) per centimeter, is treated in the manner described in Example 1 with a bath which contains 10 grams of the afore-described alkyl-alkylene urea dispersion, 25 grams of the afore-described emulsion of the polymerisate having perfluoroalkyl radicals, and additionally 15 grams of 100% dimethylol urea and 4 grams ammonium chloride per liter.

The bath is prepared by first dissolving the dimethylol urea in the ten-fold amount of hot water, permitting the solution to cool, and adding thereto isobutyl alcohol. This mixture is combined with the other ingredients, and the ammonium chloride is added last in the form of a 5% aqueous solution.

The cotton fabric finished in the bath described above has an initial water absorption of 18.1%, good water repellency, and an oil repellency rating of 90. After the fabric is laundered three times at 60°, the water absorption and the oil repellency are not significantly affected. The recovery angle of the finished material is 100° (average of warp-wise and filling-wise test) as compared to a recovery angle of 56° of the unfinished fabric.

#### Example 3

Samples of wool gabardine weighing 300 grams per square meter and having a twill weave with 27 warp threads per centimeter (Nm. 19) and 20 filling threads per centimeter (Nm. 22) are respectively saturated with the finishing bath described below, extracted to a pick-up of approximately 65%, dried at 120° and cured 5 minutes at 130°.

An alkyl-alkylene urea dispersion is prepared as follows:

A mixture of 250 parts water, 3 parts potassium carbonate, 40 parts stearyl alcohol polyglycol ether (20 mols ethylene oxide per mol stearyl alcohol) and 28.5 parts ethylene imine is gradually added drop by drop to 200 parts heptadecyl isocyanate. When the reaction is completed 450 parts water containing 2 parts potassium car-

bonate are added, and the dispersion formed is homogenized by means of a high speed stirrer.

3 grams of the dispersion obtained are stirred in small portions into the five-fold amount of water. The diluted emulsion is then added to a mixture of 20 cc. isobutanol, 20 cc. isopropanol, and 700 cc. water. In this mixture,

30 parts of an aqueous 30% dispersions of a copolymer of 80 mol percent of a monomer of the formula



and of 20 mol percent butadiene is dispersed by stirring.

The woolen fabric treated with the solution prepared as described above has excellent water repellency after the treatment, and this water repellency is practically unaltered after three laundry cycles. After three cycles of commercial dry cleaning it is reduced only to a rating of "good." The oil repellency has an initial rating of 100+ and is reduced after three launderings as well as after three cycles of dry cleaning to a rating of 100.

A further improvement can be achieved by adding to the bath prior to the addition of the polymer dispersions 0.1 to 50 cc. of an acidified aqueous dispersion containing about 10 percent of one of the products described herein-after. This addition improves the processing characteristics of the bath as far as freedom from formation of coatings on the padding rolls is concerned, and also improves the initial oil and water repellency, as well as the resistance of the finish to laundering and dry cleaning.

**Precondensate (a).**—90 parts stearic acid are melted in a three-neck flask equipped with a condenser, a stirrer, and a thermometer. 148 parts of methanol, 75 parts of paraformaldehyde, and 25 parts of melamine are added to the molten acid with continuous stirring while a temperature of approximately 60° is maintained. As soon as all the ingredients are mixed, the temperature is slowly increased to 120° within about 2 hours, and within an additional hour from 120° to 130° while the methanol is permitted to distill off. When as a temperature of 130° is reached, 25 parts of triethanolamine are added whereby the temperature is reduced to about 115°. This temperature is maintained while the mixture is being stirred. As soon as a sample is clearly soluble in hot, aqueous, 6% acetic acid, 190 parts of trichloroethylene are stirred in, and the clear solution obtained is permitted to cool. When 10 to 15% of acetic acid are added thereto in the form of a strong aqueous solution, and the resultant mixture is diluted with water, a stable emulsion having small dispersed particles is obtained. If this dispersion is to be prepared in large amounts it is preferably made up with the aid of a mechanical high speed stirrer.

Triethanolamine may be replaced in the above reactions by tripropanolamine.

**Precondensate (b).**—182 parts of methanol, 35 parts of triethanolamine, 90 parts of paraformaldehyde, and 190 parts of a technical grade of 1,3-diamino-5-hexadecyl-2,4,6-triazine containing 80% of the pure compound while the remainder consists essentially of fatty acid nitriles having an average molecular weight of about 255, are mixed in a three-neck flask equipped as described above, and heated to a temperature of 140–145° within about 2 to 3 hours while the alcohol is permitted to distill off. The maximum temperature is maintained until a sample of the product in the flask is completely and clearly soluble in hot, 6% acetic acid. The main body of the re-

action mixture is then cooled to about 90°, and 260 parts of trichloroethylene are added. A light yellow solution is obtained which is readily emulsified in water in the presence of 15 to 30% of acetic acid. The emulsion is very stable.

**Precondensate (c).**—525 parts of isobutanol are mixed in a three-neck flask fitted with a stirrer, a reflux condenser, and a thermometer, with 35 parts diethanolamine, 90 parts of paraformaldehyde, and 150 parts of a product obtained by jointly heating 1 mol of melamine with 2 mols of heptadecyl isocyanate to about 240° C. The mixture obtained is refluxed for 3 hours whereupon the reflux condenser is replaced by a descending condenser, and the alcohol is distilled off over a period of 2 to 3 hours while the temperature is increased to 150–155° C. This temperature is maintained until the product is soluble in hot, 6% acetic acid. It is then cooled to about 110° and mixed with 240 parts of toluene. An almost transparent, light brown solution is obtained which in the presence of 12 to 28% acetic acid forms a good, stable dispersion in water.

Instead of the approximately 50% solutions of the precondensates of the invention with organic solvents, mixtures of the precondensates with about equal amounts of paraffin may be made, and these mixtures may be added to the treating bath instead of the solvent solution. If such paraffin mixtures are employed, it is necessary to fuse the waxy mixtures at temperatures of approximately 60–80° before they are stirred with approximately equal to three-fold amounts of 30% aqueous, acetic acid having a temperature of about 80°. The mixtures obtained may be diluted gradually with hot water, and finally chilled with 3 to 5 volumes of cold water whereupon they are ready to be added to the treating bath.

When di-propanolamine is employed in the condensation reaction to replace an equimolecular amount of the diethanolamine, closely similar results are obtained.

#### Example 4

A nylon fabric similar in weave and weight to the polyester fabric described in Example 1 is saturated with the bath described below, extracted to a pick-up of about 60%, dried at 110°, and cured for 5 minutes at 130°.

One of the finishing agents in the bath is an alkyl-alkylene urea prepared as follows:

A mixture of 250 parts water, 15 parts of aqueous concentrated ammonia solution (d. 0.90), 45 parts of tricrinolein polyglycol ether (30 mols ethylene oxide per mol tricrinolein), and 28.5 parts ethylene imine are slowly added, drop by drop to 200 parts heptadecyl isocyanate with strong agitation. After the reaction is completed, 450 parts of water containing 10 parts aqueous ammonia solution are added, and the dispersion formed is homogenized by means of a high speed stirrer. It is diluted with a solution of 66 parts of hexadecylhydroxymethylene-pyridinium chloride in 134 parts of water, and mixed by stirring with 25 parts of the solution of a water insoluble precondensate soluble in organic acids prepared as described below:

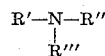
370 parts methanol, 69 parts triethanolamine, 187 parts paraformaldehyde, and 63 parts melamine are mixed in a three-neck flask equipped with a descending condenser, a stirrer, and a thermometer. While the mixture is continuously stirred, its temperature is slowly raised. When it reaches 40°, 225 parts of a technical grade of stearic anhydride (acid number approximately 3 to 7) are added, and the temperature is gradually raised within about 2 to 3 hours to about 120° while the alcohol is permitted to distill off. The mixture is held at this temperature until the product formed is soluble in hot, 6% acetic acid. 475 parts of a mixture of one part of volume of tetrachlorethylene and 3 parts of volume of benzene are added.

Various modifications are contemplated, and may be obviously resorted to by those skilled in the art without

departing from the spirit and scope of the invention as hereinafter defined by the appended claims, as only preferred embodiments have been disclosed.

What we claim is:

1. A method of treating textile materials and other fibrous materials which comprises impregnating said material with an aqueous treating bath containing a first organic compound having a plurality of perfluoroalkyl radicals, each of said radicals having at least four carbon atoms; and a second organic compound which is an N-alkyl-N', N'-alkylene urea, the alkyl radical of said second compound having more than ten carbon atoms, and the alkylene radical of said second compound having two to three carbon atoms; drying the impregnated material; and curing the dried material, wherein said bath further contains a water insoluble third organic compound soluble in dilute aqueous solutions of monocarboxylic lower alkanolic acids, said third compound being a precondensate of an aminotriazine having at least two amino radicals directly bound to the triazine ring, said ring being free of directly bound hydroxyl radicals, with formaldehyde and a monohydric lower alkanol, said precondensate having for each triazine ring at least one alkyl radical of more than ten carbon atoms and at least 0.2 mol equivalent of the basic amino group of an alkanolamine of the formula



wherein R' is a member selected from the group consisting of hydrogen, an alkyl radical having one to four carbon atoms, a hydroxyalkyl radical having two to four carbon atoms, and the radicals  $-\text{CH}_2-\text{CH}_2-\text{NR}''\text{R}'''$  and  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NR}''\text{R}'''$ ; R'' is a hydroxyalkyl radical having two to four carbon atoms; and R''' is selected from the group consisting of hydrogen and a hydroxyalkyl radical having two to four carbon atoms.

2. A method according to claim 1, wherein said bath contains between substantially 2 and 15 grams per liter of said first compound, said first compound being a polymer essentially consisting of monomer units, at least one half of said units having a perfluoroalkyl radical of at least four carbon atoms, and wherein said bath contains between one and fifteen grams per liter of said second compound, said alkyl radical of said second compound having between fifteen and nineteen carbon atoms, and said alkylene radical thereof having two carbon atoms; and wherein said bath contains 0.002 to 10 grams per liter of said third organic compound.

3. A method according to claim 2, wherein said third compound is used in form of a mixture with an about equal amount of a water insoluble organic substance selected from the group consisting of hydrocarbons and waxes.

4. A method according to claim 2, wherein said alkanolamine is a dialkanolamine having two to three carbon atoms in each hydroxyalkyl radical.

5. A method according to claim 2, wherein said alkanolamine is a trialkanolamine having two to three carbon atoms in each hydroxyalkyl radical.

6. A textile material treated according to claim 1.

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