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PROCESS FOR MAKING DURABLE PRESS AND SOIL RELEASE TEXTILE AND RESULTANT ARTICLE

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ABSTRACT OF THE DISCLOSURE

Process for improving the soil release properties of a textile by treating the same with a mixture of a fluoroacrylic polymer and a water-insoluble acrylic hydrophilic polymer.

The present invention is concerned with improving the soil (or oil) release properties of textile materials. The invention is of particular importance when used in connection with cellulosic fabrics, although other types of textiles may also be processed in the manner described herein as will be hereinafter apparent.

In existing or conventional procedures for treating cellulosic fabrics, i.e. fabrics composed entirely of cotton or blends thereof with man-made fibers such as polyester fibers (as in the case of durable press goods of the precured or post-cured type), a substantial amount of thermosetting resin is applied to the fabric in order to obtain properties not obtainable with the untreated textile (e.g. durable press or wrinkle resistance). This has its advantages but, like many other textile processing techniques it also introduces certain problems. One of the most important of the latter is the difficulty in removing oily stains by laundering and the problem becomes increasingly acute as the amount of solids add-on is increased as necessary to impart essential wash and wear, wrinkle resistance, permanent crease or permanent press and/or hand or other aesthetic properties.

One reason which has been suggested for the difficulty in removing oily stains from resin-treated cellulosic textiles is that the large amounts of thermosetting resin which are employed apparently result in a high degree of crosslinking with the cellulosic fibers and thus prevent these fibers from swelling when washed. This reduction in swelling with resultant loss in absorbency makes it difficult for detergent or the like to penetrate into the fibers and remove the oily stains.

The severity of the staining problem increases in the case of fabrics where man-made fibers, such as polyester fibers, are blended with cotton or the like. Polyesters and other man-made fibers have a marked tendency to absorb oily stains but are generally quite hydrophobic and, therefore, resist effective laundering.

Several procedures have been described for improving the soil release properties of fabrics composed of cellulosics, man-made fibers such as polyesters or blends thereof. For instance, procedures in this regard are described in the commonly assigned U.S. applications, Ser. Nos. 645,599, now abandoned, and 683,139, now U.S. Pat. 3,521,993, the subject matter of which is incorporated herein by reference. In Ser. No. 645,599, the soil release properties of textile materials of, for example, the durable press type, are improved by treating the textile with a synthetic polymer having certain water-absorbing properties. The process of Ser. No. 683,139 represents a further improvement in the process of Ser. No. 645,599 wherein an aryl stearic acid, notably phenyl stearic acid, is used with the synthetic water-absorbing polymer for soil release purposes.

The soil release composition and procedures of Ser. No. 645,599 and Ser. No. 683,139 are contemplated for use herein with certain unique modifications which provide even further improvements in soil release and other properties of textile fabrics. The invention is particularly important with respect to fabrics composed entirely of cellulosic fibers or polyester fibers or blends thereof, whether in woven, knitted or nonwoven form. However, fabrics containing other natural or man-made fibers which suffer from only stains that are difficult to remove by laundering may also be effectively processed according to the invention. Hence, the invention is normally applicable to any type of fabric where the release of oily stains in laundering is a problem, with particular emphasis on cellulosic and/or polyester fabrics which have been treated with a thermosetting resin for wash/wear, wrinkle resistance, hand, durable press or the like.

In most prior soil release processes, a high solids add-on of soil release agent is usually needed to obtain the desired soil or oil release properties. This "overloading" causes many undesirable side effects such as "mark-off" on the fabric, i.e., the surface of the fabric is prone to show white scratches or marks caused by abrasion or the equivalent in subsequent handling, e.g. by a garment maker during the process of sewing as a result of needle scratching, contact with sharp edges, scissors, etc.

Another problem in the case of most prior soil release procedures is that, with the high add-on of soil release material, pressing of the fabric causes a slight color change between the pressed and unpressed sections. This is apparently due to the fact that the press flattens out the add-on solids in the pressed section and thereby causes it to assume a duller appearance than an unpressed section. Additionally, in some prior procedures, the fabric treated for soil release takes on a dry powdered, stiff feeling or hand which diminishes the attractiveness of the product.

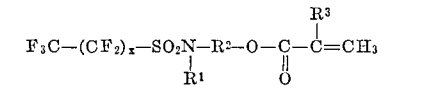
There are some soil release processes which do not require overloading the fabric, but these usually involve the use of fluoro chemicals which suffer from the disadvantage that they are not particularly durable to washing. Consequently, where durability is important, a higher add-on of the fluorochemical must be used in order to compensate for the lack or durability. However, the available fluorochemicals are expensive and the finisher must, therefore, compromise between cost and the degree of durability he can afford to put into a fabric so as to keep within the marketable or economic range of acceptance. Another disadvantage of the fluorochemical finishes is the lack of durability to drycleaning.

In view of the above the principal object of the invention is to provide certain improvements in soil release compositions and procedures whereby the prior disadvantages noted above. e.g. mark-off and color change are eliminated while obtaining effective soil release and maintaining other important fabric properties. Another object of the invention is to provide a novel process and composition for providing soil release properties while otherwise improving other aesthetic or essential fabric properties e.g. hand or feel and eliminating such undesirable characteristics as the chalkiness or oiliness frequently encountered in fabrics treated by other means for soil releases. Other objects will also be apparent from the following detailed description of the invention.

Broadly stated the objects of the invention are realized by treating the textile with a soil release composition containing as the essential soil release agent a mixture of a fluoroacrylic polymer and an acrylic hydrophilic or water-absorbing polymer as described in Ser. No. 645,599 and Ser. No. 683,139. Suprisingly, the application of this mixture of components, usually in the form of an aqueous dispersion, to cellulosic and/or polyester fabrics, gives

outstanding soil release properties at low solids add-on and with improvement in other important textile properties such as hand, etc. The exact reason for this result is not understood but apparently the fluoroacrylic polymer and acrylic hydrophilic polymer co-act in some unique way to give a synergistic soil release effect.

The fluoroacrylic polymer used herein may be any of those which are available with water-repellent properties, as described, for example, in Pats. Nos. 2,803,615, 3,068,-187 and 3,252,932. Typically suitable fluoroacrylic polymers are those available under the "Scotchgard" trade name, e.g., Scotchgard FC–216, 205 and 208 and "Zepel B." Of these compounds, the Scotchgard products, which are available in emulsion form, may be described according to U.S. Pat 2,803,615 by the following formula:



in which X is a value between 3 and 13 inclusive, R^1 is lower alkyl, such as methyl, ethyl, propyl, and the like, having 1–6 atoms, R^2 is alkylene containing 1–12 carbon atoms and R^3 is H, methyl or ethyl. The product "Zepel" is also available in emulsion form and while it is chemically different from the Scotchgard products, it is a fluoroacrylic oil repellent containing fluorocarbon tails composed of CF_2 groups which may end in a terminal CF_3 group.

The water-absorbing acrylic polymer may be any such polymer as described in the above-mentioned applications, i.e., one which absorbs at least about five times its weight of water under alkaline conditions or, more specifically, at least about 550% by weight of water when immersed in an aqueous detergent solution for 2 minutes at 140° F. (pH about 8–12). Particularly useful materials for use herein as the water-absorbing or swellable component are: polyacrylic acid, acrylic acid or methacrylic acid copolymers for example copolymers of styrene and acrylic acid, copolymers of itaconic acid and acrylic acids; and copolymers of ethyl acrylate and methacrylic acid; the copolymers of styrene, e.g., copolymers of styrene and maleic anhydride; and methacrylic acid and acrylic acid terpolymers such as terpolymers of methacrylic acid, butadiene and styrene; and terpolymers of monomethyl itaconate, acrylic acid and itaconic acid.

Especially useful for present purposes is a 60/40 copolymer of methacrylic acid and ethyl acrylate with molecular weight in the range of 800,000 to 1,500,000 although other copolymers of these or different monomers with higher or lower molecular weights may also be used, as indicated, provided they meet the indicated water-absorbing requirements.

Preferably the water-absorbing polymer is one which absorbs at least about 1000% by weight of water. This is evidenced by very substantial swelling of the polymer although the polymer should not be soluble in alkaline solutions. The suitability of a polymer for use herein can be readily determined by measuring its water absorbing capacity or swellability. To do this, fabric treated with the polymer only is weighed, and the original weight of fabric is subtracted. The fabric is then immersed in detergent solution for two minutes at 140° F., blotted dry with paper towels and then weighed. A correction is made for the liquid absorption by the fabric itself by repeating the procedure with uncoated fabric. The swelling is equal to:

$$\frac{\text{weight gain in coating}}{\text{dry weight of coating}} \times 100$$

A typical detergent solution which may be used for this purpose is .15% Tide detergent in water. Tide comprises sodium sulfate 16%, alkyl alcohol sulfate 6%, sodium polyphosphate 30%, sodium pyrophosphate 17% and 31% sodium silicate and sodium sulfate combined.

The water absorbing (or swelling) characteristic of the soil release polymer is related to molecular weight. In general, low molecular weight polymers of the type described above are water soluble whereas higher molecular weight polymers are insoluble in water but will swell. For the most part, suitable polymers will have a number average molecular weight of 1,000 to 3,000,000, although this is subject to some variation provided the desired degree of water absorption or swelling is realized without dissolution of the polymer.

Another factor affecting the water absorbing property or swellability of the polymer is the degree of crosslinking therein. The polymers used herein are essentially linear polymers. A certain degree of crosslinking may be introduced into the polymers during subsequent treatments. Although such crosslinking is not absolutely essential, it is desirable for durability. However, excessive crosslinking tends to connect the polymer molecules into a rigid three dimensional network which will not swell and this is not particularly useful for present purposes. Suitable crosslinking agents are formaldehyde, polyfunctional alcohols, formaldehyde amine precondensates, polyfunctional epoxides, etc. These may be included, as desired, to improve durability.

The ratio of fluoroacrylic polymer and water-swellable acrylic polymer used for the soil release mixture employed herein can be widely varied depending on other factors, e.g., the nature and construction of the fabric involved, and other additives in the soil release composition. However, the fluoroacrylic polymer will usually be used in the range of 5–35%, preferably about 10%, based on the weight of water-swellable acrylic polymer (solids basis).

As noted earlier, the fluoroacrylic polymer and water-swellable polymer are usually applied to the fabric in the form of an aqueous dispersion or emulsion. The application may involve impregnating the fabric, usually by padding, although other means such as spraying or dipping may be used, followed by drying to normal moisture regain and then curing. Drying and curing conditions will vary depending on the fabric composition and other conditions but usually will involve heating at 175–220° F. for 1–5 minutes for drying and somewhat higher temperatures, of the order of 275–320° F. for 5–15 minutes, to cure. Wet pickup in the fabric impregnation will also vary depending on fabric construction, etc., but will usually run in the neighborhood of 60–75%, based on the dry weight of the fabric. Soil release solids pickup generally amounts to about 0.05 to 2% based on the weight of the treated fabric for effective soil release, although more or less than the indicated pickup may be used in special cases as desired. However, for equivalent soil release porperties, the total add-on of fluoroacrylic polymer and water-swellable acrylic polymer will usually be 25–75% lower than the add-on when the polymer components are used separately under otherwise identical circumstances to obtain an equivalent degree of soil release. This reduction in the amount of soil release solids add-on obviates such prior problems as mark-off, color change, harshness of hand and other undesired side effects of previous soil release finishes. As noted earlier, this reduction in total solids add-on, while obtaining the desired soil release effect, including durability of the finish to washing, is apparently due to some sort of synergistic co-action between the two soil release components although the mechanism involved is not understood.

Special processing is necessary to prepare the mixture of fluoroacrylic polymer and acrylic hydrophilic or water-swellable polymer for use herein since, although these materials both have the acrylic structural backbone, they are ionically different and, therefore, not compatible. Accordingly, an important aspect of the invention is the use of one or more selected emulsifiers or stabilizers which make it possible to mix the two components together in water to obtain a stable mixture for application to the textile. Examples of suitable stabilizers include

alkylphenoxypolyethoxyethanols having alkyl groups of about seven to eighteen carbon atoms and 6 to 60 or more oxyethylene units, such as heptylphenoxypolyethoxyethanols, octylphenoxypolyethoxyethanols, methyloctylphenoxypolyethoxyethanols, nonylphenoxypolyethoxyethanols, dodecylphenoxypolyethoxyethanols, and the like; polyethoxyethanol derivatives of methylene linked alkyl phenols; sulfur-containing agents such as those made by condensing 6 to 60 or more moles of ethylene oxide with nonyl, dodecyl, tetradecyl, t-dodecyl, and the like mercaptans or with alkylthiophenols having alkyl groups of six to fifteen carbon atoms; ethylene oxide derivatives of long-chained carboxylic acids, such as lauric, myristic, palmitic, oleic, and the like or mixtures of acids such as found in tall oil containing 6 to 60 oxyethylene units per molecule; analogous ethylene oxide condensates of long-chained alcohols, such as octyl, decyl, lauryl, or cetyl alcohols, ethylene oxide, derivatives of etherified or esterified polyhydroxy compounds having a hydrophobic hydrocarbon chain, such as sorbitan mono-stearate containing 6 to 60 oxyethylene units, etc.; block copolymers of ethylene oxide and propylene oxide comprising a hydrophobic propylene oxide section combined with one or more hydrophilic ethylene oxide sections. Preferred emulsifiers or stabilizers for use herein include the following: nonylphenoxy poly(ethylene oxy) ethanol ranging from 1.5 to 100 mole ratio of ethylene oxide/hydrophobe; polyethylated fatty alcohol such as polyethylated stearyl alcohol or the like; octylphenoxy poly(ethylene oxy), ethanol, nonionic detergents, alkyl-aryl polyether alcohols, sulfonates and sulfates (e.g. the Tritons such as Triton X–100, Triton X–155 and Triton X–200) and Basanyl BM, sulfonated aliphatic polyester. These emulsifiers or stabilizers also seem to improve the "flow" properties of the total polymeric system and thus apparently give a more effective or continuous film on the surface of the fibers leading to the improved results of the invention. However, other alternative emulsifiers and stabilizers, which contain the appropriate compatible functional groups are also available and may be used to give stable formulations of the fluoroacrylic polymer and acrylic hydrophilic polymer for use herein. In any case, however, it will be appreciated that care must be taken in the sequence of combining the various components of the formulation employed, i.e., the soil release components and emulsifiers or stabilizers and other optional additives such as wetting agents, crosslinking agents, catalysts, hand builders, softeners and durable press imparting resin or reactant. Usually the formulation employed will contain, on a weight basis, from 0.5 to 5% of the fluoroacrylic polymer and from 1 to 20% of the acrylic water-swellable polymer with other optional components included in conventional amounts.

While the invention is not limited to use in the finishing of durable press fabrics of the post-cured or pre-cured types, an important aspect of the invention is that the soil release mixture described herein may be added with the durable press resin. In other words, the fabric may be impregnated with a stable aqueous formulation containing the soil release mixture, emulsifier, a durable press type of aminoplast resin or the equivalent, catalyst for the resin and other conventional additives such as hand builders (e.g. the Rhoplex type of acrylics) and wetting agents. Phenyl stearic acid or the like may also be included in the formulation to help in soil release as described in Ser. No. 683,139 and Ser. No. 690,079, pending.

Any durable press-type of resin or reactant may be used for present purposes. This includes any of the water-soluble precondensates of formaldehyde with such amino compounds as urea, thiourea, cyclic ethylene ureas (e.g. dimethylol cyclic ethylene urea or dimethylol dihydroxy cyclic ethylene urea), melamine, ethyl carbamate, urons, triazones and triazines. Blocked isocyanates may also be effectively used.

The invention is illustrated, but not limited, by the ensuing examples wherein percentages are given on a weight basis:

EXAMPLE 1

The following formulation was prepared in cold water (tap) by adding the components in the order listed:

	Percent
Wetting agent (Igepal CO–897) which is nonylphenoxypoly(ethyleneoxy)ethanol	1.0
Resin (Reactant 183–cyclic ethylene urea)	20.0
Phenyl stearic acid	5.0
Scotchgard FC–216 (fluorinated acrylic polymer)	1.0
(60/40 methacrylic acid/ethyl acrylate copolymer)	10.0
Rhoplex HA–8 (acrylic hand builder)	1.0
Citric acid catalyst	2.5
Ammonium chloride catalyst	1.0

The fabric (50/50 polyester/cotton medium weight) was padded through this solution to about 75% wet pickup, dried at 5–7% moisture and then cured by heating for fifteen (15) minutes at 300° F.

Samples of the fabric were stained (1) before washing and (2) after nine (9) washings with four types of oils; mineral, motor, butter and vegetable. After staining, the samples were given a single washing in a home laundry agitator type washing machine using a low sudsing detergent (e.g. "ADD," pH about 10) in wash water at 140° F. After washing for 10 minutes, the samples were rinsed at 105° F., extracted and tumble dried at 150–170° F. After conditioning, the samples were placed on a black surface under a fluorescent light. The samples were visually rated under these conditions with numerical ratings as follows:

Class 5—No staining
Class 4—Slight, but not appreciable staining
Class 3—Noticeable staining
Class 2—Very noticeable staining
Class 1—Very extreme staining

In each instance the samples of fabric processed in the manner described herein gave values of 5.0 after one wash and after the ten washings, the latter indicating the durability of the finish to repeated washings. No color change was noted after pressing and there was no mark-off. All other aesthetic properties of the fabric, such as hand, permanent press and wash/wear, were outstanding.

EXAMPLE 2

In this example, types of fluorochemicals commonly used for water repellency and in rainwear were used in the following formulation:

	Percent
Triton X–200	0.1
Igepal CO 897	1.0
Reactant 183	20.0
Phenyl stearic acid	5.0
Fluorochemical	1.0
60/40 methacrylic acid/ethyl acrylate copolymer	10.0
Citric acid catalyst	2.5
Ammonium chloride catalyst	1.0

Fluorochemical used:
(1) FC–205
(2) Zepel B

After one (1) wash, soil release ratings were 4.0 for both formulations.

EXAMPLE 3

The formulation of Example 2 was used substituting Nekal WS25 (sulfonated aliphatic polyester) for Triton X–200 and using FC–205 as the fluorochemical. A soil release rating of 5.0 was obtained after one washing.

EXAMPLE 4

In order to build the hand or thickness without interfering with oil release properties, selected hand builders were first padded onto the fabric of Example 1 and dried, after which the fabric was treated with the oil release formulation of Example 1.

Typical pretreat formulations were:

(A)

1.078% nonionic detergent
4.000% polyvinyl acetate—firm hand

(B)

2.5% methacrylic acid and ethyl acrylate copolymer
3.0% polyvinyl acetate—very firm hand

(C)

0.15% Triton X–155
3.00% acrylic polymer—full hand

Soil release ratings of 5.0 were obtained after one washing.

This example illustrates the use of other polymer systems to develop aesthetic properties of fabric by way of pretreatment in case these systems are not compatible with and prevent the preparation of a stable mix with the oil release finish.

EXAMPLE 5

The following is a typical formulation which can be used to increase the thickness of a fabric without interfering with the oil release properties or permanent press quality, using a one step procedure. The necessary hand builders are included in the soil release finish without effecting undesirably the soil release ratings.

	Percent
Igepal CO–897 (nonylphenoxy poly(ethylene oxy) ethanol)	0.5
Reactant 183	20.0
(Polyvinyl acetate homopolymer emulsion)	3.0
Phenyl stearic acid	5.0
Fluorochemical (Example 1)	1.15
60/40 methacrylic acid/ethyl acrylate copolymer	10.0
Citric acid catalyst	2.5
Ammonium chloride catalyst	1.0

Soil release ratings of 5.0 were obtained after one and ten launderings. The hand and other chraacteristics of the fabric were also outstanding.

It will be appreciated that various modifications may be made in the invention described herein without deviating from the scope thereof as defined in the following claims, wherein, what is claimed is:

1. In a process for improving the soil release properties of a textile material wherein the textile material is impregnated with a composition including a durable press textile reactant selected from water-soluble precondensates of formaldehyde with amino compounds and blocked isocyanates and a water-insoluble acrylic hydrophilic polymer which absorbs at least five times its weight of water when immersed in an aqueous detergent solution for 2 minutes at 140° F., said polymer being an addition polymer of at least one ethylenically unsaturated monomer having one or more acid groups, and then drying and curing, the improvement which comprises applying said durable press reactant and hydrophilic polymer to said textile in a stable aqueous mixture with an oil and water repellent fluoro-acrylic polymer characterized by (CF_2) groups and a terminal CF_3 group, the amount of fluoro-acrylic polymer being in the range of 5–35% based on the weight of said hydrophilic polymer, said fluoro-acrylic polymer and hydrophilic polymer providing a synergistic soil release effect whereby the total add-on of said polymers is 25–75% lower than the add-on necessary when said polymers are used separately for the same degree of soil release.

2. The process of claim 1 wherein said material is cellulosic, polyester, or a mixture thereof.

3. The process of claim 1 wherein said mixture is applied as an aqueous emulsion including an ethylene oxide emulsifying agent.

4. The process of claim 3 wherein the mixture is prepared by adding said emulsifying agent to water and then adding in sequence the fluoro-acrylic polymer and the water-insoluble acrylic polymer.

5. The process of claim 1 wherein the mixture also includes phenyl stearic acid.

6. A process according to claim 1 wherein said water-insoluble, acrylic hydrophilic polymer is a methacrylic acid/ethyl acrylate copolymer.

7. The process of claim 1 wherein said polymer is one selected from the group consisting of polyacrylic acid; acrylic acid and methacrylic acid copolymers with styrene; copolymers of itaconic acid and acrylic acid; copolymers of ethyl arylate and methacrylic acid; copolymers of styrene and maleic anhydride; terpolymers of methacrylic acid, butadiene and styrene; and terpolymers of monomethyl itaconate, acrylic acid and itaconic acid.

8. A durable press textile having improved soil release properties, said textile being finished with a cured durable press and soil release finish consisting essentially of a mixture of durable press reactant selected from water-soluble precondensates of formaldehyde with amino compounds and blocked isocyanates, water-insoluble acrylic hydrophilic polymer which absorbs at least five times its weight of water when immersed in an aqueous detergent solution for 2 minutes at 140° F., said polymer being an addition polymer of at least one ethylenically unsaturated monomer having one or more acid groups, and oil and water repellent fluoro-acrylic polymer characterized by (CF_2) groups and a terminal CF_3 group, the amount of fluoro-acrylic polymer being in the range of 5–35% based on the weight of hydrophilic polymer, said fluoro-acrylic polymer and hydrophilic polymer providing a synergistic soil release effect whereby the total add-on of said polymers is 25–75% lower than the add-on necessary when said polymers are used separately for the same degree of soil release.

9. The textile of claim 8 wherein said finish includes phenyl stearic acid in said mixture.

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U.S. Cl. X.R.

117—138.8, 139.4, 143; 260—29.6

Notice of Adverse Decision in Interference

In Interference No. 98,439 involving Patent No. 3,592,686, R. P. Barber, G. R. Moses and D. L. Waugh, PROCES FOR MAKING DURABLE PRESS AND SOIL RELEASE TEXTILE AND RESULTANT ARTICLE, final judgment adverse to the patentees was rendered Aug. 29, 1975, as to claims 1, 2, 3, 6, 7 and 8.

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