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PROCESS FOR PRODUCTION OF PERFLUOROALKANOYL ESTERS OF CELLULOSE

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A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to cellulose esters. More particularly, this invention relates to the production of perfluoroalkanoyl esters of cellulose.

A primary object of the present invention is to provide an improved esterification process for the esterification of hydroxyl group-containing cellulosic textile fibers with perfluoroalkanoic acids without destroying the textile properties of the fibers. A further object is to provide a process of modifying the properties of cellulosic textiles that contain hydroxyl groups, to impart or enhance properties such as a resistance to wetting by liquids such as water, oil, and the like. Another object is to provide perfluoroalkanoyl esters of cellulose in textile fiber form wherein the esterification treatment is durable to dry cleaning and water washing in the presence of neutral detergents.

The application of fluorochemicals to cellulosic materials to obtain oil and water repellent surfaces are known in the prior art. In most of these prior art processes, metal complexes of fluorine-containing monocarboxylic acids are employed to treat the cellulosic textile, or else perfluoromonocarboxylic acids are applied to textiles which have been impregnated with a mordant to bond the acids to the textile. In these processes, the fluorochemical is not strongly bonded to the cellulose by formation of a chemical derivative of the cellulose, and consequently the oil and water repellency treatment is not durable, particularly to aqueous laundering.

Another method of applying fluorochemicals to cellulosic textiles is to esterify hydroxyl groups of the cellulose with an esterifying agent of a perfluoroalkanoic acid to produce perfluoroalkanoyl esters of cellulose. Conventional esterification procedures employing a heterocyclic tertiary aromatic amine, particularly pyridine, to dissolve the esterifying agent and to neutralize acidic reaction products can be used for this purpose. We have found, however, that these conventional esterification procedures have many disadvantages when used to prepare perfluoroalkanoyl esters of cellulose. The treated textile has an uneven or "spotty" finish, and has low tear strength. If the esterification reaction is allowed to proceed for a considerable length of time, particularly when a perfluoroalkanoic halide is used as the esterifying agent, the textile frequently disintegrates. Esterification under these conventional conditions proceeds relatively slowly, and high degrees of substitution (D.S.) of the cellulose are required to achieve the desired extent of oil- or water-repellency. As a consequence of this, the treated textiles are generally stiff, boardy, and discolored. In addition, the oleophobic property of the treated textiles is not durable to aqueous laundering—a serious drawback to practical, commercial applications of the treated textiles.

We have discovered an improved esterification process for the production of partial perfluoroalkanoyl esters of cellulosic materials whereby the treated cellulosic material is rendered oil and water repellent even at low degrees of substitution, said oil and water repellency being durable to aqueous laundering in the presence of neutral detergents and to dry cleaning. The improved esterification process of the present invention does not alter significantly the strength, color, appearance, hand, or fibrous form of the cellulosic material.

In general, in accordance with the present invention, a hydroxyl group-containing cellulosic material is esterified by reacting it with an esterifying agent of a perfluoroalkanoic acid wherein the alkanoyl radical contains from 4 to 10 carbon atoms. In carrying out the esterification process of the invention, the esterification is accomplished by a reaction between the cellulosic material and one or more of the perfluoroalkanoyl halide esterifying agents, in the presence of dimethylformamide solvent and a quantity of a tertiary aromatic amine sufficient to neutralize acidic reaction products to their respective amine salts. The process of the present invention is characterized by a critical sequence of addition of the reactants and of washing the esterified cellulosic material, which sequences are described below.

Substantially any cellulosic material containing hydroxyl groups can suitably be employed in the present processes. Illustrative examples of such materials include cellulose derived from cotton, flax, ramie and the like vegetable materials, wood cellulose, regenerated cellulose such as viscose rayon and the like, partial esters of cellulose such as partially acetylated cellulose, beta-propiolactone-reacted cellulose, and the like, partial ethers of cellulose such as partially cyanoethylated, partially aminoethylated, partially carboxymethylated, and the like partially etherified cellulosic materials. In general, the the cellulosic textile fibers, in the form of free fibers, slivers, yarns, threads or fabrics, including the natural fibers and partial ethers or partial esters thereof which are produced by reactions in which the fibers retain their cellulosic textile properties, are preferred starting materials. The cellulose textile fibers in the form of spun textiles, i.e., yarns, threads, or cloths, are particularly suitable starting materials.

A perfluoroalkanoyl halide of substantially any perfluoroalkanoic acid wherein the alkanoyl radical contains from 4 to 10 carbon atoms can be employed as the esterifying agent in the present process. Acids whose esterifying agents can be employed include perfluorobutyric acid, perfluorooctanoic acid, perfluorodecanoic acid, and the like acids. The alkanoyl chlorides of these perfluoroalkanoic acids are the preferred esterifying agents in the present invention. It is important that pure perfluorinated halides be used in the process. If perfluoroalkanoic acids are present as impurities in the halides, an uneven or "spotty" finish on the treated cellulosic material will result.

In reacting the cellulosic material with the esterifying agent of the perfluoroalkanoic acid, substantially any apparatus usually employed in the esterification of cellulose can be employed. In carrying out the improved esterification process, the cellulosic material to be reacted is first thoroughly wetted with dimethylformamide. The rate of wetting with the dimethylformamide is very rapid, being almost instantaneous for all except dense textile fabrics. The amount of dimethylformamide used is not critical. It is usually preferred to employ from about 5 to 20 moles of dimethylformamide for each mole of anhydroglucose units of the cellulose. After the cellulosic material is thoroughly wetted with the dimethylformamide, the perfluoroalkanoyl halide is added to the reaction system. The quantity of halide used and the rate of addition of the halide is not critical. It is preferable to use agitation to thoroughly disperse the halide as it is added, thus assuring its uniform reaction with the cellulose. Sufficient halide must be present to react with hydroxyl groups of

the cellulose to give the degree of substitution desired by the operator. It is generally preferred to use about 1 to 2 moles of the halide for each mole of anhydroglucose units of the cellulose. It is usually unnecessary and uneconomical to employ much larger amounts of halide than this, as the desired properties can usually be achieved at low degrees of substitution of the treated cellulosic material. After completion of the addition of the perfluoroalkanoyl halide, a quantity of a tertiary aromatic amine at least sufficient to neutralize acidic reaction products to their respective amine salts is added. In general, about 2 to 4 moles of the amine are preferred for 1 mole of perfluoroalkanoyl halide. The amine employed can be either a heterocyclic tertiary aromatic amine like pyridine, or a tertiary aromatic amine like N,N-dimethyl aniline. Since the perfluoroalkanoyl halides are much more soluble in the dimethylformamide solvent of the present invention than in pyridine, it is necessary to use large amounts of pyridine in the present process as is required in prior art processes. In general, it is preferable to have present enough dimethylformamide and amine to dissolve the esterifying agent and to neutralize any acid formed in the course of the esterification reaction. Where it is desired to use N,N-dimethylaniline in place of pyridine in the process of the present invention, it is preferable to dissolve the amine in several parts of dimethylformamide solvent prior to adding it to the reaction mixture. The aforementioned order of addition of reactants is of utmost importance and must be followed in the esterification process of the present invention. It is unsatisfactory, for example, to dissolve the esterifying agent in dimethylformamide and pyridine, then treat the cellulosic textile with this mixture. When this procedure is followed, there is considerable loss in tear strength of the resultant textile and its soil repellency is poor.

The extent of reaction, and thus the degree of substitution (i.e. the number of the three reactive hydroxyls per anhydroglucose unit which have been substituted, by replacing a hydrogen atom with an acyl radical, as indicated by the proportion of acyl groups per unit weight of cellulosic material) can be varied widely.

The degree of substitution can be varied primarily by (*a*) varying the proportion of esterifying agent in contact with the cellulose material during the esterification reaction, and (*b*) varying the time and temperature of the esterification reaction. In general, it is preferable to conduct the esterification reaction at a temperature above the freezing point of the solution used for the esterification and below a temperature at which an undesirable amount of cellulose degradation occurs. Reaction temperatures of from about room temperature (25° C.) to about 90° C. are preferred. Under the preferred esterification conditions, durably oil- and water-repellent cellulosic materials can be produced using reaction times as low as about 3 minutes at 90° C. or in less than 1 hour at room temperature. These rates of reaction are considerably faster than those of prior art processes. The oil- and water-repellency, which is durable to dry cleaning and to aqueous laundering with neutral detergents, is achieved at extremely low degrees of substitution of the cellulose. It is generally preferred to esterify the cellulose to a D.S. between about 0.02 and 0.10 to impart the aforementioned properties. If desired, the operator can esterify the cellulose to considerably higher degrees of substitution and impart durable oil- and water-repellency without significant alteration of the strength, color, appearance, or fibrous form of the cellulosic material.

Following completion of the esterification reaction, it is very important that the treated cellulosic material be washed free of the reactant solution before washing the cellulosic material with hot water. In the preferred washing procedure, the treated material is segregated from the reaction mixture and is first quenched by washing for about 2 to 3 minutes with running water at room temperature (25°–30° C.); it is then washed with absolute methanol or ethanol for several minutes; and it is finally washed again with room temperature water for several minutes. A total washing time of about 5 to 6 minutes is generally sufficient to completely wash the treated cellulosic material using the preferred procedure. If the washed cellulosic material is free of odor, this is a good indication that the washing is complete. We have found, contrary to expectations, that it is unsatisfactory to first wash the treated cellulosic material with hot (60° C.) water, prior to washing with cold water and other solvents. If the treated material is first washed with hot water before unreacted chemicals are removed, it loses the ester treatment and does not possess oil and water repellent properties. A possible explanation of this phenomenon is that the hot water, in the presence of the unreacted chemicals, can reach and break the cellulosic ester linkages. If the chemicals are first removed with cold water according to the process of the present invention, evidently the perfluoro chains are oriented such that subsequent treatment with hot water, or even with aqueous neutral detergents at temperatures as high as 100° C., does not break the ester linkages.

The washed, esterified cellulosic material can be dried using substantially any of the procedures conventionally employed for the drying of cellulosic materials. It is preferable to conduct the drying at relatively low temperatures—up to a temperature of about 110° C.

The following examples are illustrative of certain details of the invention. The perfluoroalkanoyl chlorides used in the examples were prepared from the corresponding acids by refluxing the acids with thionyl chloride in the presence of a minute quantity of pyridine catalyst.

EXAMPLE 1

(*Preferred method of treatment*)

A 1.2 g. sample of 80 x 80 cotton fabric (scoured and bleached) was placed in a flask and thoroughly wetted with 5 ml. of dimethylformamide at 25° C. Then 2 ml. of pure perfluorooctanoyl chloride (B.P., 130° C. at 744 mm.) were added, with shaking. This was followed by the addition of 1 ml. of pyridine with shaking. The shaking was continued for 4 minutes, after which time the fabric was removed, washed for several minutes with cold, running tap water, then methanol, and then cold tap water again. The fabric was dried in an oven at 90° C. The resultant fabric consisted essentially of perfluorooctanoyl esters of cellulose having a D.S. of 0.10 (as indicated by a weight gain of 27%).

The treated fabric had physical properties like those of the original fabric—that is, its tear strength, color, appearance, hand, and fibrous form were not altered by the treatment. It possessed excellent oil and water repellent properties which were durable to 1-hour Soxhlet extractions with CCl_4 and ethanol, as well as to two water boils of 20 minutes each in the presence of neutral detergents.

EXAMPLE 2

Cotton fabric was treated according to the procedure of Example 1 except that the reaction time was reduced to 3 minutes. The resultant fabric had a D.S. of 0.02 (weight gain, 4%) and exhibited the properties of the treated fabric described in Example 1.

EXAMPLE 3

A 1.6 g. sample of 80 x 80 cotton fabric was treated according to the procedure of Example 1 except that the reaction time was increased to 1 hour. The resultant fabric had a D.S. of 0.58 (weight gain, 145%) and exhibited the properties of the treated fabric described in Example 1.

Infrared absorption spectra of the treated fabric were obtained using the conventional procedures. The characteristic band obtained at 5.64 microns demonstrated the presence of perfluoro ester linkages with the cellulose.

Normal carboxylic esters usually exhibit a band at about 5.75 microns [Rasmussen, J. Am. Chem. Soc. 71, 1073 (1949)], but fluorine substituents cause a shift in the ester band to shorter wavelengths [Rappaport, Hauptschein, O'Brien and Filler, J. Am. Chem. Soc. 75, 2695–97 (1953)].

[In all of the above examples, the mole ratios of acid chloride to anhydroglucose was ≤ 1, and all of the pyridine was added immediately after the addition of acid chloride.]

EXAMPLE 4

A sample of scoured and bleached 48 x 48 cotton fabric weighing 0.9 g. was thoroughly wetted with 5 ml. of dimethylformamide, then 2 ml. of a purified perfluorooctanoyl chloride were added before the addition of 2 ml. of pyridine was begun. The pyridine was added slowly and the reaction was allowed to take place for 45 minutes at room temperature (25° C.). The treated fabric was washed and dried as described in Example 1. The resultant fabric had a D.S. of 0.03 as indicated by a weight gain of 8%, and exhibited the properties of the treated fabric described in Example 1.

EXAMPLE 5

A 1.6 g. sample of 48² cotton fabric (scoured and bleached) was wetted with 5 ml. of dimethylformamide; then 2 ml. of purified perfluorooctanoyl chloride were added, followed by 1 ml. of pyridine. An additional 5 ml. of dimethylformamide was added, and after 15 minutes, an additional 1 ml. of pyridine was added to the reaction mixture, which was then shaken at room temperature (25° C.) for 3½ hours. The resultant fabric, after washing and drying as described in Example 1, was the perfluorooctanoyl ester of cellulose having a D.S. of 0.03 (as indicated by the weight gain of 7.1%). It exhibited the properties of the treated fabric described in Example 1.

EXAMPLE 6

A 1.6 g. sample of 48² cotton fabric was wetted with 5 ml. of dimethylformamide, then 2 ml. of purified perfluorooctanoyl chloride were added, followed by 1 ml. of pyridine. One additional ml. of pyridine was added after 15 minutes of reaction. The reaction was allowed to proceed for 15 hours at 25° C. with shaking. The resultant fabric, after washing and drying as described in Example 1, had a D.S. of 0.12 (as indicated by a weight gain of 27%). It exhibited the properties of the treated fabric described in Example 1.

EXAMPLE 7

A 1.6 g. sample of 48² cotton fabric (scoured and bleached) was wetted with 5 ml. of dimethylformamide. Then 2 ml. of pure perfluorooctanoyl chloride were added. Two ml. of pyridine were mixed with 5 ml. of dimethylformamide and the mixture was added slowly to the reaction mixture during 45 minutes of reaction time at room temperature with shaking. The resultant fabric, after washing and drying as described in Example 1, had a D.S. of 0.02 as indicated by a weight increase of 4%. It exhibited the properties of the treated fabric described in Example 1.

EXAMPLE 8

An 8.74 g. sample of 48² cotton fabric was wetted with 75 ml. of dimethylformamide, then 15 ml. of pure perfluorooctanoyl chloride and 15 ml. of pyridine were added in succession. The reaction was allowed to proceed for 1 hour at 25° C. with shaking. The resultant fabric, after washing and drying as described in Example 1, had a D.S. of 0.03 (as indicated by a weight increase of 5.5%). Quantitative analyses showed that the fabric contained 3.13% fluorine. The treated fabric retained 80% of the original breaking strength, and it exhibited the properties of the treated fabric described in Example 1.

The following two examples illustrate the importance of using a pure perfluorinated chloride in the process of the present invention. For example, if the perfluorinated chloride employed contains some unreacted perfluorinated acid as an impurity (as detected by B.P. range), treated fabric with a very "spotty" oil and water repellent finish is produced.

EXAMPLE 9

To a 1.2 g. sample of 48 x 48 cotton fabric wetted with 10 ml. of dimethylformamide was added 2 ml. of an impure sample of perfluorooctanoyl chloride (B.P. range, 125°–135° C. at 744 mm.) and then 2 ml. of pyridine. The reaction was allowed to proceed for 50 minutes at 25° C. and the treated fabric was washed and dried as in Example 1. The resultant fabric had only 1.5% weight gain and a very uneven or "spotty" oil and water repellent finish.

EXAMPLE 10

A sample of cotton fabric identical to that used in Example 9 was treated in exactly the same manner as described in Example 9, except that a pure perfluorooctanoyl chloride (B.P. 130° C. at 760 mm.) was used. In this instance, a treated fabric with an 8.7% weight gain was obtained, the finish was not spotty, and the fabric possessed excellent oil and water repellent properties.

The following example illustrates that an acid scavenger other than pyridine can be used in the process of the present invention—provided the order of addition of reagents is the same as in Example 5.

EXAMPLE 11

A 1.031 g. sample of 48 x 48 cotton fabric was wetted with 5 ml. of dimethylformamide. After this, 2 ml. of purified perfluorooctanoyl chloride were added. After the addition of the acid chloride, 5 ml. of dimethylformamide containing 1 ml. of N,N-dimethylaniline was added. The reaction was allowed to take place at room temperature for 13 hours, then the treated fabric was washed and dried as described in Example 1. The resultant fabric had a weight gain of 26% (D.S. of 0.12), and possessed an excelent oil and water repellent finish that was durable to the launderings in organic solvents and aqueous solutions of neutral detergents described in Example 1.

The following two examples illustrate the use of perfluorobutyryl chloride in place of perfluorooctanoyl chloride, and the importance of the order of addition of the reactants.

EXAMPLE 12

A 1.6 g. sample of 80 x 80 cotton fabric was treated according to the procedure of Example 3, except that an equivalent quantity of a purified perfluorobutyryl chloride was used in place of the perfluorooctanoyl chloride. The resultant washed and dried fabric consisted essentially of perfluorobutyryl esters of cellulose and had a D.S. of 0.37 (weight gain, 46.6%). The fabric possessed good oil and water repellency.

EXAMPLE 13

A 1.6 g. sample of 80 x 80 cotton fabric was treated according to the procedure of Example 12, except that the dimethylformamide, pyridine, and perfluorobutyryl chloride were mixed in that order and then the mixture was used to treat the fabric. The resultant washed and dried fabric showed a weight gain of only 19% and its oil repellency was poor. (Oil droplets placed on the surface of the fabric spread and wet the fabric within 1 minute.) There was considerable loss in tear strength of the fabric as a result of the treatment, and the treated fabric was discolored.

The following example shows the detrimental effect of first washing off unreacted chemicals with hot water

rather than with cold water at the end of the reaction time.

EXAMPLE 14

Cotton fabric (80 x 80) was treated exactly according to the procedure of Example 1, except in this case the treated fabric was first washed with hot (60° C.) water prior to washing with cold water, methanol, and cold water and drying as in Example 1. The resultant fabric had no weight gain and it did not possess oil and water repellent properties.

The following example illustrates the use of the process of the invention on cotton yarn.

EXAMPLE 15

A 1.2 g. sample of scoured and bleached cotton yarn was wetted with 20 ml. of dimethylformamide, then 5 ml. of purified perfluorooctanoyl chloride were added, followed by 5 ml. of pyridine. The reaction was allowed to proceed for 1 hour at room temperature. The resultant yarn, after washing and drying as described in Example 1, had a D.S. of 0.11 (weight gain, 30%). The yarn was strongly resistant to wetting by oil and water.

The following three examples illustrate the inadequacies of conventional esterification processes for preparing perfluoroalkanoyl esters of cellulose, and particularly the non-durability of the oil repellency finish imparted by such processes.

EXAMPLE 16

A 2.23 g. sample of 80 x 80 cotton fabric (scoured and bleached print cloth) was treated with 9 grams of purified perfluorobutyryl chloride in 45 ml. of pyridine, by immersing the cotton in the treating solution for 1 hour at room temperature. The treated fabric was washed thoroughly with pyridine, followed by acetone, and was then dried overnight (16 hrs.) at room temperature (25° C.). The resultant fabric showed a weight gain of 3.73 grams, corresponding to a D.S. of 1.3 (167% weight gain). The fabric was very low in tear strength, was rough in hand, but was oil and water repellent.

A 0.995 g. portion of the above treated fabric was boiled in an aqueous solution of neutral detergent for 20 minutes, using an exactly comparable solution and procedure as employed in Example 1. The fabric was rinsed in hot and then cold water, and was dried in an oven at 90° C. The fabric lost 0.17 g. in weight, and its oil repellency was greatly reduced—that is, oil droplets placed on the surface of the fabric spread and wet the fabric in less than 3 minutes. (In the case of good oil repellency, the fabric would not have been wetted for at least 12 hours.) After a second 20-minute boil in the neutral detergent solution, the fabric had completely lost its oil repellency, but was still water repellent.

Another portion of the treated fabric was Soxhlet-extracted for 1 hour with CCl_4, and a third portion was Soxhlet-extracted for 1 hour with ethanol. The oil repellency of both samples was considerably decreased, but the water repellency remained.

EXAMPLE 17

A 2.28 g. sample of 80 x 80 cotton print cloth (scoured and bleached) was treated as described in Example 16, except that the reaction was allowed to continue for 4 hours at room temperature. The resultant fabric had a D.S.>1 (weight gain, 135%). The oleophobic property of the fabric was destroyed by a single 20-minute boil in neutral detergent solution, but the water repellency remained. The oleophobic property of the fabric was reduced by 1-hour Soxhlet extractions in CCl_4 or ethanol.

EXAMPLE 18

A 2.23 g. sample of the 80 x 80 scoured and bleached cotton print cloth was treated as described in Example 16, except that the reaction was allowed to continue for 15 hours at room temperature. The fabric was completely disintegrated at the end of the reaction period—only a pulpy, fibrous mass remained.

We claim:

In a process for converting a cellulosic textile fiber having free hydroxyl groups in the cellulose molecule to an esterified cellulosic textile fiber containing perfluoroalkanoyl radicals attached to oxygen atoms of cellulose molecules by esterifying the cellulosic textile fiber having free hydroxyl groups in the cellulose molecule with a perfluoroalkanoyl halide wherein the alkanoyl radical contains from 4 to 10 carbon atoms, the improvements which impart durable oil- and water-repellency even at low degrees of ester substitution of the cellulosic textile fiber comprising the sequential steps of wetting said hydroxyl group-containing cellulosic textile fiber with dimethylformamide, adding the perfluoroalkanoyl halide, then adding a quantity of a tertiary aromatic amine sufficient to neutralize acidic reaction products to their respective amine salts, reacting said cellulosic textile fiber to the desired degree of ester substitution; and washing with water, at a temperature not exceeding about 30° C., to free the so-reacted fiber from reactant solution.

No references cited.