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TREATMENT OF TEXTILES TO IMPART
WATER-REPELLENCE

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This invention relates to cellulosic materials and particularly to the treatment of these materials to render them repellent to water.

Cellulosic materials are not naturally water-repellent. Methods of water-proofing fabrics by filling the interstices thereof by means of rubber, resins, etc. have long been practiced, with some degree of success. This is not, however, a sufficient answer to the problem since for many uses it is highly desirable that the fabric be water-repellent but that the interstices be left substantially unchanged and that the fabric in general be left substantially unchanged in appearance and feel. Methods have been devised for example heating with soap and alum, impregnating with an emulsion or solution of waxy materials, etc., which attempt to attain this latter end but these methods in general suffer from the defect that the water-repellency is not permanent and is more or less readily removed in a few launderings. (See Business Week, July 24, 1937, page 24). The finish produced by such treatments is not permanent and the fabric soon loses its water-repellency.

This invention has an object the improvement of cellulosic materials, fibers, or fabrics such as cotton, regenerated cellulose, artificial silk, paper, etc., by a treatment designed to markedly decrease their ability to wet with water without in any way injuring the structure, appearance or feel. A further object is the imparting to vegetable or artificial cellulosic fibers or fabrics made therefrom a high degree of water-repellency which is not lost upon subjection to the usual laundering procedures. A further object is the preparation of spot-proof fabrics. A still further object is the preparation of improved awning materials, shower curtain materials, and the like. Another object is the preparation of materials suitable for shower-proof suits, dresses, coats, and clothing generally, also for straw hats, umbrellas, shades, curtains, etc. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a cellulosic material is impregnated with an aqueous or other dispersion of an isothiocyanate or isocyanate having an aliphatic carbon chain containing at least eight carbon atoms, then dried and (subsequently or simultaneously) heated under conditions more thoroughly detailed below.

In carrying out the process of this invention, an aliphatic isocyanate or isothiocyanate containing a hydrocarbon radical of at least eight carbon atoms, e. g., dodecyl isothiocyanate, 9,10-

octadecenyl isothiocyanate, octadecyl isothiocyanate, decamethylene diisothiocyanate, dodecyl isocyanate or octadecyl-isocyanate or mixtures of two or more of these materials may advantageously be employed. In order to avoid the use of expensive solvents, it is advantageous to use the said compound in the form of an aqueous emulsion employing, for example, ordinary household or laundry soap as the emulsifying agent. The use of a soap emulsion also insures better penetration and quicker impregnation. The fabric may then be squeezed free of excess liquor to avoid too rapid exhaustion of the bath and then allowed to dry and/or immediately subjected to an elevated temperature such as 125° C. for a period of at least several minutes, or until the fabric is found to have been rendered water-repellent to the desired degree. After this baking operation the fabric is washed free of soap and dried. It is then found to be difficult to wet with water.

The more detailed practice of the invention is illustrated by the following examples, wherein parts given are by weight unless otherwise stated. There are of course many forms of the invention other than these specific embodiments.

Example I

Two parts of dodecyl isocyanate was added slowly to a solution of 3 parts soap in 95 parts water with rapid stirring. A piece of cotton muslin was impregnated with the resulting emulsion, squeezed free of excess liquor, then heated for 1½ hours at 100° C. After rinsing and drying, the fabric was found to be very water-repellent and not wet by drops of water even after washing with hot benzene and acetone.

Example II

Two parts of octadecyl isocyanate was slowly added to one part of soap and 37 parts of water with rapid stirring. In the emulsion thus formed cotton muslin fabric was immersed, then freed of excess liquor and subjected to a temperature of 135° C. for 30 minutes. After rinsing and drying, the fabric was not again easily wetted, nor was the water-repellency impaired after laundering for ½ hour in ½ % soap solution followed by rinsing with water.

Example III

Ten parts dodecyl isothiocyanate was added slowly to a solution of 5 parts Castile soap in 70 parts water, the solution being stirred rapidly throughout the addition. In the resulting emul-

sion 3.5 parts cotton muslin and 6 parts loose cotton fibers were immersed until thoroughly wet. The fabric and fibers were then squeezed free of excess liquor after which they weighed 6.7 parts and 10.4 parts respectively. After allowing to dry they were then subjected to a temperature of 130° C. for 4 hours. Following this baking treatment the cotton was washed with water and finally acetone to remove the soap and excess unreacted material. Both the fabric and fibers were then dried and found to be very water-repellent which effect was not appreciably impaired by subjection to two one-half hour washings in boiling ½% soap solution. The appearance of the fabric was unchanged while the feel was somewhat softer. The fibers floated on water indefinitely without wetting while the fabric was capable of supporting drops of water until they evaporated. The treated cotton had an increased affinity for acid dyestuffs normally used on animal fibers while the affinity for most direct dyes was unchanged.

Example IV

Ten parts octadecyl isithiocyanate was melted with two parts of stearic acid and poured very slowly and with rapid stirring into a solution consisting of 4 parts of 10% caustic potash solution, two parts 10% soda solution and 182 parts of water. The emulsion was then run through a colloid mill and was found to be a stable gel when cooled. Cotton muslin was impregnated for 30 seconds in this emulsion at 28° C., squeezed free of excess liquor and heated for 15 minutes at 140° C. It was then rinsed with water and ironed dry. The fabric was then very water-repellent, even after boiling for ½ hour in ½% soap solution.

Example V

Three parts of cotton muslin was impregnated in an emulsion prepared by adding 0.3 parts of octadecyl isothiocyanate to 0.5 parts soap and 30 parts water with rapid stirring. The fabric was then wrung to a weight of 6 parts and subjected to a temperature of 105° C. for 5 minutes. After rinsing the fabric with water and again drying, it was found to be very water-repellent which effect was resistant to the action of acetone.

Example VI

Ten parts 9,10-octadecenyl isothiocyanate was added slowly to a solution of 5 parts castile soap in 70 parts water, the solution being stirred rapidly throughout the addition. In the resulting emulsion 3.5 parts cotton muslin and 6 parts loose cotton fibers were immersed until thoroughly wet. The fabric and fibers were then squeezed free of excess liquor after which they weighed 6.7 parts and 10.4 parts respectively. After allowing to dry they were then subjected to a temperature of 130° C. for 4 hours. Following this baking treatment the cotton was washed with water and finally acetone to remove the soap and excess unreacted material. Both the fabric and fibers were then dried and found to be very water-repellent which effect was not appreciably impaired by subjection to two one-half hour washings in boiling ½% soap solution. The appearance of the fabric was unchanged while the feel was somewhat softer. The fibers floated on water indefinitely without wetting while the fabric was capable of supporting drops of water until they evaporated. The treated cotton had an increased affinity for acid dyestuffs normally used on animal fibers while the affinity for most direct dyes was unchanged.

Example VII

Ten parts 9,10-octadecenyl isothiocyanate was melted with two parts stearic acid and poured very slowly and with rapid stirring into a solution consisting of 4 parts of 10% caustic potash solution, two parts 10% soda solution and 182 parts of water. The emulsion was then run through a colloid mill and was found to be a stable gel when cooled. Cotton muslin was impregnated for 30 seconds in this emulsion at 28° C., squeezed free of excess liquor and heated for 15 minutes at 140° C. It was then rinsed with water and ironed dry. The fabric was then very water-repellent, even after boiling for ½ hour in ½% soap solution.

Example VIII

Three parts of cotton muslin was impregnated in an emulsion prepared by adding 0.3 parts of 9,10-octadecenyl isothiocyanate to 0.5 parts soap and 30 parts water with rapid stirring. The fabric was then wrung to a weight of 6 parts and subjected to a temperature of 105° C. for 5 minutes. After rinsing the fabric with water and again drying, it was found to be very water-repellent which effect was resistant to the action of acetone.

Example IX

Ten parts octyl isothiocyanate was added slowly to fifty parts of a 5% aqueous solution of soap with rapid stirring. A piece of cotton muslin weighing 5.6 parts was impregnated with this emulsion and squeezed free of excess liquor to a weight of 11.0 parts. The fabric was then dried overnight at 100° C., then washed with water and ironed. It was then "spot-proof," being capable of shedding drops of water placed thereupon momentarily.

Example X

Five parts decamethylene diisothiocyanate was emulsified in 15 parts of a 3% aqueous soap solution. Five parts cotton voile fabric was thoroughly wet out in this emulsion and wrung to a weight of 9 parts. Half of this fabric was dried over night at 95-100° C. and the other half 45 minutes at 125° C. Each half was then rinsed with water and dried. Both pieces of voile, although of open weave, were very water-repellent and supported drops of water without wetting even after repeated washing with actone or soap.

Example XI

Ten parts of 9,10-octadecenyl isothiocyanate was emulsified by adding slowly and with rapid stirring to 100 parts of a 3% solution of soap in water. Viscose artificial silk was immersed in this emulsion and after becoming thoroughly wet was squeezed and dried for 15 minutes at 140° C. After rinsing out the soap the fabric was definitely water-repellent.

There may be employed in the process of this invention any water-insoluble aliphatic compound containing at least 8, and preferably from 12-18, carbon atoms and one or more isocyanate or isothiocyanate radicals attached by the nitrogen atom to one or more carbon atoms, respectively, of the hydrocarbon chain. While the examples disclose isocyanates and isothiocyanates of alcohols of eight to eighteen carbon atoms in the alkyl group, isocyanates and isothiocyanates wherein the hydrocarbon is of higher carbon content may be employed, e. g. melissyl. The isocyanates and isothiocyanates of alcohols of twelve to eighteen carbon atoms are greatly pre-

ferred because of the effectiveness of the water-repellency treatment and the availability of the isocyanates and isothiocyanates.

The aliphatic hydrocarbon isocyanates and isothiocyanates $R(NCX)_y$, where R is an aliphatic hydrocarbon radical of at least eight carbon atoms having a valence of y , X is oxygen or sulfur and y is an integer which is at least one, are particularly useful and are of generic utility.

In addition to the isocyanates and isothiocyanates of the examples there may be employed such compounds as the isocyanic or isothiocyanic esters of linolyl-, linoleyl-, eleostearyl-, mellissyl-, and 1,2-chloro-octadecyl alcohol, or the isocyanate or isothiocyanate of such glycerol ester-alcohols as castor oil or hexahydro-castor oil (glyceryl tris-hydroxystearate).

Any fabric, yarn or fiber may be used so long as it is cellulosic, as for example, cotton, linen, jute, ramie, viscose silk, etc. The term "cellulosic" is used to include cellulose but not cellulose ethers or esters.

The process of the present invention is most effective in causing fibrous cellulosic materials to attain water repellency and this forms a preferred class of cellulosic materials. In the case of non-fibrous cellulosic materials, e. g., those sold under the registered trade-mark "Cellophane," the process while effective to some extent is not commercially feasible.

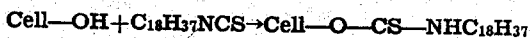
The reagents may be applied to the cellulosic material in any manner desired though preferably in the form of an aqueous emulsion using any neutral soap, such as "castile" alkaline soap, himolal salts, etc. in sufficient quantity to disperse the oil in the aqueous phase. The reagent may be employed in any concentration in excess of about 1%, or even less, of the total solution or emulsion while the preferred concentration ranges from about 1% to about 25%. The ratio of the amount of reagent to the amount of textile material is immaterial as long as sufficient liquid is present to cause uniform wetting. The time necessary for immersion is in no way limited, except that the goods must be uniformly impregnated. They may or may not be freed of excess liquor and may or may not be dried at room temperature before baking, as desired. The temperature of the baking treatment may be varied from about 80° C. to about 160° C., (i. e., from the temperature at which the reaction rate begins to be appreciable, up to the temperature at which charring begins), the time required with given materials being in inverse proportion to the temperature. At and below approximately 100° C., the reaction rate is so slow that several hours may be required to obtain the desired result, while the desired effect may be obtained in a few minutes when using a temperature approaching that at which scorching of the fabric occurs (i. e. approximately 160° C.). In general no harm results from continuing the baking beyond the point where the reaction is completed, providing it is not continued until charring or scorching is appreciable.

The baking step is not a mere drying since drying at room temperature does not produce water-repellent effects. A reaction either with the cellulose or intramolecularly is caused by the baking.

The temperatures and times given in the examples are not intended to be the minima necessary. Temperatures between 80° and 160° C. and preferably between 95° and 145° C. are selected and the baking is continued until the goods after

washing are found to be water-repellent to the required degree.

When a cellulosic material, e. g., a fabric, is made water-repellent according to the methods already known, namely by impregnation with an emulsion or solution of a material such as a high molecular weight ester or a waxy hydrocarbon or other material which is deposited in or on the fibers, thereby imparting to said fibers the inherent water-repellent properties of the agent used, permanent laundry fastness is not obtained. Adhering mechanically to the fibers, this material is of course removed by laundering with soap or cleaning with organic solvents. We do not wish to be limited by any theory but it appears that when a fabric is treated in accordance with this invention with a long chain alkyl isocyanate or isothiocyanate, the cellulose on the surface of the fibers reacts to form a urethane or thio-urethane in the following manner, where Cell-OH stands for a portion of the cellulose molecule:



Since the cellulose thus becomes chemically attached to the water-repellent agent, the effect is not lost by mechanical treatment with soaps or organic solvents. The invention is not however limited to this theory. The water-repellency of the treated fabric is not adequate unless the R of $R-N=C-X$ contains at least eight carbon atoms and is more satisfactory when R contains at least twelve carbon atoms.

The products of this invention are particularly useful in any application where a water-repellent fabric is desired and where the fabric must occasionally be laundered or dry cleaned as for example in the case of shower-proof dresses, suits and coats; in fact cotton or cellulose-containing clothing in general, also spot-proof table cloths, doilies, etc. Even paper may be given water-repellent properties by this treatment. It has been pointed out above that the process herein described for the production of water-repellent textile materials is superior to methods involving filling of the interstices of the fabric or surface-coating the fiber in that the goods are left substantially unchanged in appearance and feel. It is also superior to methods involving simple mechanical impregnation with water-repellent agents in that the water-repellent effect is not readily removed by laundering.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

We claim:

1. Process which comprises baking at a temperature of 80-160° C. a cellulosic fabric impregnated with an isothiocyanic acid ester of an aliphatic alcohol of at least eight carbon atoms, until the fabric becomes water-repellent.

2. Process which comprises baking at a temperature of 80-160° C. a cellulosic fabric impregnated with an alkyl isothiocyanate, the alkyl group of which contains at least eight carbon atoms, until the fabric becomes water-repellent.

3. Process which comprises baking at a temperature of 80-160° C. a cellulosic fabric impregnated with an alkyl isothiocyanate, the alkyl group of which contains 12 to 18 carbon atoms, until the fabric becomes water-repellent.

4. Process which comprises baking a cellulosic fabric, impregnated with octadecyl isothiocyanate, at a temperature between about 80° and

160° until the fabric becomes water-repellent.

5. Process which comprises impregnating a cellulosic fabric with an aqueous dispersion of octadecyl isothiocyanate and baking the impregnated fabric at a temperature between about 80° and 160° until the fabric becomes water-repellent.

6. Process which comprises impregnating a cellulose-containing fabric with an aqueous dispersion of octadecyl isothiocyanate and baking the impregnated fabric at 95°-145° until the fabric becomes water-repellent.

7. Water-repellent material comprising a cellulosic material impregnated with octadecyl isothiocyanate, and baked at a temperature of 80°-160° C. until the fabric becomes water-repellent.

8. Water-repellent fabric obtained by baking at a temperature of 80-160° C. a cellulosic fabric impregnated with an isothiocyanic acid ester of an aliphatic alcohol of at least eight carbon atoms, until the fabric becomes water-repellent.

9. A process which comprises impregnating a cellulose textile material with an isothiocyanate of the formula $RNCS$ in which R is an aliphatic hydrocarbon radical containing more than seven carbon atoms, and heating the impregnated material until the material becomes water-repellent.

10. A process which comprises impregnating a cellulose textile material with octadecyl isothio-

cyanate and heating the impregnated material until the material becomes water-repellent.

11. A process which comprises impregnating a cellulose textile material with an isothiocyanate of the formula $RNCS$ in which R is an aliphatic hydrocarbon radical containing more than ten carbon atoms, and heating the impregnated material until the material becomes water-repellent.

12. Water-repellent material comprising a cellulosic material impregnated with 9,10-octadecenyl isothiocyanate and baked at a temperature of 80 to 160° C. until the fabric becomes water repellent.

13. Water-repellent material comprising a cellulosic material impregnated with dodecyl isothiocyanate and baked at a temperature of 80 to 160° C. until the fabric becomes water repellent.

14. Process which comprises baking at a temperature of 80 to 160° C. a cellulosic fabric impregnated with 9,10-octadecenyl isothiocyanate until the fabric becomes water repellent.

15. Process which comprises baking at a temperature of 80 to 160° C. a cellulosic fabric impregnated with dodecyl isothiocyanate until the fabric becomes water repellent.

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