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PROCESS OF WATERPROOFING

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This invention relates to a new process of rendering textile fibers, yarns, fabrics and similar materials water-repellent. It particularly deals with a new means of chemically altering the surface of organic fibers to make them water-repellent and non-absorptive without materially changing their general appearance. It further relates to imparting a desirable soft hand to textile fabrics.

Heretofore, textile fabrics have been rendered water-repellent with superficial coatings of wax or metallic soaps. When the fabric was laundered or dry-cleaned, the layer of water-repellent substance was removed and the property of water-repellency lost.

It is the object of this invention to provide a process by which water-repellency is imparted to textile fibers, more particularly to cellulosic fibers or fabrics. It is also an object to provide a water-repellent finish for such materials which is not removed upon repeated laundering or dry-cleaning. It is a further object to render fibers water-repellent throughout a fabric rather than merely at the surface of the fabric. It is another object to provide a water-repellent finish for cellulosic fabrics or other textiles which imparts a soft, pleasing hand which is free from greasiness. A further object is to provide an agent and process for rendering waterproof any organic material which may be impregnated with the agent and heated without damaging the material and which is reactive to said agent. Other objects will appear hereinafter.

These objects are attained by treating fibers, yarns, or fabrics with amine condensates of the type described in United States Patent No. 1,952,008 which contain an aliphatic or substituted aliphatic hydrocarbon chain of 12 or more carbon atoms. These amine condensates are prepared by reacting amides with formaldehyde and a strongly basic, non-aromatic, secondary amine. We have found that when the amide contains a sufficient number of aliphatic carbon atoms to yield a relatively long hydrocarbon chain which is hydrophobic and when the secondary amine bears not more than about seven carbon atoms consisting of lower alkyl groups, relatively small cycloaliphatic groups or divalent groups jointly forming with the nitrogen atom a heterocyclic ring, these amide-formaldehyde-amine condensates react with organic fibers to produce a hydrophobic layer on the surface of these fibers.

The most suitable condensates are made from such amides as the amides of stearic, oleic, 12-

hydroxystearic, lauric, myristic, palmitic, phenylstearic, arachidic, ricinoleic, linoleic, carnaubic, and montanic acids or the monoalkyl amides thereof. Amines suitable for the condensates include dimethylamine, diethylamine, piperidine, morpholine, methylcyclohexyl amine, triethylene tetramine, etc. When these amides and amines are condensed with formaldehyde, the resulting products are waxy masses or soft oily or jelly-like substances, as described in United States Patent No. 1,952,008.

The condensates are free tertiary amine bases and may be used as such, or they may be converted into acid salts, preferably with weak water-soluble organic acids, such as formic, acetic or lactic acids. The bases or salts are soap-like in nature and are dispersible in water, particularly on warming. Since they are good wetting and penetrating agents, they are readily taken up by fibers. Without doubt their cationic nature is responsible for their ready adsorption. When cellulose fibers or fabrics are heated, a reaction occurs between the cellulose of the fibers and the water-proofing agent, which results in a stable water-repellent complex which cannot be broken down by ordinary physical means. Other organic materials, such as wool and silk, also appear to react with the condensates, but the reaction is not entirely understood. An advantage of the tertiary amine condensates herein disclosed is the preservation of the strength of fabric.

In our process of rendering cellulosic or other fibers water-repellent a solution or dispersion of the condensation product is prepared by stirring the compound into, preferably, warm water. The material in solution is quite stable and can be safely used even at the boiling point of water. Auxiliary solvents, such as alcohol or dioxane, may be added, if desired, although this is not necessary. The reaction time may be shortened by the use of a suitable catalyst, which may be either weakly acidic or mildly alkaline. Acetic, formic and lactic acids are examples of suitable acid catalysts, while sodium carbonate and bicarbonate, borax, and sodium acetate are examples of suitable alkaline catalysts. The latter type of catalyst is more desirable because it usually gives a more water-repellent finish and because there is no danger of tendering fabric during the reaction.

The cellulosic or other material is impregnated with a solution containing preferably about 5 to about 10% of the above type of condensate, and then with or without preliminary drying, is sub-

jected to a temperature of 120° C. or more. In the case of condensates which are hard and waxy, application has been made successfully with a powder sprinkled over the fabric, and reacted with the fibers by ironing. The time required for heating is determined by the nature of the fabric and the temperature. At 150° C. two or three minutes are usually sufficient. At lower temperatures longer times become necessary. It is usually desirable, although not essential, to remove by-products of the reaction by washing the fabric after the step of heating.

The fibers or fabrics resulting from this process are highly water-repellent and retain this property through repeated laundering or dry-cleaning operations. In addition, treated fabrics possess a soft, pleasing hand, free from greasiness.

Various methods by which the condensates described may be successfully applied are illustrated in the following examples, but these examples are not to be construed as limitations of the process.

Example 1

Cotton broadcloth was immersed in a solution prepared from 800 g. of water, 100 g. of acetic acid and 100 g. of the condensation product obtained by condensing stearamide with equimolecular quantities of formaldehyde and dimethylamine. This solution was soapy and creamy at room temperature. The material was dried in a current of air at 30° C. and then placed in an oven at 120° C. for 30 minutes. Thereafter, it was well washed in warm soap solution. When dry, it was very resistant to wetting.

Example 2

Cotton sheeting was treated as above in a solution of 400 g. of water, 25 g. of formic acid and 50 g. of the condensation product prepared by condensing stearamide with equimolecular quantities of formaldehyde and diethylamine. After drying, it was baked 20 minutes at 130° C. A permanent water-repellent finish was obtained.

Example 3

Cotton sheeting was immersed in a solution containing 1200 g. of water, 100 g. of acetic acid and 100 g. of the condensation product prepared from one mol each of 12-hydroxystearamide, formaldehyde and dimethylamine. After drying, it was baked 30 minutes at 130° C. Good water-proofing was obtained.

Example 4

Cotton lawn was immersed in a solution containing 100 g. of ethyl alcohol, 50 g. of acetic acid, 750 g. of water and 100 g. of the condensation product prepared from one mol each of montanic acid amide, formaldehyde and dimethylamine. It was dried and heated at 125° C. for 30 minutes. A very water-repellent finish was obtained.

Example 5

Viscose rayon was treated with a solution containing 750 g. of water, 20 g. of acetic acid and 80 g. of the condensation product prepared from one mol each of stearic amide, formaldehyde and morpholine. When dry, it was baked 45 minutes at 120° C. Good water-repellency was obtained.

Example 6

Cotton sheeting was immersed in a solution

containing 200 g. of isopropyl alcohol, 50 g. of acetic acid, 650 g. of water and 100 g. of the condensation product prepared from one mol each of stearic amide formaldehyde and piperidine. After drying at room temperature, it was pressed with a hot flat iron. Good repellency to water was obtained.

Example 7

Cotton sheeting was immersed in a solution containing 100 g. of acetic acid, 800 g. of water and 100 g. of the reaction product obtained from equimolecular quantities of stearamide, formaldehyde and triethylene tetramine. After drying, it was baked 30 minutes at 130° C. Good water-repellency was obtained.

Example 8

Cotton broadcloth was immersed in a solution at 70° C. containing 5 g. of sodium carbonate, 950 g. of water and 50 g. of the reaction product obtained from equimolecular quantities of stearamide, formaldehyde and dimethylamine. Without previous drying, it was heated in an oven 5 minutes at 150° C. An excellent water-repellent finish was obtained.

Example 9

Viscose rayon was treated with a solution containing 10 g. of sodium bicarbonate, 400 g. of water and 40 g. of the reaction product obtained from equimolecular quantities of stearamide, formaldehyde and diethylamine. Without previous drying, it was heated in an oven at 140° C. for 10 minutes. A good, permanent water-repellent finish was obtained.

Example 10

Cotton lawn was immersed in a solution containing 10 g. of sodium carbonate, 5 g. of urea, 1450 g. of water and 50 g. of the condensation product of stearamide, formaldehyde and dimethylamine. It was then heated 30 minutes at 130° C. A very pleasing, soft finish was obtained, which had water-repellent properties.

Example 11

Cotton sheeting was padded through a bath containing 5% of soda ash, 5% of the condensation product of N-methyl stearamide, formaldehyde, and dimethylamine, and a trace of capryl alcohol. It was then heated for 30 minutes at about 130° C. After the fabric was washed in a soap solution and dried, it was found to be water-repellent and soft.

This process is particularly applicable to the treatment of cellulosic materials, such as cotton, linen, paper, straw, viscose rayon, acetate rayon, or other regenerated cellulose esters or ethers.

While cellulosic fibers give the best results, our new process may also be applied to wool and silk or to textile materials containing a mixture of different types of fibers. In general, the process is applicable to any organic materials which may be impregnated with the amide-formaldehyde-amine condensates and heated to over 120° C. without being damaged and which possess groups capable of reaction with said condensation products.

There are some types of fabrics which do not require the high degree of permanent repellency which is possible by our process, but in which some degree of permanency is still a factor. Such materials may be treated at a saving in cost with an emulsion of inexpensive paraffin wax or other suitable waxes, with or without metallic soaps,

such as aluminum stearate, zinc palmitate and the like. Such emulsions may be made with the condensates herein described which are effective not only as wetting and penetrating agents but also as emulsifying agents. High initial repellency may thus be secured with a fair degree of permanency.

The physical properties of the solutions may be materially improved by the addition of other materials which prevent foaming and reduce the viscosity. Urea or capryl alcohol, added to the extent of $\frac{1}{4}$ to 1%, is particularly effective in this respect and is very helpful in the application of the longer chained condensates.

Textile materials treated with the condensation products of the type herein disclosed possess both water-repellency and a soft, pleasing hand. The softening effect is likewise a permanent effect and differs therein from the softness obtained with the usual sulfonated oils or oil emulsions. The fabrics softened by our new process have the further advantage over those fabrics carrying the ordinary softeners in that there is no danger of sweating out of oil, discoloration, or development of rancidity. Since a complex seems to be formed, treated materials are free from greasiness often encountered with oil softeners. When the concentration of the condensation product is less than 5%, water-repellency is se-

cured to some degree and softening is still marked.

We claim:

1. The process of rendering cellulosic fabrics water-repellent which comprises impregnating said fabrics with a solution containing between about 5% and about 10% of a condensation product of a fatty acid amide of at least 12 carbon atoms, formaldehyde, and a strongly basic, non-aromatic secondary amine of not more than seven carbon atoms, a small amount of a water-soluble basic catalyst for accelerating the reaction between fabric and condensate, and $\frac{1}{4}$ % to 1% of urea, and heating the impregnated fabrics to a temperature between about 120° C. and about 150° C. to react said fabric with said condensate.

2. The process of rendering cellulosic fabrics water-repellent which comprises impregnating said fabrics with a solution containing $\frac{1}{4}$ % to 1% of urea and between about 5% and about 10% of a condensation product of a fatty acid amide of at least 12 carbon atoms, formaldehyde, and dimethylamine, and heating the impregnated fabric to a temperature between about 120° C. and about 150° C. to react said fabric with said condensate.

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