TREATMENT OF CELLULOSE TEXTILES WITH LONG CHAIN VINYL ETHERS

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12 Claims.

This invention relates to the chemical modification of textile materials and more particularly to the treatment of textile materials to impart thereto a desirable finish or resistance to wetting with water.

This invention has as an object the provision of a process for the fluid treatment of textiles. A further object is the provision of a process for the chemical modification of textiles. Another object is the provision of a process for imparting to textiles a high resistance to wetting with water and aqueous fluids. A still further object is the provision of a process whereby the water resistance is permanent to laundering. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a textile fabric, preferably a cellulosic textile fabric, is impregnated with a vinyl ether of a monohydric alcohol having at least eight carbon atoms in an open chain and the ether baked on the fabric under non-alkaline conditions.

The treatment of textiles to obtain water-repellent effects has been effected in the past in several ways. One type of method is that wherein the textile fabric is impregnated with a material such as paraffin wax.

While improved results are obtained with such processes, one of the best of which is the process disclosed by McQueen and Merril in U. S. Patent 2,947,217, nevertheless these processes suffer from the defect that the waterproofing effect is lost after a sufficient number of launderings.

The present process is of a different type. It depends for its efficiency upon a superficial modification of the fiber surface. This is obtained by impregnating the textile fabric, etc., with an acid material and a long chain vinyl ether, preferably in dilute solution in an inert organic solvent, removing excess solution, drying and heating to obtain the desired effect.

The more detailed practice of the invention is illustrated by the following examples, wherein parts are by weight and temperatures are in centigrade degrees unless otherwise noted.

Example I

Ten pieces of mercerized unfinished broadcloth are steeped in 5% aqueous lactic acid, wrung, and dried. They are then placed in a solution composed of 20 parts of octadecyl vinyl ether and 100 parts of carbon tetrachloride. After a refluxing time of 8 hours, one of the fabrics is removed (Sample A). After a total refluxing time of 21 hours a second fabric (Sample B) is removed. After a total refluxing time of 29 hours a third piece of fabric (Sample C) is removed. After a total refluxing time of 48 hours the last fabric (Sample D) is removed. The fabrics are then washed with hot water. The fabrics are all found to be water-repellent, the degree of repellency increasing with the time of heating with the octadecyl vinyl ether. The fabrics are still water-repellent after two severe launderings. This example illustrates the treatment of cotton fabrics by heating with a solu-
tion of octadecyl vinyl ether in an organic solvent over a considerable period of time.

Example III

A solution is prepared from 30 parts of octadecyl vinyl ether, 180 parts carbon tetrachloride and 1 part acetic anhydride. Four pieces of mercerized cotton broadcloth are placed in this solution and the mixture refluxed. After 5 hours one piece of broadcloth (Sample A) is removed. After a total of 21 hours of refluxing a second piece of fabric (Sample B) is removed. After 29 hours of refluxing a third fabric (Sample C) is removed. After a total refluxing time of 45 hours the remaining fabric (Sample D) is removed. The samples are allowed to dry and are then rinsed with a 0.2% solution of mild soap at 160° F. for 5 minutes. The samples are then washed well with hot water and ironed. All of the fabrics are water-repellent, the degree of repellency increasing up to a 21 hour reaction time and thereafter being constant. After two severe launderings at the boil the fabrics are still quite water-repellent, Sample A, however, being not quite as good as the other three fabrics.

Example IV

Six pieces of broadcloth are steeped in a 5% solution of sodium carbonate and are then wrung to twice the weight of the original fabric and dried at room temperature. The fabrics are next steeped in a solution composed of 5 parts of octadecyl vinyl ether and 95 parts of carbon tetrachloride, wrung to twice the original weight and then allowed to dry at room temperature. Baking is effected as follows:

Sample 1 20 minutes at 120° C.
Sample 2 120 minutes at 120° C.
Sample 3 20 minutes at 150° C.
Sample 4 120 minutes at 150° C.
Sample 5 5 minutes at 170° C.
Sample 6 20 minutes at 170° C.

The fabrics are then rinsed in 0.25% mild soap solution at 160° C. for 5 minutes and then washed well with hot water. The fabrics show only slight repellency in all cases and after being given a severe laundering were found to be badly wet by water.

This example shows the necessity for operating under non-alkaline conditions. The results of this example when compared with the results obtained in Example I show the desirability of acidic conditions.

The long chain vinyl ethers may be made by the reaction of acetylene with a long chain alcohol in the presence of an alkaline catalyst. Thus, acetylene at 200 lbs. per square inch is passed into a mixture of 100 parts of octyl alcohol and 4 parts of sodium hydroxide in a shaker autoclave at 180° C. until the theoretical amount of acetylene is absorbed, which usually takes place in about five hours. The octadecyl vinyl ether is isolated by vacuum distillation, B. P. 176° C. at 2 mm.

To prepare the other ethers the appropriate alcohol, e.g., octyl, dodecyl, myristyl, decyl, etc. is substituted for the octadecyl alcohol.

Example V

Six pieces of cotton broadcloth are steeped in 5% lactic acid, wrung to twice the weight of the dry fabric and dried at room temperature. They are next steeped in a solution composed of 5 parts of cetyl vinyl ether in 95 parts of carbon tetrachloride and wrung to twice the weight of the original fabric and dried by allowing to hang at room temperature. Baking is effected as follows:

Sample 1 20 minutes at 120° C.
Sample 2 120 minutes at 120° C.
Sample 3 20 minutes at 150° C.
Sample 4 120 minutes at 150° C.
Sample 5 5 minutes at 170° C.
Sample 6 20 minutes at 170° C.

The fabrics are rinsed in a 0.25% mild soap solution at 160° F. for 5 minutes, washed with hot water and then ironed. All of the fabrics show good water repellency when tested by placing a drop of water about 1 cm. in diameter on the fabric and allowing the drop to remain for 3 minutes. The repellency of the fabric which has been heated at higher temperatures or for longer times is slightly better than that of the other samples. After subjecting to a severe laundering the samples are still water-repellent.

Example VI

Three sets of fabrics are prepared from mercerized unfinished cotton broadcloth. The first set is steeped in 2% lactic acid, wrung to twice the weight of the original fabric and dried. The second set is steeped in 10% sodium carbonate, wrung to twice the weight of the original fabric and dried. The third set of fabrics is taken from the same bolt as the first two but is not pre-treated. All of the samples are steeped in a solution of 5 parts of dodecyl vinyl ether in 45 parts of benzene, wrung to twice the weight of the original fabric and baked as follows:

One fabric of each series... 5 minutes at 170° C.
One fabric of each series... 20 minutes at 170° C.

The treated fabrics are rinsed in 0.25% mild soap solution at 160° F. for 5 minutes and then washed well with hot water. The samples pretreated with lactic acid are quite water-repellent and the water repellency is not removed by laundering. The fabrics treated with sodium carbonate are not water-repellent. The samples prepared without the use of a catalyst are water-repellent although not to quite as pronounced a degree as the samples treated with lactic acid. The effect is resistant to laundering. The water-repellency exhibited by the samples heated for 5 minutes is about the same as that produced in 20 minutes.

Example VII

(A) Three pieces of unfinished mercerized cotton broadcloth are steeped for 5 minutes in a solution of 4 parts of octadecyl vinyl ether in 96 parts of benzene. The fabrics are wrung until they weigh twice the original weight of the fabric, dried before an electric fan at room temperature and then baked for 5, 10 and 20 minutes at 170° C. After soaking with 0.2% mild soap at 160° F. for 5 minutes, rinsing well with hot water and ironing, the fabrics are found to be very water-repellent. After a severe laundering they are of substantially the same water-repellency. After extraction with benzene for 16 hours in a Soxhlet extractor, the repellency was somewhat diminished but was still good. All three of the fabrics were of about the same degree of repellency, indicating that the 5 minute reaction time was about as effective as a 20 minute reaction time.

(B) Three pieces of unfinished mercerized
cotton broadcloth are impregnated with 5% aqueous lactic acid, wrung until the weight of the impregnated fabric is approximately twice the weight of the dry fabric and then dried at room temperature. The fabrics containing acid are steeped in an octadecyl vinyl ether solution of the same concentration as that described in (A). They are wrung until the impregnated fabrics weigh twice the weight of the original fabric and are then baked for 5, 10, and 20 minutes at 170° C., respectively. They are then rinsed in 0.2% sodium hydroxide for 5 minutes and then rinsed well in hot water and ironed. The fabrics are found to be of excellent water-repellency when tested by placing a drop of water on the fabric for several minutes and noting the tendency to wet the fabric. After a severe laundering with soap and soda ash, the water-repellency is still most excellent. Extraction with benzene overnight in a Soxhlet extractor reduces the repellency somewhat but does not completely remove it.

This example illustrates the treatment of fabrics with octadecyl vinyl ether both with and without acidic materials as catalysts. It also shows the effectiveness of the finish after laundering and extraction with organic solvents.

In carrying out the steeping operation it is generally preferable to avoid the presence of water since this may interfere with the subsequent reaction. If operation is carried out rapidly, however, water may be present, or even lower alcohols. In some cases it is even possible to operate using an aqueous emulsion of the long chain vinyl ether. The concentration of ether in the water is not critical over a wide range. Concentrations as low as 0.1% although they do not give a high degree of water-repellency, give a desirable softness to the fabric. Solutions containing as much as 50% of product may be used where especially pronounced effects are desired. In general, however, the concentration of treating solution will vary between 1 and 15% in order to obtain an economic degree of efficiency.

The steeping temperature is not important but is best maintained at about room temperature, especially when organic solvents are used since this minimizes evaporation and fire hazard. As solvents there may be used practically any material in which the long chain vinyl ether is soluble. Obviously solvents which are quite reactive toward the ether should not be used, and where the term solvent is used in this specification such relatively inert solvents are indicated. In general, materials such as the lower alcohols, chlorinated solvents, ethers, esters, hydrocarbons and ketones are suitable. The steeping time is not important so long as good impregnation is obtained. In most instances it is desirable to remove the excess of treating solution by a wringing operation, since this insures uniformity. However, in some instances it may be desirable simply to remove the fabric from the treating bath and to allow it to dry. Treatment with the agent may also be effected by other methods besides impregnation, such as spraying or padding. Treatment with the agent may also be effected by exposure to vapors of the boiling ether. This is not a desirable procedure, however, because of the danger that the vinyl ether may decompose on standing.

The impregnated fabrics may be dried at room temperature or at elevated temperatures; low temperature drying is preferable where organic solvents are used because this facilitates recovery and reduces the fire hazard. The results obtained also seem somewhat more uniform under these conditions. However, it is permissible to carry out the drying and baking operation in one step. This is desirable where a more rapid operation is necessary. Intermediate temperatures may also be used. The treated fabric may be laundered or rinsed following the treatment if desired, or this treatment may be omitted. It is not important except in certain instances such as where a strong acid catalyst has been used which may degrade the fabric on storage.

The treatment is best carried out in the presence of an acid catalyst although neutral conditions are also suitable. In general, non-alkaline conditions are satisfactory. Representative acid catalysts which may be used are acetic acid, monochloroacetic acid, succinic acid, citric acid, phosphoric acid, ammonium dihydrogen phosphate, cinnamic acid, ammonium chloride, lactic acid, and sodium bisulfite. The fabrics may either be pretreated with the catalyst or the treatment may be dissolved in the treating solution. Pretreatment with catalyst is especially desirable where the treating agent is being applied in the form of an emulsion.

The vinyl ethers which are most suitable for the treatment are those derived from long chain alcohols. In this group are included those products derived from alcohols containing 8 or more carbon atoms. The vinyl ethers, therefore, with which this invention is concerned are the vinyl ethers containing 10 or more carbon atoms. Lower ethers do not appear to give the water-repellent effects with which the invention is primarily concerned. The long chain radical present in the ether may contain substituents such as phenyl or other aromatic radicals or halogen, ether or unsaturated groups which do not interfere with the reaction. In general it may be said that all vinyl ethers of medium - long chain alcohols having at least eight carbon atoms in an open chain which are moderately stable at room temperature may be used since those groups which do not interfere with the stability of the ether also do not interfere with the finishing operation. Examples of suitable vinyl ethers are octadecyl vinyl ether, hexadecyl vinyl ether, dodecyl vinyl ether, octyl vinyl ether, decyl vinyl ether, beta-phenoxycetyl vinyl ether and octadecyloxyethyl vinyl ether. Vinyl oxide substituted higher aliphatic hydrocarbons are preferred.

Although the examples presented for illustration have all been concerned with treatment of cotton fabrics, the treatment is also applicable to other textile materials. These include visco rayon, cuprammonium rayon, regenerated cellulose in general, cellulose rayons such as ethyl cellulose and cellulose acetate, and linen. This group of fabrics is generally known as products of cellulose or vegetable origin. The process is also applicable to textile materials produced from synthetic resins and to products of animal origin such as silk and wool. The textile materials may consist of fibers in loose, woven, spun or other form.

The effect produced depends upon the time of baking. Short baking times give a soft handle of moderate resistance to laundering while longer times give more water repellent effects of better laundry fastness. The optimum time also depends upon the temperature and may be as short as 10 seconds when a moderate waterproofing effect is desired or for a longer time, even up to
several hours, to obtain a more complete waterproofing effect. The reaction is continued at least until a small sample of fabric after light agitation in an 0.2% solution of mild soap for three minutes at 140°F, and thorough rinsing in warm water, is not wet through instantly by the application of a drop of distilled water to the surface. At temperatures of above 90°C, baking times of at least one minute up to about one hour are preferred. Temperatures from 60°C to 205°C are operative, providing the time of treatment is suitably adjusted.

The precise nature of the reaction taking place during treatment of fabrics with long chain vinyl ethers has not been established. It may involve polymerization of the vinyl ether to an insoluble compound which is not easily removed from the fibers or, more probably, reaction of the vinyl ether through the unsaturated groups with reactive groups, e.g., alcohol groups, in the fabric. The fact that the reaction goes best under acid conditions lends support to the theory that reaction with the vinyl group rather than polymerization is involved. We prefer, however, not to commit ourselves upon the nature of the reaction involved.

The principal use which has been found for the invention is in the treatment of fabrics to render them substantially permanently water-repellent. The fabrics are softened to some extent at the same time that they are made water-repellent.

The advantage of this invention lies in the fact that the finish is substantially permanent, i.e., resistant to laundering. The use of long chain vinyl ethers as repellents offers advantage in that they are cheaply and simply made by reaction of long chain alcohols with acetylene, they are soluble in a wide range of solvents which makes them easy to apply to the fabric, and they do not degrade the fabric due to vigorous chemical action as do some products, such as acid anhydrides or acid chlorides. No undesirable by-products are formed during the treatment, as is the case with certain other finishing treatments of this type.

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

We claim:
1. Process which comprises impregnating a cellulose textile material with a monomeric vinyl ether of a monohydric alcohol having an open chain of at least eight carbon atoms and baking the same under non-alkaline conditions until a sample of the fabric after light agitation in a 0.2% solution of mild soap for three minutes at 140°F, and thorough rinsing in warm water is not wet through instantly by the application of a drop of distilled water to the dry surface.
2. Process which comprises impregnating a cellulose textile material with an acid catalyst and a monomeric vinyl ether of a monohydric alcohol having an open chain of at least eight carbon atoms and baking the same until a sample of the fabric after light agitation in a 0.2% solution of mild soap for three minutes at 140°F, and thorough rinsing in warm water is not wet through instantly by the application of a drop of distilled water to the dry surface.
3. Process which comprises impregnating a cellulose textile material with a monomeric vinyl ether of a long chain aliphatic monohydric alco-
rinsing in warm water is not wet through instant-
ly by the application of a drop of distilled water
to the dry surface.

11. A cellulosic textile material of improved
water repellence having impregnated thereon the
product obtained by baking thereon the mono-
meric vinyl ether of dodecanol.

12. A cellulosic textile material of improved
water repellence having impregnated thereon the
product obtained by baking thereon the mono-
meric vinyl ether of hexadecanol.

JULIAN WERNER HILL.
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CERTIFICATE OF CORRECTION.


JULIAN WERNER HILL, ET AL.

It is hereby certified that error appears in the printed specification
of the above numbered patent requiring correction as follows: Page 4, first
column, line 68, claim 2, for the word "is" read --in--; and that the said
Letters Patent should be read with this correction therein that the same
may conform to the record of the case in the Patent Office.
Signed and sealed this 30th day of September, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)