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MANUFACTURE OF WATER-SOLUBLE TEXTILE MATERIALS

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8 Claims. (Cl. 8—116.2)

1

This invention relates to the manufacture of water-soluble textile materials.

According to the invention textile materials which are soluble in cold water are made by uniformly impregnating cellulose textile materials with a concentrated caustic alkali solution, and subjecting the impregnated materials to the action of an etherifying agent under conditions such that the cellulose is wholly converted into a water-soluble cellulose ether without at any time during the operation undergoing solution.

The process of the invention can be used to give products of differing degrees of solubility in water; thus by a suitable choice of etherifying agent and reaction conditions it is possible to make products which are soluble in cold water and insoluble in hot water (i. e., water at a temperature between about 50° C. and the boiling point), or products which are soluble in both cold and hot water.

As the textile starting materials there may be used fibres, yarns, and fabrics of naturally occurring forms of cellulose or of regenerated cellulose. The application of the new process to cotton yarns and fabrics is specially valuable, but very useful products can also be obtained from regenerated cellulose materials, especially materials comprising regenerated cellulose yarns made by stretching and saponifying cellulose acetate yarns or other yarns having a basis of a cellulose ester. For the sake of simplicity the invention will be described in detail by reference to the production of materials which are soluble in cold water but not in hot by methylating cotton materials by means of methyl chloride.

I have found that when cotton fabrics or yarns which have been given only the usual conventional treatments are treated by the process of the invention, using for example methyl chloride as the etherifying agent, it is very difficult to obtain products which are wholly soluble in water. Investigation has shown that the products are in fact very incompletely methylated, and that the reason for this is that the caustic alkali solution has not uniformly and completely impregnated the materials. This in turn is due to the presence in the cotton materials of certain substances, apparently of an oily nature, which effectively prevent the necessary uniform impregnation. I have now found that this difficulty may be overcome by treating the cotton materials with an agent capable of removing these oily substances before bringing the materials into contact with the alkali solution with which they are to be impregnated. In one method of doing this

2

the cotton materials are scoured with an aqueous soap solution. For example the cotton materials may be boiled for between about half an hour and two hours with an aqueous soap solution of concentration less than 1%, for example 0.2 to 0.4%. In another method the cotton materials are boiled under pressure with a dilute caustic alkali solution. For instance, they may be boiled at a temperature above about 150° C., e. g. between 150° and 170° C., with a caustic soda solution of concentration between about 1% and 3%.

After this preliminary treatment, the cotton materials can be uniformly impregnated with the concentrated caustic alkali solution simply by immersion in the solution followed by removal of excess solution. Preferably the concentration of the caustic alkali solution exceeds 35%. Thus cotton yarns, for example, may be passed through a caustic soda solution of concentration of the order of 40% at about 30° C., and then through nip rollers or some other device whereby excess alkali solution is removed. However, as this is a somewhat laborious procedure, it is usually better to impregnate cotton yarns in the form of hanks or of loosely wound packages; thus a number of hanks may be immersed together in the 40% caustic soda solution, and excess solution subsequently removed, for example by centrifuging. Cotton fabrics, which may with advantage be held on a frame, may be impregnated in a similar manner. The amount of 35–40% caustic alkali solution remaining on the cotton materials is preferably such that the materials weigh after impregnation approximately three to four times as much as before.

The impregnated cotton materials are preferably methylated as soon as practicable. For this operation the materials may be introduced into an air-tight reaction vessel, which is then evacuated, after which methyl chloride vapour is fed into the vessel under pressure. After the methyl chloride has been introduced, the temperature in the reaction vessel may be raised above 50° C., and preferably to 70 to 80° C., and the treatment continued for two to five hours. The methylation may be rendered more uniform by employing a rotating reaction vessel. At the end of the reaction unreacted methyl chloride may be removed, for example by distillation, and the treated materials washed several times with hot water, preferably at temperatures exceeding 70° C. The materials may be finally dried, still at a high temperature, for example by means of a current of air heated to about 100° C. Materials so treated, and having a methoxy content of the

order of 30%, are found to have when dry a tenacity not much less than that of the original cotton, but to be soluble in cold water.

In place of methyl chloride there may be used other etherifying agents capable of forming water-soluble cellulose ethers. For example, by treatment with ethylene oxide under conditions similar to those described above, cotton or other cellulose textile materials may be converted into water-soluble hydroxy-ethyl cellulose materials, while under the same conditions acrylonitrile gives water-soluble carboxy-ethyl cellulose materials. By employing two or more etherifying agents mixed ethers may be made. For example, by allowing first acrylonitrile and then methyl chloride to act on the impregnated cellulose materials a mixed carboxy-ethyl methyl ether of cellulose which is soluble in both cold and hot water can be produced. These various ethers may be purified by the same general method as that described for purifying methyl cellulose materials, but the precise mode in which they are washed must, of course, be varied in accordance with their solubilities. For example such carboxy-ethyl cellulose or carboxy-ethyl methyl cellulose materials as are soluble in both cold and hot water may be washed with hot concentrated aqueous alcohol.

When the water-soluble cellulose ether materials are made from fibres, yarns, or fabrics having a basis of regenerated cellulose, the initial scour or alkali boil can be omitted.

When it is desired that textile materials made by the process of the present invention should be dissolved by water particularly rapidly, as for example when the materials are used in mine-laying parachutes, it is advantageous to add to the material a wetting agent. This may be done for example by treating the materials with a solution of the wetting agent in an organic liquid which is not a solvent for the water-soluble ether of cellulose, and removing the organic liquid by evaporation. An example of a suitable wetting agent is pine oil, which may be applied to the materials in solution in benzene.

The new materials are valuable for various purposes. As already indicated, they may be employed in making parachutes for mine-laying and other purposes which are dissolved by sea or river water. Another very useful application of the new materials is in the production of cotton fabrics in which the cotton is practically without twist. For example a cotton yarn having a very low degree of twist may be doubled with a water-soluble yarn having a similar but opposite twist; the resulting yarn is woven into a fabric, and the fabric washed with water to dissolve out the water-soluble yarn. The resulting fabric is composed of cotton yarns which are practically without twist and is very strong; such fabrics are useful, for example, for covering the lifting surfaces of aircraft. Yet another use for the water-soluble yarns is in the manufacture of wire-textile fabrics by the method described in U. S. application S. No. 542,386 filed June 27, 1944, now Patent No. 2,412,562.

The following examples illustrate the invention. Examples 1 and 2 describe the production of yarns which are soluble in cold water but insoluble in hot.

Example 1

A singles 30 count low twist cotton yarn in hank form is boiled for an hour in a 0.25% soap solution, and is then immersed in a 38.5% solution of sodium hydroxide at 32° C. for 30 minutes, the alkali solution being gently stirred at intervals. The cotton is then removed from the alkali solution, drained, and centrifuged for a few minutes.

The alkali-impregnated cotton is transferred to a reaction vessel capable of being rotated about a horizontal axis, and the vessel is evacuated. Methyl chloride is fed into the vessel to a pressure of about 220 lbs./square inch; the vessel is then slowly rotated, and its temperature raised to 75° C.

After three hours the rotation of the vessel is stopped, and unreacted methyl chloride removed by distillation. The hanks are then removed from the vessel and repeatedly washed with water at 70° C.–80° C. until free from alkali. They are then centrifuged to remove the greater part of the water, and are finally dried in a current of air at 100° C.

The product is a slightly brown yarn having a dry tenacity not very much less than the original cotton, but no tenacity at all when wet. The yarn is completely soluble in cold water. Owing to its substantial dry tenacity and other properties the yarn may be worked up into fabrics by knitting or weaving. If the slight colour is a disadvantage, it may be removed by washing the yarn in hot 0.5% sulphuric acid.

Example 2

A singles 30 count low twist cotton yarn is kier-boiled at 160° C. with a 1.6% solution of sodium hydroxide for four hours, and is then impregnated with alkali and methylated with methyl chloride by the method described in Example 1. The final product is similar to that obtained by the method of Example 1, its dry tenacity being slightly higher, though still a little below the dry tenacity of the original yarn, and its wet tenacity again being zero. The yarn is soluble in cold water.

If the alkali impregnation and methylating treatment described in these examples are not preceded by an initial treatment with a soap solution or an alkali solution, a product is obtained which has a low methoxy content, usually about 5%, and is for the most part insoluble in cold water.

Examples 3 and 4 describe the production of fabrics which are soluble in both cold and hot water.

Example 3

A regenerated cellulose fabric, woven from yarn made by stretching and saponifying cellulose acetate yarn, is held on a metal frame and impregnated with a 40% medium hydroxide solution.

The fabric, still held on the frame, is inserted into a reaction vessel capable of being rotated about a horizontal axis, and the reaction vessel is evacuated. Acrylonitrile is then introduced in amount about 4.5 times the original dry weight of the fabric, and the vessel is slowly rotated. The reaction is allowed to proceed at room temperature for 16 hours. Unreacted acrylonitrile is then removed by distillation under low pressure, and the fabric which has become soluble in cold and hot water, is washed with methylated spirits until free from alkali.

It is is desired to treat a cotton fabric or yarn by the process of this example, it should first be given a scour with a soap solution, or be kier-boiled, for instance as described in Examples 1 and 2.

Example 4

A regenerated cellulose fabric, or a scoured or kier-boiled cotton fabric, is impregnated with a 40% sodium hydroxide solution and etherified with acrylonitrile as described in Example 3. At the end of the 16 hours' treatment with the acrylonitrile the reaction vessel is evacuated, and methyl chloride introduced to a pressure of 50 lbs./square inch. The temperature is raised to 70° C. for 45 minutes, and then allowed to fall to room temperature. The reaction with the methyl chloride is allowed to continue for 19 hours in all. During the whole of the treatment with the acrylonitrile and methyl chloride the reaction vessel is slowly rotated. At the end of the treatment unchanged methyl chloride is removed by distillation and the fabric washed with methylated spirits. It is soluble in both hot and cold water.

Example 5

A solution of pine oil in benzene is applied to a methyl cellulose or other cellulose ether yarn or fabric obtained by the method of any of the preceding examples, and the benzene allowed to evaporate at room temperature. After this treatment the yarn is yet more quickly dissolved by cold water.

Having described my invention, what I desire to secure by Letters Patent is:

1. Process for the manufacture of textile fabrics having a relatively high tenacity when dry but capable of being dissolved by water, which comprises impregnating a cellulose fabric with a caustic alkali solution of concentration at least 35%, removing excess alkali solution until the fabric retains 2 to 3 times its original weight of the alkali solution and, without allowing the alkalized cellulose material to age, subjecting it first to the action of acrylonitrile at about room temperature and then to the action of methyl chloride at a temperature above 50° C.

2. Process for the manufacture of textile fabrics having a relatively high tenacity when dry but capable of being dissolved by water, which comprises scouring a cotton fabric with a boiling aqueous soap solution, impregnating the scoured fabric with a coustic alkali solution of concentration at least 35%, removing excess alkali solution until the fabric retains 2 to 3 times its weight, after scouring, of the alkali solution and, without allowing the alkalized cotton material to age, subjecting it first to the action of acrylonitrile at about room temperature and then to the action of methyl chloride at a temperature above 50° C.

3. Process for the manufacture of textile fabrics having a relatively high tenacity when dry but capable of being dissolved by water, which comprises boiling a cotton fabric under pressure with a caustic alkali solution of concentration less than 3%, impregnating the boiled fabric with a caustic alkali solution of concentration at least 35%, removing excess alkali solution until the fabric retains 2 to 3 times its weight, after boiling, of the alkali solution and, without allowing the alkalized cotton material to age, subjecting it first to the action of acrylonitrile at about room temperature and then to the action of methyl chloride at a temperature above 50° C.

4. Process for the manufacture of textile fabrics having a relatively high tenacity when dry, but capable of being dissolved by cold and hot water, which comprises impregnating a cellulose fabric with a caustic alkali solution of concentration at least 35%, removing excess alkali solution until the fabric retains 2 to 3 times its original weight of the alkali solution and, without allowing the alkalized cellulose material to age, subjecting it first to the action of acrylonitrile for a number of hours at about room temperature and then to the action of methyl chloride at a temperature above 50° C. for at least 45 minutes.

5. Process according to claim 1, wherein a solution of a wetting agent in an organic solvent is applied to the treated fabric and the solvent is removed by evaporation.

6. Process according to claim 2, wherein a solution of pine oil in benzene is applied to the treated fabric and the benzene is removed by evaporation.

7. Process according to claim 3, wherein a solution of pine oil in benzene is applied to the treated fabric and the benzene is removed by evaporation.

8. Process according to claim 4, wherein a solution of a wetting agent in an organic solvent is applied to the treated fabric and the solvent removed by evaporation.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
362,318	Scheppers et al.	May 3, 1887
1,741,637	Lilienfeld	Dec. 31, 1929
1,800,944	Lilienfeld	Apr. 14, 1931
1,863,208	Shorgel	June 14, 1932
1,955,582	Golding	Apr. 17, 1934
2,098,335	Dreyfus	Nov. 9, 1937
2,101,262	Maxwell	Dec. 7, 1937
2,101,263	Maxwell	Dec. 7, 1937
2,131,733	Haskins	Oct. 4, 1938
2,141,729	Thompson	Dec. 27, 1938
2,160,782	Maasberg	May 30, 1939
2,264,229	Wallach	Nov. 25, 1941
2,289,039	Reichel	July 7, 1942

FOREIGN PATENTS

Number	Country	Date
550,525	Great Britain	Jan. 13, 1943
478,259	Great Britain	Jan. 17, 1938
518,225	Great Britain	Feb. 21, 1940

OTHER REFERENCES

Lenher: Use of Wetting Agents—Text. Colorist, April 1941; pages 265–267.

I & Chem., January 1941, Surface-Active Agents—pages 18–20.

Certificate of Correction

Patent No. 2,439,865. April 20, 1948.

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It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 4, line 57, for the word "medium" read *sodium*; column 5, line 48, for "coustic" read *caustic*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of June, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.