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CELLULOSIC TEXTILES REACTED WITH UREA - VINYL SULFONE ADDITION PRODUCTS

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This invention relates to the finishing of textile materials. More particularly the invention relates to the coating or impregnating of textile materials, such as yarns, filaments, fibers, fabrics, and the like, whether natural, artificial, or synthetic, with addition products formed by reacting an amine with a sulfone-activated ethylenic compound, i. e., compounds having ethylenic (C=C) linkages which are activated by a sulfone ($-SO_2-$) group adjacent said ethylenic linkages, in order to enhance the water retentive and wet elongation properties of the textile materials, as well as to stabilize such materials against repeated washings and to set crimp therein when the textile materials are, or are formed from, crimped fibers.

While the present invention is applicable to the treatment or finishing of yarns, filaments, fibers, fabrics, and the like, whether natural, cellulosic, artificial, or synthetic, for purposes of illustration the same will be described as it is applicable to the treatment of rayon yarns, etc., formed by the regeneration of cellulose from viscose solutions in conventional manner, it being understood that the invention is only to be limited as the same is defined in the appended claims. "Cellulosic" as used herein is intended to include regenerated cellulose, and cellulose derivatives, such as cellulose esters and ethers, for example, nitrocellulose, cellulose acetate, ethyl cellulose, hydroxy ethyl cellulose, which contain a reactive hydroxyl group.

It is well known to impregnate rayon with many types of compounds that form resins, for various and sundry purposes. These resins, however, are simply deposited in the base material and do not react with the constituents of the material. This is evidenced by the fact that such resins may be dissolved out of the material by their usual solvents, for example, alcohol, or a mixture of alcohol and benzene. The general type of resins that have been employed in the past are those derived from condensation products of phenol, urea and the like with formaldehyde. However, in these types of resins, the polymerization process proceeds so rapidly that a compound formation with the base material, such as cellulose, cannot take place and therefore the resins do not react with the cellulose.

Workers in the rayon industry are continually striving to find improved ways to reduce the water retentive property of rayon as well as to stabilize fabrics formed therefrom against repeated washing and to find some improved means to set the crimp in textile materials. Various

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means have been proposed such as numerous impregnating agents, coating agents, and the like. While these agents have accomplished their purpose to a certain extent, they have not proved entirely satisfactory and there still is room for improvement.

It is an object of the present invention to provide a method of treating textile materials whereby the water retentive property of the same is greatly reduced.

It is another object of the invention to provide a method of treating textile materials whereby the same are stabilized against repeated washing.

It is another object of the invention to provide a method of treating textile materials comprising crimped fibers whereby the crimp therein is set.

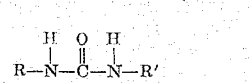
It is another object of the invention to impregnate yarns, fibers, filaments, fabrics, and the like, whether natural, cellulosic, artificial, or synthetic, with a polymerizable compound formed by the reaction of urea and a sulfone activated ethylenic compound.

It is another object of the present invention to treat cellulosic textile materials with a resin forming compound which will react with the cellulose contained therein.

Other objects and advantages of the present invention will be obvious from the following description of the same which is merely intended to be illustrative and not limitative.

In general, the objects of the present invention are accomplished by immersing the textile material to be treated in an aqueous bath of a resin forming material, formed by the reaction of urea with a sulfone-activated ethylenic compound, removing the excess solution, and then heating the impregnated textile material to dry the same and to cure or polymerize the resin forming material or addition product therein. The preparation of the resin forming materials and addition products within the purview of the instant invention are described in my copending application S. N. 177,344, filed August 2, 1950, entitled "Addition Products of an Amine and Sulfone-Activated Ethylenic Compounds."

The addition products suitable for use in the present invention are those having the general formula:



where R represents the radical derived from a monomeric sulfonyl chemical having from one to two intermediate sulfonyl radicals, each linked

to a terminal vinyl group or a hydrocarbon substituted vinyl group and R' may be either the same as R or hydrogen.

When compounds represented by the above general formula are polymerized, it is believed that the addition products have the general formula:



where R is the same as above described and m is an integer of variable value according to the degree of polymerization.

Compounds having the above general formulas are formed by reacting urea with a sulfone-activated ethylenic compound, the following list of which is representative:

Di-vinyl sulfone (vinyl sulfone)

$CH_2{=}CHSO_2CH{=}CH_2$

Isopropenyl sulfone



Propenyl sulfone

$(CH_3CH{=}CH{-})_2SO_2$

1,2-bis (vinyl sulfonyl) ethane

$CH_2{=}CHSO_2CH_2CH_2SO_2CH{=}CH_2$

1,4-bis (vinyl sulfonyl) butane

$CH_2{=}CHSO_2(CH_2)_4SO_2CH{=}CH_2$

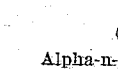
Bis (vinyl sulfonyl) methane

$(CH_2{=}CHSO_2)_2CH_2$

Styryl sulfone

$(C_6H_5CH{=}CH)_2SO_2$

Alpha-ethyl vinyl sulfone



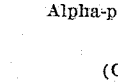
Alpha-n-propyl vinyl sulfone



1-butenyl sulfone

$(C_2H_5CH{=}CH)_2SO_2$

Alpha-phenyl vinyl sulfone



Bis (beta,beta'-vinyl sulfonyl) ethyl ether

$(CH_2{=}CHSO_2CH_2CH_2)_2O$

Yarns, fabrics, etc., to be treated are immersed in an aqueous solution of the resin forming compound of approximately 2 to 10% concentration at room temperature, or higher if desired, until thoroughly wet. Aqueous solution is intended to include solutions of dioxane, Carbitols, and the like, with water in the ratio of 80 parts to 20 parts, and 50:50. Preferably, a catalyst is added to the solution just prior to application in order to facilitate polymerization of the compound when the rayon or other textile material is heated. Suitable catalysts for the polymerization reaction are any base or alkali which is unreactive with the resin, for example, there may be employed quaternary ammonium hydroxides, the alkali and alkaline earth metals, their oxides, hydrides, and carbonates, such as sodium hydroxide, sodium ethoxide, sodium hydride, phenyl lithium, potassium carbonate, metallic sodium, barium, calcium, etc., trimethyl benzyl ammonium hydroxide, tetramethyl ammonium hydroxide, and the like, etc. The amount of catalyst necessary is small, e. g. .001–1% or more.

The excess solution is removed in any convenient manner and the impregnated material is then heated at a temperature within the range of 75–200° C. for a period, such as of 30 minutes or greater, depending upon the degree of polymerization desired. Products treated in such a manner show a decrease in water retention of approximately 50–60%. In addition, the products are stabilized against repeated washing and the crimp is set when the products comprise crimped fibers. "Water retention" as used herein is defined as the percentage of water retained by the fiber or other textile material after centrifuging under standard conditions and is based on the conditioned weight of the material.

The treating solution may be applied to the textile material in any of several ways. Staple fibers may be dipped in the solution and squeezed or centrifuged to remove excess solution. Yarn may be passed continuously through the solution or it may be dipped in skein form in the solution and then squeezed or centrifuged to remove excess solution. Flat fabrics may be passed through the solution or the solution may be applied from rolls or by spraying and the excess may be removed by squeezing between rolls, passing between wiper or doctor blades, or the like, or by vacuum extracting. Articles, as of clothing, may be dipped in the solution or sprayed. Fabrics or articles of clothing may be treated locally by spraying.

Resin forming compound solutions of the present invention are stable under ordinary conditions up to 5% for periods of one week or more. It should be pointed out, however, that solutions to which a catalyst has been added, for example sodium hydroxide, are stable for periods of 30 minutes to one hour. Therefore, application of the solution to a textile material should preferably be carried out upon addition of the catalyst to the solution. If desired, the material to be treated may be first treated or impregnated with the catalyst prior to application of the resin forming solution. In this case, however, care must be taken that the catalyst chosen is not one which will injure the particular textile material to be treated. It should be further pointed out that attempts to neutralize the catalyst in the resin forming solution will yield an unreactive resin, i. e. one which will not react with the cellulose to be impregnated.

In addition to the resin forming compound having the above general formula, the sulfones when used alone are useful for treating textile materials to stabilize the same against repeated washing and to set the crimp therein. Divinyl sulfone is particularly useful in this respect. The procedure is essentially the same as that hereinbefore outlined. However, due to the lachrymatory and vesicant properties of divinyl sulfone, necessary precautionary measures must be taken when using the same in order to protect the workers against poisoning. Therefore, while the sulfones alone produce the desired results, it is preferred to employ the above-named resin forming compounds which have greatly reduced or negligible lachrymatory properties.

As illustrative of the present invention, the following examples are given but it should be understood that the invention is not to be limited thereby.

EXAMPLE I

The resin forming compound in this case was prepared by reacting 2 mols of divinyl sulfone with one mol of urea by adding the former very slowly to a 25% aqueous solution of urea containing 0.38% by weight of sodium hydroxide. The reaction temperature was maintained at 20°

C. The resultant resin forming compound solution was then diluted in 3 parts to yield 3, 5, and 7% solutions. Into each of these solutions was immersed 300 denier/80 filament regular bright viscose rayon yarn in the form of skeins for a period of approximately 30 seconds, the solutions being maintained at room temperature. The skeins of yarn were removed from the solutions and the excess solution removed by centrifuging. The skeins were dried at 100° C. and then cured at 150° C. for a period of 30 minutes. The scoured or impregnated skeins were then tested and compared to a control, i. e. the same type viscose rayon yarn without the resin treatment, with the following results:

Table No. 1

Percent Resin Conc.	Percent Water Retention	Tensile (gms./denier)		Percent Elongation	
		Dry	Wet	Dry	Wet
0—Control	85	2.3	1.3	19.9	27.8
3	58	2.3	1.3	17.9	19.4
5	51	2.2	1.3	15.2	14.9
7	44	2.3	1.3	13.2	13.7

Thus by treating the rayon with the resin the water retention of the yarn is greatly decreased without affecting the tensile strength to any appreciable extent.

EXAMPLE II

In this case divinyl sulfone was added to a 50% aqueous solution of urea, in equimolar proportions. After addition was complete, the solution was refluxed for one hour under 760 mm. pressure. The solution was then allowed to cool and divided into 4 portions, two of which were diluted to contain 5% resin and two to contain 10% resin. Each of the four solutions was catalyzed by the addition of 0.25% sodium hydroxide. 300 denier/80 filament regular bright viscose rayon yarn, in the form of skeins, was immersed in each of the solutions for a period of approximately 30 seconds, the solutions being maintained at room temperature. Upon removal of the yarn the excess solution was removed by passing the yarn through squeeze rolls. The yarn that had been treated with a 5% solution and a 10% solution was dried at 100° C. and yarn treated with 5 and 10% resin solutions was dried at 100° C. and then cured at 150° C. for approximately 30 minutes. The treated yarn was tested with the following results:

Table No. II

Percent Resin	Process	Percent Water Retention	Tensile (gms./denier)		Percent Elongation	
			Dry	Wet	Dry	Wet
0	Control	80	2.5	1.4	20.7	29.1
5	Dry @ 100° C.	58	2.0	1.4	13.8	15.1
5	Cure @ 150° C.	48.2	2.1	1.4	14.7	15.4
10	Dry @ 100° C.	45.5	2.3	1.6	14.1	14.4
10	Cure @ 150° C.	38.2	2.3	1.5	14.7	14.6

Again the water retention was greatly reduced with no appreciable effect on tensile strength. An increase in concentration of resin plus curing of the same after impregnation gave the best results.

Similar tests to the above were run using isopropenyl sulfone and propenyl sulfone. In all cases the results were comparable with those given in Tables I and II. There was an appreciable reduction of the percentage water retention without hindering the tensile strength.

EXAMPLE III

The procedure outlined in the above examples was essentially followed in impregnating crimped viscose rayon tow with an aqueous 3% solution of divinyl sulfone. The dry tow had been previously wound on stainless steel spools. The spooled tow was centrifuged and then immersed in an aqueous solution of 2% NaOH plus 20% NaCl for 30 seconds and then centrifuged again. After 30 minutes the tow was washed in water and dryed. Tow serving as a control was wound on a stainless steel spool with the same tension on the treated tow.

A 10 inch length of tow from both the treated and control was mounted between two clamps with a very low tension. The tow was wetted and then loaded with a 25 gram weight. The tow was then permitted to dry at the extended length and then finally released from the clamps, rewetted and dryed while in a relaxed state. Individual filaments were removed from the treated and untreated tow at various steps to observe change in crimp. The treated filaments remained as well crimped as the unstretched filaments while the untreated filaments had practically no crimp left at all. This is believed to be due in part to the reaction which takes place between the cellulose and divinyl sulfone.

The concentration of the divinyl sulfone may be varied between 2 and 10%.

The treatment with divinyl sulfone and the like may take place on the filaments, fibers, or the fiber or filament tow, or the material may be treated after being spun into a yarn or woven or knit into a fabric. The same is true when employing the resin forming compounds, such as the reaction product of urea and divinyl sulfone.

By means of the present invention, it is possible to produce textile articles which have a greater drying rate due to the fact the yarn, from which the article is made, will take up or retain less water after washing. There will be less swelling of the yarn thus alleviating a great deal of the distortion in fabricated articles after washing. The cellulose reacts with the resin hence the latter is not removed from the textile material upon repeated washing. Crimped fibers or filaments, yarns, fabrics, etc., when treated in accordance with the present invention, have their crimp set. Numerous other advantages will be obvious to those skilled in the art.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. A cellulosic textile material produced by the process of claim 2, thereby having its water retention and the difference between its dry and wet extensibilities reduced.

2. A method for treating a cellulosic textile material which contains a reactive hydroxyl group to reduce the water retention and difference in dry and wet extensibility thereof comprising treating said cellulosic textile material with an aqueous solution of a resin-forming addition product of one mol of urea and one to two mols of a monomeric sulfonyl compound having from one to two intermediate sulfonyl radicals, each of said radicals being linked to a terminal group selected from the class consisting of vinyl and mono-hydrocarbon-substituted vinyl, and then

heating the treated material in the presence of an alkaline catalyst at a temperature in the range of 75° to 200° C. to dry it and to polymerize the resin-forming compound in situ.

3. The method of claim 2 wherein the aqueous solution contains an alkaline catalyst comprising sodium hydroxide.

4. The method of claim 3 wherein the aqueous solution contains about 2 to 10% of the resin-forming compound.

5. The method of claim 4 wherein the textile material is regenerated cellulose.

6. A cellulosic textile material produced by the process of claim 5, thereby having its water retention and the difference between its dry and wet extensibilities reduced.

7. A method for treating regenerated cellulose to reduce the water retention thereof comprising impregnating the regenerated cellulose with an aqueous 2 to 10% solution of a resin-forming compound having the formula $(CH_3CH{=}CHSO_2CH_2CH_2CH_2NH)_2C{=}O$, said solution containing 0.001 to 1.0% sodium hydroxide, then drying the impregnated regenerated cellulose and heating the dried regenerated cellulose at a temperature of 75° to 200° C. to cure the resin thereon.

8. A cellulosic textile material produced by the process of claim 7, thereby having its water retention and the difference between its dry and wet extensibilities reduced.

9. A method for treating regenerated cellulose textile materials to reduce the water retention thereof comprising impregnating the regenerated cellulose with an aqueous 2 to 10% solution of a resin-forming compound having the formula $(CH_2{=}CHSO_2CH_2CH_2NH)_2C{=}O$, said solution containing 0.001 to 1.0% sodium hydroxide, then drying the impregnated regenerated cellulose and heating the dried regenerated cellulose at a temperature of 75° to 200° C. to cure the resin thereon.

10. A cellulosic textile material produced by the process of claim 9, thereby having its water retention and the difference between its dry and wet extensibilities reduced.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,867,035	Stocker	July 12, 1932
2,208,632	Dreyfus	July 23, 1940
2,390,253	Henke	Dec. 4, 1945
2,524,399	Schoene et al.	Oct. 3, 1950

FOREIGN PATENTS

Number	Country	Date
865,455	France	Feb. 24, 1941