United States Patent Office 3,124,414 Patented Mar. 10, 1964

3,124,414

TEXTILE FINISHING PROCESS

Hans Dolmetsch, Siegburg, Germany, assignor to Phrix-Werke Aktiengesellschaft, Hamburg, Germany

No Drawing. Filed Feb. 2, 1960, Ser. No. 6,097
Claims priority, application Germany Feb. 11, 1959
10 Claims. (Cl. 8—116.2)

This invention relates to a process for finishing cellulosic materials. More particularly, the present invention is concerned with a process for finishing filaments, fibers, threads and fabrics derived from native or regenerated cellulose by treating the material to be finished with a substance containing at least one N=C— halogen group.

It is well known to prepare cellulose derivatives by contacting reactive cellulose, such as cellulose pretreated with strong alkali, with a substance containing one or more N=C— halogen groups, e.g. cyanuric chloride or cyanuric bromide. The cellulose derivatives thus obtained can be further reacted if desired with a compound containing a replaceable hydrogen atom attached to nitrogen, oxygen or sulfur, such as a primary or secondary amine. It has also been proposed to react esterified or etherified cellulose with a substance containing at least one N=C— halogen group in the presence of a tertiary base.

The known finishing processes involving a reaction of alkali cellulose, acyl cellulose or alkyl cellulose with a substance containing at least one N=C— halogen group and resulting in a substitution of cyanuric acid groups for the hydroxyl groups of the cellulose, are carried out in order to render the cellulose inert to direct cellulose dyestuffs and to impart to it an affinity for basic dyestuffs or—upon further reaction with amines—acid dyestuffs. These processes necessitate a pretreatment of the cellulose with a strong alkali or an esterification or etherification of the cellulose prior to the reaction with the N=C— halogen compound. Another condition for these finishing processes is the use of a large quantity of the modifying substance, e.g. cyanuric chloride, said quantity amounting to at least half of the quantity of the cellulose to be treated. The prior art finishing processes are conducted in an organic solvent and require a considerable amount of time, the duration of the reaction being in the order of several hours. Moreover, the above finishing processes result in a considerable deterioration of the mechanical strength of the fibrous material treated, the loss in strength amounting frequently to as much as 12 to 26% of the original strength of the cellulose fibers subjected to the reaction with the cyanuric halide.

It is a primary object of the present invention to provide a process for finishing cellulose in the form of fibers, fabrics and the like so as to decrease its water absorption and to increase its resistance to scouring.

Another object of the present invention is to provide a process for reacting cellulose with a substance containing at least one N=C— halogen group, e.g. cyanuric chloride, which can be effected in an aqueous medium and proceeds at a high rate.

A further object of the present invention is to provide a process for preparing cellulose derivatives from native and regenerated cellulose in the form of fibers, fabrics and the like which is not accompanied with a substantial loss in mechanical strength of the fibrous material.

Still further objects will appear hereinafter.

With the above objects in view, the present invention provides a process for finishing cellulosic materials which comprises treating the material for a short period of time with a dispersion of a compound containing at least one N=C— halogen group, said dispersion having a pH within the range of about 7 to about 10; drying the material thus treated; and subjecting the material to a heat treatment at a temperature above 100° C.

A preferred embodiment of the process of this invention involves treating a fibrous material derived from cellulose with an aqueous dispersion of a compound containing at least one N=C— halogen group at a temperature between about 15° and about 60° C. for a period of about 1 to about 30 minutes, preferably for about 5 minutes, the pH of said dispersion being kept within the range of about 7 to about 10, preferably at about 8, said dispersion containing about 10 g. to about 100 g., preferably about 30 g. to about 60 g. of said compound per 1 kg. of cellulose; drying the fibrous material thus treated; and subjecting the dried material to a heat treatment at a temperature above 100° C., preferably at a temperature between about 110° and about 120° C.

The process of the present invention is applicable to filaments, fibers, threads and fabrics derived from native or regenerated cellulose. The fibrous material subjected to the process of this invention may be dry or wet. As distinguished from the prior art finishing processes, the process of the present invention does not necessitate a pretreatment of the fibrous material with alkali or an esterification or etherification of the cellulose prior to the reaction with the N=C— halogen groups.

In order to achieve a nearly complete substitution of cyanuric acid radicals for the hydroxyl groups of the cellulose, the known finishing processes serving to make the cellulose immune to direct dyestuffs use strong alkali, a long reaction time and generally high temperatures. In other words, the known finishing processes involving a treatment with a cyanuric halide are conducted under conditions which ensure a rapid replacement of the halogen atoms of the heterocyclic reagent, e.g. cyanuric chloride, so that reactive halogen is left over only if an excess of the cyanuric halide is applied.

In contrast thereto, the process of the present invention is distinguished by the application of a very small amount of the N=C— halogen-containing finishing agent, which however is utilized to the maximum extent. After a short treatment with a dilute aqueous dispersion of the finishing agent, e.g. cyanuric chloride, the heating of the reaction product at a temperature above 100° C. results in cross-linking of the hydroxyl groups of the cellulose. Before the cross-linking reaction is initiated by heating, a maximum of unsaponified, reactive halogen atoms is available since under the conditions of the first step only a small number of halogen atoms is split off.

As indicated above, the process of this invention makes it possible to substantially decrease the water absorption and to considerably increase the resistance to scouring of the fibrous material treated. This desirable result can be obtained without an adverse effect on the tensile strength and elongation values. As compared with the known hardening of cellulose fabrics with formaldehyde and the finishing methods involving the incorporation of urea- or melamine-formaldehyde resins, the process of the present invention has the advantage that the fibrous material subjected thereto does not become brittle. The process of this invention also avoids the known difficulties caused by an uneven distribution of the condensation resins, which are not directly absorbed from the bath.

As distinguished from such resins, cyanuric halides and similar heterocyclic compounds are easily attached to cellulose in an alkaline medium. Accordingly, the N=C— halogen compound contained in the finishing bath is distributed evenly over the fibrous material in the process of the present invention.

The process of this invention permits to react the finishing agent containing at least one N=C— halogen

group with other reactive compounds after or before the former is coupled to the cellulose. In this manner, it is possible to impart certain desired properties to the fibrous material. The reactive compound attached to the finishing agent may undergo a cross-linking reaction either with the cellulose or with itself.

By way of example, a fibrous material derived from cellulose which has been treated with a cyanuric-halide may be reacted with an amino compound, such as urea, melamine and aliphatic amine or the like, said amino compound being present either in the same bath as the N=C— halogen finishing agent or in a subsequent bath, whereupon the material is heated at a temperature above 100° C. Thus, it is possible to accomplish a very high improvement of the resistance to scouring while at the same time bringing about a sufficient decrease in the swelling number. It is also possible to introduce hydrophobic groups into the cellulose molecule by reacting the cyanuric ring attached to the cellulose with a long-chain aliphatic amine, such as heptyl amine, oleyl amine, stearyl amine, etc.

In accordance with another embodiment of the present invention, the fibrous material reacted with a dispersion of the finishing agent containing at least one N=C— halogen group, e.g. cyanuric chloride, and with an organic amino compound, e.g. urea, is treated also with the solution of an aldehyde, such as formaldehyde or glyoxal. Subsequently, the material is dried and heated at an elevated temperature. In this embodiment of the invention, the amino compound is linked to the cellulose by means of a cyanuric halide whereupon the desired cross-linking reaction is brought about by an acid aldehyde condensation in the absence or in the presence of a suitable catalyst such as ammonium biphosphate. Such a treatment results in an extremely large decrease in the swelling number coupled with a manifold increase in the scouring resistance. Furthermore, this process permits a saving of the N=C— halogen group-containing finishing agent. The nitrogen-containing bodies go on the cellulose like a direct dye-stuff while the pressing-off difficulties encountered in the impregnation with these substances are avoided. Finally, the cross-linking reaction prevents the fibrous material from becoming brittle.

It is also within the purview of this invention to react an amino compound, such as urea, melamine, an aliphatic amine, and the like, with a cyanuric halide in an aqueous alkaline medium to thereby form a reaction product. The fibrous material to be finished is then placed in a bath containing this reaction product whereupon the fibrous material is dried and heated to a temperature above 100° C. In this embodiment of the present invention, previously prepared reaction products of a cyanuric halide with suitable compounds are attached to the cellulose by means of one or more free halogen atoms still contained therein.

The finishing agents of the present invention are heterocyclic compounds containing one or more N=C— halogen groups. Representative examples of these compounds are cyanuric chloride, cyanuric bromide and other members of the triazine series having at least one reactive halogen atom.

The finishing agent is applied in an aqueous dispersion and the fibrous material to be subjected to the treatment with the finishing agent may be dry or wet (as obtained from a spinning bath).

It is advisable to carry out the treatment with the aqueous dispersion of the finishing agent at a temperature not substantially higher than 60° C. since otherwise the finishing agent may decompose. On the other hand, the reaction is too slow for commercial operation at low temperatures. It is therefore preferred to effect the finishing treatment at a temperature ranging from about 15° to about 60° C.

Within the preferred temperature range, an increase in the temperature of the treating bath results in a considerable acceleration of the reaction. As the temperautre rises, the cross-linking reaction of the OH groups of the cellulose concentrates more and more on the periphery of the fiber. By varying the temperature of the finishing bath, it is therefore possible to produce either a fiber evenly cross-linked over its entire cross-section or a fiber cross-linked only in the outer layer.

In a preferred embodiment of the present invention a buffer substance such as borax is added to the aqueous dispersion of the finishing agent in order to prevent the pH of the bath from falling below 7 on account of the hydrohalic acid formed in the reaction. An alkaline buffer substance, e.g. borax, is preferably present also during the final heat treatment carried out to promote the condensation reaction since otherwise the hydroxyl groups of the cellulose will not react satisfactorily. This applies to all finishing operations in accordance with the present invention except where the cyanuric halide-containing reaction product of the first step is further reacted prior to drying with such compounds as urea or an organic amine. The condition of having a buffer substance present during the heat treatment is met if the fibrous material treated with the aqueous dispersion containing the finishing agent and the buffer substance is not washed before drying. However, the fibrous material may be freed from excess finishing liquor by presiding or flinging if desired.

While the fibrous material recovered from the bath may be dried without a preceding removal of the bulk of the finishing dispersion adhering thereto, the drying time may be shortened by pressing or flinging the treated material so as to free it from excess liquor. After the drying step, the fibrous material is heated at a temperature above 100° C. It is preferred to conduct the heat treatment between about 110° and about 120° C. but temperatures up to 160° C. with correspondingly shorter heating periods may be used if desired.

The following examples further illustrate the present invention without in any way limiting it.

Example 1

1 kg. of staple rayon (Zellwolle) is treated at 20° C. for a period of 5 minutes with the 20-fold amount of a 2% aqueous borax solution containing 60 g. of cyanuric chloride dispersed therein. It is also possible to recycle the borax solution and to contact it with the corresponding amount of cyanuric chloride separated therefrom by means of a filter.

The cyanuric chloride is absorbed completely by the cellulose fibers from the bath having a pH of about 8 during the indicated period. The fibrous material is then taken out of the bath and liquor adhering to its surface is removed by pressing or flinging. Thereupon the material is dried as usual without washing and heated at about 120° C. for about 30 minutes.

The fibers thus finished are insoluble in cellulose solvents, nearly incapable of swelling and have the following characteristics.

Sample	Swelling Value	Resistance to Scouring T./m. (1.5 thread, km.)	Tensile Strength, g./den.	Elongation (wet) percent
Control (untreated) Finished Staple Rayon	94	184	2.5	21.6
	68	4,300	2.6	20.8

Example 2

In order to provide spun rayon fibers with an external layer insoluble in cellulose solvents, the procedure of Example 1 is repeated except that the temperature of the bath is kept between 40° and 50° C.

Example 3

A staple rayon fabric is finished by the procedure described in Example 1. As a result, the fabric becomes

insoluble in cellulose solvents. The swelling value of the fabric falls from 90% to 78% while its resistance to scouring rises from 285 to 940. The tensile strength and the elongation values of the threads remain practically unchanged.

Example 4

1 kg. of freshly spun desulfurized staple rayon (still moist) is treated at 20° C. for a period of 5 minutes with the 20-fold quantity of a 2% aqueous solution of borax containing 60 g. of cyanuric chloride dispersed therein. The fibrous material is removed from the bath and freed from excess liquor by pressing or flinging. Then the material is dried without being washed and heated at 120° for about 30 minutes.

The treatment with cyanuric chloride can be followed immediately by an impregnation in a brightening bath containing 2% borax, a fatty alcohol sulfate or the like. After the impregnation, the material is dried and heated at an elevated temperature.

The following table shows the decrease in swelling and the improvement of the resistance to scouring obtained as a result of this treatment.

Kind of Treatment	Swelling Value, percent	Resistance to Scouring T./m. (1.5 thread, km.)
No cyanuric chloride, no brightening (control)	106	1,500
With cyanuric chloride, no brightening	75	5,360
With cyanuric chloride, with brightening	78	10,020

Example 5

1 kg. of spin bath-moist staple rayon is treated in a suspension of 50 g. of cyanuric chloride in a 2% solution of borax at 20° C. for a period of 5 minutes. After the absorption of the cyanuric chloride, the material is rinsed for 5 minutes at 20° C., with a 5% solution of urea buffered with borax to a pH of 8.0. After pressing or flinging off this solution, the material is impregnated with a 2.5% solution of formaldehyde containing 0.2% of ammonium biphosphate as a catalyst. Upon removal of excess solution the material is dried as usual and heated at about 120° C. for about 30 minutes.

The fibers thus finished have a swelling value of 50.2% and a scouring number of 1839 as compared with a swelling value of 105%, and a scouring number of 210 of the untreated, dried fiber.

Example 6

Following the procedure described in Example 1, fibrous material derived from cellulose is reacted with 60 g. of cyanuric chloride per 1 kg. of cellulose in a borax-alkaline solution. After the absorption of the cyanuric chloride 30 g. of oleyl amine dissolved in acetone are added to the bath. The fibrous material is then freed from excess liquor dried and heated at 120° C. for 30 minutes. The fibrous material thus obtained is water-repellent.

Example 7

5 g. of urea are dissolved in 20 l. of a 2% borax solution. Then 60 g. of cyanuric chloride dissolved in acetone are added to the borax solution at 20° C. while sitrring. After completion of the reaction (about 5 minutes), 1 kg. of viscose fiber from sulfite cellulose obtained from beech wood are placed in the bath and the latter is heated to 50° C. in order to add the urea-cyanuric chloride reaction product on to the cellulose. The final condensation occurs after drying the fibrous material by heating at 120° C. During the condensation reaction borax residue adhering to the material bind the hydrochloric acid liberated.

The fibers thus finished have a swelling value of 84% and resistance to scouring of 21,400 while the corresponding values of the untreated fibers are 102% and 4,350, respectively.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. Process for treating a fibrous material derived from cellulose, comprising the steps of treating said fibrous material substantially without prior alkali treatment, esterification and etherification of the same for a short period of time with a small proportion of an aqueous dispersion of a cyanuric halide, said dispersion having a pH within the range of between about 7 to 10; drying the thus-treated material; and subjecting the material to a heat treatment at a temperature between above 100° C. and 160° C., whereby a material of substantially decreased swelling characteristics, substantially insoluble in solvents for cellulose, and of high resistance to scouring is obtained.

2. Process for treating a fibrous material derived from cellulose, comprising the steps of treating said fibrous material substantially without prior alkali treatment, esterification and etherification of the same for a period of between about 1 and 30 minutes at a temperature of between about 15° C. and 60° C. with an aqueous dispersion of a cyanuric halide, said dispersion having a pH within the range of between about 7 to 10 and containing between about 10 and 100 grams of said cyanuric halide for each kilogram of said material being treated; drying the thus-treated material; and subjecting the material to a heat treatment at a temperature between above 100° C. and 160° C., whereby a material of substantially decreased swelling characteristics, substantially insoluble in solvents for cellulose, and of high resistance to scouring is obtained.

3. Process for treating a fibrous material derived from cellulose, comprising the steps of treating said fibrous material substantially without prior alkali treatment, esterification and etherification of the same for a period of between about 1 and 30 minutes at a temperature of between about 15° C. and 60° C. with an aqueous dispersion of a cyanuric halide selected from the group consisting of cyanuric chloride and cyanuric bromide, said dispersion having a pH within the range of between about 7 to 10 and containing between about 10 and 100 grams of said cyanuric halide for each kilogram of said material being treated; drying the thus-treated material; and subjecting the material to a heat treatment at a temperature between above 100° C. and 160° C. whereby a material of substantially decreased swelling characteristics, substantially insoluble in solvents for cellulose, and of high resistance to scouring is obtained.

4. Process for treating a fibrous material derived from cellulose, comprising the steps of treating said fibrous material substantially without prior alkali treatment, esterification and etherification of the same for a period of about 5 minutes at a temperature of between about 15° C. and 60° C. with an aqueous dispersion of a cyanuric halide, said dispersion having a pH of about 8 and containing between about 30 and 60 grams of said cyanuric halide for each kilogram of said material being treated; drying the thus-treated material without washing; and subjecting the material to a heat treatment at a temperature between about 110° and 120° C., whereby a material of substantially decreased swelling characteristics, substantially insoluble in solvents for cellulose, and of high resistance to scouring is obtained.

5. Process for treating a fibrous material derived from cellulose, comprising the steps of treating said fibrous material substantially without prior alkali treatment, esterification and etherification of the same for a period of between about 1 and 30 minutes at a temperature of between about 15° C. and 60° C. with an aqueous dispersion

of a cyanuric halide in a dilute aqeuous borax solution, said dispersion being maintained at a pH of about 8; drying the thus-treated material; and subjecting the material to a heat treatment at a temperature between above 100° C. and 160° C., whereby a material of substantially decreased swelling characteristics, substantially insoluble in solvents for cellulose, and of high resistance to scouring is obtained.

6. Process for treating staple rayon substantially without prior alkali treatment, esterification and etherification of the same, comprising the steps of treating said staple rayon for a period of about five minutes at a temperature of between about 40° C. and 50° C. with a dispersion of a cyanuric halide in a dilute aqueous borax solution, the pH of said dispersion being maintained at about eight and said dispersion containing between about 30 grams and 60 grams of cyanuric halide for each kilogram of said staple rayon; drying the thus-treated staple rayon without washing; and subjecting the staple rayon to a heat treatment at a temperature of between about 110° C. and 120° C. for a period of about 30 minutes.

7. Process for treating a fibrous material derived from cellulose, comprising the steps of treating said fibrous material substantially without prior alkali treatment, esterification and etherification of the same for a period of between about 1 and 30 minutes at a temperature of between about 15° and 60° C. with an aqueous dispersion of a cyanuric halide, said dispersion having a pH within the range of between about 7 to 10 and containing between about 10 and 100 grams of said cyanuric halide for each kilogram of said material being treated; contacting the material with an organic amino compound selected from the group consisting of urea, melamine and aliphatic amines; drying the thus-treated material; and subjecting the material to a heat treatment at a temperature between above 100° C. and 160° C., whereby a material of substantially decreased swelling characteristics, substantially insoluble in solvents for cellulose, and of high resistance to scouring is obtained.

8. Process for treating a fibrous material derived from cellulose, comprising the steps of treating said fibrous material substantially without prior alkali treatment, esterification and etherification of the same for a period of between about 1 and 30 minutes at a temperature of between about 15° C. and 60° C. with an aqueous dispersion of a cyanuric halide, said dispersion having a pH within the range of between about 7 to 10 and containing between about 10 and 100 grams of said cyanuric halide for each kilogram of said material being treated; contacting the material with an organic amino compound

selected from the group consisting of urea, melamine and aliphatic amines; treating the material with an aldehyde; drying the thus-treated materials; and subjecting the material to a heat treatment at a temperature between above 100° C. and 160° C., whereby a material of substantially decreased swelling characteristics, substantially insoluble in solvents for cellulose, and of high resistance to scouring is obtained.

9. Process for treating a fibrous material derived from cellulose, comprising the steps of treating said fibrous material substantially without prior alkali treatment, esterification and etherification of the same for a period of between about 1 and 30 minutes at a temperature of between about 15° C. and 60° C. with an aqueous dispersion of a cyanuric halide, said dispersion having a pH within the range of between about 7 to 10 and containing between about 10 and 100 grams of said cyanuric halide for each kilogram of said material being treated; contacting the material with an organic amino compound selected from the group consisting of urea, melamine and aliphatic amines; treating the material with an aldehyde selected from the group consisting of formaldehyde and glyoxal in the presence of ammonium biphosphate; drying the thus-treated material; and subjecting the material to a heat treatment at a temperature between above 100° C. and 160° C., whereby a material of substantially decreased swelling characteristics, substantially insoluble in solvents for cellulose, and of high resistance to scouring is obtained.

10. In a process for treating a fibrous material derived from cellulose, the steps of treating the material substantially without prior alkali treatment, esterification and etherification of the same with a dispersion of a product obtained by reacting in an aqueous alkaline medium a cyanuric halide with an organic amino compound selected from the group consisting of urea, melamine and aliphatic amines; drying the thus-treated material; and subjecting the material to a heat treatment at a temperature higher than 100° C. and up to 160° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,873,269	Fasciati et al.	Feb. 10, 1959
2,892,670	Alsberg et al.	June 30, 1959
2,892,671	Alsberg et al.	June 30, 1959
2,892,674	Sause et al.	June 30, 1959

OTHER REFERENCES

Warren et al.: Textile Research Journal, vol. 22, No. 9, pages 584–590.