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[54] **CROSSLINKING OF CELLULOSIC MATERIALS WITH PRODUCTS PRODUCED BY THE REACTION OF ALKYL SULFONAMIDES AND FORMALDEHYDE UNDER ALKALINE CONDITIONS**

3 Claims, No Drawings

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[50] **Field of Search** 260/556; 8/116.3

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ABSTRACT: Formaldehyde is reacted with alkyl sulfonamides under alkaline conditions. The resulting products are useful modification agents for cellulosic fibers.

CROSSLINKING OF CELLULOSIC MATERIALS WITH PRODUCTS PRODUCED BY THE REACTION OF ALKYL SULFONAMIDES AND FORMALDEHYDE UNDER ALKALINE CONDITIONS

The invention relates to a class of addition products and the use of the same in the cross-linking of cellulosic materials. More particularly, the invention concerns formaldehyde-alkyl sulfonamide addition products and the use of the same to chemically modify cellulosic fibrous textile products in order to impart improved shape retention thereto.

Within recent years various methods have been devised for treating cellulosic textile products, such as cotton cloth, in order to impart durable wrinkle resistance or better resilience thereto. For instance, mono- and dimethylol derivatives of carboxylic amides and ureas are used extensively for the cross-linking of cotton cellulose, so that easy-care properties are produced. While these and other known cross-linking agents have made a significant contribution to the cotton finishing art, the results have been less than perfect. For instance, in some cases the cross-linking treatment has tended to lack permanency since the finishing agents tend to be gradually removed from the treated article by repeated laundering. In other cases, such treatment substantially impaired the abrasion resistance of the fabric or resulted in objectionable chlorine retention after hypochlorite bleaching, etc. For this and similar reasons the industry is continuing its effort to develop new and better finishing agents.

It is an object of the invention to provide a new class of addition products which find outstanding utility in the textile finishing art.

It is another object of the invention to provide an improved process for imparting easy-care properties to cellulosic materials.

It is a more specific object of the invention to provide a process for imparting easy-care properties to cellulosic fibrous textile products which properties are not significantly diminished after repeated laundering.

A further object is to impart significantly improved wet and dry crease recovery to cellulosic fibrous textile products, with a minimum impairment of their abrasion resistance.

Still another object is to provide a textile finishing process which results in a cellulosic fibrous textile product possessing high moisture regain and which does not discolor, even after extended periods of use and the accompanying exposure to the atmosphere, bleaching agents, etc.

It is a further object of the invention to provide a process for enhancing the properties of cellulosic fibrous textile products which may be conducted with the use of standard textile finishing equipment.

These and other objects, as well as the scope, nature and utilization of the invention will become more clearly apparent from the following description and appended claims.

It has been discovered that a class of addition products which yield outstanding results in textile finishing applications may be produced by the catalyzed reaction of an alkyl sulfonamide and formaldehyde.

The alkyl sulfonamide compounds which may be employed in accordance with the invention may if desired contain a plurality of sulfonamide groups. Illustrative examples of alkyl bis-sulfonamides which may be utilized are methylene-bis-methanesulfonamide, ethylene-bis-methanesulfonamide, 1, 3-propane-bis-methanesulfonamide, etc. Alkyl sulfonamides containing a single sulfonamide group per molecule and containing one to about four carbon atoms per alkyl group have been found particularly effective in the formation of addition products according to the invention. Illustrative examples of such alkyl sulfonamides are methanesulfonamide, ethanesulfonamide, n-propanesulfonamide, isopropanesulfonamide, n-butanesulfonamide, isobutanesulfonamide, etc. As indicated, the alkyl groups may possess either straight or branched carbon chains. Formaldehyde addition products of aromatic sulfonamides, such as benzenesulfonamide, p-benzenedi-sulfonamide, p-toluenesulfonamide, have been produced, but were found to be ineffective as cellulosic cross-linking agents.

The addition products in accordance with the invention may be satisfactorily produced by reacting at least about one mole of formaldehyde with each mole of the alkyl sulfonamide. A mole ratio of formaldehyde to alkyl sulfonamide of about 2 to 1 is particularly preferred, and a molar ratio of as high as about 4 to 1 may be utilized, but such additional quantity of formaldehyde fails to produce any further improvement in ultimate cellulose cross-linking properties. The reaction may be conducted at a temperature of between about 0° C. and 100° C. and preferably at a temperature between about 40° C. and 80° C. The reaction is catalyzed by a basic type catalyst, maintaining an alkaline pH, preferably a pH of between about 9 and 11. Illustrative examples of suitable catalysts are the hydroxides and carbonates of alkali metals, such as NaOH, KOH, Na_2CO_3, etc. A reaction time of at least about 60 minutes, and preferably between about 60 and 120 minutes is usually required for the reaction to progress to a sufficient degree of completion.

An aqueous solution containing 10 percent alkyl sulfonamide and an amount of formaldehyde theoretically sufficient to form the dimethylol product is heated to 50—80° C. for 60 minutes during which the pH is maintained at 10 with suitable base, such as NaOH. After this time the pH is lowered to 3 with dilute acid such as dilute sulfuric acid. The addition product is very soluble in water. The reaction can be run at room temperature for an extended period of time, e.g. 24 hours. The use of 4 moles of formaldehyde per mole of alkyl sulfonamide tends to force the reaction nearer to completion, but the fabrics treated with such a solution are of substantially the same quality as those treated with the solution containing 2 moles of formaldehyde per mole of alkyl sulfonamide.

Basic solutions of the cross-linking compositions may be stored for considerable periods of time with no apparent loss in efficiency as a chemical finish.

The exact chemical structure of the addition product of the alkyl sulfonamide and formaldehyde is not known with certainty and its structure is considered to be incapable of simple description or explanation. There is some evidence, however, that once a molecule of the mono or dimethylol derivative of an alkyl sulfonamide has formed that it next condenses with either a molecule of unreacted alkyl sulfonamide or with another monomethylol alkyl sulfonamide molecule to produce a more complex product. If it ever be shown that the resulting reaction product results from both addition and condensation reactions, the product is nevertheless to be considered within the purview of the term "addition product" as used herein. The outstanding utility of the product as a cellulose cross-linking agent is in no way dependent upon exact knowledge of its structure or of the complex chemical reactions involved in its formation. Once the cross-linking step has occurred a finished product of exceptional stability is produced.

A satisfactory process for cross-linking cellulose in accordance with this invention comprises padding or otherwise wetting the cellulose material with a solution of the alkyl sulfonamide-formaldehyde addition product, drying the impregnated material and curing it by heating under acidic conditions to produce a treated cellulose possessing improved properties. Cellulose in the form of cotton fabric may be wetted with an aqueous solution of the addition product, dried, and cured according to standard pad-dry techniques which are well known in the art. The solution may satisfactorily contain about 5 to 20 percent addition product by weight. A particularly preferred solution contains about 10 percent addition product by weight. An acidic catalyst such as magnesium chloride, zinc nitrate, an aluminum salt, or an organic and inorganic acid is desirably included in the solution in a concentration of from about 10 to 30 percent based on the weight of the addition product. Cure temperatures from about 140° C. to 170° C. for a duration of about 2 to 10 minutes are recommended. Particularly outstanding results are produced when a cure temperature of about 150° C. is employed for about 5 minutes.

The invention is useful for treating cotton yarns and fibers as well as cotton fabric. Also, it is applicable to other cellulosic materials such as viscose rayon, and to fiber blends, for example, blends containing 15 percent to 75 percent cotton and correspondingly 85 percent to 25 percent of a synthetic fiber such as polyester, nylon, etc. As will be obvious to those skilled in the art, the cross-linking systems disclosed herein can also be used to treat paper for the purpose of increasing its wet strength and similar properties.

If desired, the addition products according to the invention may be formed in situ, with an appropriate mixture of the alkyl sulfonamide, formaldehyde and catalyst used to wet the cellulosic material, dried, and cured at elevated temperatures. Under such conditions the addition reaction and the cross-linking of the cellulosic material may be accomplished in a single operation.

When it is desired to produce white goods possessing a cross-linked structure it is desirable that any soluble residue of the alkyl sulfonamide-formaldehyde addition product remaining after curing be removed from the treated cellulosic material prior to the bleaching. The removal of such soluble portions may be accomplished by ordinary laundering or scouring. Bleaching may then be conducted by any standard procedure such as the use of a hypochlorite bleach, without resulting in objectionable chlorine retention. In the prior art, chlorine retention of resin treated cellulosic materials has quite often lead to undesirable scorching. The removal of the soluble products present upon the cellulose in no manner detracts from the improved properties resulting from the finishing treatment. In fact, such removal improves the moisture regain of the finished product which produces a further improvement of the hand and enables greater wearing comfort.

The following detailed examples will illustrate the invention:

EXAMPLE 1

To 0.1 mole of methanesulfonamide dissolved in 75 cc. of water is added 0.1 mole of formaldehyde (as 37 percent formalin solution). The pH of the solution is adjusted to 10 by addition of 10 percent NaOH. The solution may be allowed to stand at room temperature for several hours, or may be heated to about 50–60° C. for 1 hour. After this time the pH of the solution is lowered to 3 with dilute HCL. Enough water is added to bring total weight to 100 g. With the addition of the acidic catalyst, the product is ready to use.

To form the 1:1.5 and 1:2 addition product, 0.15 mole and 0.20 mole of formaldehyde respectively are added to the original methanesulfonamide solution.

EXAMPLES 2–20

In Examples 2 through 20 addition products according to the invention are formed in situ upon 80+80 cotton print cloth, and the mechanical properties of the cross-linked fabric measured. The results obtained are presented in Table I which follows, together with data obtained from testing a sample of the untreated fabric, and samples of the identical fabric treated with the well known cross-linking agent, dihydroxydimethylolethylene urea ("DHDMEU"). The fabric in Examples 2–20 was padded with an aqueous treating solution of methanesulfonamide and formaldehyde. Add-ons of about 5 percent were achieved in each instance. The fabrics were dried at 60° C. for 10 minutes and subsequently cured for 5 minutes at 150° C. with the exception of the fabric of Example 8 which was dried but received no cure after treatment. All fabrics were afterwashed and tumbled dry with the exception of those present in Examples 11 and 16. The afterwash was conducted by machine washing in warm, alkaline water with a conventional neutral, alkyl aryl sulfonate detergent added. A 3 percent concentration of $MgCl_2.6H_2O$ catalyst was present in the aqueous treating solution of Examples 2–15, and a 1 percent concentration of $Zn(NO_3)_2.6H_2O$ catalyst was employed in Examples 16–20. The aqueous treating solution contained 10 percent by weight methanesulfonamide in each example with the exception of

TABLE I

	Molar equivalents of HCHO per mole sulfonamide	Degrees: Dry crease recovery angle (W+F)	Degrees: Wet crease recovery angle (W+F)	Tear strength (W), g.	Percent moisture regain	Abrasion (percent of untreated)	HCHO/N	Percent N	Special conditions
Example No.:									
2	1.0	228	210	592	7.6	95			
3	1.0	186	144	800	7.3	110		0.40	Cured with no catalyst.
4	1.0	236	206	576	7.4	100	0.5	0.28	5% solution.
5	1.5	252	230	544	7.1	90	0.5	0.59	
6	1.5	258	236	528	7.2	94	0.4	0.35	Do.
7	2.0	270	274	480	7.2	66	0.75	0.74	
8	2.0	182	142	800	7.2	100		0.41	Dried only, no cure.
9	2.0	256	228	554	7.1	90	0.80	0.34	5% solution.
10	2.0	256	284	480	7.5	90	0.85	0.61	
11	2.0	286	272	432	6.4	68	0.80	0.95	Not afterwashed.
12	2.0	260	254		9.7		1.7	0.22	Hydrolyzed at pH 2.
13	2.0	272	278		10.0		3.2	0.18	Hydrolyzed at pH 6.
14	2.0	262	278		10.0		2.5	0.24	Hydrolyzed at pH 10.
15	2.0	258	280		9.0	76			
16	2.0	298	290	432	5.7	65	0.9	1.19	Not afterwashed.
17	2.0	264	280		9.2		1.6	0.44	Hydrolyzed at pH 2.
18	2.0	278	294		9.7		2.0	0.32	Hydrolyzed at pH 6.
19	2.0	284	286		9.5		2.5	0.28	Hydrolyzed at pH 10.
20	2.0	278	290		9.1				20 launderings.
Untreated control		170	140	1,040	7.8	100			
"DHDMEU" treated		302	275	530	5.6	48	2.0		Single afterwash.
Do		182	238						Hydrolyzed at pH 2.
Do		250	202	644	5.8		2.0		20 launderings.

Examples 4 and 6 which utilized 5 percent methanesulfonamide. The hydrolysis after treatments at various pH values of Examples 12–14 and 17–19 were conducted by (1) soaking fabrics for 30 minutes at 80° C. in a solution containing 1.5 percent phosphoric acid and 5 percent urea at a pH of 2; (2) boiling fabrics in distilled water at a pH of 6 for 30 minutes; (3) soaking fabrics for 30 minutes at 80° C. in a sodium carbonate-bicarbonate buffer solution at a pH of 10. It is believed that the reduction in nitrogen content resulting from hydrolysis may be attributed to the removal of soluble nonbonded dimers, trimers or low molecular weight polymers. The retention of satisfactory wet and dry crease recovery at such exceptionally low nitrogen contents is considered remarkable. The 20 launderings employed in Examples 15 and 20 were conducted by machine washing in warm, alkaline water with a neutral, alkyl aryl sulfonate detergent added.

The fabrics marked "DHDMEU" were, for purposes of comparison, padded with a solution containing 15 percent of Permafresh Reactant 183 (a solution of dihydroxydimethylolethyleneurea marketed by Sun Chemical Corp.) and 2.7 percent of a solution of Catalyst X-4 (a solution of zinc nitrate). Fabrics were dried for 10 minutes at 60° C., cured for 5 minutes at 150° C., afterwashed, and tumble dried.

EXAMPLES 21–26

In Examples 21 through 26 as reported in Table II results obtained according to the invention utilizing a wide variety of alkyl sulfonamides to cross-link a cellulosic material are reported. In each instance the addition products were formed in situ upon 80×80 cotton pring cloth, and the mechanical properties measured. The fabrics were padded with aqueous

TABLE II

Example No.	Compound	Molar equivalents of HCHO per mole sulfonamide	Degrees: Dry crease recovery angle (W+F)	Degrees: Wet crease recovery angle (W+F)	Tear strength (W), g.	Percent moisture regain	HCHO/N
21	N-methylmethanesulfonamide	1.0	160	150	560		
22	Methylene-bismethanesulfonamide	2.0	240	232			
23	1,3-propane-bismethanesulfonamide	2.0	240	266	400	8.4	1 1.2
24	Ethanesulfonamide	2.0	200	225	460		
25	n-Butanesulfonamide	2.0	256	226			
26	N-(methanesulfonyl)-glycine	2.0	249	202	600	8.5	

solutions containing 10 percent by weight of the respective alkyl sulfonamides, formaldehyde as indicated in the table, and 3 percent $MgCL_2.6H_2O$ catalyst. Add-ons of about 5 percent were achieved in each instance. Fabrics were dried for 10 minutes at 60° C., cured for 5 minutes at 150° C., afterwashed, and tumble dried.

As has been indicated, the present invention provides a class of addition products, and a process for significantly improving mechanical properties of cellulose fibers utilizing the same. High dry and wet crease recovery angles are achieved. A somewhat greater resistance to abrasion than found in common commercial finishes is produced. Treated fabrics possess a high moisture regain (7–10percent) as compared to a moisture regain of about 5 percent in common finished goods. Wash-wear ratings of 4 to 5 commonly result. White fabrics retain their whiteness after long periods of use, and fabrics possess the outstanding attribute of being capable to withstand repeated commercial laundering without a significant diminution of the resulting enhanced properties as is a common result with many of the prior art processes.

Although the invention has been described in connection with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

The described invention is particularly pointed out and claimed in the appended claims.

What is claimed is:

1. A process for cross-linking a cotton-containing fabric which comprises:

impregnating the fabric with a treating solution containing 5 to 20 percent by weight of an addition product of formaldehyde and a sulfonamide selected from the group consisting of methane sulfonamide and ethane sulfonamide, said product being formed by heating an aqueous solution containing 1 to 4 moles of formaldehyde per mole of sulfonamide at a pH between about 9 and 11 and at a temperature between about 40° and 80° C. for from about 60 to about 120 minutes;

drying the resulting impregnated material;

heating the dried material at a temperature between about 140° and 170° C. for from about 2 to 10 minutes in the presence of an acidic curing catalyst to produce a fabric possessing improved shape retention properties; and

washing residual water soluble addition product from the fabric, thereby minimizing subsequent chlorine retention.

2. A process according to claim 1 wherein said sulfonamide is methane sulfonamide.

3. A process according to claim 1 wherein the sulfonamide is ethane sulfonamide.

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