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3,720,500

TEXTILE MATERIALS AND PROCESSES FOR MAKING THE SAME

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No Drawing. Continuation-in-part of application Ser. No. 77,284, Dec. 21, 1960, which is a continuation-in-part of abandoned application Ser. No. 863,217, Dec. 31, 1959. This application Oct. 12, 1970, Ser. No. 80,206
Int. Cl. D06m *13/28, 13/54, 15/54*
U.S. Cl. 8—115.7 26 Claims

ABSTRACT OF THE DISCLOSURE

Cellulosic materials, particularly textile materials consisting of cellulosic fibers or blends of cellulosic and non-cellulosic fibers, are treated with compounds containing sulfato ethyl sulfone groups which function as vinyl sulfone group precursors. The compounds may be applied to the cellulosic material either concomitantly with thermosetting resins or subsequent to modification of the cellulosic material with thermosetting resins.

This application is a continuation-in-part of my copending application, Ser. No. 77,284, filed Dec. 21, 1960, now abandoned, which in turn is a continuation-in-part of my copending application, Ser. No. 863,217, filed Dec. 31, 1959, now abandoned.

This invention relates to modified cellulose fibers having an improved configurational memory, and to methods and chemicals used in making the same. More particularly the invention relates to modified cellulose yarns and fabrics having an improved tendency to return to an original flat, creased or similar configuration when washed and thereafter dried and to modified papers having increased wet strength, crease recovery, and rate of absorbability.

It is well known that fabrics can be formed which have a tendency to return to a predetermined configuration after washing. For example, by applying certain resins to fabrics and curing the resin while the fabric is in a flattened condition, one can obtain a fabric that, when allowed to dry in a flat condition, has a pressed appearance and requires no ironing. In a similar manner, one can form "permanent" pleats in a fabric so that the pleats are not removed by washing. The fabric dries flat between creases, and no ironing of the fabric is required. Any such fabric, or yarns capable of resulting in such fabrics, are referred to in this specification as "flat drying" and it will be understood that this term is employed broadly to include any textile material which normally requires no ironing, pressing or the like for a satisfactory appearance.

These fabrics which obtain their flat drying properties as a result of resin application, commonly referred to in the trade as Wash and Wear fabrics, have the following disadvantages: (a) lack of durability, (b) odor formation, (c) chlorine retention, (d) loss of strength and (e) are highly subject to wrinkling when wet. On account of the latter disadvantage, these fabrics must be drip dried since they give a low degree of recovery from creases when wet. The inconvenience of drip drying is well known.

Other treatments include the cross linking of cellulose by means of dichloropropanol or epichlorohydrin in the presence of strong alkali. Such treatments inevitably were accompanied by severe losses in tensile and tear strength.

Another way of producing like effect is to treat the fabric with divinyl sulfone and alkali according to U.S. Pat. 2,524,399. The disadvantage of this last treatment is that the divinyl sulfone is a very toxic and lacrimatory material, that the divinyl sulfone is subject to polymerization upon exposure to the alkaline solution. Therefore when the fabric is treated with the solution of divinyl sulfone and alkali, the divinyl sulfone reacts partially with the cellulose and polymerizes partially. All of the above mentioned treatments are also defective in that the cotton so treated suffers from alkaline oxidation.

Fabrics woven of certain synthetic materials, such as glycolterephthalate fibers, also display flat drying qualities but such fabrics likewise have several inherent disadvantages. For example, flat drying polyester fabrics are expensive, have a tendency to collect static electricity, and, if formed from staple fibers, generally display a tendency to pill badly. In addition, polyester fabrics have a low moisture absorptivity so that they feel cold to the touch and are incapable of absorbing perspiration from the body. Still another disadvantage is that they become dingy after repeated washings and cannot be readily bleached.

Flat drying fabrics prepared by other methods generally must be "drip dried"; that is, they must be hung immediately after they are withdrawn from the wash and before they are wrung. It is therefore inconvenient to drip dry even a single item of clothing and almost prohibitive to drip dry large quantities of clothing.

Cross linking agents which have been used in treating cellulosic fibers to make flat drying fabrics have not been as chemically reactive as desirable, and in many cases not as water soluble as desirable, and in some cases have been rather volatile, at least under reaction conditions so that they tend to escape into the room. Therefore, special ventilating procedures and apparatus are required for handling such materials. Moreover, it would be desirable to reduce or to eliminate the "wet slickiness" that seems to be inherent in fabrics treated with some cross linking agents.

An object of the present invention is to obtain reagents and procedures for preparing flat drying fabrics that overcome the many disadvantages of the resin treated fabrics.

Another object of the invention is to obtain such reagents that are more chemically reactive than other cellulose cross linking agents, so that the reaction can take place in a short time thereby facilitating continuous operations.

Still another object is to obtain such reagents which are more specific in their cross linking reaction with cellulose so that there will be fewer side reactions.

Still another object of the invention is to obtain such reagents that are soluble in water so they can be readily used in solution instead of in emulsion form.

Still another object of the invention is to obtain such reagents that have practically no volatility and therefore do not create any ventilation problems in the mill.

Another object of the invention is to produce flat drying cellulosic fabrics that do not have to be drip dried but will retain their configurational memory as long as they are wet and therefore can be put through a roller or a centrifugal wringer before they are hung.

Other objects and advantages of the invention will be apparent from the following description:

The invention resides in the discovery of certain reagents which are novel compositions of matter and which are effective in imparting flat drying properties to cellulosic fibers, and also in the use of such reagents in treating cellulosic fibers. According to the invention cellulosic fibers in any desired form, while in a swollen condition, are reacted with a cross link agent having the formula:

$$X\text{-}[CHR^1—CHR^2—O—SO_3—Y]_2$$

in which R^1 and R^2 are hydrogen or saturated alkyl groups having 1 to 3 carbon atoms such as methyl, ethyl or propyl,

Y is hydrogen or any metal ion or nitrogen base that produces a soluble reagent.

X is $-SO_2-$; $-O_2S-R-SO_2-$; $-SO-$; or $-OS-R-SO-$

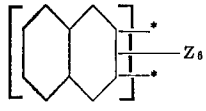
These compounds are of particular interest because they may be in the form of salts and therefore non-volatile and easy to handle in the mill. Such compounds are also water-soluble.

In the formula for this group of compounds, R may be any of several groups of radicals, as follows:

(a) A saturated aliphatic radical of from 1 to 10 carbon atoms, hydrogen, 0 to 4 oxygen atoms, 0 to 2 sulfur atoms, and positive ions, e.g., metal ions or nitrogen base ions, in amount not exceeding that necessary to replace carboxylate and sulfonate acid hydrogens. The oxygen in the saturated aliphatic radical is present in ether, sulfonate or carboxylate groups. The sulfur is present in thio ether or sulfonate groups; or

(b) Cycloaliphatic radicals of 4 to 7 carbon atoms, 0 to 3 oxygen atoms, 0 to 1 sulfur atoms, and positive ions, e.g., metal ions or nitrogen base ions, in amount not exceeding that necessary to replace the carboxylate and sulfonate acid hydrogens. The oxygen of the cycloaliphatic radical is present in sulfonate, ether or carboxylate groups. The sulfur is present in thio ether or sulfonic groups. Moreover, the sulfone or sulfoxide groups of the radical X are attached directly to —CH— groups in the cycloaliphatic ring; or

(c) The aromatic groups of meta or para phenylene, meta or para phenylene substituted with hydrocarbon groups having 1 to 3 carbon atoms, or



where the groups Z in the aggregate consist essentially of hydrogen, 0 to 3 carbon atoms (present as an alkyl group), 0 to 2 sulfur atoms, and 0 to 6 oxygen atoms, the oxygen and sulfur being in the form of sulfonate groups. The valence bonds * are linked to the sulfone or sulfoxde groups of the radical X. Moreover, there are no two sulfur oxide groups ortho to each other on the naphthalene ring whether from the sulfone or from any sulfonate substituents.

The reagents represented by the first general structural formula given above may be a metallic (or nitrogen base) salt of the sulfuric ester. Any metal or nitrogen base that produces a soluble reagent may be used to supply the cation. The alkali metal salts such as lithium, sodium, and potassium are readily available and therefore acceptable. The alkaline earth metal salts such as barium, calcium, and magnesium are also suitable (except that barium and calcium should not be used when a sulfonate group is present because of the insolubility problems). However, other metallic ions that produce water soluble reagents and therefore also lend themselves to being used include lead, tin, zinc, iron, nickel, cobalt, ammonium, and manganese.

The choice of nitrogen bases is also very broad. Even very weak bases such as aromatic and aliphatic amines including aniline, methyl and ethyl amines can be used. Of course, the strong quaternary hydroxide amines are satisfactory. These include benzyl trimethyl ammonium hydroxide, tetramethyl ammonium hydroxide, trimethyl phenyl ammonium hydroxide and others.

As will be explained later, it is believed that the cross linking agent of the present invention react with the hydroxy groups of the cellulose molecule through the medium of the sulfated ethyl group. The sulfone groups $-SO_2-$ are believed to be important in imparting the desired activity and specific reactivity with cellulose hydroxyls desired in the sulfated groups. It follows also that the character of the group R is of secondary importance,

the object merely being to select groups which will not interfere with the reaction of the sulfated ethyl groups with the cellulose hydroxyls.

The radicals R are classified under three main headings:

(a) Saturated aliphatic radicals,
(b) Cycloaliphatic radicals, and
(c) Aromatic groups.

Taking up first the group (a) saturated aliphatic radicals, it is desirable to avoid groups such as alcohol (—OH) and nitrogen ($-NO_2,NH_2$) groups. However, oxygen and sulfur-containing groups such as ether, thioether, sulfonate, and carboxylate groups are permissible. In order to exclude unduly complicated radicals which may interfere with the cross linking reaction through steric hindrance or insolubility, the number of such groups is generally restricted so that the total number of oxygen atoms is not greater than two, the number of sulfur atoms is not greater than two, and the total number of carbon atoms in the group R is restricted to one to ten inclusive. In instances where sulfonate and carboxylate groups are present, the acid hydrogens may be partly or entirely replaced with weak or strong positive basic ions.

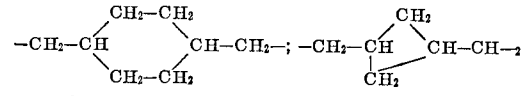
Aliphatic radicals that may be included in the cross linking agents of this invention include:

$-CH_2-CH_2-$; $-CH_2-CH_2-CH_2-$

C_4H_8-(such as $-CH_2-CH_2-CH_2-CH_2-$)

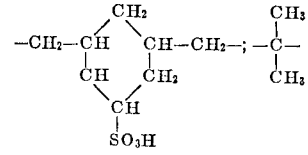
$-CH_2-CH_2-O-CH_2$; $-CH_2-CH_2-S-CH_2-CH-$)

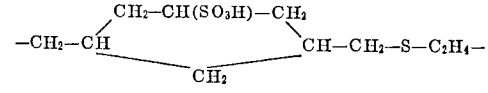
$-CH_2-CH_2-CH(COOH)-CH_2-CH_2-$



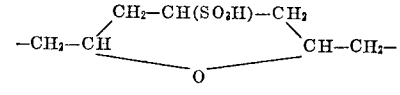
$-CH_2-CH(C_2H_5)-CH_2-CH_2-CH(C_2H_5)-CH_2-$

$-CH_2-CH(CH_2-SO_3Na)-CH_2-$; $-CH_2-CH(CH_2-SO_3H)-CH_2-$



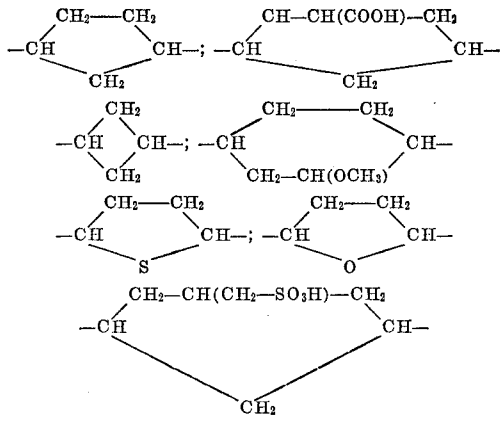


and



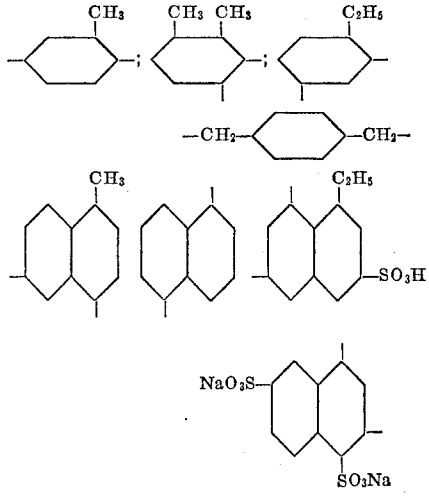
The second classification of the radical R is the cycloaliphatic radicals. It is intended to include within this class compounds in which the sulfone groups of the group X are attached directly to the ring, i.e., directly to a —CH— group of such ring.

As in the case of the aliphatics, the character of the group R is only of secondary importance. The object is to avoid interfering with the reactivity of the sulfated ethyl group. Therefore, the group R is generally restricted to those having 4 to 7 carbon atoms. Although oxygen and sulfur may be present, such elements would be in the form of ether, sulfonate, carboxylate or thioether groups. Moreover, the total number of oxygen atoms in the cycloaliphatic radical is from 0 to 3, and the total number of sulfur atoms is 0 to 1. The following cycloaliphatic radicals are examples of those which may be present in the group X of the cross linking agents of the present invention.



In addition to the 4 to 7 carbon atoms, 0 to 3 oxygen atoms, and 0 to 1 sulfur atoms which make up the cycloaliphatic radical R, any carboxylate or sulfonate group may have its acid hydrogen partly or wholly replaced by a strong or weak metal ion.

The third kind of group R is aromatic. The aromatic group may be phenylene (or substituted phenylene), or it may have a naphthalene base. In this case also, the number and type of substituents are restricted to exclude those that may interfere with the desired reaction. The substituents on the naphthalene group are preferably no more than one hydrocarbon group having 1 to 3 carbon atoms, and such naphthalene groups having no more than two sulfonate substituents. Recognizing that $-SO_2-$ groups of the radical X will be attached to the naphthalene groups and that sulfonate substituents (if present) may supply additional $-SO_2-$ groups, it is desirable that there shall be no $-SO_2-$ substituents that are ortho to each other on the naphthalene nucleus. Examples of radicals R that fall within the category of aromatics are:



The following are examples of specific compounds that may be used as cross linking agents:

$[NaO_3S-O-CH(CH_3)-CH(CH_3)-]_2SO_2$

$[NaO_3S-O-CH(CH_3)-CH_2-]_2SO_2$

$[NaO_3S-O-CH(C_3H_7)-CH_2-]_2SO_2$

$[NaO_3S-O-CH_2-CH_2-SO_2-CH_2-]_2$

and

$NaO_3S-O-CH_2-CH_2-SO_2-$phenylene$-O_2S-CH_2-CH_2-O-SO_3Na$

The process can be satisfactorily performed on natural cellulose fibers, regenerated cellulose fibers and/or chemically modified cellulose fibers having a portion of the hydroxy groups thereof blocked by ester or ether groups such as cellulose acetate or methyl cellulose provided

that the fibers retain their general form when wetted with water.

The fibers may be treated in any desired form, e.g., yarn (either staple or multifilament), fabric, non-woven batts, and the like. The treatment may be provided at any stage of the processing of the desired form. In the textile field, for example, the treatment may occur at any stage from raw material to finished fabric.

Generally, the cellulosic fibers should have an average of at least 1.8 free hydroxy groups per glucose unit. Cellulosic materials having a smaller number of free hydroxy groups do not give satisfactory results even though, in the case of cellulose esters, the ester groups might theoretically be removed by hydrolysis during the cross linking reaction.

Satisfactory results can also be achieved with cellulosic fibers partially composed of other than cellulosic materials and this is particularly true where the noncellulosic fibers have some known flat drying properties of their own. For example, the flat drying tendencies of yarn spun from a mixture of glycol-terephthalate fibers and cotton fibers can readily be increased by the process of this invention, even if the percentage of cotton fibers is as small as 10%. Even when the noncellulose fibers display no flat drying properties, yarn and fabrics containing the same can be caused to display flat drying properties by the present process if the yarn or fabrics contain at least about 40% by weight of cellulosic fibers.

It is believed that the reaction between the cross linking agent and the cellulose molecule takes place according to the following equation:

$$+2Cell-OH+X[CHR^1-CHR^2-O-SO_3Y]_2+2YOH \rightarrow X[CHR^1-CHR^2-O-Cell]_2+2H_2O$$

wherein Cell—OH means the cellulose molecule and R^1, R^2, X and Y have the values given above.

Apparently, the reaction with the cellulose proceeds through a substitution of the alkali cellulose for the sulfato group which is split off from the ethyl radical forming a cellulose ethyl ether. This reaction takes place without the formation of intermediate vinyl sulfone and has the specific advantage over the reaction of the vinyl sulfone with the cellulose in that the alkali which is present in the cellulose micelle during the reaction with the sulfato ethyl sulfone is neutralized by the sulfato radical which is split off from the ethyl group, thus avoiding alkali damage to the cellulose. The cellulose is first treated with an aqueous solution of the cross linking agent and dried and then immersed in a strong solution of alkaline medium, preferably an aqueous alkaline solution. Suitable alkaline materials are the alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, the alkali metal sulfides such as sodium sulfide, quaternary ammonium hydroxides such as benzyl trimethyl ammonium hydroxide, tetramethyl ammonium hydroxide, or trimethyl phenyl ammonu hydroxide or any other alkaline material which will provide a pH of at least 10 as a 1% solution in water. The amount of strong alkaline material present during the cross linking reaction is at least two equivalents per molecule of the cross linking agent in addition to any that may be needed to neutralize acidic hydrogen atoms in the molecule. For example, if the agent contains a sulfonic acid or a carboxylic acid group, the amount of alkali would be increased accordingly.

A sufficient amount of cross linking agent should be used in order to provide enough cross linkages to give the degree of cross linking that will produce a noticeable amount of flat drying in fabrics, and high wet strength, absorbability and crease recovery in papers. Due to the high chemical efficiency of these cross linking agents, only a very small amount is required Generally at least 0.005 mole per anhydro-glucose unit is sufficient. Preferably a somewhat larger quantity of 0.01 mole of cross linking agent per anhydro-glucose unit is used. Larger amounts can be used, though with some sacrifice of flexibility and

strength (as well as economy). Hence, I prefer to keep the amount of cross linking agent below 0.05 mole per anhydro-glucose unit.

The manner of applying the agent and the strong alkali to the cellulosic fibers is also subject to wide variation. In many cases, it is preferred first to place the cross linking agent on the fibrous material as an aqueous solution, then dry the material and apply just enough strong alkali to meet the requirements set forth above. In this way, there is almost no leaching out of the cross linking agent into the alkali solution. Both the treating agent solution and the alkali solution can be applied by conventional padding or by spraying techniques. In one process the treated material containing the agent is passed downwardly through the nip between two rubber covered rollers and the alkaline solution is also fed into the nip in just the right amount to saturate the material and be carried through the nip with it. If leaching of the agent from the material by the aqueous caustic is or becomes a problem, salt such as sodium chloride may be desirable in the aqueous alkali to reduce the solubility of the agent therein.

It is not necessary to put the cross linking agent on the fibers first. The alkaline material may be applied first or the two may be applied simultaneously.

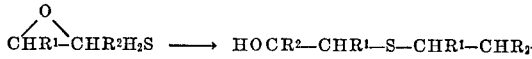
Substantial advantages of the invention arising out of the solubility of the cross linking agent in water are its low volatility and its high selective reactivity for cellulose. The greater reactivity and selectivity make it possible to carry out the reaction in a shorter time and thereby make continuous operation possible. Because of the lower volatility of the acid and the salt forms, the material is easier to handle in the plant and ventilation problems are greatly simplified. The solubility of the agents in water not only avoids the problem of preparing emulsions, but also greatly improves the penetration and uniform distribution of the treating agent through and over the fibrous material as the case may be.

The temperature of the reaction and the time of reaction are mainly interdependent. The reaction may, if desired, be carried out as low as room temperature, in which case a reaction time of 30 minutes may be expected. If the material is heated slightly, say to 40° C., the reaction will be completed in as little as 30 seconds. If still a higher temperature is maintained, say 95° C., reaction is complete in only a few seconds. Some heat is generated from the reaction itself and this effect alone may account for a temperature rise in the material from 40° C. to about 60° C.

The cross linking reaction tends to fix permanently the configuration of the fibrous material as that prevailing during the reaction. In other words, if one desires a fabric that will have a flat and pressed appearance after washing, it is necessary that the fabric be retained in a flat and slightly tensioned condition during the cross linking reaction. This can be accomplished by conducting the reaction while the fabric is in a tenter frame. Of course, if it is desired that the fabric display permanent pleats or the like, then it is necessary that the cross linking reaction be conducted while the fabric is in a pleated condition.

Following the cross linking reaction, the fibrous material should be thoroughly scoured employing any suitable detergent. This serves mainly to remove reaction by-products such as sodium sulfate and also to remove any excess alkali and sodium chloride that may be present.

The cross linking agents can be prepared in the following manner when the group Xis $-SO_2-$



$$CHR^1{-}CHR^2 + H_2S \longrightarrow HOCR^2{-}CHR^1{-}S{-}CHR^1{-}CHR_2{-}OH$$

This reaction is the well known addition reaction of hydrogen sulfide to ethylene oxide or substituted ethylene oxide to produce bishydroxyethyl sulfide. The latter compound is then oxidized with about one or two chemical equivalents of an oxidizing agent, for example, hydrogen peroxide or potassium permanganate as an oxidizing agent to produce bishydroxyethyl sulfone

$$O_2S{-}[CHR^1{-}CHR^2{-}OH]_2$$

Finally, the bishydroxyethyl sulfone is treated with sulfuric acid to form bissulfatoethyl sulfone

$$O_2{-}S{-}[CHR^1{-}CHR^2{-}O{-}SO_3H]_2$$

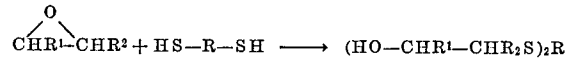
The bissulfatoethyl sulfones may be applied directly to the cellulosic fibers (in which case, as explained above, additional quantities of alkali will be required) or they may first be neutralized with an alkaline material to replace the acidic hydrogen of the sulfonic acid group with a metallic or equivalent ion.

Instead of treating the cellulosic with the acid sulfatoethyl compound, any salt of such acid with a weak or strong base may be used. By reacting the bissulfatoethyl sulfone acid with any metal oxide or hydroxide from the group described above (in defining the symbol Y), the bissulfatoethyl sulfone salt of such a metal may be formed. If the metal oxide or hydroxide is insoluble it should be used in finely divided form, giving enough time, preferably with some heat, for the reaction with the acid compound to take place.

Another way of forming the bissulfatoethyl sulfone salts of metal is to pass a solution of the corresponding acid through an ion exchange bed containing the metallic ion that is to be substituted for the acidic hydrogen.

The sulfatoethyl sulfones in the acid and salt forms are stable compounds and therefore can be isolated and stored for future use or they can be used immediately in the solutions in which they are first prepared.

The cross linking agents in which the group X is $-SO_2-R-SO_2-$ may be formed by similar reactions using a bis mercaptan instead of H_2S.

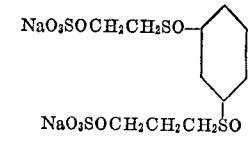


$$CHR^1{-}CHR^2 + HS{-}R{-}SH \longrightarrow (HO{-}CHR^1{-}CHR_2S)_2R$$

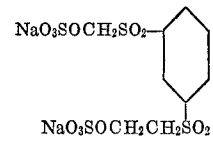
The intermediate product is oxidized with peroxide or permangate as described before to form the sulfone $[HO{-}CHR^1{-}CHR^2{-}SO_2]_2R$. The latter compound is then treated in a manner similar to the bishydroxyethyl sulfone mentioned above, i.e., with sulfuric acid or SO_3 to form the corresponding bissulfatoethyl sulfone, which may be used as such or may be converted to any of the metal or nitrogen base salts described above.

Compounds in which R is an aliphatic, cycloaliphatic or aromatic group may be prepared from dithiols. For example, 142 grams of m-benzenedithiol and 2 grams of dihydroxy ethyl sulfide are placed into a three neck, round bottom flask equipped with a stirrer, thermometer and reflux condenser. Ethylene oxide is bubbled into the mixture at 50° C. until a weight gain of about 90 grams is registered. The product is vacuum distilled to remove excess ethylene oxide and then diluted with an equal amount of water. The mixture is cooled in an ice bath and stirred while 30% hydrogen peroxide is added. After 2 moles of hydrogen peroxide have been added, the disulfoxide is formed. The product is dried and sulfated by the addition of 30% fuming sulfuric acid at 5–10° C.

The reaction product is held for about 4 hours at room temperature, then poured into ice water with stirring and neutralized with sodium carbonate. The product is purified by vacuum evaporation of water until a slurry forms. Acetone is added to the slurry and the precipitate filtered and recrystallized from a 25/75 water-acetone solution. The disulfoxide has the following formula:



In the same way, the disulfone



can be obtained employing the same procedure by adding 4 moles of hydrogen peroxide instead of 2 moles thereof.

The m-benzenedithiol can be obtained by sulfonating benzene, separating the sulfonate salt by crystallization, chlorinating with phosphorus pentachloride and reducing the dichloride with zinc and hydrochloric acid.

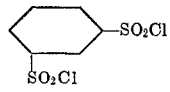
The compounds in which the R group is cycloaliphatic may also be prepared using the same procedure. For example, the cyclohexane derivative may be prepared employing cyclohexane dithiol in the above procedure with the sulfoxide being produced with 2 moles of hydrogen peroxide and the sulfone with 4 moles. Likewise, 1,2-ethane dithiol may be employed in the above procedure to form the corresponding sulfoxide and sulfone.

The compounds in which the group X is

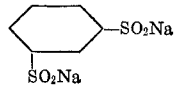
$$—SO_2—R—SO_2—$$

wherein the group R is aromatic and the two sulfones are attached directly to the aromatic ring, also can be readily prepared by the following procedure:

The compound



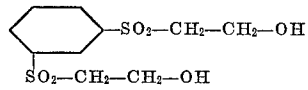
is prepared by known procedures by treating benzene with chlorosulfonic acid. The material is then treated with sodium sulfite in an aqueous solution of sodium hydroxide to form the compound



The material so formed is then treated with

$$Cl—CH_2—CH_2—OH$$

while refluxing in aqueous solution to form the compound



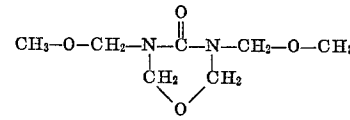
which is treated with 30% fuming sulfuric acid according to the procedure described above for the hydroxyethyl sulfone.

One aspect of the present invention is directed to the combined application, particularly in the treatment of yarns and fabrics, of resin materials of the class to be described more fully hereafter and the cross linking agents set forth above. Such resins, when used alone, at least in amounts sufficient to impart flat drying characteristics, have the undesirable characteristic of imparting poor hand to fabrics with a tendency to become discolored when repeatedly bleached with household bleaches. Furthermore, the resin tends to be removed from fabrics after a number of launderings. If the amount of resin is reduced, then the dry crease resistance as normally imparted by the resin treatment is decreased or even lost.

By combining the resin treatment with the cross linking agent of the present invention, however, it has been found that the two reagents exert a synergistic action upon each other so that by reducing the amount of resin, the normal undesirable properties of resin treatment are minimized, but the flat drying characteristics are retained.

The resinous materials which can be employed and which will hereinafter be referred to simply as "textile resins" are low molecular weight (less than 1,000), water soluble, acid or acid salt catalyzed materials which are

thermosetting at least in the presence of cellulosic materials as above defined. The largest class of resins within this group comprises the amino-plast resins formed by reacting compounds such as urea and melamine with formaldehyde, and specific examples of resins within this class include urea formaldehyde resins such as the resin commercially available from Rohm & Haas under the trade name of "Rhonite 610"; methyl ethers of urea formaldehydes such as the resin sold by Rohm & Haas under the trade name of "R–2 Resin"; acrolein urea formaldehyde resins; cyclic ethylene urea formaldehyde resins such as the resin sold by E. I. du Pont under the trade name of "Zeset" and the resin sold by Rohm & Haas under the trade name of "R–1 Resin"; trimethylol acetylene diurea; tetramethylol acetylene diurea; melamine formaldehyde resins such as the resins sold by Monsanto under the trade name of "Resloom H.P." and "Resloom L.C."; methylated melamine formaldehyde resins such as the resin sold by American Cyanamid under the trade name of "M–3 Resin"; or the resin sold by Monsanto under the trade name of "M–75 Resin"; copolymers such as a copolymer of melamine formaldehyde and ethylene urea formaldehyde; and the resin known to the trade as Uron which has the formula



In addition to resins of the above type, one can suitably employ epoxy resins and specific examples of suitable resins of this class include the diglycidyl ether of ethylene glycol, the triglycidyl ether of glycerol, and the epoxy resins sold by Shell Chemical Company under the name of "Eponite 100." Still another class of resins which can suitably be employed are triazinone resins and any member of this type of resins coming within the above defined group can give satisfactory results according to the process of this invention. Still another resin which can be employed is tris (1-aziridinyl) phosphine oxide which is prepared by reacting 3 moles of ethyleneimine with 1 mole of $POCl_3$ and which is known to the trade as "APO Resin" or "Imine I.P. Resin." One need not employ a single resin material but can employ blends of resins of the above type or copolymers where available. Likewise, it is not necessary that the resins be entirely free from water insoluble components since it has been found that dispersed particles of water insoluble materials in the resin solution are not deleterious even though any portion of the resin that is water insoluble does not contribute to the beneficial results obtainable according to this invention. Some of the commercially available resinous materials mentioned above contain small percentages of water insoluble polymeric materials and while an aqueous mixture of such resins can be filtered if desired, equally satisfactory results are generally obtained by employing the unfiltered material.

Suitable acid catalysts for resins of the above types are well known in the art. Urea formaldehyde and melamine formaldehyde resins are best catalyzed by chloride or nitrate salts of hydroxyalkyl amines such as monoethanol amine hydrochloride or 2-amino-2-methyl-propanol nitrate. Cyclic ethylene urea formaldehyde resins, acetylene diurea formaldehyde and uron resins are preferably catalyzed by zinc nitrate or by magnesium chloride. The epoxy resins are preferably catalyzed by acid fluoride salts, such as catalyst compositions available from Shell Development Company under the trade names of "Curing Agent 48" and "Curing Agent 20." The above catalysts are all characterized by their ability to furnish hydrogen ions which are necessary for the condensation or etherification reactions taking place during the curing cycle. Generally any amount of catalyst up to about 5% by weight of the solution will give satisfactory results

with the preferred range being from about 0.5% to 2% by weight of the resin solution.

The amount of resin which is applied to the fibrous material according to this aspect of the invention can be varied within wide limits and the most advantageous amount is dependent upon a number of variables, especially the particular type of resin being employed. It is a general rule that the greater the degree of cross linkage, the smaller the amount of textile resin which can effectively be employed, and one can obtain results by employing only a relatively small amount of resin on a highly cross linked cellulosic fibrous material that is comparable to those obtained by employed a relatively larger amount of textile resin on a material, the fibers of which are to be cross linked only to a slight degree. In most instances, it is desirable to employ only a small amount of resin material and from 1% to 5% resin solids on the weight of the fibrous material generally gives optimum results. Due to the synergistic action of the cross linking agent and the textile resin, the effectiveness of the textile resin is greatly increased as compared to prior art procedures of resin applications to cellulosic fibrous materials and satisfactory minimum care characteristics and wrinkle resistance can sometimes be obtained employing as little as 0.5% resin solids based on the weight of the fabric. At the other extreme, the amount of resin materials in some instances up to as much as 10% to 15% by weight of the material can be employed without imparting an unacceptable hand, but the addition of such large amounts of resin is generally not necessary and is not economically desirable.

A unique feature of this aspect of the invention when both cross linking agent and textile resin are used is that both can be and are applied from the same aqueous solution containing the desired amount of textile resin, catalyst therefor, and cross linking agent (but without the catalyst for the cross linking agent). Conventional padding equipment is suitable for applying the solution and with such apparatus, the fibrous material can be passed through the aqueous solution to give sufficient solution pickup by the fabric to provide the desired amount of resin solids and cross linking agent to the material. Following the application of the solution, the material is dried and heated to cure the resin. The most advantageous curing temperature depends upon the particular resin and catalyst employed. As a general rule, the curing temperature is a range from 100° C. to 200° C. and preferably between 150° C. and 180° C. The curing temperature should be maintained for from 10 seconds to 30 minutes with the preferred range being from 30 seconds to 5 minutes, depending upon the temperature, amount, and kind of material and the particular resin compound.

After the textile resin has been cured, the material still containing the uncured cross linking agent, is treated with alkaline catalyst to bring about the reaction between the functional groups of the cross linking agent and the cellulose hydroxyl groups as described above. The strong alkaline catalyst, several types of which have been mentioned previously, may be applied by known techniques including the padding technique used for applying the resin and the cross linking agent.

The amount of sulfato sulfone linking agent may be varied within relatively wide limits, but the amount will generally be somewhat smaller that that used without the resin. In most instances, 0.005 mole of cross linking agent per anhydro-glucose unit will be sufficient to give the product noticeable flat drying, wet crease resistance, and wet configurational memory to fabrics and high absorbability rate, wet strength and wet crease recovery to papers. Best results are generally obtained when the fibrous material is reacted with 0.01 to 0.02 mole of cross linking agent per anhydro-glucose unit. Amounts of the agents greater than 0.03 mole per anhydro-glucose unit are generally avoided because it may produce excessive stiffnesss and degradation of the fiber.

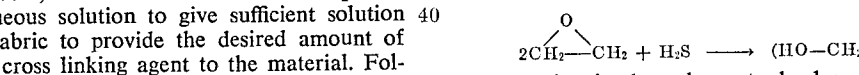
The important advantages of the invention are attributable to the fact that both the resin and the sulfato sulfone cross linking agents are present in a single solution that is applied to the fibrous material in one step. At the time the resin is being cured as a catalyst, the cross linking agent remains unaffected because it is nonvolatile and nonreactive in acid medium. However, it is still present on the fibers and still in immediate contact with the fibers and therefore in a position where it can exert its effect when the proper conditions are present. Furthermore, it is believed that the cross linking agent may react with some of the active hydrogens of the resin. Wet slickiness and excessive hydrophobic properties have been attributed to the presence of too many active hydrogens, and hence the removal of some of them by the cross linking agent is desirable.

After the resin has been cured, the alkaline conditions are produced to cure the cross linking agent. Such alkaline conditions would normally have a bad effect on the resin, but because the resins have been cured, they are not harmed under the controlled conditions and limited time of exposure that are maintained to cure the cross linking agent.

The invention will now be described more specifically in terms of examples in which all parts are by weight unless otherwise indicated.

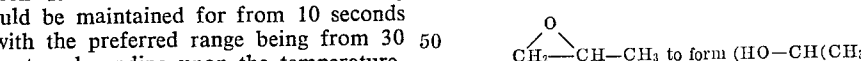
EXAMPLE I

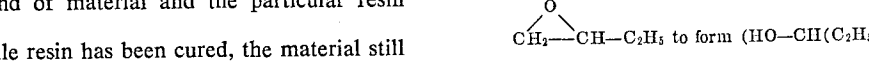
Preparation of the sulfide.—The sulfide is a known material available on the market. It was prepared by introducing gaseous ethylene oxide and hydrogen sulfide in the proportion of 2 moles of the former to 1 mole of the latter into the bottom of a packed column containing a small amount of the reaction product to initiate the reaction. The exothermic reaction took place in the column to form the sulfide, which flowed down through the column and was withdrawn.

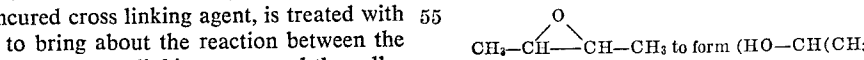


The reaction in the column took place at about 45° C. to 60° C. The yield was about 95% to 100% of the theory.

In a similar way using known procedures, substituted ethylene oxides (which are liquids) can be used to prepare substituted sulfides by reaction with H_2S as follows:







Preparation of the sulfoxide.—Bis(hydroxyethyl) sulfide $(HO—CH_2—CH_2)_2S$, for example, which is a liquid, is diluted with water in the proportion of about 500 parts of the sulfide to 200 parts of water. The mixture is cooled in an ice bath and stirred while adding 30% hydrogen peroxide. About 1.0 to 1.2 moles of peroxide are added per mole of sulfide. The reaction is strongly exothermic but the temperature is kept below 65° C. by stirring and cooling. The corresponding sulfoxide

$$(HO—CH_2—CH_2)_2SO$$

is formed in about 95% to 100% yield.

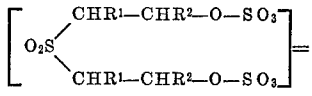
Preparation of the sulfone.—After all of the peroxide needed for the preparation of the sulfoxide has been added, the mixture is heated and refluxed at the pot temperature of 100° to 110° C. Another mole of 30% H_2O_2 is added slowly while continuing the refluxing. After all peroxide has been added, refluxing is continued for two

to five hours to decompose excess peroxide. The end point is determined by carrying out starch-iodine tests. Water is then evaporated under vacuum to give the sulfone in a yield of 90% to 95%, i.e., about 600 parts of the sulfone $(HO—CH_2—CH_2)_2SO_2$. These compounds are also known.

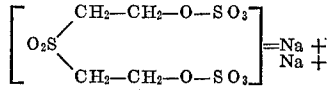
Preparation of the bissulfatoethyl sulfone.—Thirty percent fuming H_2SO_4 is added to the sulfone, which is a viscous oil or solid, with cooling and stirring. 2.2 moles of SO_3 (including free SO_3 and the SO_3 equivalent of the H_2SO_4 present) are used per mole of the sulfone. The reaction is exothermic and it is preferred to hold the temperature in the range of about 5° to 10° C. during the addition. Thereafter, the mixture is allowed to come to room temperature, where it is kept about two to four hours. With cooling and stirring to maintain a temperature below 20° C. the mixture is poured into an equal volume of water. The product at this point has the structure $(HO_3SO—CH_2—CH_2)_2SO_2$. The acid form of the bissulfatoethyl sulfone can be used as such as a cross linking agent for treating cellulosic fibers following the same procedure described above, or it can be converted to the metal salt.

Preparation of the metal salt.—In making the sodium salt, sodium hydroxide or preferably sodium carbonate is added in amount sufficient to replace all of the acid hydrogens of the sulfatoethyl groups. Sodium sulfate precipitates at the high concentration of sodium ion prevailing and can be filtered off. The yield of the sodium salt is about 50% based on the sulfone. To get the solid sodium salt, water is evaporated under vacuum until the liquid in the pot begins to solidify. The pot is cooled and the material is recrystallized from a solution of 25% water and 75% acetone by volume. An alternative procedure is to evaporate until the liquid slurry is present in the pot. Acetone is then added to the slurry in the pot to precipitate the desired sodium salt. The impurities are mainly retained in the solution.

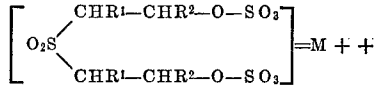
The product contains the ion



in association with positive, e.g., metallic ion or ions. The product having the chemical formula



exists as a monohydrate having a melting point of 162° C. and as a nonhydrated material having a melting point of 141.5° C., both of which are white crystalline solids. More generally, the materials in which the ethylene hydrogens may be substituted with alkyl groups having 1 to 3 carbon atoms are described by the structural formula:



where M refers to positive ions having two valences matched by the divalent bissulfatoethyl sulfone anion. The divalent anion is believed to be present as described in the structural formula irrespective of the particular cation associated therewith and irrespective of whether the compound is in the form of a liquid, a solid, or in solution.

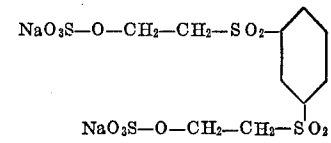
Treatment of cloth.—A 15% aqueous solution of the bissulfatoethyl sulfone sodium salt or other metal salts is fed to padding rolls while the cotton cloth to be treated (4 yard per pound 80 x 80) is passed downwardly between the rolls. The amount of solution supplied is sufficient to give 75% liquid pickup by the cloth. The fabric is then dried, preferably at room temperature, after which it is again padded with 2% aqueous sodium hydroxide solution saturated with sodium chloride (to retard any tendency of the sulfone to go into solution). The caustic padded cloth is held at room temperature for one hour, then washed thoroughly with detergent, rinsed, and dried. The finished fabric has the desired flat drying qualities while retaining a high degree of strength. It also has wet crease resistance and configurational memory.

EXAMPLE II

The procedure of Example I is carried out except that the fabric is treated with the bissulfatoethyl sulfone and dried, then immersed in 2% aqueous sodium hydroxide saturated with sodium chloride at 40° C. for thirty seconds. It is then removed, washed thoroughly with a detergent, rinsed and dried. The fabric obtained has the desirable flat drying and other qualities substantially like the product of Example I.

EXAMPLE III

A 21% by weight solution of the compound



in water is prepared and is padded on a viscose rayon fabric having a count of 97 x 51 and a weight of 6.5 oz. per yard and made of 19.8/1 warp and 19.8/1 filling of spun viscose staple fiber, to give a pickup of 70% by weight of the solution based on the weight of the unpadded fabric. It is air dried and then padded again with 2% aqueous sodium hydroxide solution saturated with sodium chloride at room temperature. The pickup of aqueous sodium hydroxide solution is also 70%. The fabric is rolled up into a roll and wrapped in aluminum foil where it is left for one hour at room temperature. The fabric is thereafter washed thoroughly with detergent in hot water, rinsed, and dried. The finished fabric has good flat drying properties, wet crease resistance, and wet configurational memory.

EXAMPLE IV

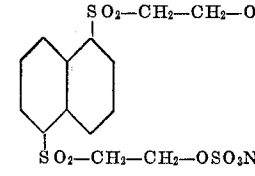
A 13% by weight of aqueous solution of the compound

$$[NaO_3S—O—CH_2—CH_2—SO_2—CH—_2]_2$$

is prepared and is padded on woven cotton fabric (4 yards per pound 80 x 80) according to the procedure described in the previous examples. The pickup of solution by the fabric is also 70%. The fabric is dried in the air and is repadded with 2% aqueous sodium hydroxide saturated with sodium chloride to a pickup of 70%. The fabric is immediately rolled and wrapped in aluminum foil and stored for one hour at room temperature and is thereafter unrolled and washed thoroughly in hot water containing a detergent, rinsed, and dried. The product has good flat drying properties, wet crease resistance, and wet configurational memory.

EXAMPLE V

A 28% by weight aqueous solution of the compound

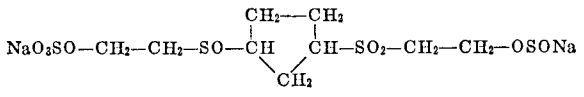


is prepared and is padded on a cotton fabric (4 yards per pound 80 x 80) to give a solution pickup of 70% by weight. The fabric is air dried and then immersed in a 2% aqueous NaOH solution without sodium chloride at 70° C. for about 15 seconds. It is then withdrawn and immediately washed thoroughly with hot water containing de-

tergent, rinsed, and allow to dry in the air. The fabric has good flat drying properties, wet crease resistance, and wet configurational memory.

EXAMPLE VI

A 24% by weight aqueous solution of the compound



is prepared and is padded on a cotton fabric to get a 70% pickup of solution, after which it is dried in the air. It is then immersed in a 5% aqueous NaOH solution saturated with sodium chloride at 35° C. for sixty seconds. At the end of that time, it is withdrawn, washed thoroughly in hot water containing a detergent, rinsed, and dried in the air. The fabric has good flat drying properties, wet crease resistance, and wet configurational memory.

EXAMPLE VII

A 16% aqueous solution of the compound

$$[NaO_3S—O—CH(CH_3)—CH_2—]_2SO_2$$

is prepared and is padded on a 4 yard per pound 80 x 80 cotton fabric. It is then immersed in a 3% aqueous solution of benzyl trimethyl ammonium hydroxide at 50° C. for 45 seconds, after which it is withdrawn and immediately washed thoroughly with hot water containing a detergent. The fabric is rinsed, dried and found to have good flat drying properties.

EXAMPLE VIII

An aqueous solution consisting of 10% of the sulfato sulfone

$$(NaO_3SO—CH_2—CH_2)_2SO_2$$

10% Aerotex 23 (containing 50% solids) a modified melamine formaldehyde resin sold by American Cyanamid Company, 0.8% zinc nitrate (catalyst), 6% Moropol 700 (emulsified polyethylene softener) made by Mortex Chemical Products, Inc. containing 30% solids is then padded onto a cotton fabric to give 70% pickup based on the weight of the fabric. It is then air dried and cured at 160° C. for one and one-half minutes. The fabric is then immersed in 2% aqueous sodium hydroxide saturated with sodium chloride at 35° C. for 30 seconds. It is immediately withdrawn and washed in hot water containing detergent, rinsed, and dried. The fabric has crease resistance comparable to fabrics treated with twice the amount of the same resin without cross linking agent. The wet crease resistance and the wet configurational memory are comparable to a fabric that has been treated with a larger amount of the same cross linking agent, but without resin.

Although this aspect of the invention has been illustrated in terms of using a specific sulfone as cross linking agents, the same effects could be obtained with any of the other cross linking agents described above.

The foregoing description has been directed to the use of sulfones as cross linking agents. Another group of cross linking agents having similar properties are the sulfoxides, which are represented by the same general structural formula

$$X[CHR^1—CHR^2—O—SO_3Y]_2$$

except that the group X is —SO— or —SO—R—SO—. In the structural formula for the sulfoxide cross linking agents, the same symbols R^1, R^2 and Y are defined in exactly the same way as they are in the case of the sulfone cross linking agents.

The effect of the sulfoxide group has been found to be substantially the same as the effect of the sulfone group described above, that is, it activates the sulfato group toward the cellulose hydroxyl groups to produce cross linking. Therefore, the reaction mechanisms and reaction conditions described above for the sulfone cross linking agent apply also to the use of the sulfoxide cross linking agents. Specifically, the molar proportions of the cross linking agent and the anhydro-glucose units, and the types and concentrations of strong alkali used during the cross linking reaction generally are the same for the sulfoxides and the sulfones. Furthermore, the sulfoxides can be used for cross linking the several types of cellulosic fibers (for example, cotton, regenerated cellulose, chemically modified cellulose) that were described in connection with the sulfones.

The following is an example giving a specific precedure for cross linking cotton fibers with a sulfoxide cross linking agent.

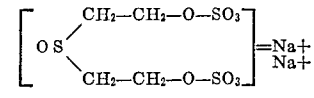
EXAMPLE IX

The following sulfoxide was prepared as an intermediate in the preparation of the sulfone used in Example I.

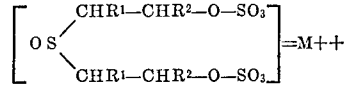
$$(HO—CH_2—CH_2)_2SO$$

The aqueous solution of the sulfoxide is evaporated to dryness under vacuum and the white crystalline product is obtained in a yield of 95% to 100% of theoretic, based on the sulfide. The sulfoxide is reacted with 30% fuming sulfuric acid in the ratio of 1 mole of sulfoxide to 3 moles of SO_3 (based on total free SO_3 and SO_3 equivalent to the H_2SO_4).

The fuming sulfuric acid is placed in a vessel equipped with a stirrer and surrounded by an ice bath. The sulfoxide is added in small amounts periodically over a period of three hours taking care that the temperature of the mixture does not go above 20° C. After all of the sulfoxide has been added, stirring is continued for two to four hours and the material is allowed to warm up to room temperature. The liquid reaction product is added slowly to an equal volume of water while cooling it to keep the temperature below 20° C. It is then neutralized to a pH of seven by adding sodium carbonate. Due to the high concentration of the sodium ion, most of the sodium sulfate is precipitated and is removed by filtration. The product is evaporated to dryness under vacuum to obtain a white crystalline product in a 50% yield based on the bishydroxyethyl sulfoxide. The product has the following composition:



This is a new composition of matter and may be represented by the same structural formula



wherein the symbols have the same meaning as described thereto in discussing the sulfones.

Treatment of cloth.—A 25% aqueous solution of the bissulfatoethyl sulfoxide is prepared and padded onto a 4 yard per pound 80 square cotton fabric to give a 70% by weight pickup of the solution. It is air dried and then immersed in a 2% aqueous sodium hydroxide solution saturated with sodium chloride. The alkaline solution is at 70° C. Immersion is for 3½ minutes. The cloth is then withdrawn and immediately washed in a hot aqueous solution containing a detergent, rinsed, and dried at room temperature. The fabric has very good flat drying properties, wet crease resistance, and wet configurational memory.

Other sulfoxides that are effective in treating cellulosic fibers according to the invention are those that have the same structural formula as the compounds used in Examples I to VIII, inclusive, and others described in the specification except that the sulfone group —SO_2— is replaced with the sulfoxide group —SO—.

EXAMPLE X

The fabric is prepared as in Example IX and immersed in an aqueous 15% acetic acid solution containing metallic zinc, and is held at a temperature of 35° to 40° C. The treatment is continued for 15 minutes in order to reduce the sulfoxide (S—O) groups in cross links to sulfide groups (S). The fabric is then withdrawn, washed thoroughly with hot water containing a detergent, rinsed, and dried in the air. The fabric still has substantially the same flat drying, wet crease resistance, and configurational memory properties, but the chlorine absorption is substantially reduced. Instead of using zinc and acetic acid to reduce the sulfoxide linkages between the cross linked cellulose chains, the reduction may be carried out in similar reducing media that do not cause decomposition of the cellulose. The advantage of being able to reduce the sulfur in the cross linkages applies to the other sulfoxide cross linking agents as well.

EXAMPLE XI

An 80 x 80 4 yard per pound cotton print cloth, bleached and mercerized, is treated with a solution containing 15% diglycidyl ether of tetraethylene glycol, 20% bis(sodium sulfatoethyl) sulfone, 1% zinc fluoroborate, and 64% water. The fabric is padded with the solution, dried and cured one and one-half minutes at 150° C. The cured fabric is then padded with 3% NaOH, rolled up damp and held at room temperature for 6 hours. The cloth is then washed and dried. It has excellent line and tumble drying properties.

EXAMPLE XII

A cotton fabric, bleached and mercerized, is treated with a solution containing 10% HCHO, 20% bis (sodium sulfatoethyl) sulfone, 1% oxalic acid and 69% water. The fabric is padded with the above solution, dried and cured two minutes at 150° C. The cured fabric is then padded with 3% NaOH, rolled up at room temperature and aged six hours. The fabric is then washed and dried. It has excellent line and tumble drying properties.

That which is claimed is:

1. The method of imparting wet memory to cellulosic fibers, which comprises treating said fibers in the presence of a strong alkali with an agent having the formula

$$X(CHR^1—CHR^2—O—SO_3Y)_2$$

in which

R^1 and R^2 are of the class consisting of hydrogen and saturated alkyl groups having 1 to 3 carbon atoms,

Y is of the class consisting of metals such that said agent is soluble in water, and hydrogen,

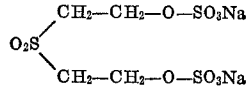
X is of the class consisting of $—SO_2—$; and —SO— thereby to chemically combine said agent with the cellulose.

2. The method of claim 1 wherein X is $—SO_2—$.

3. The method of claim 1 wherein R^1 and R^2 are hydrogen.

4. The method of claim 1 wherein Y is an alkali metal.

5. The method of claim 1 wherein the agent is



6. The method of claim 1 wherein the agent is

$$[NaO_3S—O—CH(CH_3)—CH_2—]_2SO_2$$

7. The method of claim 1 in which the strong alkali is an alkali metal hydroxide.

8. The method of claim 1 in which the amount of alkali is at least about two equivalents per mole of cross linking agent in excess of that necessary to neutralize any acidic hydrogens present on the sulfonate groups of the cross linking agent.

9. The method of claim 1 in which the amount of agent is in the approximate range of 0.005 to 0.05 mole per anhydro-glucose unit of the cellulose.

10. The method of claim 1 in which the amount of cross linking agent is at least about 0.01 mole per anhydro-glucose unit of the cellulose.

11. The method of claim 1 wherein the cross linking agent is first applied to the fibers, the fibers are then dried, and the fibers thereafter treated with the strong alkali to cross link the cellulose chains.

12. The method of claim 1 wherein the cellulosic fibers are cotton.

13. The method of claim 1 wherein the cellulosic fibers are viscose rayon.

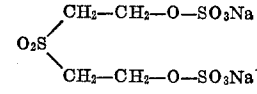
14. The method of claim 1 wherein the cellulosic fibers are mixed with non-cellulosic fibers having flat drying properties, and the amount of cellulosic fibers is at least 10% by weight based on the total weight of cellulosic and non-cellulosic fibers.

15. The method of claim 1 wherein cellulosic fibers are mixed with non-cellulosic fibers and the amount of cellulosic fibers is at least 40% by weight based on the total weight of the cellulosic and non-cellulosic fibers.

16. The method of claim 1 wherein a solution of said agent, an acid catalyzable, water soluble thermosetting textile resin having a molecular weight less than 1000 and an acid catalyst is prepared, said solution is applied to cellulosic fibers, the fibers are then heated to cure said thermosetting resin without activating substantially said agent, and the fibers are then treated with said strong alkali, thereby to cross link the cellulose chains of said fibers.

17. The method of claim 1 in which cellulosic fibers are first modified with a water soluble, acid catalyzed thermosetting textile resin having a molecular weight less than 1000 and are thereafter treated with said agent, thereby to impart both wet memory and dry crease resistance to the fibers.

18. The method of claim 17 in which the thermosetting resin is a melamine formaldehyde resin, the amount thereof is in the approximate range of 1% to 5% based on the weight of the cellulosic fibers, and the agent is



the amount of said agent being in the approximate range of 0.01 to 0.02 mole per anhydro-glucose unit.

19. The method of claim 17 in which the thermosetting resin is an aminoplast resin.

20. The method of claim 19 in which the resin is a melamine formaldehyde resin.

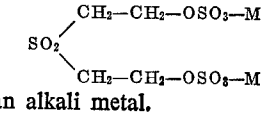
21. The method of claim 17 in which the amount of thermosetting resin applied is in the approximate range of 0.5% to 15% based on the weight of the cellulosic fibers and the amount of said agent is in the approximate range of 0.005 to 0.03 mole per anhydro-glucose unit.

22. The method of claim 21 wherein the amount of thermosetting resin is in the approximate range of 1% to 5% based on the weight of the cellulosic fibers.

23. The method of claim 1 wherein X is —SO—.

24. The method of claim 23 in which cellulosic fibers after being treated with the agent and the strong alkali are treated with a mild reducing agent to reduce the sulfoxide groups chemically attached to the cellulose chains to sulfide groups without substantial degradation of the fibers.

25. A process of chemically modifying a fibrous cellulosic material which comprises treating the material in the presence of an alkaline catalyst with a sulfone having the structural formula



where M is an alkali metal.

26. Cellulosic fibers prepared according to the method of claim 1.

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8—115.6, 120, 116.2, 116.3, 129, Dig. 2; 117—140 A; 260—230, 232, 458, 460, 607 A, 851, 856, 29.4 R, 231 A