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[21] Appl. No. **747,015**
[22] Filed **July 17, 1968**
[45] Patented **Jan. 11, 1972**
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**Continuation of application Ser. No.
242,604, Dec. 6, 1962, now abandoned.
This application July 17, 1968, Ser. No.
747,015**

[51] Int. Cl. **D06m 1/24,
D06f**
[50] Field of Search **8/DIG. 18,
115.6**

[56] **References Cited**
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2,922,768 1/1960 Mino et al. 260/17.4
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[54] **MODIFICATION OF CELLULOSIC FIBERS WITH
ETHYLENICALLY UNSATURATED COMPOUNDS**
4 Claims, No Drawings
[52] U.S. Cl. **8/116,**
8/116.2, 38/144, 2/243, 260/17.4

ABSTRACT: Cellulosic textile materials are reacted with ethylenically unsaturated compounds which, in polymer or copolymer form, have a glass transition temperature in excess of 50° C. to produce a material which may be set under heating conditions in a desired configuration which is durable to the effects of wetting with water.

MODIFICATION OF CELLULOSIC FIBERS WITH ETHYLENICALLY UNSATURATED COMPOUNDS

This case is a continuation of U.S. application, Ser. No. 242,604, filed Dec. 12, 1962, and now abandoned.

This invention relates to a novel process for producing s) having a high degree of settability and crease retentivity, and to fabrics and garments produced therefrom.

Cellulosic materials, particularly cotton, are used extensively in the production of garments. These garments have excellent insulating and aesthetic properties but in some instances, such as after wetting, the garments lose their otherwise neat appearance. This difficulty has been generally overcome by various processes involving treatment of the garments, or of the fabrics from which the garment is made, with various cross-linking reagents. These processes invariably involve an increased cost in the garment due to the extensive process control requirements on the part of the fabric manufacturer. In addition, the configuration set in the garment by one of the cross-linking procedures is substantially permanent and cannot be altered without extensive further treatment.

Furthermore, present techniques involve treatment to produce flat cellulosic fabrics. Prior to the present invention there was no known procedure for producing cellulosic fabrics having a propensity for subsequent durable setting in any desired configuration, i.e., flat, creased, pleated or the like.

It is an object of this invention to treat cellulosic materials in such a manner as to impart thereto a high degree of settability and a correspondingly high degree of retention of the configuration in which the fibers are set.

It is a further object of this invention to produce yarns, fabrics and garments having a similar settability and capacity to contain the set configuration.

Another object of this invention is to produce cellulosic materials which can be set in any given configuration with the further capability of having that configuration readily altered to other configurations as desired.

Yet another object of this invention is to provide a cellulosic fabric which may be durably set in any desired configuration, as by a garment manufacturer, without any further chemical treatment.

These objects are accomplished in accordance with this invention by reacting cellulosic materials with a particular class of ethylenically unsaturated compounds. Yarns, fabrics and/or garments constructed of these cellulosic materials may be set in any given configuration and that configuration will be durable to wetting.

By "settability" as used herein is meant the capacity of a cellulosic material to be set in a predetermined configuration which will be retained even after prolonged exposure to wet conditions. By "crease retentivity" as used herein is meant the ability of a cellulosic material to retain a crease or pleat after prolonged exposure to wet conditions.

Cellulosic materials have been reacted with a wide variety of ethylenically unsaturated compounds, but there has been no realization heretofore that a certain class of ethylenically unsaturated compounds may be reacted with cellulosic materials so that yarns, fabrics, and garments produced therefrom may be durably set without further chemical treatments in any given configuration, for example, flat, creased, pleated or otherwise under conditions of heat and pressure. These configurations, furthermore, may be readily altered to other configurations as desired under the same conditions of heat and pressure. Generally, the temperature of setting exceeds the glass transition temperature of the compound system utilized, although adequate results are obtained at any elevated temperature, e.g., in excess of about 40 C. At lower temperatures, it may be desired to use higher pressures to produce the most satisfactory set.

The class of ethylenically unsaturated compounds suitable for use in accordance with this invention includes those compounds which, in polymer or copolymer form, have a glass transition temperature in excess of about 50 C., preferably above about 75 C. The glass transition temperature is a well-known property and is the temperature at which a sheet of a polymer is transformed from a glasslike solid state to a soft-

tened state. Above the glass transition temperature, the volume of the sheet increases more rapidly with an increase in temperature. The point at which this volume increase begins may be readily determined in a plot of volume versus temperature. These glass transition temperatures may be readily determined by standard A. S. T. M. heat deflection temperature measurements, for example A. S. T. M. Designation D648-45T, issued 1941, revised 1944, 1945.

Among the suitable compounds, there are included acrylamides and the monomeric or low polymeric forms of N-dialkyl acrylamides, such as N,N-dimethyl, -diethyl, -dipropyl, -dibutyl, -dihexyl, -dioctyl etc., acrylamides; N-(p-anisyl) methacrylamide, N-(p-chlorophenyl) methacrylamide, N-phenyl methacrylamide, N-ethylmethacrylamide, N-methylmethacrylamide, N-(p-tolyl) methacrylamide and the like; unsaturated acids and anhydrides, such as acrylic, methacrylic, ethacrylic, propacrylic, chloroacrylic, bromoacrylic, aconitic, itaconic, maleic, crotonic, fumaric citraconic and the like; the phenyl, benzyl, phenylethyl, etc., esters of the aforementioned acids; vinyl aromatic compounds, such as styrene and methylstyrenes, such as m-methylstyrene, o-methylstyrene, p-methylstyrene and dimethylstyrenes, such as 2,5-dimethylstyrene; halogenated styrenes, such as m-bromostyrene, p-bromostyrene, p-iodostyrene, pentachlorostyrene, a, -trifluoro-styrene, 2,5-bis(trifluoromethyl) styrene, 3-trifluoromethyl styrene, dichlorostyrene, and the like; the various cyanostyrenes; the various methoxystyrenes, e.g., p-methoxystyrene; vinyl naphthalenes, etc., e.g., 4-chloro-1-vinylnaphthalene, 6-chloro-2-vinylnaphthalene; vinyl halides, e.g., vinyl chloride, bromide, etc.; itaconic and maleic diesters containing a single $\text{CH}_2=\text{C}-$ grouping, e.g., the dimethyl, diethyl, di- β -chloroethyl, diethylchloro, diisopropyl, dipropyl, dibutyl, diisobutyl, dinonyl and other saturated aliphatic monohydric alcohol diesters, e.g., diphenyl itaconate, dibenzyl itaconate, di-(phenylethyl) itaconate, etc., and corresponding maleates; methyl and ethyl methacrylate; nitriles containing a single $\text{CH}_2=\text{C}-$ grouping, e.g., acrylonitrile, methacrylonitrile, a-acetoxyacrylonitrile and the like.

Preferred compounds within this class include acrylonitrile (glass transition temperature ca. 95 C.), styrene (ca. 100 C.), dichlorostyrene (ca. 130 C.) methyl methacrylate (ca. 105 C.), vinyl chloride (ca. 80 C.) and copolymers containing a sufficient amount of such compounds, including copolymers containing compounds having glass transition temperatures below about 50 C., to provide a copolymer having a glass transition temperature above about 50 C., e.g., styrene/acrylonitrile (ca. 110 C.) styrene/fumaronitrile (ca. 125 C.), styrene/dichlorostyrene (ca. 110 C.), vinyl chloride/vinyl acetate (ca. 60 C.), vinyl chloride/vinylidene chloride (ca. 60 C.), styrene/butyl acrylate 90/10 (ca. 77 C.), styrene/butyl acrylate 85/15 (ca. 67 C.), methyl methacrylate/ethyl acrylate 80/20 (ca. 71 C.) and the like.

Of the above compounds, acrylonitrile, styrene and methyl methacrylate are highly preferred for availability, cost and performance.

While some improvement is obtained at any significant pickup of the above compounds, e.g., above about 10 percent by weight, the desired improvement is obtained to a significant level only at pickups in excess of about 50 percent by weight of the above compounds.

This class of ethylenically unsaturated compounds can be reacted with keratinous and cellulosic materials by a number of well-known processes. For example cellulosic fibers may be reacted with the desired compounds in the presence of a catalyst or initiator system for inducing polymerization of the compound. Among such systems are included irradiation under the influence of high energy fields, including the diverse actinic radiations, such as ultraviolet X-ray and gamma radiations, as well as radiations from radioactive material such as cobalt-60.

Redox catalyst systems composed of a reducing agent and an oxidizing agent initiator may also be utilized. Although the catalytic mechanism is not completely understood, it is believed that the interaction of these agents provides free radicals which cause polymerization of the compounds, which preferably are in monomeric or low polymeric form, onto the cellulosic material.

The reducing agent may be an iron compound, such as the ferrous salts including ferrous sulfate, acetate, phosphate, ethylenediamine tetra-acetate, metallic formaldehyde sulfoxylates, such as zinc formaldehyde sulfoxylate; alkali-metal sulfoxylates, such as sodium formaldehyde sulfoxylate; alkali-metal sulfites, such as sodium and potassium bisulfite, sulfite, metabisulfite or hydrosulfite; mercaptan acids, such as thioglycolic acid and its water-soluble salts, such as sodium, potassium or ammonium thioglycollate; mercaptans, such as hydrogen sulfide and sodium or potassium hydrosulfide; alkyl mercaptans, such as butyl or ethyl mercaptans and mercaptan glycols, such as beta-mercaptoethanol; alkanolamine sulfites, such as monoethanolamine sulfite and mono-isopropanolamine sulfite; manganous and chromous salts; ammonium bisulfite, sodium hydrosulfide, cysteine hydrochloride, sodium thiosulfate, sulfur dioxide, sulfurous acid and the like, as well as mixtures of these reducing agents. In addition, a salt of hydrazine may be used as the reducing agent, the acid moiety of the salt being derived from any acid, such as hydrochloric, hydrobromic, sulfuric, sulfurous, phosphoric, benzoic, acetic and the like.

Suitable oxidizing agent initiators for use in the redox catalyst system include inorganic peroxides, e.g., hydrogen peroxide, barium peroxide, magnesium peroxide, etc., and the various organic peroxy catalysts, illustrative examples of which are the dialkyl peroxides, e.g., diethyl peroxide, dipropyl peroxide, dilauryl peroxide, dioleoyl peroxide, distearyl peroxide, di-(tert.-butyl) peroxide and di-(tert.-amyl) peroxide, such peroxides often being designated as ethyl, propyl, lauryl, oleyl, stearyl, tert.-butyl and tert. amyl peroxides; the alkyl hydrogen peroxides, e.g., tert.-butyl hydrogen peroxide (tert.-butyl hydroperoxide), tert.-amyl hydrogen peroxide (tert.-amyl hydroperoxide), etc.; symmetrical diacyl peroxides, for instance peroxides which commonly are known under such names as acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearoyl peroxide, malonyl peroxide, succinyl peroxide, phthaloyl peroxide, benzoyl peroxide, etc.; fatty oil acid peroxides, e.g., coconut oil acid peroxides, etc.; unsymmetrical or mixed diacyl peroxides, e.g., acetyl benzoyl peroxide, propionyl benzoyl peroxide, etc.; terpene oxides, e.g., ascaridole, etc.; and salts of inorganic peracids, e.g., ammonium persulfate, potassium persulfate, sodium percarbonate, potassium percarbonate, sodium perborate, potassium perborate, sodium perphosphate, potassium perphosphate, etc.

Other examples of organic peroxide initiators that can be employed are the following: tetralin hydroperoxide, tert.-butyl diperphthalate, cumene hydroperoxide, tert.-butyl perbenzoate, 2,4-dichlorobenzoyl peroxide, urea peroxide, caprylyl peroxide, p-chlorobenzoyl peroxide, 2,3-bis(tert.-butyl peroxy) butane, hydroxyheptyl peroxide and the diperoxide of benzaldehyde.

The above oxidizing agent initiators, particularly the salts of inorganic peracids, may be utilized alone to initiate the reaction, although faster reactions at lower temperatures may be conducted when the oxidizing agent is combined with a reducing agent to form a redox catalyst system. Ferric salts can be used as oxidizing agents and form a redox catalyst system with hydrogen peroxide, in which case the peroxide functions as a reducing agent.

In addition to the above initiating systems, ceric ions also may be utilized, for example, in the form of ceric salts, such as ceric nitrate, ceric sulfate, ceric ammonium nitrate, ceric ammonium sulfate, ceric ammonium pyrophosphate, ceric iodate and the like.

The reaction between cellulosic materials and ethylenically unsaturated compounds most readily takes place in the presence of water. This generally presents no problem since only small amounts are necessary for this improvement and since catalyst components and/or monomers or low polymers are generally applied to the fibers in an aqueous medium. If the substrate is dry at the time of treatment, the reaction rate will be slower. Consequently, it is preferred that the substrate be wet with water when the reaction takes place. Ionic or nonionic surface active agents may be utilized in any aqueous medium used in applying the reagents.

In the presence of the above systems, it is believed that the ethylenically unsaturated compounds react with the cellulosic materials, although the mechanism of the reaction is by no means completely understood. It is known, however, that when acrylonitrile or another ethylenically unsaturated compound of the desired class, is applied to cellulosic fibers in the presence of one of the above initiating systems, the resulting cellulosic material increases considerably in weight and the reacted compounds cannot be readily removed by extraction techniques utilizing solvents for the homopolymers of such compounds. It is, consequently, believed that the reacted compounds, to a large extent, are covalently bonded to the cellulosic material. Similar effects are obtained, however, when the reacted compound is otherwise bonded to the fibers, but these compounds are generally extractable and therefore not as permanent. Where permanence is not essential, this type reaction is suitable though not as desirable as are the covalently bonded reacted compounds.

The reaction of the above monomers, or their derivatives, with cellulosic fibers may be conducted at room temperature, although temperatures between 40° and 60° C. are generally preferred. Temperatures in excess of about 100° C. are generally not preferred when the redox catalyst system is utilized, since undue degradation of some of the components of this system occurs at this elevated temperature. In general, such conditions as concentrations of the reagents, pH, time and temperature of reaction may be modified to suit the individual circumstances.

The cellulosic substrate may be exposed to the monomer in vapor, liquid or emulsion form. Exposure to the vapors of the monomer is conveniently carried out by entraining the vapor in an oxygen-free gas, such as nitrogen, and then interposing the substrate in a stream of the gas and vapor. Inert volatile liquids, such as water or an alcohol, may be mixed with the compound being vaporized. Similarly, the fibrous substrate may be immersed in a liquid system, either solution or emulsion type, containing the desired amount of monomer.

Any desired apparatus may be used to apply one or more of the above class of ethylenically unsaturated compounds to cellulosic materials, such as by padding, spraying or the like. The preferred apparatus includes forced flow equipment such as disclosed in the compending application Ser. No. 243,671 now U.S. Pat. No. 3,291,560. With this apparatus the desired systems can be repeatedly forced back and forth through cellulosic materials at controllable flow rates to provide particularly good reaction results.

The term "cellulosic material" when used herein means any material, preferably textile, comprising fibers having the free hydroxy group characteristic of cellulose, for example, natural cellulose fibers such as cotton, paper, linen, jute, flax and the like; regenerated cellulose fibers such as viscose rayon; fibers containing a limited number of acetyl groups, such as cellulose acetate; fibers containing a limited number of methyl ether groups, such as partially methylated cellulose.

Although this invention is directed primarily and preferably to cellulosic textile materials, both knitted and woven, the advantages of this invention can also be achieved by treating cellulosic yarns or threads employed to produce these fabrics. Ordinarily this will be cotton thread or yarn. The thus-treated thread or yarn, when woven into fabric, will provide a fabric having improved aesthetic and strength properties over an identical fabric reacted as such with the ethylenically unsaturated compound.

Cellulosic fibers or yarns or threads treated in accordance with this invention may be blended with synthetic or other natural fibers to provide desirable fabrics. The preferred natural fibers include keratin fibers, such as wool, mohair, alpaca, cashmere, vicuna, guanaco, camel's hair, silk, llama and the like. The preferred synthetic fibers include polyamides, such as poly(hexamethylene adipamide), polyesters, such as poly(ethylene terephthalate) and acrylic fibers, such as acrylonitrile, homopolymer or copolymers of the acrylonitrile containing at least about 85 percent combined acrylonitrile, such as acrylonitrile/methyl acrylate (85/15).

Reacted fiber, yarn or thread treated in accordance with this invention may be mechanically crimped as with gear-crimping apparatus, heated or not, prior to processing in the fabric. In many instances, this will facilitate fiber processing as well as provide a more luxurious fabric.

In the following examples, the best modes as presently known of practicing the invention are shown.

EXAMPLE I

Cotton yarn (578 gms. -6's) is wound on the spindle of a 2-lb. Gaston County package dyeing machine and placed in the machine. After scouring by passing through the package dyeing machine and yarn, an aqueous solution containing 0.5 percent on the weight of cotton of Surfonic N-95, a nonionic surface active agent, and 1.5 percent on the weight of wool of glacial acetic acid for 20 minutes at 140° F., the cotton is rinsed in water at 100° F. for 15 minutes. Deionized water is used in preparing all aqueous media in this example.

The yarn is then rinsed and the system is filled with deionized water. Methyl methacrylate (463 g.) is circulated through the yarn at a cycle of 3 minutes outside-in and 2 minutes inside-out for 15 minutes. This cycling is utilized throughout this example.

Ceric ammonium nitrate (400 milliliters of 0.1 M in 1 N HNO₃) is added to the system over a 5-minute period and circulation of the resulting system (initial pH of 1.3) is continued for 1 hour at 80° F. During the next hour, the temperature of the system is increased at 0.5° per minute until 100° F. is reached and circulation is continued at this temperature for 20 minutes. The final pH of the system is 1.1. The resultant yarn is rinsed with water, neutralized with NaHCO₃ (5 g. in 10.5 liters of water) and rinsed again until a pH of 6.8 is reached. The sample so treated is weighed and found to have increased in weight by 69 percent.

A 4-inch length of this yarn is mounted as a tight loop with a 5-millimeter diameter piano wire. The loop is then pressed at

about 100 lbs. per square inch at 100° F. for 3 minutes in a hydraulic press. The pressed loop is then placed in water heated to 140° F. for 20 minutes and dried. The angle formed by the creased yarn is measured at 95°. A similar length of untreated cotton yarn pressed in the same manner retains an angle of 132°. In this measurement, the lower the number the greater the crease retention of the creased fiber. At 97 percent pickup of reacted methyl methacrylate, the retained crease angle is 63°.

The procedure is repeated on cotton yarn containing 80 percent by weight of styrene and similar effects are noted.

EXAMPLE II

A pair of boy's trousers is produced from the methyl methacrylate reacted yarn of example I. These trousers are then pressed in a Hoffman press using 30 seconds steam, 30 seconds bake and 10 seconds vacuum. The samples are all creased to a very sharp degree and retain a sharp crease after heating in water at 100° F. for 20 minutes, where as a control fabric containing no reacted methyl methacrylate shows little or no crease whatsoever. The trousers are purposely recreated in the same manner in a different location. No double crease appears after recreasing in this manner or after testing in water at 100° F.

That which is claimed is:

1. A process of preparing garments having a creased configuration which is durable to the effects of wetting with water and which is capable of being removed under conditions of heat and pressure similar to those employed in the forming thereof comprising reacting cellulosic fibers to a level exceeding about 50 percent by weight of said fibers with an ethylenically unsaturated compound having, in polymer form, a glass transition temperature greater than about 50° C. or with two ethylenically unsaturated compounds having, in copolymer form, a glass transition temperature greater than about 50° C.; forming a fabric from said modified fibers; preparing a garment from said fabric and pressing said garment in a creased configuration at a temperature in excess of the glass transition temperature of the compound system utilized.

2. The process of claim 1 wherein a compound system characterized by a glass transition temperature in excess of about 75° C. is utilized.

3. The process of claim 1 wherein the garment is pressed on a press using a cycle or 30 seconds steam, 30 seconds bake and 10 seconds vacuum.

4. A garment produced by the process of claim 1.

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