United States Patent Office 3,423,163 Patented Jan. 21, 1969

3,423,163

CELLULOSIC TEXTILE FIBERS BEARING GRAFTED N-METHYLOL AMIDE

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No Drawing. Original application June 3, 1959, Ser. No. 817,881. Divided and this application July 19, 1966, Ser. No. 566,258
U.S. Cl. 8—116.3 2 Claims
Int. Cl. D06m *13/40*

ABSTRACT OF THE DISCLOSURE

A cellulosic textile fiber bearing polymeric chains grafted to the cellulosic fiber, the said chains being derived from an N-methylol amide of an unsaturated acid, said chains being grafted to said cellulosic fiber via carbon-to-carbon bonds in which one of the carbons of the bond is a cellulosic carbon. Among the fibers exemplified are cotton and rayon grafted with N-methylolacrylamide.

This application is a division of United States application 817,881, filed June 3, 1959, now abandoned, which was a continuation-in-part of United States applications Nos. 500,032, filed Apr. 7, 1955, and now abandoned, and 503,792, filed Apr. 25, 1955, and now abandoned.

This invention relates to cellulosic textile fibers having grafted thereto an organic compound.

The fibers of nature, i.e., those from natural carbonaceous cellulose, protein and isoprene polymers have many deficiencies when employed for apparel purposes. Attempts to cure these deficiencies by surface treatments with resins, etc., have not been satisfactory. For example, thin resin coatings on the filaments are not permanent to laundering. Heavy deposits of resins, rendered more durable and self-supporting by cross-linking, stiffen the fabric, making it harsh and unpleasant to handle or wear. Carried to an extreme, the fabric becomes bonded into a stiff unitary structure lacking in aesthetic appeal and good wear properties.

OBJECT

An object of this invention is to provide a textile formed from a natural carbonaceous polymer which is permanently modified to make it, for instance, more free from static, more dyeable, more resilient or crease resistant or more flame resistant, than textiles heretofore obtainable from the said polymers. Products having moisture absorption, hand and strength characteristics differing from the natural counterparts are also provided.

This and other objects will become apparent in the course of the following specification and claims.

STATEMENT OF INVENTION

The fibers of this invention are described as cellulosic textile fibers bearing polymeric chains grafted to the cellulosic fibers, the said chains being derived from an N-methylol amide of an unsaturated acid, said chains being grafted to said cellulosic fibers via carbon-to-carbon bonds in which one of the carbons of the bond is a cellulosic carbon.

DEFINITIONS

By the term "textile produced from a fiber-foaming carbonaceous material of nature" is meant a structure produced from filaments or films having a cellulose, protein or isoprene polymeric composition and formed in plant or animal growth and to fiber- and film-forming derivatives and regenerated forms of the natural carbonaceous

polymers such as protein, cellulose acetate and regenerated cellulose.

By "graft copolymer" is meant a polymer which is modified, after shaping, by chemically bonding thereto, molecules of a chemically dissimilar organic compound.

By "irradiation" is meant the process by which energy is propagated through space, the possibility of propagation being unconditioned by the presence of matter (as distinguished from mere mechanical agitation in a material medium such as is characteristic of energy produced by a sonic or ultrasonic transducer), although the speed, direction, and amount of energy transferred may be thus affected.

By "ionizing radiation" is meant radiation with sufficient energy to remove an electron from a gas atom, forming an ion pair; this requires an energy of about 32 electron volts (ev.) for each ion pair formed. This radiation has sufficient energy to nonselectively break chemical bonds; thus, in round numbers radiation with energy of about 50 electron volts (ev.) and above is effective for the process of this invention. The ionizing radiation of this process of this invention is generally classed in two types: high energy particle radiation, and ionizing electromagnetic radiation. The effect produced by these two types of radiation is similar, the essential requisite being that the incident particle or photons have sufficient energy to break chemical bonds and generate free radicals.

The preferred radiation for the practice of this invention is high energy ionizing radiation, and has an energy equivalent to at least 0.1 million electron volt (mev.). Higher energies are even more effective; there is no known upper limit, except that imposed by available equipment.

EXPERIMENTAL PROCEDURES AND UNITS

Compositions are given in parts by weight or weight percent, unless otherwise noted.

Radiation dosages are given in units of "mrad" (millions of rads), a "rad" being the amount of high energy radiation of any type wich results in an energy absorption of 100 ergs per gram of water or equivalent absorbing material. Alternatively, dosages may be indicated in terms of exposure in watt seconds per square centimeter of substrate treated.

The "standard washing" to which samples are subjected consists of a 30-minute immersion in 18 liters of 70° C. water contained in a 20-liter agitation washer. The wash solution contains 0.5% of detergent. The detergent employed is that sold under the trademark "Tide". This detergent contains, in addition to the active ingredient, well over 50% (sodium) phosphates (Chemical Industries, 60, 942, July, 1947). Analysis shows the composition to be substantially as follows:

	Percent
Sodium lauryl sulfate	16
Alkyl alcohol sulfate	6
Sodium polyphosphate	30
Sodium pyrophosphate	17
Sodium silicates and sodium sulfate	31

The static propensity of the fabric is indicated in terms of direct current resistance in ohms per square, measured parallel to the fabric surface, at 78° F. in a 50% relative humidity atmosphere. High values, reported as the logarithm (to the base 10) of the resistivity (log R) indicate a tendency to acquire and retain a static charge. A meter suitable for this determination is described by Hayek and Chromey, American Dyestuff Reporter, 40, 225 (1951).

Crease recovery is evaluated by crumpling a fabric in the hand, and observing the rate at which it recovers from this treatment. Numerical values are obtained using

the "vertical strip crease recovery test" described in the American Society for Testing Materials Manual, Test No. D1295–53T. In determining crease recovery by this method, the specimens are creased under a standard weight; the weight is then removed, and the recovery after 300 seconds is measured, averaging results obtained in the filling and warp directions.

The following examples are cited to illustrate the invention. They are not intended to limit it in any manner.

When a Van de Graaff generator is used for the irradiation treatment, the following conditions are typical:

Voltage-mev.	2
Tube current, microamperes	290
Conveyor speed, in./min.	40
Dose per pass, mrad	2

Example I

Pieces of scrubbed cotton sheeting (80 x 80 count) and scrubbed rayon challis are immersed in aqueous solutions of N-methylol acrylamide (MAA) at room temperature, and squeezed between rubber rolls to remove excess solution. The soaking and squeezing are repeated. The amount of N-methylol acrylamide padded on the fabrics is calculated from the wet-pickup and the pad bath concentration. A few fabrics are sealed in polyethylene bags while wet but in most cases fabrics are air-dried prior to sealing. The fabrics in polyethylene bags are exposed at about 25° C. to β-radiation from the 2 mev. vertical Van de Graaff electrostatic generator. After irradiation the fabrics are rinsed several times in distilled water, in water containing 0.2% Duponol ME [1] at 50° C. for 30 minutes, and finally in distilled water. The amounts of MAA grafted are determined by weight gains (dried at 110° C. for 1 hour) or from microKjeldahl nitrogen analyses. The data are summarized in Table 1 below:

TABLE 1

Sample	Fabric	Percent MAA in pad bath	Radiated wet or dry	Radiation dose, mrad	Percent gain
10A	Cotton	3.3	D	2	2.9
10B	do	5	D	2	4.9
10C	do	10	D	2	9.4
10D	do	15	D	2	14.4
10E	do	10.3	W	2	10.6
10F	do	10.3	W	15	14.2
10G	Rayon	10	D	0	−0.6
10H	do	10	D	2	11.4
10I	do	10	W	2	10.2

To develop improved crease recovery and resilience (fabric "bounce"), the fabrics containing grafted N-methylol acrylamide are soaked in a one percent aqueous solution of tartaric acid and squeezed between rubber rolls. Fabrics are cured, after air drying, at 160° C. for 5 minutes, and are then rinsed well in distilled water. Crease recovery and tensile strength data are summarized in the following table. Data from conventional dimethylol ethylene urea (DMEU) treatment are included for comparison.

TABLE 2

Sample	Percent MAA grafted	Before acid treatment, crease	After acid treatment, crease
Cotton sheeting:			
Control	0	168	----------
10A	2.9	151	192
10B	4.9	154	251
10C	9.4	160	268
10D	14.4	154	268
10J	4% DMEU	----------	250
Rayon challis:			
10G	0	217	----------
10I	10.2	213	235
10H	11.4	213	233

Comparisons of cotton fabric properties produced by curing grafted N-methylol acrylamide (MAA) fabrics and dimethylol ethylene urea (DMEU) applied in the conventional way are given in Table 3, rated subjectively.

[1] The sodium salt of technical lauryl alcohol sulfate.

TABLE 3

Sample	Cotton	Vertical strip crease angle (degrees)	Fabric bounce	Stability to acid*
Untreated		160	Poor	
10J	DMEU (4% wt. gain).	250	Good	Poor.
10B	MAA (4.9% wt. gain).	251	Very good	Good.

*Acid stability of finish estimated by boiling in 0.2% acetic acid and then comparing swelling and solubility of fibers in cuprammonia solution.

It is apparent that at approximately the same weight gain, the fabics treated in accordance with this invention not only have crease recovery equivalent to conventional dimethylol ethylene urea treatments, but show improved fabric "bounce" or resilience, as well as improved stability to acid. Increased amounts of grafted, cured N-methylol acrylamide give some additional improvement. The amount of grafted N-methylol acrylamide required for improving crease-resistance on cellulosics is about 2 to 5%, although as much as 15% can be used.

TEXTILE SUBSTRATE

As illustrated in the examples, the textile produced from the fiber-forming, carbonaceous polymer of nature acts as a substrate to which the organic compound is bonded by means of radiation.

The textiles treated in accordance with this invention include natural fibers such as cotton, flax, jute, hemp, ramie, sisal, abaca, phormium, silk, wool, fur, hair and materials produced from derivative and regenerated forms of natural polymers, such as cellulose acetate, cellulose triacetate, regenerated cellulose, protein fiber derived from peanut protein, zein, casein and the like. Indeed, film such as regenerated cellulose or natural rubber film may be treated in accordance with the process of this invention, and thereafter be slit to form fine ribbon-like filaments useful for making fabrics, etc. The process of the present invention may be applied to a funicular structure such as a continuous fiber, a filament, a spun yarn, cord, tow, floc, bristle, artificial straw, staple or the like. It may likewise be applied to a fabric of a woven, knitted, felted or other construction.

The shaped article, where its nature will permit, such as in cellulose acetate, may be in the form of finely comminuted particles which may, after having the organic compound grafted to it, be dissolved and shaped by dry spinning into a fiber. However, since the grafted natural polymer must be soluble or melt-spinnable the versatility of this embodiment of the process is limited; thus, it is preferred to perform the grafting operation on the polymer in its final shape, e.g., in textile form. In this way, the location of the grafted modification may be controlled, whether upon the surface, partially penetrating the filament, or completely penetrating it, effecting a "bulk" modification.

OPERABLE MODIFIERS

Any organic compound may be employed as the modifying material which may be grafted to the textile. Compounds with aliphatic unsaturation are especially preferred since a minimum radiation dose is required to graft a given weight of modifier.

UNSATURATED MODIFIERS

Among suitable materials are hydrocarbons such as ethylene, propylene, styrene, α-methyl styrene, divinyl benzene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-chloro-2, 3-butadiene, isoprene, cyclopentadiene, chloroprene; acids such as maleic acid, crotonic acid, dichloromaleic acid, furoic acid, acrylic acid, methacrylic acid, undecylenic acid, cinnamic acid; amides such as acrylamide, methacrylamide, N-methylolacrylamide, N-methyl, N-vinyl formamide, N-vinyl pyrrolidone, methyl substituted N-vinyl pyrrolidone, vinyl oxyethyl formamide,

methylene-bis-acrylamide, N-allyl-caprolactam; acrylate esters such as methyl acrylate, ethyl acrylate, benzyl acrylate, octyl acrylate, methyl methacrylate, butyl methacrylate, vinyl acrylate, allyl acrylate, ethylene diacrylate, diallyl itaconate, diethyl maleate, N,N-diethylaminoethyl methocrylate, dihydroxy dipyrone; nitriles such as acrylonitrile, methacrylonitrile; acrylyl halides such as acrylyl chloride; vinylic alcohols such as allyl alcohol, furfuryl alcohol, 3-hydroxycyclopentene, dicyclopentenyl alcohol, tropolone; aldehydic compounds such as acrolein, methacrolein, crotonaldehyde, furfural, acrolein diethyl acetal; vinyl amines such as vinyl pyridine, allyl amine, diallyl amine, vinyloxyethylamine, 3,3-dimethyl - 4 - dimethylamino-1-butene, N, N - diacryltetramethylene diamine, N,N-diallyl melamine, diamino octadiene; quaternized amines such as tetraallyl ammonium bromide, vinyl trimethyl ammonium iodide, the quaternary methiodide of methylene-3-aminometheylcyclobutane; vinyl esters such as vinyl acetate, vinyl salicylate, vinyl stearate, allyl formate, allyl acetate, diallyl adipate, diallyl isophthalate; vinyl ethers such as allyl glycidyl ether, vinyl 2-chloroethyl ether, dihydropyrane, methoxy polyethyleneoxymethacrylate; vinyl halides such as vinyl chloride, vinyl fluoride, tetrachloroethylene, tetrafluoroethylene, 1,1-dichloro-2,2-difluoroethylene, vinylidene chloride, hexachloropropene, hexachlorocyclopentadiene, p-chlorostyrene, 2,5-dichlorostyrene, allyl bromide, 2-bromoethyl acrylate, vinyl tetrafluoropropionate, 1,1,7-trihydroperfluoroalkylacrylate such as 1,1,7-trihydroperfluoroheptylacrylate; isocyanate type compounds such as vinyl isocyanate, acrylyl isocanate, allyl isothiocyanate; vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone; cyanides such as methacrylyl cyanide, allyl isocyanide; nitro compounds such as 2-nitropropene, 2-nitro-1-butene; phosphorous containing vinyls such as diethyl vinyl phosphate, diphenyl vinyl phosphine oxide, 1-phenyl-3-phosphacyclopentene-1-oxide, diallyl benzene phosphonate, potassium vinyl phosphonate, bischloroethyl vinyl phosphonate; also included are alkyl, aryl, aralkyl phosphonates, phosphites and phosphonates; sulfur containing vinyls including sulfonates, sulfonamides, sulfones, sulfonyl halides; thiocarboxylates, such as diallyl sulfide, ethylene sulfonic acid, allyl sulfonic acid, methallyl sulfonic acid, styrene sulfonic acid, 2-methylpropene-1,3-disulfonic acid, also including salts and esters of the sulfonic acids; epoxy vinyls, such as butadiene oxide, glycidyl methacrylate.

Acetylenes such as phenylacetylene, acetylene dicarboxylic acid, propiolic acid, propargylsuccinic acid, proparagyl alcohol, 2-methyl-3-butyn-2-ol, 2,2,3,3-tetrafluorocyclobutylvinylethylene and the like may be used successfully.

NONPOLYMERIZABLE MODIFIERS

In addition to compounds containing ethylenic unsaturation, it has been found that compounds can be grafted, according to the process of this invention, which are ordinarily regarded as nonpolymerizable. By nonpolymerizable is meant those compounds, free from aliphatic unsaturation, which do not polymerize by free radical initiation. Due to the efficiency of the high-energy radiation in producing free radicals, it is theorized that free radicals are produced simultaneously on the polymer substrates and on the saturated nonpolymerizable compounds, whereupon grafting ensues. The preferred nonpolymerizable compounds are those which have functional groups which are useful in modifying polymer properties. Thus, such compounds are included as hydrocarbons, alcohols, acids, ethers, ketones, esters, aldehydes, isocyanates, sulfonates, mercaptans, thioethers, disulfides, nitriles, nitro compounds, amines, amides and halides. Typical of suitable alcohols are the alkanols such as methanol, ethanol, laurol, the polyols, such as glycerine, pentaerythritol, sorbitol, mannitol, their partial esters and the like. Dialkyl ethers such as dimethyl, diethyl, ethylmethyl and the glycol ethers as well as the oxyalkylated ethers of partial esters of the polyols, such as the polyoxyethylene derivative of a fatty acid partial ester of sorbitol are suitable. Oxides such as 1,2-diisobutylene oxide are useful. Mercaptans and thioethers analogous to the above may be used as may also disulfides of a similar nature. As amines may be mentioned the alkyl amines such as methyl amine, ethyl amine, hexamethylene diamine and dodecylamine. The amides of these amines formed with acids such as formic acid, adipic acid, suberic acid, stearic acid and the like are useful; alternatively, the acids alone are often desirable modifiers. Halides within the preferred class include the alkyl halides such as chloromethane, chloroform, carbon tetrachloride, chloroethane, chloroethylene, dichlorodifluoromethane, dodecafluoroheptyl alcohol and similar materials.

Of the nonpolymerizable compounds, those organic compounds, the bonds of which are easily broken, as, for instance, chain transfer agents, are particularly preferred, since larger amounts of modifier are grafted with a given irradiation dose.

It is, of course, obvious that low molecular weight nonpolymerizable modifiers are preferred, when it is desirable to have the modifier penetrate into the polymer substrate, to make a bulk modification. It has been observed that modifiers with functional groups which have a swelling effect upon the polymer substrate are usually especially effective in penetrating the substrate.

POLYMERIC MODIFIERS

Polymeric modifiers are a preferred class for grafting to substrates which are in the form of fibers, filaments, fabrics or the like. These modifiers are especially suitable when a surface coating is desired, since it is obvious that their ability to penetrate will be limited. When irradiating these compositions, it is believed that the coating is grafted by chemical bonds, probably carbon-carbon bonds, to the fiber surface. Therefore, the process of this invention gives a much more durable coating than those obtainable by prior art processes which require polymerization initiators to cross-link the coating, and depend on mere physical bonds to retain the coating upon the textile. The polymeric modifiers are especially adaptable to the process of this invention, since relatively few bonds are needed to graft each large macromolecule to the fiber surface.

The process of this invention is especially suitable for washfast modification of fibers and fabrics, as has been shown by the examples hereinabove. These advantages are obtained by selecting polymeric modifiers which can be applied in a relatively fluid state, e.g., from solution, emulsion or as a melt. Viscosities up to about 100 centipoises may be employed, but lower viscosities are preferred. When these conditions are met the modifier migrates into the yarn bundles so that each filament in the fabric is individually coated, and a large excess of the modifier is avoided. Excess amounts of modifier result in a deleterious effect on fabric hand, and often render the fabric unfit for apparel use. The preferred polymeric modifiers are those which are soluble or dispersible in aqueous solutions, although other solvents may be used in some cases. However, water is the preferred solvent because of its cheapness, availability, and freedom from hazards. Thus, such polymers are preferred as the polyether glycols, polypropylene ethers, polymeric alcohols, polymeric acids, polymeric amines, polymeric amides and the like. These compounds are useful, for example, in increasing moisture regain, antistatic effect, and wickability, even beyond that which is characteristic of natural polymers. Alternatively, water repellence can be improved by grafting hydrophobic polymeric materials, usually utilizing a solvent other than water. Examples of such hydrophobic polymers are polytetrafluoroethylene, polyvinyl chloride, polymeric esters and the like.

REACTION CONDITIONS

Once free radicals are produced on the carbon atoms of the polymer chain in the presence of a vinyl monomer,

vinyl polymerization is initiated, and polyvinyl chains grow from the initiating site.

Magat et al. in U.S. Patent No. 3,188,228, dated June 8, 1965, gives a general discussion of the structure of a graft copolymer product, effective radiation, radiation energy, radiation dose reaction conditions and irradiation conditions.

Prior to treatment, the textile may be oriented by hot or cold drawing. It may contain additives such as pigments, antioxidants, fillers, polymerization catalysts and the like. After the irradiation, the product may be after-treated. Frequently a certain amount of homopolymer formation occurs at the surface which is readily removed by solvent extraction or washing. This treatment is usually preferred. In other aftertreatments, the shaped article may be dyed, bleached, hot or cold drawn, chemically recated, or given coatings of lubricants, sizes or the like or other similar treatments.

UTILITY

The process of the present invention is valuable in creating both surface and bulk effects upon textiles produced from carbonaceous natural polymers. It may be employed upon textiles to affect softness, resilence, tendency to shrink, static propensity, resistance to hole-melting, pilling, hydrophilicity, wickability, and the like. It is useful in changing such properties as tenacity, elongation, modulus, creep, compliance ratio, work recovery, tensile recovery, decay of stress, wet properties, high-temperature properties, abrasion and wear resistance, moisture regain, flex life, hydrolytic stability, heat-setting properties, boil-off shrinkage, dry-cleaning properties, heat stability, light durability, zero strength temperature, melting point, soilability, ease of soil removal, laundering properties, wash-wear properties, liveliness, crease resistance, crease recovery, torsional properties, hysteresis properties, fiber friction, dyeability (depth, rate, permanence and uniformity), printability, washfastness of dyes or finishing treatments (resins, ultraviolet absorbers, etc.), handle and drape properties (stiffening or softening), heat-yellowing, snag resistance, elasticity, density, ease in textile processability, solubility (insolubilization or increase in solubility), bleachability, surface reactivity, delustering action, drying properties, fabric life, crimpability, stretchability, fabric stabilization, compressional resilience (rugs), thermal and electrical conductivity, transparency, light transmittance, air and water permeability, fabric comfort, felting ion exchange properties, germicidal properties, adhesion, overall appearance and combinations of these as well as others.

It is apparent that those properties which are not primarily a function of surface characteristics of the filament (e.g., tenacity, elongation, modulus, and the like) may be more conveniently modified by using modifiers which penetrate the filaments prior to irradiation-grafting, thus producing a graft copolymer extending throughout the penetrated volume. It is also apparent that at times it may be desirable to allow one or more modifiers to penetrate the filaments, and coat one or more modifiers on the surface of the filaments, then initiate grafting simultaneously by irradiating them.

Although the invention has been described in terms of treating filamentary structures in the form of yarn or woven or knitted fabric, the process is applicable to fabricated textiles for clothing or industrial use, reinforcement for composite structures (such as cords for mechanical rubber goods, fiber for laminates, etc.), bristle or artificial straw, and the like.

Many other modifications will be apparent to those skilled in the art from a reading of the above description without a departure from the inventive concept.

What is claimed is:

1. A cellulosic textile fiber bearing polymeric chains grafted to the cellulosic fiber, the said chains being derived from an N-methylol amide of an unsaturated acid, said chains being grafted to said cellulosic fiber via carbon-to-carbon bonds in which one of the carbons of the bond is a cellulosic carbon.

2. The textile fiber of claim **1** in which the amide is N-methylol acrylamide.

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U.S. Cl. X.R.

117—139.4, 143; 204—154; 260—17, 4, 117.4, 8, 879