United States Patent Office 3,254,939 Patented June 7, 1966

3,254,939

PROCESS OF MODIFYING CELLULOSIC MATERIALS WITH IONIZING RADIATION

Fritz Munzel, Schwerzenbach, Switzerland, assignor, by mesne assignments, to Herberlein & Co. AG., a corporation of New York

No Drawing. Continuation of application Ser. No. 125,088, July 19, 1961. This application Feb. 1, 1965, Ser. No. 429,617

28 Claims. (Cl. 8—116)

This application is a continuation-in-part of application S.N. 30,056, filed May 17, 1960, and now abandoned; a continuation-in-part of application S.N. 111,900, filed May 23, 1961; and a continuation of application S.N. 125,088, filed July 19, 1961.

This invention relates to improved cellulosic textile products and to new methods for finishing cellulosic textiles to improve certain of their physical characteristics, and more particularly it relates to irradiated cellulosic textile materials of improved crease resistance, tearing strength, and abrasion resistance and to a method facilitating the action of ionizing radiation upon the cellulosic textile material to produce a vastly improved cellulosic textile product.

For purposes of this application the term "textile material" as employed herein shall be understood to include textiles of all kinds, including fibers, yarns, threads, and more manner of knit or woven fabrics, as well as nonwoven or felted fabrics. Further, for purposes of this application the terms "cellulosic textile material" and "cellulosic textile sheet material" shall be understood to include sheets or films of regenerated cellulose in fabrics of all kinds, whether woven, knit, felted or non-woven, which fabrics consist entirely of natural and/or regenerated cellulose and mixtures thereof as well as all manner of knit or woven fabrics, films, or sheets in which the cellulosic constituents constitute a major portion and noncellulosic constituents make up the remaining minor portion thereof. Generally for purposes of simplicity, the present invention is described with reference to cotton fabrics, and in certain of its aspects as hereinafter indicated is primarily directed to the finishing of cotton, rayon, or mixed cotton and rayon fabrics.

Attempts have been under way for some time to achieve improvements in cellulosic textiles through the use of ionizing radiation, but it has been noted that radiation of this type causes a change in the physical structure of the cellulose polymer molecule similar to a chemical decomposition. For example, in tests conducted with cellulosic textiles it was found that a relatively large dose of ionizing radiation causes a very great reduction in the degree of polymerization of the cellulose, and to all intents and purposes destroys the utility of the textile. With small doses of irradiation there was found to be no appreciable increase in the physical properties of the textile.

According to application Serial No. 30,056, it was found that the physical properties of cellulosic textile materials could be substantially improved with the aid of ionizing radiation under certain conditions of textile moisture, followed by heating where irradiation was carried out in the presence of oxygen. In that application it is pointed out that at conditions of about 20 to 50% moisture in the cellulosic textile ionizing radiation and subsequent heating effect substantial improvement in the physical properties of the textile as a result of cross-linking of the cellulosic molecule. The favorable results obtained by the process of application Serial No. 30,056 are believed from a radiation chemical standpoint to be due to the fact that during irradiation of the cellulosic textile under the above moisture conditions, which approximate the range of maximum swelling of the cellulose, substantially more active ions

are formed from the water present than are formed on the cellulose molecule, and that these excited ion species can transfer their energy to the cotton molecule, and in fact very likely react with excited centers on the cellulose causing cross-linking.

The present invention constittues a substantial improvement over the process of application Serial No. 30,056, in that cross-linking may now be very easily effected, with resulting substantial improvement in the physical properties of the cellulosic textile material, without resort to irradiation of the cellulose in water-swelled condition or at a critical moisture content. Furthermore, in the present process it is no longer necessary to apply heat to the cellulosic textile during or following irradiation.

In accordance with the method of the present invention it has now been found that cross-linking may be achieved to a desired degree and the physical characteristics of the cellulosic textile thereby very substantially enhanced when the textile is subjected to ionizing radiation in the presence of certain chemical substances hereinafter termed "sensitizers" in contact with the textile which contains molecular groups, presumably ionizable atoms, capable of absorbing the radiation energy to an extent that they are excited to oscillate or resonate and so transfer or transmit excitation energy to the electrons of the atom or atoms of the cellulosic molecule which enter into the cross-linking reaction thus facilitating the establishment of a cross-linking between the cellulosic polymers. Furthermore, in the present process subsequent heating of the irradiated material is not required. Also, upon treatment with the sensitizer the cellulosic textile material may be irradiated at ambient moisture conditions, which are generally between about 1 and 10% depending upon conditions of humidity in the finishing plant.

While the above explanation as to the manner of functioning of the sensitizer is believed to be correct, it is a fact that regardless of the phenomena involved cellulosic textile materials to which the sensitizer has been applied prior to irradiation are in a condition which is more advantageous for receiving ionizing radiation energy than textiles irradiated in the absence of the sensitizer.

It is well known that cellulosic fabrics, particularly cotton fabrics, become capable of recovering in a short time after creasing in a dry condition if they have been treated with the well-known finishing resin precondensates, for example methylol precondensates with urea and urea derivative or melamine precondensates. The precondensate penetrates the cellulose fibers of the fabric and is converted to an insoluble resin by polycondensation when heated in the presence of a catalyst. However, these conventional resin-finishing techniques do not appreciably enhance the ability of the finished fabrics, as compared with the starting fabrics, to recover from creases imparted during washing or when the fabric is in a wet condition. While such conventionally finished textile materials may be considered crease-resistant so long as the creases are imparted to the fabric while it is dry, they often do not exhibit entirely satisfactory wet-crease resistance, which resistance is the criterion of the wash-and-wear properties of a fabric.

Therefore in accordance with another aspect of the present invention it has been discovered that excellent wet crease resistance, as well as dry crease resistance and improved strength, can be imparted to the cellulosic textile material if it is first treated with a radiation sensitizer as indicated above and subsequently at least one graftable organic finishing chemical is grafted onto the cellulosic molecule.

In a related application, S. N. 147,380, filed on July 19, 1961, there is described a process for improving mechanical properties of a cellulosic textile material by first subjecting the unfinished textile to ionizing radia-

tion of a critical total dose and then applying a condensible or resin-forming material to the textile which condenses thereon. In accordance with that process, heat is not required to condense the resin-forming substances as in conventional prior art finishing techniques.

According to the aspect of this invention involving subsequent treatment with a graftable organic finishing chemical, the cellulosic textile material is subjected to ionizing radiation of a critical dose between about 5×10^4 and 3×10^6 rad in the presence of the radiation sensitizer, and the graftable organic finishing chemical is applied to the fabric and grafted thereon. More specifically, the cellulosic textile is first treated with the radiation sensitizer, then irradiated and then subsequently at least one graftable organic finishing chemical is applied thereto, preferably (although not necessarily) at an elevated temperature between about 40 and 100° C. In some instances, particularly where the graftable chemical is dissolved or dispersed in aqueous media, the graftable chemical may be applied to the cellulosic textile during irradiation. For example, the cellulosic textile may be irradiated while immersed in or wetted with a solution or dispersion of the graftable chemical. The graftable organic finishing material may be a polymerizable monomer, an unpolymerizable chemical or an already polymerized substance. The term "nonpolymerizable" as employed herein is intended to designate chemicals of the latter two categories, namely, already polymerized materials and chemicals which are incapable of polymerization.

Surprisingly it has been found that some cellulosic fabrics cannot be cross-linked and thus improved even under the most favorable conditions of moisture as set forth in application Serial No. 30,056, presumably because the textile contains small quantites of metal soaps which cannot be removed. When such fabrics are treated in accordance with the method of the present invention cross-linking is easily effected and the desired physical improvements realized.

By reason of the high efficiency of the sensitizer desired improvement of the physical characteristics of the textile may be obtained at substantially lower radiation doses. Accordingly, degradation of the cellulosic molecule as a result of having been subjected to ionizing radiation is very significantly reduced.

The sensitizers useful for carrying out the process of the present invention comprise both organic and inorganic materials which possess in common the ability to absorb ionizing radiation energy and transfer excitation energy to the cellulose molecule.

The inorganic sensitizers comprise heavy metal oxides and inorganic salts and heavy metal salts of organic acids containing about 1 to 4 carbon atoms. Suitable materials are, for example, the oxides or salts of titanium, chromium, zinc, tungsten, osmium, thorium, and uranium.

Organic sensitizers include certain unsaturated aliphatic compounds and aromatic compounds containing about 1 to 6 benzene rings. The suitable aliphatic compounds are olefinic and contain 4 to 20 carbon atoms in the aliphatic chain as well as 1 to 3 olefinic unsaturations. The unsaturated linkages, i.e. carbon-carbon double bonds, may be either conjugated or isolated from one another, but in the latter case the unsaturations are separated by at least two carbon atoms. These aliphatic olefinic sensitizers may be either hydrocarbons, aldehydes, such as crotonaldehyde or citral, ketones, or primary or secondary amines.

The aromatic compounds suitable as sensitizers in the present process are those containing up to about 6 benzene rings, and preferably those containing 2 or 3 condensed or uncondensed benzene rings. Typical uncondensed ring compounds include the diphenylbenzenes, di- and triphenyl methane, polyphenylethanes, fluorene and benzal fluorenes. Compounds of this type containing two or three uncondensed rings are very effective.

A particularly preferred sensitizer of this type is 1,4-diphenylbenzene.

Further typical aromatic compounds suitable as sensitizers include ketones and primary and secondary amines. Representative ketones of the 2 and 3 condensed and uncondensed ring types include quinone, naphthoquinones, benzoylfluorenes, benzil, benzalacetophenone, dicyannamylideneacetone, diphenoquinone and hydroxyacetophenone. Two particularly preferred sensitizers of this latter class are α-naphthoquinone (1,4-diketo-2,3-dihydro-naphthalene) and benzophenone. Of the aforementioned aromatic amines, those consisting of three condensed benzene rings with one to three amino groups on said rings are especially preferred. Examples of such amines are aniline, diphenylamine, tributylamine, cyclohexylamine.

The sensitizers are effective in the present process when present, in contact with the cellulosic textile material being irradiated, in exceedingly small quantities. For example, the sensitizers perform eminently satisfactorily when present on the textile in amounts insufficient to change the external appearance of the goods.

The sensitizer is applied to the cellulosic textile before irradiation. Application of the sensitizer to the fabric is preferably from an aqueous solution, dispersion or emulsion in order that the cellulosic molecule may swell in the presence of water which permits uniform and complete deposition of the sensitizer. Since such small quantities of the sensitizer are effective in the present process the aqueous solution or dispersion may be very dilute, for example between about 0.1 and about 5%.

Following application of the sensitizer, the textile material is subjected to ionizing radiation to a total dose between about 10^3 and 10^7 rad. As noted above cross-linking is now more efficiently realized than heretofore and the irradiation dose may be lower than required in other earlier processes. Accordingly, the preferred irradiation dose is between 10^4 and 10^6 rad. It has been found that cellulosic textiles which had previously required doses in excess of 10^6 rad to effect substantial cross-linking in the presence of 20–50% water can in many instances now be cross-linked to a greater extent, resulting in further improved physical characteristics, in accordance with the present process at doses ranging from about 10^4 rad to not above about 10^6 rad. This fact is particularly important in the treatment of certain of the regenerated celluloses, which are considerably more sensitive to ionizing radiation with resulting decomposition than is cotton.

The ionizing radiation may be electromagnetic in character, as roentgen or gamma rays, the latter being permitted by $cobalt^{60}$, $cesium^{137}$, burnt uranium slugs, or the fission products of $uranium^{235}$. Beta rays having a particle energy between about 0.05 and 1 mev., as produced by the usual electronic accelerators such as the cascade, Van de Graaff, or linear accelerators are also satisfactory, as are the beta particles derived from radioactive materials such as $strontium^{90}$. Generally speaking the irradiation time to reach the aforementioned total dose will vary between 10 seconds and 4 hours, depending upon the desired total dose and the quality of the source.

The process of the present invention is applicable to both heavy and light-weight cellulosic textile materials. It is particularly well adapted to the improvement of crease resistance, wash and wear properties, tearing strength and abrasion resistance of organdies and parchmentized fabrics as well as mercerized or bleached goods.

The process is also applicable to the treatment of cellulosic textile materials, especially fabrics, which have been previously subjected to conventional resin finishing to improve crease resistance and dimensional stability, and the conventionally finished wash and wear cotton or mixed cotton and artificial fiber fabric may be further substantially improved in accordance with the present invention. Conventional wash and wear finishing referred to is

achieved by applying to the cotton textile a condensible resin, for example methylol ureas, methylol amines, condensates of formaldehyde with phenol and phenol derivatives, ketone-aldehyde precondensates, aziridinyl compounds, diglycide ethers. Other suitable resin-forming substances are N-substituted urea formaldehyde resin compositions such as ethylene urea, dioxy ethylene urea or N,N'-bis (methoxymethyl) uron and tetrahydro-1,3-bis (methoxymethyl)-5-methyl-2(1) - s - triazone. A typical finish is dihydroxymethylurea in the presence of a zinc nitrate condensation catalyst. Following application of the resin precondensate the fabric must be heated to temperatures above 100 C. for a period of time in order to affect condensation of the resin. Crease-resistance is thereby improved, but fiber strength is very substantially reduced by the resin finish, and as a result the tensile or tearing strength of the goods as well as their abrasion resistance is appreciably lowered. Surprisingly, when this conventionally treated textile is subjected to the process of the present invention tearing strength and abrasion resistance are very greatly increased, as is also the crease resistance.

The present invention is further illustrated by the following examples:

Example I

A cotton poplin fabric was treated at 20° C. in a water bath containing approximately 1% by weight 1,4-diphenylbenzene, after which it was subsequently dried at about 60–70° C. It was then irradiated at an ambient moisture content of about 8% to a total dose of 10^5 rad from a cobalt^{60} source. The resulting fabric was insoluble in cuprammonium solution. The tensile strength of the fabric was measured in warp and fill directions with a Schopper pendulum apparatus on strips 2.5 cm. wide. Abrasion resistance was measured with a standard testing apparatus having a disc covered with a standardized wool cloth which was rotated on the surface of the fabric until the fabric failed, and the number of revolutions to failure was noted. Crease resistance was also determined, as evidence by crease angles in warp and fill directions. These angles were determined as follows: Strips of the fabric 3 x 5 cm. were conditioned for 24 hours at 21° C. and 65% R.H., and thereupon folded and placed under a 1 kg. weight for one hour. Upon removal of the weight, the fabric samples were left unweighted for fifteen minutes and the crease angle was measured. The values for crease angle, tensile strength and abrasive strength were as follows:

	Crease Angle (degrees)		Tensile Strength (kg.)		Abrasive Strength (revolutions)
	Warp	Fill	Warp	Fill	
Starting material	55	55	22.0	13.6	15,700
Irradiated material	108	110	22.8	13.0	34,600

Example II

An untreated piece of cotton imitation poplin fabric which could not be successfully cross-linked by simple irradiation at a moisture content of 30–40%, presumably because of the presence of very small quantities of adhering metal soaps, was treated as set forth in Example I with the 1,4-diphenylbenzene solution, and then dried to a moisture content of about 9%. It was subsequently exposed to cobalt^{60} to a total dose of 9×10^4 rad. The resulting fabric was insoluble in cuprammonium solution and the following table compares its properties with those of the starting material, including the degree of polymerization of the cellulose:

	Crease Angle		Tearing Strength		Abrasive Strength
	Warp	Fill	Warp	Fill	
Starting material	40	45	18.6	12	13,400
Irradiated material	110	114	20	12.3	40,500

Example III

A cotton imitation poplin fabric was treated in the bath containing 1,4-diphenylbenzene and dried as described in Example I. A section of the starting material (I) and a section of the fabric treated with the sensitizer (II), both having moisture contents of about 10%, were then subjected to electron radiation of a particle energy of 0.08 mev. to a total dose of 6×10^5 rad. The fabrics had the following properties:

	Crease Angle		Tearing Strength (g.)		Abrasive Strength
	Warp	Fill	Warp	Fill	
Starting material	60	46	644	540	14,350
I	80	80	924	844	19,063
II	110	105	934	996	25,436

Tearing strength was measured with a pendulum apparatus, specifically an Elmendorf tearing tester, on strips of a width of 6.3 cm. and a length of 16.5 cm.

Example IV

A cotton voile was treated in a bath containing 1,4-diphenylbenzene and dried as described in Example I. A section (I) of the starting material and a section (II) of the treated fabric, both having moisture contents of about 10% were subsequently subjected to electron radiation of a particle energy of 0.08 mev. to a total dose of 2×10^5 rad. The properties of the fabrics were as follows:

	Crease Angle		Tearing Strength		Abrasive Strength
	Warp	Fill	Warp	Fill	
Starting material	73	62	1,056	1,058	7,870
I	66	72	767	912	10,800
II	118	120	2,510	2,730	30,600

Example V

A mercerized bleached cotton muslin was parchmentized with sulphuric acid of 52° Bé. at 15° C. for a period of 16 seconds, subsequently remercerized, washed until neutral and dried. The resulting fabric was transparent. A section (I) of the parchmentized fabric, and another section (II) of the parchmentized fabric which had been treated with the solution of Example I, and then dried to about 10% moisture, were subjected to electron radiation of a particle energy of 0.12 mev. to a total dose of 2×10^4 rad. The properties of the fabrics were as follows:

	Crease Angle		Tearing Strength		Abrasive Strength
	Warp	Fill	Warp	Fill	
Starting material	7	8	-------	312	1,650
I	40	45	295	564	3,270
II	100	95	520	540	3,780

Example VI

Several portions of a cotton imitation poplin fabric were treated with 1% solutions or dispersions of several metal compounds and benzophenone, after which they were dried to a moisture content of about 10%. All sections were then subjected to a cobalt^{60} source to a total dose of 10^6 rad. The properties for the starting and resulting fabrics were as follows:

Compound	Crease Angle		Tearing Strength		Abrasive Strength
	Warp	Fill	Warp	Fill	
Starting material	60	55	610	550	14,120
Thorium oxide	95	90	850	810	18,340
Zinc oxide	90	95	1,170	1,210	21,220
Titanium oxide	95	90	930	970	18,930
Osmium tetroxide	80	82	890	900	18,800
Uranyl acetate	100	105	1,205	1,140	22,350
Benzophenone	100	105	1,180	1,140	22,300

Example VII

Several sections of a cotton muslin fabric were treated with 1% solutions or dispersions of tungsten oxide, zinc oxide and benzophenone, respectively, dried to a moisture content of about 10% and subsequently subjected to a cobalt^{60} source to a total dose of 10^6 rad. The properties of the starting and resulting fabrics were as follows:

Compound	Crease Angle		Tearing Strength		Abrasive Strength
	Warp	Fill	Warp	Fill	
Starting material	0	8	280	225	2,840
Tunsgten dioxide	80	85	660	700	5,400
Zinc oxide	85	100	500	500	6,720
Benzophenone	75	80	540	380	5,300

Example VIII

Two sections of a cotton imitation poplin fabric were treated in an aqueous solution containing 1% α-naphthoquinone and subsequently dried at about 60–70° C. to a moisture content of about 10%. Thereupon one section of the thus treated fabric (I) was subjected to gamma radiation from a cobalt^{60} source to a total dose of 10^6 rad. The other section (II) was bombarded with accelerated electrons of a particle energy of 0.12 mev. to a total dose of 10^6 rad. The mechanical properties of the fabrics were as follows:

Compound	Crease Angle		Tearing Strength		Abrasive Strength
	Warp	Fill	Warp	Fill	
Starting material	43	46	680	590	16,500
I (gamma)	135	130	1,580	1,570	28,300
II (beta)	145	140	1,775	1,800	62,300

It will be noted that the beta-irradiated material is superior to the section which was subjected to gamma radiation, even though the total doses were the same.

Example IX

A cotton imitation poplin fabric was treated in the conventional manner to impart crease resistance or wash and wear properties thereto by impregnating with a solution containing 110 g. of dimethylurea dissolved in 1 liter of water, which also contained 11 g. of zinc nitrate condensation catalyst. It was thereupon squeezed and dried at 60–70° C., subsequently heated to 140° C. for four minutes to condense the resin and then washed and dried.

A section (I) of the thus treated fabric and a second section (II), which latter was treated in a bath containing 1% 1,4-diphenylbenzene and dried as described in Example I, were subjected at fabric moisture contents of about

8–10% to a cobalt^{60} source to a total dose of 10^6 rad. The properties of the resin-finished starting material, the irradiated resin-finished starting material (I) and the sensitizer-treated irradiated resin-finished material (II) exhibited the following properties:

Compound	Crease Angle		Tearing Strength		Abrasive Strength
	Warp	Fill	Warp	Fill	
Resin-finished starting material	45	40	650	580	14,250
I	110	105	260	230	10,530
II	105	110	1,120	1,050	32,750

The products of the present invention are thus ionizing radiation-finished cellulosic textile materials of improved crease resistance, wash and wear properties, tearing strength and abrasion resistance as compared with the starting material. The starting material may be in the form of previously unfinished or already conventional resin-finished parchmentized or otherwise preliminary finished cellulosic materials.

According to the aspect of this invention wherein a graftable organic finishing chemical is applied to the material after irradiation, said finishing chemical is applied to the cellulosic material during or following irradiation from aqueous or organic solutions or dispersions, as is customary in the conventional textile finishing art. As graftable polymerizable polymers there may be employed unsaturated compounds, more particularly vinyl or allyl compounds, such as acrylamide, acrylates, methacrylates, styrene, vinyl acetate, vinyl chloride, or vinylidine chloride, or one of the ethylenically unsaturated monomers, for example ethylene, tetrafluoroethylene, butadiene or isoprene, or the like. Among the non-polymerizable graftable chemicals are those materials which are incapable of polymerization as well as already polymerized materials, including higher alcohols, aldehydes, ketones, sulfones, acetals, halogenated compounds, amines, ethers, esters, phenols, ethylene polymers, and vinyl and acrylic polymers.

The use of low energy accelerated electrons forms an important part of this aspect of the present invention. The importance of low energy particles (below about 1 mev.) is described in related application S.N. 125,089, filed July 19, 1961. Therein it is pointed out that the degradation of the cellulosic molecule of the textile is greatly reduced when low energy particles are employed.

Where accelerated electrons are employed as the source of ionizing radiation, the accelerator is so arranged with respect to the surface of the cellulosic textile material that the stream of electrons (beta particles) is directed at an acute angle thereto. Their passage into and through the textile material is thus oblique and the particles describe a slightly longer path in the material, which results in improved irradiation efficiency. Good results are achieved if the total ionizing radiation imparted to the textile whether electromagnetic or beta radiation, is to a dose range of about 5×10^4 to 3×10^6 rad, preferably about 2 to 7×10^5 rad. Within this dose range degradation of the cellulosic molecule of the textile is at a minimum consistent with the very substantially increased wet and dry crease resistance and increase in the physical properties of the textile material. With low energy accelerated electrons and the aforementioned dose range there is virtually no deterioration of the cellulose.

The method of the present invention will be further apparent from the following typical examples, employing various graftable organic chemicals, which illustrate practical applications of the present method and set forth the improved physical characteristics of the novel finished textile product. Attention is particularly directed to the very substantial and unexpected improvement in wet crease resistance of the novel product.

Example X

A cotton poplin fabric was treated at 20° C. in an aqueous bath containing about 1% 1,4-diphenylbenzene and thereupon dried at 60–70° C. Several sections, A through F, were subjected to gamma radiation from a Co^{60} source for different times in order to impart different total doses. The irradiated fabric sections were then treated with the aid of a foulard with an aqueous solution containing 5% by weight of acrylamide at 90° C., washed out and the wet crease angle measured. The sections were then dried at about 60° C. and the dry crease angle, tearing strength and abrasive strength were then measured. The following table illustrates the dose of ionizing radiation to which each of the sections was subjected and the improved results obtained as compared with the starting material. Attention is particularly directed to the very substantially improved wet crease angle.

	Starting Material	A	B	C	D	E	F
Irradiation Time (hours)		½	1	2	3	4	5
Irradiated Dose (rad)		1.25×10^5	2.5×10^5	5×10^5	7.5×10^5	10^6	1.25×10^6
Wet Crease Angle (degrees):							
Warp	60	125	143	140	110	95	80
Fill	65	130	145	142	110	96	85
Dry Crease Angle (degrees):							
Warp	45	95	110	125	110	115	100
Fill	40	96	115	123	110	120	105
Tearing Strength (g.):							
Warp	560	1,105	1,410	1,290	1,050		
Fill	540	1,100	1,360	1,305	1,020		
Abrasive Strength [1]	12,310	24,830	29,330	31,310	22,810		

[1] In number of revolutions.

Results equivalent to those set forth in the above table were obtained by substituting 1,4-naphthoquinone for the 1,4-diphenylbenzene.

Crease angles were determined with wet and dry sections as follows: 3 x 5 cm. strips of the starting and treated fabric were folded in the warp or fill direction respectively and placed under a weight of 1 kg. for one hour. Following removal of the weight the materials were left unweighted for 15 minutes and the crease angle was thereupon measured.

Tearing strength was determined with an Elmendorf Tearing Tester, as described in the ASTM-Standards on Textiles of the American Society for Testing Materials, 1956 Edition, pages 250–254, on strips having a width of 6.3 cm. and a length of 16.5 cm. Abrasive strength was measured with a testing apparatus having a disc covered with a standardized wool cloth which was rotated on the surface of the fabric until the fabric failed at which time the number of revolutions was noted.

Example XI

A cotton poplin fabric was treated with a 1% aqueous solution of 1,4-diphenylbenzene as described in Example X. Several sections, A through F, were thereupon subjected to gamma radiation from a Co^{60} source for different times to achieve different total doses. The sections were then treated with an aqueous solution containing 15% by weight of divinyl sulfone with the aid of a foulard at 90° C., washed out, and the wet crease angle determined. The sections were then dried and the dry crease angle, tearing strength and abrasive strengths were measured. The results are shown in the following table:

	Starting Material	A	B	C	D	E	F
Irradiation Time (hours)		½	1	2	3	4	5
Irradiated Dose (rad)		1.25×10^5	2.5×10^5	5×10^5	7.5×10^5	10^6	1.25×10^6
Wet Crease Angle (degrees):							
Warp	60	139	161	142	142	110	100
Fill	65	140	160	145	145	110	100
Dry Crease Angle (degrees):							
Warp	45	95	119	125	125	110	100
Fill	40	90	120	125	120	110	100
Tearing Strength (g.):							
Warp	560	1,230	1,410	1,580	1,410	1,200	
Fill	540	1,300	1,505	1,560	1,380	1,180	
Abrasive Strength [1]	12,310	32,820	40,810	42,350	38,210	29,900	

[1] In number of revolutions.

From Examples X and XI it will be apparent that with the particular fabric and the particular graftable chemical employed very superior wet and dry crease angles as well as superior tearing and abrasive strengths are obtained at doses between about 2.5×10^5 and 5×10^5 rad.

Example XII

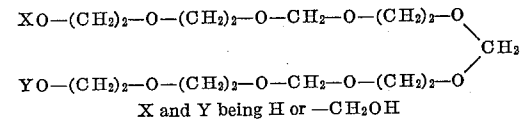
A cotton poplin fabric was treated with a 1% aqueous solution of 1,4-diphenylbenzene as described in Example X, and thereupon subjected to gamma radiation from a Co^{60} source to a total dose of 2.5×10^5 rad. The fabric was subsequently treated with an aqueous solution containing 5% by weight of nonyl alcohol at 90° C. with the aid of a foulard. The wet crease angle was measured, and the fabric was then dried and dry crease angle, tearing and abrasive strengths were determined. The results were as follows:

	Starting Material	Irradiated Fabric
Irradiation Time (hours)		1
Irradiated Dose (rad)		2.5×10^5
Wet Crease Angle (degrees):		
Warp/Fill	60/65	135/130
Dry Crease Angle (degrees):		
Warp/Fill	45/40	110/108
Tearing Strength (g.):		
Warp/Fill	560/540	1,060/1,000
Abrasive Strength [1]	12,310	23,810

[1] In number of revolutions.

Example XIII

A cotton poplin fabric was treated with a 1% aqueous solution of 1,4-diphenylbenzene as described in Example X, and four sections, A through D, were then detached and subjected to gamma radiation from a Co^{60} source to different total doses, as determined by the time of exposure. The irradiated sections were subsequently treated at 90° C. with the aid of a foulard in an aqueous solution containing 5% by weight of a glycol polyacetal of the following general formula:



X and Y being H or $-CH_2OH$

as described in U.S. Patent No. 2,786,081. The sections were then washed out, the wet crease angle measured. They were dried and dry crease angle, tearing strength and abrasive strength were measured. The results are set forth in the following table:

	Starting Material	A	B	C	D
Irradiation Time (hours)		½	1	2	3
Irradiated Dose (rad)		1.25×10^5	2.5×10^5	5×10^5	7.5×10^5
Wet Crease Angle (degrees):					
Warp	60	130	165	160	142
Fill	65	130	170	165	150
Dry Crease Angle (degrees):					
Warp	45	105	125	120	115
Fill	40	100	130	125	110
Tearing Strength (g.):					
Warp	560	1,580	2,030	1,990	1,832
Fill	540	1,430	2,110	1,900	1,750
Abrasive Strength [1]	12,310	40,280	63,810	60,210	52,880

[1] In number of revolutions.

Equivalent results were achieved by substituting a 1% aqueous dispersion of zinc oxide for the 1,4-diphenylbenzene sensitizer.

From the above examples it will be apparent that excellent wet crease resistance can be imparted to a cellulosic fabric without any decrease whatsoever in fiber strength. In fact fiber strength appears to be increased.

The present invention is also applicable to the finishing of fine fabrics of cotton or regenerated cellulose which have been subjected to stiffening or transparentizing by treatment with concentrated sulfuric acid, cupric oxide-ammonia solution or sodium zincate cellulose solution, as well as to fine fabrics having relatively highly twisted yarns, such as voiles and marquisettes.

What is claimed is:

1. A process for improving the properties of a cellulosic textile material of the group consisting of cellulose and regenerated cellulose textiles, which comprises applying to the textile from dilute aqueous media an organic sensitizer which contains molecular groups capable of absorbing ionizing radiation and transferring excitation energy to the cellulose molecules of said textile selected from the group consisting of diphenylbenzenes, diphenylmethane, triphenylmethane, phenylethanes, fluorene, benzalfluorene, quinone naphthoquinones, benzoylfluorenes, benzil, benzalacetophenone, dicinnamylideneacetone, diphenoquinone, hydroxyacetophenone, benzophenone, aniline, diphenylamine, tributylamine, cyclohexylamine, crotonaldehyde, citral and mixtures thereof, and subsequently subjecting the textile with the sensitizer thereon to ionizing radiation to a total dose in the range of about 10^3 to 10^7 rad.

2. A cellulosic textile material of improved crease resistance, tearing strength and abrasive strength produced by the process of claim **1**.

3. A parchmentized celluloisc textile material of improved crease resistance produced by the process of claim **2**.

4. A process as set forth in claim **1** wherein the total dose of ionizing radiation is about 10^4 to 10^6 rad.

5. The process of claim **1** wherein the sensitizer is 1,4-diphenylbenzene.

6. The process of claim **1** wherein the sensitizer is α-naphthoquinone (1,4-diketo-2,3-dihydro-naphthalene).

7. The process of claim **1** wherein the sensitizer is benzophenone.

8. A process for improving the wet crease resistance and the strength of a cellulosic textile sheet material which comprises subjecting said material to ionizing radiation to a total dose in the range of about 5×10^4 to 3×10^6 rad in the presence of an organic sensitizer in contact with said material which contains molecular groups capable of absorbing said radiation energy and so transferring excitation energy to the cellulosic molecule as to facilitate grafting thereon and applying a graftable organic finishing chemical to the material.

9. A process as set forth in claim **8** wherein the cellulosic textile material is irradiated to a total dose between about 10^5 and 5×10^5 rad.

10. A process as set forth in claim **8** wherein the graftable organic finishing chemical is applied to the material from a liquid vehicle.

11. A method as set forth in claim **10** wherein the liquid vehicle is at a temperature between about 40 and 100° C.

12. A process as set forth in claim **8** wherein the material is subjected to the action of accelerated electrons of a particle energy below about 1 mev.

13. A process as set forth in claim **8** wherein accelerated electrons of a particle energy between about 0.05 and 0.6 mev. are directed at an acute angle to the surface of the material.

14. A method as set forth in claim **8** wherein the graftable organic finishing chemical is a polymerizable monomer.

15. A method as set forth in claim **14** wherein the polymerizable monomer is selected from the group consisting of acrylates, methacrylates, acrylamide, styrene, vinyl acetate, vinyl chloride, vinylidene chloride, ethylene, tetrafluoroethylene, butadiene and isoprene.

16. A method as set forth in claim **8** wherein the graftable organic finishing chemical is a nonpolymerizable chemical.

17. A method as set forth in claim **16** wherein the nonpolymerizable chemical is selected from the group consisting of alcohols, aldehydes, ketones, sulfones, acetals, halogenated compounds, amines, ethers, esters, phenols, ethylene polymers, acrylic polymers and vinyl polymers.

18. A method as set forth in claim **8** wherein the sensitizer is an unsaturated aliphatic compound of 4 to 20 carbon atoms containing 1 to 3 olefinic unsaturations,

with at least two carbon atoms between plural unsaturations.

19. A method as set forth in claim **18** wherein the unsaturated aliphatic compound is selected from the group consisting of aldehydes, ketones and primary and secondary amines.

20. A method as set forth in claim **8** wherein the sensitizer is an aromatic compound having 1 to 6 benzene rings.

21. A method as set forth in claim **20** wherein the aromatic compound contains two to three uncondensed benzene rings.

22. A method as set forth in claim **21** wherein the aromatic compound is 1,4-diphenylbenzene.

23. A method as set forth in claim **21** wherein the aromatic compound is benzophenone.

24. A method as set forth in claim **20** wherein the aromatic compound contains two to three condensed benzene rings.

25. A method as set forth in claim **24** wherein the aromatic compound is 1,4-naphthoquinone.

26. A finished cellulosic textile fabric of improved wet crease resistance and strength produced by the process of claim **8**.

27. A finished fine cellulosic textile fabric of improved wet crease resistance and strength produced by the process of claim **8**.

28. A method as set forth in claim **14** wherein the polymerizable monomer is acrylamide.

References Cited by the Examiner

UNITED STATES PATENTS

2,956,899	10/1960	Cline.
2,986,507	5/1961	Steck.
2,998,329	8/1961	Sovish.
3,001,922	9/1961	Zimm.
3,092,512	6/1963	Magat.
3,097,960	6/1963	Lawton et al.
3,101,276	8/1963	Hendricks.

FOREIGN PATENTS

758,735	10/1956	Great Britain.

OTHER REFERENCES

Blouin, Textile Research Journal, vol. 28, pp. 198–204 (1959).

Gilfillan, Textile Research Journal, vol. 25, pp. 773–777 (1955).

Pan, Textile Research Journal, vol. 29, pp. 415–421 (1959).

J. TRAVIS BROWN, *Acting Primary Examiner.*