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PROCESS FOR RADIATION GRAFTING ONTO A PARTIALLY SWOLLEN CELLULOSE SUBSTRATE

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14 Claims

This application is a continuation of U.S. application 817,881 filed June 3, 1959 which is a continuation-in-part of U.S. 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 a product and process. More particularly it concerns a process for grafting an organic compound to a fiber produced from a natural carbonaceous material of the class consisting of cellulose, protein and isoprene polymer and the product formed thereby.

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.

OBJECTS

It is an object of the present invention to provide a process for grafting an organic compound to a textile produced from a carbonaceous material of nature as defined hereinafter.

Another object 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.

Still another object is to provide a process which comprises applying a highly fluid organic compound or highly fluid solution of an organic compound to a textile formed from natural or man-made polymer filaments and thereafter inducing chemical bonding between the said textile and organic compound, producing a permanently modified filament and textile.

A further object is to provide a process for permanently modifying a filament derived from a natural polymer throughout its bulk comprising the sequence of applying a suitable vinyl monomer to the surface of the filament, permitting the monomer to penetrate through the filament, exposing the structure to ionizing radiation to induce grafting between the monomer and the filament and thereafter scouring or extracting to remove any ungrafted modifier.

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

STATEMENT OF INVENTION

In accordance with the present invention, all of the filamentary surfaces of a textile produced from a fiber-forming carbonaceous material of nature of the class consisting of cellulose, protein and isoprene polymer, are

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coated with an organic compound modifier, a flowable excess being avoided when necessary to prevent inter-filament bonding at the radiation dose employed, subjecting the combination to ionizing radiation, producing chemical bonds between the textile and the organic compound and finally extracting ungrafted excess of the said modifier. For deep seated modifications the organic compound is permitted to diffuse into the filamentary substrate prior to the irradiation. Alternatively, the organic compound modifier, especially when it is of high molecular weight, may remain upon the surface of the textile during the irradiation step, thus producing a uniform chemically grafted coating on each filament. The organic compound modifiers employed in the practice of this invention are either per se highly fluid at the temperature at which they are applied or they are employed in highly fluid solution so that they readily migrate over the filament surfaces.

In a typical embodiment the process of the present invention is applied to a yarn or tow, which after being impregnated with organic compound modifier, is irradiated and thereafter extracted to remove ungrafted material. The product is then dried, and may be used as continuous filament yarn, or alternatively, it may be cut to form staple fiber which is then spun to yarn and woven to textiles following conventional procedure.

Alternatively, the textile may be wrung out or centrifuged prior to irradiation, to remove excess treating solution.

In a batch or a continuous process, it is merely necessary to provide sufficient yarn "dwell time" in each step, for instance by using multiple yarn passes during coating, impregnation or irradiation, so that the desired result will be obtained.

DEFINITIONS

By the term "textile produced from a fiber-forming 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 non-selectively 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 the 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 (m.e.v.).

Higher energies are even more effective; there is no known upper limit, except that imposed by available equipment.

By an "organic compound" is meant a material having the formula CX_n where X is a member of the group consisting of hydrogen, halogen, nitrogen, nitrogen radical, oxygen, oxygen radical, sulfur, sulfur radical or organic radical. By "organic radical" is meant a radical predominantly hydrocarbon except for the presence of substituents immediately hereinbefore listed. Where one or more of the X's is organic radical, it is preferred that it be linked to the CX residue by a carbon-to-carbon bond. Furthermore, the C may be doubly bonded to no more than $S=$ or $O=$ atom; i.e., only one pair of X's may be replaced by a divalent oxygen or sulfur atom. Typical compounds included are hydrocarbons, alcohols, acids, ethers, ketones, esters, aldehydes, isocyanates, sulfonates, mercaptans, thioethers, disulfides, nitriles, nitro compounds, amines, amides and halides. Compounds with ethylenic unsaturation are especially preferred, since a minimum radiation dose is required to graft a given weight of modifier. However, non-polymerizable organic compounds (free from aliphatic unsaturation) are also readily grafted, to produce effective modification of polymer properties. Of these compounds, the chain transfer agents are preferred.

Another useful class of modifiers is the high molecular weight compounds, especially polymers. These compounds are readily and effectively grafted since a single site of attachment bonds a relatively large weight of modifier, due to the large molecular weight. The large molecule tends to prevent penetration by these modifiers, and hence they are especially useful in creating surface effects. The polymeric modifiers especially preferred for textile uses are those which may be applied to the textile as a low viscosity solution or melt, thus ensuring that each filament is completely coated.

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 which 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" of Procter and Gamble Company of Cincinnati, Ohio. 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 Monsanto Crease Recovery Method, described as the "vertical strip crease recovery test" 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.

EXAMPLE 1

A sample of wool fabric is coated by being immersed in a solution of 16 parts polyethylene glycol 20,000¹ and 84 parts water, the solution having a viscosity of 119 centipoises at 25° C. The excess liquid is squeezed out. While still wet it is enclosed in an aluminum foil wrapper and subjected to electron irradiation in a 1 mev. resonant transformer with a beam-out current of 560 microamperes. The sample is placed on a conveyor belt which carries it through the electron beam at a rate of 16 inches per minute. At the sample location, the beam supplies irradiation of 5.6×10^6 rad (5.6 mrad) per pass. The sample is traversed back and forth across the beam until a total dose of 3 mrad is attained. The coated, irradiated fabric along with an uncoated, irradiated comparative control and a swatch of the original fabric are given 15 consecutive washings. After two washings the wool has a slightly waxy hand; after 15 washings, the hand is similar to the original, untreated fabric. The coated, irradiated sample retains its original dimension without unravelling at the edges. It has a log resistivity of 9.1. Both comparative controls unravel badly during washings. They are also observed to develop numerous small fibrous balls (known as "pills") on their surfaces, whereas the test fabric develops few, if any, pills. The log resistivity of each control sample is 13.3. Thus, by treatment according to the process of this invention, the wool has been made washable.

EXAMPLE 2

A piece of silk fabric is coated by being immersed in liquid methoxydecaethyleneoxy methacrylate. The excess reagent is squeezed out. While still wet it is wrapped in aluminum foil and irradiated, using a Van de Graaff generator under the conditions listed below:

Voltage mev.	2
Tube current, microamperes	290
Conveyor speed, in./min.	40
Dose per pass, mrad	2
Number of passes	20
Total dose, mrad	40

The coated, irradiated fabric is given 15 standard washings after which its log resistivity is 10.3. The filaments are not bonded together; no surface deposit is observed. The strength and hand of the original fabric are retained. A similarly irradiated control has a log resistivity of 13.3, while that of the original fabric is 12.9 after similar washings. Another control sample immersed in the methoxydecaethyleneoxy methacrylate, but not irradiated, and thereafter subjected to the 15 standard washings, shows no change in log resistivity over the original fabric.

EXAMPLE 3

A fabric woven from continuous filament cellulose acetate yarn is dipped in liquid methoxydecaethyleneoxy methacrylate and the excess liquid is squeezed out. The sample is then irradiated with the equipment and in accordance with the technique of Example 2 to a radiation dosage of 20 mrad. Washing removes surface deposits of ungrafted polymer. The log resistivity of the product

¹ The figure indicating molecular weight.

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after 15 standard washings is 9.9. The value for the original fabric is 10.8.

EXAMPLE 4

A piece of cotton fabric is immersed in liquid methoxydecaethyleneoxy methacrylate and the excess liquid is squeezed out. The coated sample is then irradiated in the equipment and in accordance with the technique of Example 2 to a total radiation dosage of 20 mrad. After 15 standard washings the log resistivity of this sample is 9.6. This compares to a value for the original fabric after 15 standard washings of 10.8.

To illustrate the practice of this invention using X-rays, fabric samples in Examples 5 and 6 are immersed in the

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After 15 standard washings, the treated irradiated sample is found to have shrunk about 20%, and to have acquired a delustered appearance. It has also become elastic, yet retained substantially all its original strength and has a bulkier hand as compared to a portion of the original material.

EXAMPLE 7

Rayon taffeta samples are soaked as shown in Table 1, then irradiated with 2 mev. electrons to give the indicated dose. After removing ungrafted material by the consecutive extractions listed, the weight gain is determined. In some cases, the sample is preswollen before irradiation.

TABLE 1

Sample No.	Swelling agent	Concentration of grafting agent	Dose, mrad	Extraction solvents	Weight gain, percent
7A.....	None.....	20% acrylonitrile in H ₂ O.....	2	Hot water, hot dimethyl formamide, hot water.	12.0
7B.....	do.....	50% diallylitaconate in CH ₃ OH.	2	do.....	1.5
7C.....	CH ₃ OH.....	100% distilled styrene.....	2	Hot benzene, hot acetone, hot water.	11.7
7D.....	None.....	100% 1,2-diisobutylene oxide.	2	Hot CH ₃ OH, hot H ₂ O.....	0.4
7E.....	Water.....	50% methyl methacrylate in CH ₃ OH.	2	CH ₃ OH, acetone, CH ₃ OH, H ₂ O.	16.0
7F.....	None.....	50% methyl methacrylate in CH ₃ OH.	2	do.....	1.1
7G.....	H ₂ O.....	100% vinyl acetate.....	2	Acetone.....	12.9
7H.....	None.....	50% 4-vinyl pyridine in H ₂ O.	2	Hot water.....	8.5

chosen treating liquid, the excess liquid squeezed out, then each fabric sample while still wet, is wrapped in aluminum foil forming a first package. A set of untreated controls is also packaged. All the foil packages are combined into a pile 1/2 inch thick, and are then simultaneously irradiated as described hereinafter.

The samples are exposed to X-radiation using a resonant transformer X-ray machine marketed by the General Electric Company of Schenectady, N.Y., known as a "Two Million Volt Mobile X-Ray Unit." This machine is described by E. E. Charlton and W. F. Westendorf in the Proceedings of the First National Electronics Conference, p. 425, October 1944. The pile of packaged samples is placed in an open top box made from 1/16 inch sheet lead, and positioned so that the top sample is 8 cm. from the tungsten tube target. At this location, using a tube voltage of 2 mev., and a tube current of 1.5 milliamperes, the irradiation rate is 1.5 mrad per hour. The beam irradiates a circle about 3 inches in diameter; all fabric tests are made on the irradiated portion.

EXAMPLE 5

A sample of wool fabric is coated by being immersed in a solution of 16 parts polyethylene glycol 20,000 and 84 parts water. The excess liquid is squeezed out. While still wet it is enclosed in an aluminum foil wrapper and subjected to X-ray radiation as described above. The sample receives a total dose of 27 mrad. The coated, irradiated fabric along with an uncoated, irradiated comparative control and a swatch of the original fabric are given 15 consecutive standard washings. The coated, irradiated sample retains its original dimension and hand without unravelling at the edges. Both comparative controls unravel badly during washings. They are also observed to develop numerous small fibrous balls (known as "pills") on their surfaces, which were not observed on the treated irradiated test sample.

EXAMPLE 6

A fabric woven from continuous filament cellulose acetate yarn is immersed in a mixture of 30 parts maleic anhydride, 70 parts methoxydecaethyleneoxy methacrylate monomer and 100 parts of water and the excess liquid is squeezed out. The sample is then irradiated with the equipment and in accordance with the technique described for Example 5 to a radiation dose of 13.5 mrad.

Some of the more outstanding property changes of the grafted, modified fibers, compared to non-irradiated, non-grafted controls, are listed in Table 2.

TABLE 2

Sample No.	Property change
7A.....	Improved resilience, drier hand, water absorption reduced by 15 to 30%, improved crease retention on wetting, 20% increase in wet breaking strength.
7C.....	Water absorption decreased 10 to 15%.
7D.....	Fabric much less wickable than ungrafted control.
7E.....	Dry breaking strength increased 21%; wet, 26%.

EXAMPLE 8

A wool flannel sample is padded with a solution of 50% methyl acrylate in methanol, then irradiated with 2 mev. electrons to give a dose of 1 mrad. After removing ungrafted modifier, the weight gain is 8.1%.

The grafted sample is wetted with dilute aqueous ammonia, and a crease is pressed into it, using a steam iron. The fabric is washable, and the crease is retained even after a 50° C. detergent wash.

EXAMPLE 9

Samples indicated in Table 3 are soaked and irradiated as shown in Table 4.

TABLE 3

Sample No.	Substrate	Trade name
9A.....	Protein fiber from peanut protein.	"Ardil," ICI.
9B.....	Protein fiber from casein.....	"Fibrolane", Courtaulds.
9C.....	Protein fiber from zein.....	"Vicara", Virginia-Carolina Chem. Co.
9D.....	Cellulose triacetate fiber.	
9E.....	Saponified cellulose acetate fiber.	"Fortisan," Celanese.
9F.....	Natural rubber sheet.....	
9G.....	Wool.....	
9H.....	do.....	
9I.....	Silk.....	
9J.....	Cellulose acetate fiber.....	
9K.....	Cotton cleaning mop.....	
9L.....	Rayon taffeta.....	
9M.....	Rayon taffeta.....	
9N ¹	Rayon taffeta, previously grafted with 12% polyacrylonitrile.	

¹ Sample 9N is prepared by soaking a swatch of rayon fabric in methanol, then in 100% acrylonitrile followed by irradiation (2Mrep); ungrafted material is removed by hot extraction with water, dimethyl formamide, then water.

TABLE 4

Sample	Treatment	Dose, mrad	Irrad. temp. (°C.)	Wt. Gain, percent
9A.....	15% aqueous acrylic acid; 2 hr., 25° C.	1	25	23.1
9B.....	10% aqueous acrylic acid; 2 hrs., 25° C.	1	25	25.0
9C.....	8% aqueous acrylic acid; 2 hrs., 25° C.	1	25	12.4
9D.....	10% aqueous acrylic acid; 1 hr., 25° C.	1	25	14.0
9E.....	15% aqueous acrylic acid; 1 hr., 25° C.	1	25	11.0
9F.....	50% acrylic acid in toluene; 5 days, 25° C.	1	25	21.8
9G.....	9% aqueous sodium styrene sulfonate; 10 min., 60° C.	2	60	11.3
9H.....	22% aqueous methacrylic acid; 2 hrs., 25° C.	1	25	58.5
9I.....	9% aqueous sodium styrene sulfonate; 10 min., 60° C.	1	60	21.0
9J.....	do.	2	60	8.9
9K.....	35% aqueous styrene sulfonic acid; 10 min., 25° C.	1	25	11.0
9L.....	40% aqueous potassium ethylene sulfonate; 10 min., 25° C.	2	25	4.5
9M.....	25% dist. styrene, 25% maleic acid, 50% CH ₃ OH; 15 min., 25° C.	2	25	3.2
9N.....	15% aqueous acrylic acid; 15 min., 25° C.	1	25	15.0

After irradiation, ungrafted acid is removed by washing four times in distilled water at 80° C. After drying, the weight gain is determined. The fibers show no evidence of surface polymer, and are not bonded to one another.

The acid-grafted samples are then dyed with basic dyes; deeper shades and more rapid dyeing is observed, as compared to an ungrafted control. Sample 9H is heavily weighted, but the fabric hand and appearance are unchanged.

The acid grafted polymer substrates are converted to the sodium salt form by heating in 1% aqueous Na₂CO₃ for 1 hour at 60° C. The property changes obtained are given in Table 5.

TABLE 5

Sample	Property changes	Log R, test vs. control
9A.....	Decreased flammability, increased moisture regain.	ND. ¹
9B.....	do.	ND.
9C.....	do.	ND.
9D.....	Improved resilience, hand; improved resistance to hole melting. ²	9.0 vs. 13.3.
9E.....	Improved wickability.	8.8 vs. 13.3.
9F.....	Improved dyeability, printability.	ND.
9G.....	Improved muss and crease resistance, wet.	9.5 vs. 11.7.
9H.....	Improved wickability, resistance to hole melting.	7.7 vs. 11.7.
9I.....	Improved muss and crease resistance.	7.8 vs. 13.3.
9J.....	Improved wickability and wet muss resistance.	7.8 vs. >13.3.
9K.....	42% increased water absorption decreased soiling.	ND.
9L.....	Improved hand, like combed cotton.	ND.
9M.....	Increased amount grafted over styrene or maleic acid alone.	ND.

¹ ND indicates properties not determined.

² Resistance to hole melting is estimated by scattering hot ashes from a burning cigarette onto the fabric.

EXAMPLE 10

Pieces of scrubbed cotton sheeting (80 x 80 count) and scrubbed rayon challis are immersed in aqueous solutions of N-methylolacrylamide (MAA) at room temperature, and squeezed between rubber rolls to remove excess solution. The soaking and squeezing are repeated. The amount of N-methylolacrylamide 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 ME¹ at 50° C. for 30 minutes,

¹ The sodium salt of technical lauryl alcohol sulfate.

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 6 below:

TABLE 6

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-methylolacrylamide 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 dimethylolethylene urea (DMEU) treatment are included for comparison.

TABLE 7

Sample	Percent MAA grafted	Before acid treatment crease angle (degrees)	After acid treatment crease angle (degrees)
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-methylolacrylamide (MAA) fabrics and dimethylolethylene urea (DMEU) applied in the conventional way are given in Table 8, rated subjectively.

TABLE 8

Sample	Cotton	Monsanto 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 fabrics treated in accordance with this invention not only have crease recovery equivalent to conventional dimethylolethylene urea treatments, but show improved fabric "bounce" or resilience, as well as improved stability to acid. Increased amounts of grafted, cured N-methylolacrylamide give some additional improvement. The amount of grafted N-methylolacrylamide required for improving crease-resistance on cellulose is about 2 to 5%, although as much as 15% can be used.

EXAMPLE 11

Increased efficiency of grafting is often obtainable by pretreating the filamentary substrate with a swelling agent for said substrate, or alternatively, dissolving the organic modifier in a solvent which has a pronounced swelling action for the fiber. This example illustrates the advantages.

A switch of rayon taffeta woven from 100 denier 40 filament rayon is soaked in a solution consisting of 10

ml. of methanol and 10 ml. of diallyl itaconate for a period of about 1 hour. Excess liquid is squeezed from the fabric sample by passing it through a wringer, the sample is then wrapped in aluminum foil and exposed to a dose of 2 mrad of electrons from a 2 mev. electron accelerator. After irradiation, the sample is washed for 30 minutes in hot methanol, followed by rinsing three times in an agitation washer containing water at 70° C. The sample is then dried; a weight gain of 1.5% is observed. The sample is much more dyeable with basic dyes, compared to an untreated, non-irradiated control.

When the test is repeated with another swatch of the same fabric, the only change being that the sample is immersed in pure diallyl itaconate without the methanol swelling agent, a weight gain less than 0.1% is observed.

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. By an "organic compound" is meant a material having the formula CX_n where the subscript n indicates the total valence bonds available for the X substituents and where X is a member of the group consisting of hydrogen, halogen, nitrogen, nitrogen radical, oxygen, oxygen radical, sulfur, sulfur radical or organic radical linked to the CX residue by a carbon-to-carbon bond. Furthermore, the C may be doubly bonded to no more than one $S=$ or $O=$ atom; i.e., only one pair of X 's may be replaced by a divalent oxygen or sulfur atom. 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 -methylacrylamide, N -methyl, N -vinyl formamide, N -vinyl pyrrolidone, methyl substituted N -vinyl pyrrolidone, vinyl oxyethyl formamide, methylenebis-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 methacrylate, 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-aminomethylcyclobutane; 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, dihydropyran, methoxy polyethyleneoxymethacrylate; 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 isocyanate, 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, bis-chloroethyl 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, propargyl alcohol, 2-methyl-3-butyn-2-ol, 2,2,3,3-tetrafluorocyclobutylvinylethylene and the like may be used successfully.

NON-POLYMERIZABLE 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 non-polymerizable. By non-polymerizable 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 non-polymerizable compounds, whereupon grafting ensues. The preferred non-polymerizable 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

at super-atmospheric pressure or in the presence of swelling agents, dye carriers, or the like. However, elevated temperatures are to be avoided when using modifiers, such as strong acids, which may degrade hydrolysis-susceptible polymers. Minor amounts of wetting agents, surface active compounds, and the like are useful for improving penetration efficiency.

When it is desirable to limit penetration of a diffusable modifier to a zone near the fiber surface, this may be accomplished by reduced contact time or temperature, or the use of modifiers with greater chain length. Alternatively, the fiber may be exposed to the modifier for the time required to effect the desired penetration, then penetration may be stopped by freezing, for example with Dry Ice. The combination may then be irradiated while frozen, and grafting will occur when the combination is warmed.

Where the modifier is applied from a solution, water is usually the preferred solvent. Other inert liquids are suitable for this purpose, however, such as alcohol, benzene, toluene, glycol, high boiling ethers and the like; where high soaking or irradiation temperatures are used, a non-volatile solvent is often advantageous.

RADIATION WHICH IS EFFECTIVE

The ionizing radiation useful in the process of this invention must have at least sufficient energy to non-selectively break chemical bonds. This radiation is to be distinguished from ultraviolet radiation, which is effective in activating or ionizing only specific chemical bonds; such bonds are responsive to ultraviolet radiation only of given wave lengths. It is often necessary to use an ultraviolet photo-initiator in such reactions, so that light of available wave lengths will initiate the desired chemical reaction. In contrast, the ionizing radiation of this invention has sufficient energy so that it exceeds that which is required to break any chemical bond. Thus, this ionizing radiation serves to activate polymer substrates so that chemical reactions are initiated with any organic compound, or, alternatively, to activate non-polymerizable organic compounds so they react with the polymer substrate.

In general, ionizing radiation is preferred which has sufficient energy so that appreciable substrate thickness is penetrated, and in addition radiation absorption by the atmosphere is sufficiently low so that it is unnecessary to operate in a vacuum. Such radiation has energy of at least 0.1 mev. Higher energies are even more effective; the only known upper limit is imposed by available equipment.

The ionizing radiation of the process of this invention is generally considered in two classes: particle radiation, electromagnetic radiation. Effects produced by these two types of radiation are similar, since in their interaction with matter, each generates secondary radiation of the other type. The important consideration is that the incident radiation exceed a minimum threshold energy. Details of the mechanism of the interaction of high energy electrons with organic matter, including polymers, are not completely known but the initial reaction is considered to be the absorption of energy by the valence electrons of the irradiated molecules in or near the path of the high energy electrons. The absorbed energy may be so great that some valence electrons will be shot off fast enough to ionize still other molecules. Some of the displaced electrons fall back to form neutral molecules and give up their energy as electromagnetic radiation, which in turn can be absorbed by other molecules and thus raise them to an excited stage. Further redistribution of the energy in the molecules results primarily in C—C bonds splitting off H atoms or molecules, producing free radicals or unsaturation.

The similarity of effect between the two types of radiation is thought to be due to the fact that an electron is ejected when an atom absorbs a quantum of high energy X- or gamma-rays; the electron has sufficient energy so

that it in turn ejects electrons from other atoms, corresponding in effect to irradiation with an electron beam. Thus, the initial effect of high energy irradiation is to produce high energy electrons, which within the irradiated substrate produce free radicals. Consequently, the effects produced by particle and electromagnetic irradiation of equivalent energy are very similar, and differ only in the rate at which the effect is produced, which is a function of dose rate. The dose rate is a function of the equipment available to produce it, rather than an inherent limitation of the type of irradiation. Thus, with present day equipment, higher dose rates are obtainable with electron irradiation than are obtainable with X-rays of equivalent energy.

Although the fundamental particles differ from one another in size and charge, their mechanism or energy loss is essentially the same. Thus, their effect on chemical reactions is also similar. Although the neutron is not a charged particle, it, however, produces protons and gamma-rays which lose energy in the normal ways and consequently is effective in the process of this invention.

Therefore, the high energy particle radiation effective in the process of this invention is an emission of highly accelerated electrons or nuclear particles such as protons, neutrons, alpha particles, deuterons, beta particles, or the like, directed so that the said particle impinges upon the textile bearing the organic compound. The charged particles may be accelerated by means of a suitable voltage gradient, preferably at least 0.1 mev., using such devices as a resonant cavity accelerator, a Van de Graaff generator, a betatron, a synchrotron, cyclotron or the like, as is well known to those skilled in the art. Neutron radiation may be produced by bombardment of selected light metal (e.g. beryllium) targets. In addition, particle radiation suitable for carrying out the process of the invention may be obtained from an atomic pile, or from radioactive isotopes or from other natural or artificial radioactive materials.

Similarly, ionizing electromagnetic radiation useful in the process of this invention is produced when a metal target (e.g., gold or tungsten) is bombarded by electrons possessing appropriate energy. Such energy is imparted to electrons by accelerating potentials in excess of 0.1 million electron volts (mev.). Such radiation, conventionally termed X-ray, will have a short wave length limit of about 0.01 angstrom units (in the case of 1 mev.) and a spectral distribution of energy at longer wave lengths determined by the target material and the applied voltage. X-rays of wave lengths longer than 1 or 2 angstrom units are attenuated in air thereby placing a practical long wave length limit on the radiation. In addition to X-rays produced as indicated above, ionizing electromagnetic radiation suitable for carrying out the process of the invention may be obtained from a nuclear reactor ("pile") or from natural or artificial radioactive material, for example, cobalt 60. In all of these latter cases the radiation is conventionally termed gamma-rays. While gamma radiation is distinguished from X-radiation only with reference to its origin, it may be noted that the spectral distribution of X-rays is different from that of gamma-rays, the latter frequently being essentially monochromatic, which is never the case with X-rays produced by electron bombardment of a target.

RADIATION ENERGY

To be efficient in the practice of the present invention, it is necessary that the high energy particles have sufficient velocities to permit penetration of several layers of material, when fabrics or films are being treated. Although an energy of about 50 ev. is enough to initiate the grafting reaction, energies of at least 0.1 mev. are preferred, for efficient penetration. The velocity required will depend on the nature of the particle and also on the nature of the substrate to a certain extent. An electron which is accelerated by a potential of a million volts

(mev.) will effectively penetrate a thickness of polyhexamethylene adipamide fabric of about 0.25 cm. A more universal measure of penetration for all substrates is in units of grams penetrated per square centimeter irradiated. Thus, 2 mev. electrons will effectively penetrate 0.7 gm./cm.² of any shaped article, while 1 mev. electrons are effective for 0.35 gm./cm.².

As stated previously, there is no known upper limit to the particle energy, except that imposed by present day equipment. Thus, energies equivalent to 24 mev. to 100 mev. may be used.

As a guide in using other charged particles which have been shown to be effective in grafting the table below shows particle energies required to give penetration equivalent to 0.1 mev. electrons.

Particle:	Accelerating potential, mev.
Electron, e ⁺ -----	0.1
Proton, H ⁺ -----	3.0
Deuteron, D ⁺ -----	4.0
Alpha, He ⁺⁺ -----	12.0

It should be recognized that the heavier charged particles are especially adapted to creating surface effects, due to their lower penetration at a given energy. In situations where surface effects are paramount, it is not necessary that the shaped article be completely penetrated by the high energy particle and lower accelerations may be employed. Under those conditions, if the surface effect is to be applied to both sides of the shaped article, it will obviously be necessary to expose each of the surfaces to the particle radiation. This is done by simultaneously bombarding both sides of the shaped article or alternatively by subjecting each side to the single source of irradiation during different runs.

High energy particle radiation has special utility for grafting modifiers to thin substrates, e.g., fabrics, filaments and films. The required irradiation doses with present day electron accelerators, such as exemplified herein, are attained rapidly, in a matter of seconds, thus promoting a high rate of throughput.

In comparison, high energy electromagnetic radiation in short wave lengths is highly penetrating, and hence readily lends itself to treating massive substrates. When grafting to the preferred substrates of this invention, this type of radiation is especially useful for irradiating materials present in multiple layers. For example, rolls of film, bolts of fabric, yarn packages, bales of staple fiber, or the like, may be irradiated as a single unit.

As an illustration, X-rays generated by electrons of 2 mev. have adequate penetration for polymer samples of several inches in thickness. Lower energy (longer wave length) X-rays are, of course, less penetrating, so that it may be necessary to reduce the thickness of material to be treated simultaneously. In addition, the very long (soft) X-rays, because of low penetration, may be especially effective in producing surface effects.

Although the treatment can be carried out using conventional X-ray equipment, the use of radioactive isotopes such as cobalt 60 is especially economical. Radiation from waste fission products, with particle irradiation screened off if desired, is also effective and offers an opportunity to utilize an otherwise useless waste product.

RADIATION DOSE

In determining the optimum dose of irradiation for any particular combination, both the nature of the organic compound and the nature of the solid substrate must be considered. For example, for vinyl monomers which are readily graftable, and polymer substrates that are readily activated by ionizing radiation, it appears that the greater part of the minimum irradiation dose is required to consume the inhibitor (including oxygen) which may be present in the vinyl monomer. After that is done, relatively low additional doses will produce enough radicals to initiate graft polymerization. For readily graftable

combinations of this type, a high propagation constant is observed. Thus, the extent of irradiation-induced graft polymerization can be increased by increasing either radiation dose, post-irradiation time, post-irradiation temperature, or all three. For instance, if a polymer soaked in acrylic acid solution is irradiated with a dose of 0.06 mrad, and the irradiated sample is kept in contact with the acrylic acid solution for 1 hour at room temperature, a large amount of the acid is grafted. In contrast, with the same dose, if monomer is removed from the sample immediately after irradiation (e.g., by a water extraction), only one-third as much acrylic acid is grafted. Therefore, for polymerizable vinyl compounds and readily graftable polymer substrates, a very small dose is required; thus, a minimum dose of 5000 rads (0.005 mrad) initiates a significant amount of grafting.

When unsaturated compounds which are not homopolymerizable (e.g., maleic acid) are used as the modifier, in combination with readily graftable substrates, doses of 0.1 mrad are required to initiate appreciable grafting. When non-polymerizable organic compounds or saturated polymeric modifiers are used, a minimum dose of 1 mrad should be employed. Radiation doses below the minimum specified fail to initiate beneficial amounts of grafting within a practical length of time. This is due to the fact that the life of free radicals produced by the irradiation depends on a balance between competing (i.e., non-grafting) reactions and those which produce grafting. It is obvious, of course, that even lower doses may be used in completely inhibitor- and oxygen-free systems, or if irradiation-initiation of grafting is supplemented by a chemical initiator.

Although the minimum doses specified are effective, higher dosages may be used and are usually highly beneficial. Dosages so high that substantial degradation of the shaped substrate occurs must obviously be avoided. High doses crosslink some polymers, which may sometimes be undesirable.

As a guide in this regard, wool fiber may be irradiated to a dosage as high as 80 mrad. However, it is preferred that the dosage applied to these substrates not exceed about 60 mrad. An upper limit of about 40 mrad is suggested for silk, while cellulose fiber substrates are preferably subjected to no more than 20 mrad.

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.

However, it has been observed that the life of free radicals is many times greater than has been found in vinyl polymerizations carried out in solution or emulsions. For this reason, at a given radiation dose, the yield of polymer grafted to the shaped substrate is much greater than would be obtained, for example, if the substrate polymer were dissolved in the vinyl monomer and the solution irradiated.

The average molecular weight of the grafted polymer chains (at a given constant weight gain) may be controlled by adjusting the radiation dose. It may also be adjusted by controlling chain transfer to the substrate polymer, e.g., by changing grafting temperatures, or modifying the substrate polymer by incorporating copolymer components which are more (or less) susceptible to chain transfer. Similarly, the molecular weight distribution of the grafted polymer chains may be adjusted. By controlling the number, length and length distribution of grafted chains, the effect produced by a given grafting agent may be modified.

It has been observed that irradiation of the modifier-treated textile in the presence of air or moisture may occasionally cause some degradation; such adverse effects can be avoided by employing an atmosphere of inert gas around the article while it is being irradiated. Alternately

tively, a satisfactory and simpler approach is to wrap the sample in a material which is substantially air and water impervious, thus limiting the quantity of air or moisture contacting the sample. Complete exclusion of oxygen is not required, although it may contribute to grafting efficiency when using a vinyl monomer. In some of the examples, the samples are wrapped in polyethylene film. Aluminum foil is satisfactory. The nature of such wrapping material is not critical, provided it is substantially impervious to air and moisture, when required, and is readily penetrated by the radiation.

IRRADIATION CONDITIONS

In the process of this invention it may be desirable to include in the combination to be irradiated, materials which may have a protective or antioxidant effect in preventing radiation degradation of either modifier or substrate or both. Compounds of this type are cysteine, carbon, polyethylene glycols and the like. It may also be desirable to include in the combination to be irradiated materials which absorb radiation and transmit the energy thus absorbed to the modifier or the organic polymeric material or both, whereby adhering is promoted and the efficiency of utilization of the radiation is increased. Compounds with this property are somewhat similar to sensitizers in photography, except that in this case useful materials absorb high energy radiation and emit the energy in a lower or more usable range. Phosphor screens containing calcium tungstate, zinc sulfide or metallic lead or the like have utility for this purpose. The phosphor materials may be used as plates contacting the material being treated, or may be incorporated in the modifying agent or even be coated on or dispersed in the organic polymeric material which it is desired to modify.

The irradiation may be accomplished over a wide range of temperatures. However, a low temperature decreases the tendency toward oxidation. Since the absorption of particle radiation frequently causes a temperature increase in the range of about 2° C. for each mrad absorbed, if high tube current is employed so that radiation absorption is complete within a short time interval, it is usually advisable to provide means to remove the heat generated to avoid injury to the sample. The use of Dry Ice to maintain a cold atmosphere is very satisfactory for this purpose. In general, irradiation at a higher temperature promotes the speed with which bonding occurs, thus promoting a higher throughput of a given piece of equipment at a constant radiation dosage. Temperatures ranging from -80° C. or below up to the melting point of the polymer substrate may be employed. More efficient grafting is often noted when irradiation temperatures are in the range of 100 to 160° C.

In general, the greatest weight of modifier is grafted for a given dose when the organic compounds are applied to the substrate as liquids or concentrated solutions. However, this finding must be followed with caution, since the "fabric" character must be preserved. In many instances, unless excess solution is removed from the textile prior to irradiation, large amounts of homopolymer may be formed on the surface of the filaments, bonding them together in a stiff, unattractive mass. This not only represents a loss of modifier, but, if not removed, will render the textile unfit for apparel use. In order to avoid this result, it is recommended that (a) modifier compositions be avoided which cross-link to an insoluble state under irradiation doses needed for grafting; (b) that excess modifier be removed prior to or after grafting.

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 after-treatments, the shaped

article may be dyed, bleached, hot or cold drawn, chemically reacted, 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, resilience, 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, washwear 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, over-all appearance and combinations of these as well as other.

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. Method for beneficially modifying substantially pure cellulosic substrates which comprises first contacting the substrate with an aqueous solution, in a substantially neutral pH, of a water-soluble ethylenically unsaturated monomer that is polymerizable in aqueous solution under the influence of a field of ionizing high energy radiation; continuing contact of said substrate with said monomeric solution until the former is at least partially swollen by the latter; then subsequently exposing the cellulosic substrate while it is in contact with the aqueous monomeric solution to a field of ionizing high energy radiation until at least the surface of the substrate has become modified with the saturated reaction product of said monomeric material that has been chemically reacted to provide said reaction product in the presence of and in intimate association with said substrate.

2. The method of claim 1, wherein the substrate is comprised of cotton fibers.

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3. The method of claim 1, wherein the substrate is comprised of regenerated cellulose.

4. The method of claim 1, wherein the substrate is comprised of viscose rayon fibers.

5. The method of claim 1, wherein the field of ionizing high energy irradiation that is employed for the modifying reaction has an intensity of at least about 40,000 roentgens per hour.

6. The method of claim 1, wherein the amount of water-soluble monomer in aqueous solution that is in contact with said substrate is an amount of the monomer between about 1 and 40 percent by weight, based on the weight of the substrate.

7. The method of claim 1, wherein the amount of water-soluble monomer in aqueous solution that is in contact with said substrate is an amount of the monomer between about 5 and 20 percent by weight, based on the weight of the substrate.

8. The method of claim 1, wherein said monomer is selected from the group consisting of acrylonitrile, methacrylonitrile, acrylamide, acrylic acid, methyl methacrylate, sulfonated styrene monomers, vinyl lactam monomers and methyl isopropenyl ketone.

9. The method of claim 1, wherein said monomer is a para-sulfonated styrene monomer.

10. The method of claim 1, wherein said monomer is vinyl pyrrolidone.

11. The method of claim 1, wherein said monomer is acrylonitrile.

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12. Modifying a cotton fiber substrate with acrylonitrile by a method according to the method set forth in claim 1.

13. Modifying a cotton fiber substrate with N-methylolacrylamide according to the method set forth in claim 1.

14. Method for modifying cellulosic substrates which comprises immersing the substrate in aqueous N-methylolacrylamide until said substrate is at least partially swollen; and subsequently exposing said substrate to a field of ionizing high energy radiation until at least the surface of the substrate has become modified by a chemical reaction in which said acrylamide is grafted to said substrate.

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