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CELLULOSIC TEXTILE FINISHING

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8 Claims. (Cl. 8—116)

This invention relates to an improved method of finishing cellulosic textile materials to improve certain physical properties thereof, particularly the crease resistance, tensile or tearing strength, and the abrasive strength of the textile, and to the novel product thereby produced. It is related to Heberlein et al. U.S. application No. 62,068, filed March 31, 1960, and constitutes an improvement over the method therein described.

The term "cellulosic textile material" as employed herein is intended to include films, yarns, fibers, filaments or threads as such or in the form of cast sheets, woven, knit, felted or non-woven fabrics, consisting of natural or regenerated cellulose, as well as such fibers, fabrics, etc., which are made up of a major portion of cellulose or regenerated cellulose, but which also contain in addition a small quantity of non-cellulosic material.

It is well known that in order to improve the crease resistance of natural or regenerated cellulose yarns or fabrics, for example, cotton, rayon, or mixed cotton and rayon goods, the yarn or fabric is impregnated with one or more well-known condensable resin-forming substances, for example a synthetic resin precondensate dispersed or dissolved in a fluid carrier containing a condensation catalyst which is usually acidic. Following impregnation the excess resin precondensate is squeezed out and the impregnataed fabric is then subjected to temperatures well above 100° C. for a time sufficient to cure the resin. Textiles finished in this conventional manner at elevated temperature are substantially less durable than the unfinished or starting material. While conventional finishing imparts improved crease resistance, this is accomplished at the expense of a marked reduction in fiber strength of the textile product, as evidenced either by appreciably reduced tensile or tearing strength or resistance to abrasion or both.

According to related Heberlein et al. U.S. application Serial No. 62,068, a method is suggested whereby the cellulosic textile to be finished is first treated with a condensable or resin-forming substance and subsequently subjected to ionizing radiation, more particularly to electromagnetic ionizing radiation, which facilitates condensation and curing of the resin-forming substance on the textile. The method thereof may be carried out with or without the usual condensation catalyst, but heat is not required. The product produced by the related method exhibits substantially improved crease resistance as compared with this property of the same conventionally finished textile. Tearing strength of the textile finished in accordance with the related application is in some instances, although not always, improved. Occasionally tearing strength is slightly reduced.

While it is generally agreed that a finish superior to that of the conventional method can be imparted to the textile by the method of the earlier related application, there is still a need for a method which will assure superior crease resistance results accompanied by improved tearing and abrasive strength, without degradation of the cellulose.

I have found that these results can be obtained by following the general procedures outlined in the related application as respects application of the condensable or resin-forming substance, but instead of subjecting the thus treated textile to electromagnetic ionizing radiation, the impregnated material is irradiated with accelerated electrons of a critical low particle energy to a critical total dose.

It has already been proposed to employ accelerated electrons (beta radiation) to effect condensation of synthetic resins on cellulosic textiles, but the methods previously described have always employed very high energy beta particles. More particularly, the prior art techniques employ beta radiation of a particle energy of 2 mev. and higher, with the total doses irradiated being between about 5×10^6 and 7×10^7 rad. These prior art techniques have been acknowledge to be insufficient for the proper finishing of cellulosic textile materials in that they cause very extensive degradation of the cellulosic substrate thus rendering its further use as a fabric impossible. Furthermore, at these high energy levels satisfactory resin condensation is not achieved and an acceptable finish is thus not imparted to the fabric.

It has been established that extensive decomposition of cellulose and regenerated cellulose occurs when it is subjected to total doses of ionizing radiation above 2.5×10^6 rad. For example, at total doses of 5×10^6 rad at least 10% of the cellulose is converted to sugars. Furthermore, many of the resin precondensates usually employed for the finishing of cellulosic textiles such as urea, melamine and ethyleneurea, are also sensitive to radiation and are extensively decomposed at total doses of more than 2.5×10^6 rad. Accordingly, the unsatisfactory results attending the aforementioned prior art attempts at finishing with the use of high energy beta particles is not surprising.

In accordance wtih the method of the present invention excellent resin condensation on the celiulosic material can be achieved without any significant degradation of the cellulose or the resin precondensate if the textile materials are subjected to the action of accelerated electrons of a critical particle energy of less than 1 mev., and if a total dose imparted is less than 2×10^6 rad. The present process contemplates the use of accelerated electrons of a particle energy between about 0.05 and 1 mev., and preferably between 0.05 and 0.6 mev., with irradiation being to a total dose above 10^4 but below 2×10^6 rad, preferably between 10^5 and 10^6 rad.

The excellent results obtained by the method of the present invention mentioned above and set forth in detail hereinafter are indeed surprising, since one skilled in the art would not expect that the irradiation of resin precondensate impregnated cellulosic textiles with accelerated electrons of such a low particle energy and at a comparatively low total dose would produce sufficient resin condensation to effect the desired crease resistance and dimensional stability improvement. From the teachings of the prior art, one would assume that sufficient resin condensation or linking of the resin to the cellulosic molecule could not be achieved with accelerated electrons since at much higher doses and particle energies poor condensation is achieved and degradation of the cellulosic substrate is appreciable.

It is believed that the success of the method of the present invention is due to the fact that electromagnetic ionizing radiation (gamma rays) pass through the irradiated material on the shortest possible path, with at most only about 1% of their energy being absorbed by the cellulosic textile. On the other hand, accelerated electrons, which possess mass, are slowed down as a result of multiple collisions with the atoms of the cellulosic material or with atoms of the resin precondensate thus forming secondary electrons which themselves collide with other atoms. At each collision of electrons energy is transferred and a relatively great part of the energy of the accelerated electrons is absorbed by the cellulosic

textile and the condensable or resin-forming substance thereon. It has now been found that accelerated electrons of a very high particle energy, that is above about 1 mev., transfer so much energy during their passage through the cellulosic material that numerous scissions of the chain of the cellulosic molecule occur with resulting decomposition and destruction of the textile. If, in accordance with the present invention, accelerated electrons of low particle energy are irradiated into the cellulosic material there is a much smaller transfer of energy so that cellulose chain scission is very greatly reduced or eliminated, but the transferred energy is sufficient, perhaps being different in kind, to provide activation energy for the cellulose or resin precondensate to effect ionization and condensation.

Furthermore, in accordance with the present invention it has been established that decomposition of the cellulose at a certain irradiated total dose, e.g., 10^6 rad, is very substantially lower where accelerated electrons having a low particle energy, i.e., below 1 mev., are used as compared with electrons of a particle energy above 1 mev. Where, in accordance with the present invention, accelerated electrons of a particle energy of between about 0.05 and 0.6 mev. are employed, the total dose to which the cellulosic textile is exposed can be maintained at a sufficiently low value so that no decomposition of the cellulose worth mentioning takes place.

Accelerated electrons employed in accordance with the preesnt process may be produced by the conventional electron accelerators, such as the cascade, Van de Graaf or linear types. Radioactive substances such as Sr^{90} emitting beta radiation of a particle energy of 0.6 mev., promethium^{147} emitting beta radiation of a particle

finishing of textiles of all kinds, as noted earlier, but is particularly useful in the treatment of sheet materials or fabrics. It is intended primarily for the crease-proof finishing and the imparting of dimensional stability to woven or knit cotton or rayon, or mixed cotton and rayon fabrics, and offers the further very significant advantage in that the tearing and abrasive strength of the starting or unfinished fabric is very substantially increased. The finished fabrics exhibit a pleasant soft hand.

In accordance with the present method it is also possible to impart to a fabric permanent embossing effects, such as goffering, ribbing, schreinering, or moire effects, as well as calendaring effects with or without friction. The method is also effective in the treatment of cellulosic textile yarns, filaments or threads. Excellent results are achieved in fabrics such as voiles and marquisettes fashioned of highly twisted yarns, which fabrics normally exhibit a strong tendency to shrink.

Moreover, fine fabrics of cotton or regenerated cellulose which have been stiffened or transparentized by treatment with concentrated sulfuric acid, cuprammonium solution or sodium zincate cellulose solution are very significantly improved by the present process, without any decrease in fiber strength.

The method of the present invention will be further apparent from the following typical examples, which illustrate practical applications of the method and describe certain characteristics of the novel finished textile products.

Example I

A cotton imitation poplin was singed, desized and bleached and thereupon impregnated with a solution con-

and abrasive strength for the starting unfinished cotton poplin fabric and for fabric Sections A, B and C.

	Crease angle in degrees		Tearing strength in g.		Abrasive strength in number of rotations
	Warp	Fill	Warp	Fill	
Starting material	62	63	770	730	42.000
Section A	81	82	680	650	30.870
Section B	76	82	780	660	32.850
Section C	108	110	1050	980	49.360

It will be noted that simply impregnating the fabric with dimethylolethyleneurea and drying at 60–70° C. appreciably increased the crease angle, but at the expense of lowered tearing and abrasive strengths. Irradiation with 2 mev. particles effected some improvement in the abrasive strength and also in the warp tearing strength, but appreciably reduced the warp crease angle. On the other hand, Section C which was irradiated in accordance with the method of the present invention employing low energy beta particles exhibited outstandingly superior crease angle, tearing strength and abrasive strength, as well as an improved hand as compared with Section B.

Example III

A cotton muslin fabric which had been pretreated in the customary manner was parchmentized with sulfuric acid of 52.5° Bé. for 16 seconds at 15° C. and thereupon aftermercerized with 30° Bé. sodium hydroxide for 15 seconds. The thus treated material was washed until neutral, dried under tension and impregnated with a 10% solution of 1-carbonyl-2,5-dimethoxy-4-ethyl-triazone-2,4, 6 dried at 60–70° C. and thereupon irradiated with accelerated electrons of a particle energy of 0.06 mev. to a total dose of 10^6 rad. The product and the starting material exhibited the following properties:

	Crease angle in degrees		Tearing strength in g.		Abrasive strength in number of rotations
	Warp	Fill	Warp	Fill	
Starting material	0	8	200	195	3.220
Irradiated	100	110	750	740	6.140

Example IV

A spun rayon gabardine fabric, pretreated in the usual manner, was impregnated with a solution of dimethylolethyleneurea, as described in Example I, and dried at 60–70° C. Thereupon it was irradiated with accelerated electrons of a particle energy of 0.12 mev. to a total dose of 10^5 rad. The thus treated fabric exhibited excellent abrasive strength and crease resistance and unimpaired tearing strength.

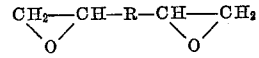
Example V

A cotton imitation poplin fabric was impregnated with an aqueous solution containing per liter 100 g. melamine-formaldehyde precondensate and 15 g. triethanolamine glycolate catalyst, squeezed out and dried at 60° C. Thereupon the fabric was irradiated with accelerated electrons of a particle energy of 0.1 mev. to a total dose of 10^6 rad. After irradiation the fabric was washed with a soap soda solution at about 60° C., dried and rinsed with cold water. The thus treated fabric had the following properties:

	Crease angle in degrees		Tearing strength in g.		Abrasive strength in number of rotations
	Warp	Fill	Warp	Fill	
Starting material	47	59	880	880	15.400
Irradiated	110	105	1,030	1,030	20.810

Example VI

The cotton imitation poplin fabric of Example V was impregnated with an aqueous solution containing per liter 102 g. of a diepoxide resin of the formula:



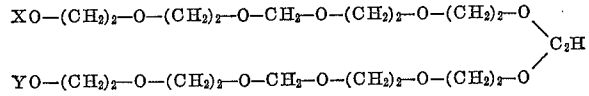
R=1 to 5 CH_2-groups

and 6 g. zinc fluoroborate catalyst. It was then squeezed out and dried at 60° C., washed, dried and rinsed as descrebed in Example V. Thereupon it was irradiated with accelerated electrons of a particle energy of about 0.1 mev. to a total dose of 2×10^6 rad. The thus treated fabric exhibited the following properties:

	Crease angle in degrees		Tearing strength in g.		Abrasive strength in number of rotations
	Warp	Fill	Warp	Fill	
Starting material	47	59	880	880	15.400
Irradiated	110	120	1,950	1,950	25.880

Example VII

The cotton imitation poplin fabric of Example V was impregnated with an aqueous solution containing per liter 100 g. of a glycol polyacetal, the polymeric condensation product of diethyleneglycol and formaldehyde of the following general formula:



where X and Y are either H or $-CH_2OH$, as described in U.S. Patent No. 2,786,081, and 40 g. $MgCl_2.6H_2O$ as catalyst. The fabric was then squeezed out, dried at 60° C. and washed, dried and rinsed as described in Example V. It was thereupon irradiated with accelerated electrons of a particle energy of about 0.1 mev. to a total dose of 5×10^5 rad. The thus treated fabric exhibited the following properties:

	Crease angle in degrees		Tearing strength in g.		Abrasive strength in number of rotations
	Warp	Fill	Warp	Fill	
Starting Material	47	59	880	880	15.400
Irradiated	110	105	1,890	1,690	26.930

I claim:

1. A method of finishing a cellulosic textile of the group consisting of cotton, rayon and mixtures thereof, which comprises impregnating the textile with a crease-resistance imparting condensable resin-forming substance disposed in a fluid carrier, and subsequently subjecting the impregnated textile to beta radiation of a particle energy between about 0.05 and 1 mev. to a total radiation dose between about 10^4 and 2×10^6 rad to condense the condensable substance on the textile and substantially improve the abrasion and tensile strengths of the starting textile.

2. A crease resistant cellulosic textile finished by the process of claim 1.

3. A method as set forth in claim 1 wherein the beta radiation is of a particle energy between about 0.05 and 0.6 mev.

4. A method as set forth in claim 1 wherein the fluid carrier is water.

5. A method as set forth in claim 1 wherein the impregnated textile is irradiated in wet condition.

6. A method as set forth in claim 1 wherein the impregnated textile is dried below about 100° C. before it is irradiated.

7. A method of finishing a fine cellulosic textile fabric of the group consisting of cotton, rayon and mixtures thereof, which comprises impregnating the textile with a crease-resistance imparting condensable resin-forming substance dispersed in a fluid carrier, and subsequently subjecting the impregnated textile to beta radiation of a particle energy between about 0.05 and 0.6 mev. to a total radiation dose between about 10^5 and 10^6 rads to condense the condensable substance on the textile and substantially improve the abrasion and tensile strengths of the starting textile.

8. A fine cellulosic textile fabric finished by the process of claim 7.

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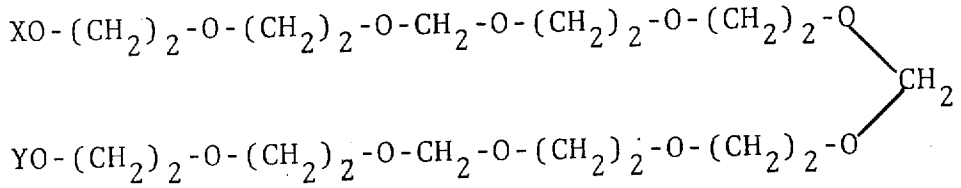
CERTIFICATE OF CORRECTION

Patent No. 3,206,273 September 14, 1965

Fritz Munzel

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, lines 11 and 12, for "descrebed" read -- described --; lines 32 to 35, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 3rd day of May 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents