

1

3,481,682

MODIFYING KERATINIC FIBERS WITH UNSATURATED SULFONIC ACIDS AND BLENDING FIBERS SO MODIFIED WITH FIBERS HAVING DIFFERENT DYE AFFINITY TO OBTAIN PRODUCTS WHICH ARE DIFFERENTIALLY DYEABLE

Greville Machell, Spartanburg, S.C., assignor to Deering Milliken Research Corporation, Spartanburg, S.C., a corporation of Delaware

No Drawing. Filed Dec. 6, 1962, Ser. No. 242,614

Int. Cl. D06p 3/02, 5/00

U.S. Cl. 8—1

6 Claims

This invention relates to a novel process for modifying the dyeing characteristics of natural fibers and, more particularly, for reducing the affinity of keratin fibers for acid dyestuffs and/or increasing the affinity of keratin fibers for basic dyestuffs and to novel keratin fibers treated in accordance with the novel process.

Keratin fibers in general, wool fibers in particular, have a marked affinity for acid dyestuffs. By reducing the affinity for acid dyestuffs of some of the wool fibers of a fabric, desirable effects can be produced during subsequent dyeing operations. For example, a fabric containing untreated wool fibers and immunized fibers (immunized being the common term for keratin fibers characterized by a reduced affinity for acid dyestuffs) may be subsequently dyed with an acid dyestuff to produce an effect fabric, wherein only the untreated fibers retain the acid dyestuff, leaving the immunized fibers undyed. This effect fabric may subsequently be dyed with a basic dye which has an affinity only for the immunized fibers so that a fabric having fibers dyed to contrasting colors may be produced.

The affinity of wool and other keratin fibers for acid dyestuffs has been reduced by means of concentrated sulfuric, sulfamic acid, mixtures of acetic anhydride, acetic acid and sulfuric acid, by treating the fibers with a solution of formaldehyde in aqueous sulfuric acid with or without the addition of aromatic sulfonation products, or also by means of tannic acid with the addition of tin, formaldehyde, zinc chloride, or pyridine.

All of these treatments, however, cause considerable damage to the fibers so treated, particularly with regard to their physical and aesthetic properties. Furthermore, none of these processes has proven satisfactory, being either too expensive or not producing the desired degree of immunization.

It is an object of this invention to provide a process for reducing the affinity of keratin fibers for acid dyestuffs whereby the fiber weight is increased while retaining many of the desirable physical properties of the fibers so treated.

It is a further object of this invention to provide such a process wherein the aesthetic properties of the wool are substantially retained.

Still a further object of this invention is to provide a process wherein the keratin fibers are more completely immunized toward acid dyestuffs than any of the above prior art processes while providing improved physical characteristics.

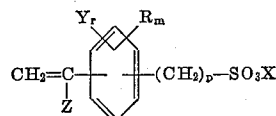
Yet another object of this invention is to provide a process wherein the keratin fibers are characterized by an increased affinity for basic dyestuffs, in most instances accompanied by a reduced affinity toward acid dyestuffs.

These and other objects are accomplished in accordance with this invention by reacting keratin fibers with at

2

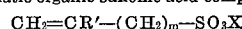
least one of the monomeric ethylenically unsaturated sulfonic acids or derivatives thereof represented by the formulae:

(I)



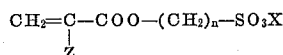
(aromatic organic sulfonic acid compounds)

10 (II)



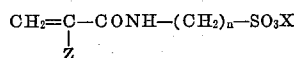
(alkenyl organic sulfonic acid compounds)

15 (III)



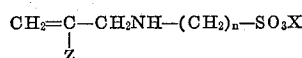
(sulfoalkylacrylate organic sulfonic acid compounds)

20 (IV)



(acryloyl taurine homologue compounds)

25 (V)



(allyl taurine homologue compounds)

wherein X is hydrogen, ammonium, substituted ammonium (preferably methyl or ethyl), an aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, an alkali-metal ion (including sodium, potassium and lithium), Y is hydrogen, chlorine or bromine; R is methyl or ethyl; R' is hydrogen, methyl, ethyl, or ---COOX ; Z is hydrogen or methyl; m has a numerical value in whole number increments from 0 to 2; n has a numerical value of 1 or 2; p is 0 or 1; and r is 1 to 4.

When one, or a combination of these monomers, is reacted with a keratin fiber under graft polymerization conditions whereby the resulting polymer, to a great extent, is chemically attached to the fiber, there is provided a high degree of immunity toward acid dyestuffs and/or enhanced receptivity toward basic dyestuffs. The amount of polymer which must be added to the substrate for complete immunization varies with each monomer, e.g., about 20% by weight of the polymer formed from sodium styrene-p-sulfonate provides complete immunity to acid dyestuffs and excellent receptivity toward basic dyestuffs. An addition of any appreciable amount of polymers from the above monomers, however, will markedly alter the dyeing characteristics of the substrate treated.

Keratin fibers so treated may then be combined with other fibers, such as untreated keratin fibers, having a different affinity for acid and basic dyestuffs. The resulting combination of fibers may then be dyed with at least one, or both, of these dyestuffs to obtain differentially dyed fibers.

Acid dyestuffs, as is well known, are those dyestuffs wherein the dyeing component is acidic, or anionic, while the dyeing component of basic dyestuffs is basic, or cationic.

Suitable acidic compounds for modifying the dyeing characteristics of keratin fibers include such organic sulfonic acids as 2-propene sulfonic acid; α -sulfopropyl acrylate; sodium vinyl toluene sulfonate; potassium ortho-chlorostyrene sulfonate 2-hydroxy-3-sulfopropyl acrylate, sodium salt; sodium 3-allyloxy-2-hydroxypropane sulfonate; 4-sulfophenyl acrylate, sodium salt, and N-allyl amino di(2-ethane sulfonic acid).

Still other organic sulfonic acids which may be employed are set forth in the following representative (but by no means exhaustive) listing, wherein they are grouped according to the several types indicated in the foregoing formulae.

Aromatic vinyl-containing sulfonic acids (corresponding to Formula I) include para-styrene sulfonic acid; ortho-styrene sulfonic acid; para-isopropenyl benzene sulfonic acid; para-vinyl benzyl sulfonic acid; ortho-isopropenyl benzyl sulfonic acid; sodium para-styrene sulfonate; potassium ortho-styrene sulfonate; methyl para-styrene sulfonate; ethyl para-vinyl benzyl sulfonate; ortho-vinyl benzene sulfonic acid, isopropyl ortho-isopropenyl benzene sulfonate; n-butyl ortho-styrene sulfonate; tertiary butyl para-styrene sulfonate; 2-chloro-4-vinyl benzene sulfonic acid; 4-bromo-2-isopropenyl benzene sulfonic acid; 3-vinyl toluene 6-sulfonic acid, sodium salt; 2-ethyl-4-vinyl benzene sulfonic acid; 2,3-dichloro-4-vinyl benzene sulfonic acid; 2,3,5-tribromo-4-vinyl benzene sulfonic acid; 2-chloro-3-vinyl-toluene-6-sulfonic acid; 2,3-diethyl-4-vinyl-benzyl sulfonate, sodium salt and the like.

Alkenyl sulfonic acids (corresponding to Formula II) include α -sulfoacrylic acid; ethylene sulfonic acid; sodium ethylene sulfonate; potassium ethylene sulfonate; methyl ethylene sulfonate; isopropyl ethylene sulfonate; 1-propene 3-sulfonic acid; 1-propene 1-sulfonic acid, sodium salt; 1-propene 2-sulfonic acid, ethyl ester; 1-butylene 4-sulfonic acid, n-butyl ester; 1-butylene 3-sulfonic acid and tertiary butylene sulfonic acid and the like.

Sulfoalkyl acrylates (corresponding to Formula III) include sulfomethyl acrylate, 2-sulfoethyl acrylate; sulfomethyl methacrylate, sodium salt; 2-sulfoethyl methacrylate, methyl ester; 2-sulfoethyl methacrylate, potassium salt and the like.

Acryloyl taurine and homologues (corresponding to Formula IV) include N-acryloyl taurine; M-acryloyl taurine, sodium salt; N-methacryloyl taurine, methyl ester; N-methacryloyl taurine, potassium salt; N-acryloyl taurine, ethyl ester; N-acryloyl-aminomethane sulfonic acid; N-methacryloyl-aminomethane sulfonic acid, sodium salt; methyl N-methacryloyl-aminomethane sulfonate and the like.

Allyl taurine and homologues (corresponding to Formula V) include allyl taurine; allyl taurine, sodium salt; allyl taurine, potassium salt; methallyl taurine; methallyl taurine, methyl ester; methallyl taurine, isopropyl ester; N-allyl-aminomethane sulfonic acid; sodium N-allyl-aminomethane sulfonate; lithium N-methallyl-aminomethane sulfonate; n-butyl n-allyl-aminomethane sulfonate

A graft polymerization technique is generally distinguished from conventional polymerization in situ procedures by covalent bonding of the polymer to the substrate involved. For example, a polymeric material grafted onto a fibrous substrate would be covalently bonded to the substrate so as to be non-extractible by a solvent for the polymer formed, whereas the polymers simply coating the substrate would be extractible to a much greater extent than the grafted polymer. The modification in dyeing properties of natural fibers is obtained, however, whether or not the reacted material is extractible. For example, modification is also derived if the reacted material is only ionically bonded to the fiber.

In graft polymerization techniques, that amount of polymer which can be extracted is designated as homopolymer, while the polymer which is covalently attached to the substrate and, therefore, is not extractible, is designated as graft polymer. It is realized, however, that some homopolymer may be occluded within the interstices of the fibers of the substrate treated and that not all of the polymeric material remaining on the substrate is graft polymer. For purposes of his invention, then, since both the occluded and graft polymer affect the dyeing characteristics of the fibrous substrate and particularly since neither type polymer can be extracted from the substrate,

the term "non-extractible" will be utilized herein to define that polymeric material remaining on the fibrous substrate after polymerization occurs under graft polymerization conditions and after the treated substrate is washed with a solvent for the particular homopolymer involved until no more homopolymer is removed.

Graft polymerization techniques are usually conducted in the presence of a redox catalyst system or some other catalyst which will initiate the polymerization of vinyl type monomers. The preferred redox catalyst system includes a reducing agent and an oxidizing agent, the interaction of which provides free radicals which cause polymerization of the monomeric material onto the keratin substrate.

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

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

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

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

5

Other suitable catalysts or initiators for the polymerization process include azo catalysts, such as azobisisobutyronitrile, as well as irradiation under the influence of high energy fields, including the various, diverse actinic radiations such as ultra-violet, x-ray and gamma radiations, as well as radiation from radioactive materials, such as cobalt-60.

In conducting the graft polymerization process, either or both of the reducing agent and oxidizing agent may be applied to the fibrous substrate prior to the application to the substrate of the monomeric material or the monomer may be applied to the substrate before either or both of the catalyst components. In general, however, it is preferred to add either the reducing agent or the oxidizing agent to the fibrous substrate and, subsequently, to add the other catalyst component and the monomeric material simultaneously. For example, a substrate can first be impregnated with a solution of a reducing agent and then immersed in an aqueous solution containing the oxidizing agent and the desired monomeric material.

When conducting the process of this invention on cellulosic substrates, such as cellulose acetate, viscose rayon, paper, cotton and the like, ceric ion initiating systems may also be used. The ceric ion may be derived from ceric salts, such as ceric nitrate, ceric sulfate, ceric ammonium nitrate, ceric ammonium sulfate, ceric ammonium pyrophosphate, ceric iodate and the like.

The graft polymerization of the sulfonic acid monomers or their derivatives may be conducted at room temperature, although temperatures between 40 and 60° C. are generally preferred. A temperature in excess of about 100° C. is not preferred since undue degradation of the preferred catalyst system, the redox system, occurs at this elevated temperature. In general, such conditions as concentrations of the reagents, pH, time and temperature of reaction may be modified to suit the individual circumstances, while still providing the desired degree of graft polymerization.

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

Graft polymerization most readily takes place in the presence of water. This generally presents no problem since the catalyst components or monomers are preferably applied to the substrate in an aqueous medium. If the substrate is dried, however, prior to exposure to the monomer, polymerization will be unduly slow. Consequently, it is preferred that the substrate be moistened with water when the polymerization takes place. Ionic or non-ionic surface active agents may be utilized in any aqueous medium used in applying any of the reagents. Improved results are obtained when the keratin fibers are in a swollen condition during reaction. This condition is most readily obtained by conducting the reaction in the presence of a swelling agent for keratin fibers, such as urea; thiourea; lithium salts, such as the chloride, bromide and iodide; guanidine compounds, such as the hydrochlorides, formamide, N,N'-dimethylformamide, acetamide, N,N'-dimethylacetamide and the like.

The process of this invention may be applied to fibers in the free form, such as in the form of top or sliver, and the resulting immunized fibers can then be blended with untreated fibers, spun into yarn, and made into fabrics which can then be dyed with an acid dye-stuff to provide an effect fabric. Similarly, yarns of keratin fibers may be treated in accordance with this invention and combined with untreated yarns for the manufacture of a fabric which can be similarly dyed to provide an effect fabric. Alter-

6

natively, the fabric itself can be treated, in whole or in part, in accordance with this invention.

As stated above, any of the fibers treated in accordance with this invention for the purpose of immunizing toward acid dyestuffs will also be characterized by a marked affinity for basic dyestuffs. Consequently, any of the effect fabrics produced in accordance with this invention can be subsequently dyed with a basic dyestuff to provide effect fabrics of even greater contrast. In another embodiment of this invention, any fabric containing a major proportion of keratin fibers may be treated with a minor amount of the sulfonic monomers or even greater amounts if desired, to increase the affinity of the resulting fabric toward basic dyestuffs. If it is desired to dye only with a basic dye, the fibers may be given the same treatment that they would be given to reduce their affinity toward acid dyestuffs and the resulting fibers would then be characterized by dyeability to deep shades with basic dyestuffs.

While the process of this invention is particularly adapted to fibrous substrates composed essentially of natural fibers, particularly those composed entirely of wool or cotton fibers, it is also applicable to substrates wherein synthetic or natural fibers are blended with these fibers and to blends with other keratin or cellulosic fibers such as mohair, alpaca, cashmere, vicuna, guanaco, camel's hair, silk, llama and the like. The preferred synthetic fibers include polyamides such as polyhexamethylene adipamide, polyesters such as polyethylene terephthalate, and acrylic fibers such as acrylonitrile, homopolymers or copolymers of acrylonitrile containing at least about 85% combined acrylonitrile, such as acrylonitrile-methylacrylate (85/15) and cellulose acetate and viscose rayon. Of the natural fibers which may be blended with the keratin fibers, cotton is preferred.

Example I

A swatch of wool fabric weighing 13.70 gms. at 22.2° C. and 65% relative humidity is impregnated at room temperature for 1 hour with 200 milliliters of a 0.2% solution of ferrous ammonium sulfate containing 0.03% by weight of the surface active agent Surfonic N-95. The swatch is then removed, blotted to a total weight of 21 gms. and air dried to a final weight of about 14.0 gms. in 1.5 hrs. at room temperature.

There is then prepared a solution of 8 gms. sodium styrene-p-sulfonate in 450 milliliters of water at a pH of 5.5 containing 0.2 gms. of Surfonic N-95. This solution is introduced into a closeable container which is flushed with nitrogen for 10 minutes at 50° C. A solution of 0.4 milliliter of 35% hydrogen peroxide in 10 milliliters of water is then added with mixing and the above impregnated swatch of fabric is introduced. The container is then tightly closed and the contents kept at 50° C. with occasional agitation for 6 hours. The fabric is removed, washed thoroughly with water and Surfonic N-95 at 50° C. to remove homopolymer and then treated with ethylenediamine tetra-acetic acid at pH 2 to remove any residual iron.

After conditioning, at 22.2° C. and 65% relative humidity, the fabric weighs 17.93 gms. for a weight increase of 31%.

A portion of the treated fabric along with an equal weight of untreated fabric is introduced into a dyebath containing 0.25% Sulphon Acid Blue RA, 10% anhydrous sodium sulfate, 3% acetic acid and 2% Surfonic N-95, the percentages being based on the total weight of treated and untreated wool. After boiling for one hour, the untreated wool is dyed to a deep blue shade, while the treated wool is completely immunized, i.e., has taken up no dye whatsoever. A further portion of the treated wool along with an equal weight of untreated wool is introduced into a dyebath containing 1% Sevron Brilliant Red 4G, a basic dyestuff, 1% acetic acid and 1% Decer-esol SE. After boiling for 1 hour, the treated wool is dyed to a deep red shade while the untreated wool is dyed to

a pale pink shade. In both dyeing procedures, the remaining solution is free of dyestuff, indicating that no additional homopolymer is extracted from the treated wool during immersion in the boiling dye bath.

Example II

The procedure of Example I is repeated except that the amount of sodium styrene-p-sulfonate is reduced to 5 gms. In this instance, the weight increase is 16% and the wool is immunized toward Sulphon Acid Blue RA to the extent of 95%.

Example III

A swatch of wooden fabric, 13.89 gms., is impregnated with ferrous iron, and treated with a solution of 11.3 gms. α -sulfoacrylic acid in 450 mls. of water as described in Example I. The washed and conditioned product is found to have increased in weight to the extent of 6% and to have become 40% immunized toward Sulphon Acid Blue RA. This fabric, furthermore, shows a marked increase in receptivity to the basic dyestuff when dyed in accordance with Example I.

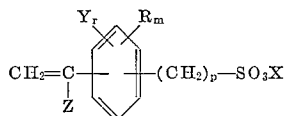
Example IV

The procedure of Example I is repeated except that sodium ethylene sulfonate, sulfomethyl acrylate, N-methacryloylaminoethane sulfonic acid (sodium salt) and sodium N-allyl aminomethanesulfonate are each substituted for the sodium styrene-p-sulfonate of Example I. The fibers so treated are much less receptive to the acid dyestuff when dyed as in Example I.

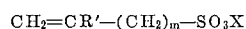
That which is claimed is:

1. A process for modifying the characteristics of wool fibers comprising reacting said fibers in the presence of a redox catalyst system with at least one sulfonic acid compound selected from the group consisting of those represented by the formulae:

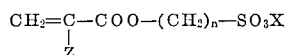
(I)



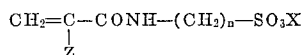
(II)



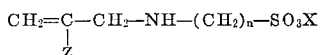
(III)



(IV)



(V)



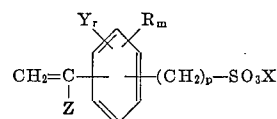
wherein X is hydrogen, ammonium, substituted ammonium, an aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms or an alkali-metal ion; Y is hydrogen, chlorine or bromine; R is methyl or ethyl; R' is hydrogen, methyl, ethyl or carboxyl; Z is hydrogen or methyl; m has a numerical value in whole number increments from 0 to 2; n has a numerical value of 1 or 2; p is 0 or 1; and r is 1-4, said catalyst system comprising a reducing agent and an oxidizing agent whereby at least a portion

of the sulfonic acid compound is polymerized and is chemically attached to said fibers, so that said fibers are characterized by both an increased affinity for basic dyestuffs and a reduced affinity for acid dyestuffs, and combining said keratin fibers with other fibers having a different affinity for said dyestuffs whereby said combination of fibers may be dyed with at least one of said types of dyestuffs to obtain a different effect among the fibers.

2. The process of claim 1 wherein the sulfonic acid compound comprises sodium styrene-p-sulfonate.

3. The process of claim 2 wherein the reducing agent comprises an iron ion and the oxidizing agent comprises a peroxide compound.

4. A process for modifying the characteristics of wool fibers comprising impregnating said fibers with a reducing agent and then contacting said fibers with an aqueous solution containing an oxidizing agent and an aromatic sulfonic acid of the formula:



wherein X is hydrogen, ammonium, substituted ammonium, an aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms or an alkali-metal ion; Y is hydrogen, chlorine or bromine; R is methyl or ethyl; Z is hydrogen or methyl; p is 0 or 1; and r is 1 to 4; m has a numerical value in whole number increments from 0 to 2 whereby at least a portion of the sulfonic acid compound is polymerized and chemically attached to said fibers, so that said fibers are characterized by both an increased affinity for basic dyestuffs and a reduced affinity for acid dyestuffs, and combining said keratin fibers with other fibers having a different affinity for said dyestuffs whereby said combination of fibers may be dyed with at least one of said types of dyestuffs to obtain a different effect among the fibers.

5. The process of claim 4 wherein the sulfonic acid compound comprises sodium styrene-p-sulfonate, the reducing agent comprises an iron ion and the oxidizing agent comprises a peroxide compound.

6. Keratin fibers prepared in accordance with the process of claim 1.

References Cited

UNITED STATES PATENTS

3,031,334	4/1962	Lundgren	8-127.6
3,036,032	5/1962	Murdock et al.	
3,006,830	10/1961	Cloninger.	
3,035,009	5/1962	Murdock et al.	

OTHER REFERENCES

Lipson et al.: Nature, vol. 157, June 1, 1946, p. 736.
Noble: abstract, Rayon Textile Monthly, October 1946, p. 565.

GEORGE F. LESMES, Primary Examiner

U.S. Cl. X.R.

8-15, 21, 23, 116, 115.7, 127.6, 128, 129

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,481,682 Dated December 2, 1969
Inventor(s) Greville Machell

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 62, "allyloxy" should read --allyloxyl--.
line 64, "amino di(2-ethane sulfonic acid)" should read --amino di-(2-ethane sulfonic acid)--.
Column 3, line 53, "covelant" should read --covalant--.
line 71, "maerial" should read --material--.
line 72, "his" should read --this--.
Column 4, line 54, "cetyl" should read --acetyl--.
Column 5, line 7, "cobalt=60" should read --cobalt-60--.
Column 7, line 12, "wooden" should read --woolen--.

SIGNED AND
SEALED

JUN 16 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, :
Commissioner of Patent