Patented Mar. 26, 1946 2,397,454

UNITED STATES PATENT OFFICE

2,397,454

POLYMERIC CELLULOSE STRUCTURE AND PROCESS FOR MAKING SAME

Harold Edward Woodward, Penns Grove, N. J., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application September 17, 1941, Serial No. 411,262

13 Claims. (Cl. 18—54)

This invention relates to colored shaped objects from cellulose derivatives and particularly to films and threads.

The coloring of shaped objects from cellulose derivative presents certain problems relating to the fastness of the color and the uniformity or levelness of the color obtained. In particular, wash fastness of textiles, especially of viscose rayons, is a problem. Rayons in general can be dyed with the same type of dyestuffs as those used on cotton, but the greater affinity for the dyestuff and the lower wet strength of the rayon create difficulties in the dyeing operation which require the careful attention of the dyer. Strain or friction on the yarn or cloth must be avoided and at the same time the yarn must be quickly and evenly turned in the dye bath in order to assure obtaining level shades.

It has been proposed in the past to add azo dye coupling intermediates or azo dyes to viscose, but the compounds used were of low molecular weight which made the possibility of loss during spinning and purification of the yarn considerable. Leuco bases have also been used as viscose modifiers, but such a process leaves no choice of color once the yarn is spun.

This invention has as an object the provision of a process for obtaining dyeings of cellulosic shaped objects of unusual fastness and uniformity. A further object is to provide a procedure for obtaining dyeings on rayons of unusual wash fastness and levelness without recourse to severe processing conditions and with a minimum of handling on the part of the dyer. Another object comprises shaped objects capable of receiving different colorings or dyeings. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a high molecular weight polymeric material containing a multiplicity of structural residues or groups capable of reacting with a diazonium salt to give an azo dye is dispersed in a solution of a cellulose derivative, the cellulosic material is regenerated from the solution, intimately associated and interspersed with said polymeric material, in a suitable solid form and the shaped object thus obtained is treated with an aqueous solution of a diazonium salt to produce an azo dye within the cellulosic material.

The cellulose derivative is one which can be brought into solution. In a particularly useful and important phase of the present invention which is described in detail below, the cellulose derivative is cellulose xanthate, but the invention is also applicable to cellulose esters of organic acids, e. g. cellulose acetate, cellulose propionate, cellulose benzoate or mixed esters, such as cellulose acetate-butyrate. Esters of inorganic acid may also be used, e. g. cellulose sulfate. It may also be applied to cellulose ethers, e. g., ethylcellulose, methylcellulose, benzylcellulose, alkali soluble glycolcellulose and celluloseglycolic acid.

In the preferred mode of operation of the process of this invention, there is added to standard commercial viscose 1–5% (based on the cellulose) of a polymeric dye coupling compound containing at least six recurring aromatic nuclei directly bearing amino or hydroxyl groups, or at least six reactive methylene groups capable of reacting with a diazonium salt. The addition of the modifying agent to the viscose may be accomplished either in the mixer during the dissolution of the cellulose xanthate in dilute alkali solution or by simply stirring the modifying agent into the viscose at any time prior to the regeneration of the cellulose. This modified viscose is ripened in the usual manner and is then spun into threads or cast into films by following the methods well known to the art. Thus, if a continuous filament yarn is to be made, the modified viscose containing, for example, 7% cellulose and 6% alkali and 2% (based on the cellulose) of a polymeric dye coupling intermediate is allowed to ripen to a salt index of 3–5 and is forced through a spinneret into a coagulating bath comprising, for example, 9–11% sulfuric acid, 19–23% sodium sulfate, 0–4% glucose, and 0.5–1.0% zinc sulfate. It is immaterial whether spinning is by the bobbin or pot process, but the examples below illustrate the use of the invention in the bobbin process. The thread may be of total denier varying from 50 to upwards of 200 denier with individual filaments ranging from 1–20 deniers. Other spinning conditions may include, for example, a bath travel of 20–200 inches, bath temperature of 45–65° C., a tension of the gel thread of 0.1–1.0 g./d., and a thread speed of 2500–5000 inches per minute. However, insofar as they effect the realization of

the central features of this invention, these conditions are not critical and are stated here merely to illustrate the ranges in which commercial yarns may be produced. If staple fibers are spun, the spinning procedure is similar to the above except that the number of holes in the spinneret is increased greatly and the bath composition, spinning tension, spinning speed, temperature, etc. are adjusted in accordance with known principles in order to produce good fiber properties. If film is produced, the modified viscose is extruded through a slit into a coagulating bath such as one containing 10–13% sulfuric acid and 18–25% sodium sulfate. The regenerated cellulose structure, whether fiber or film, is washed free of acid, desulfured by treating with a dilute alkaline solution such as 0.2 to 0.3% sodium carbonate, sodium sulfide, or other rayon purification salt, and, if desired, is bleached before drying. These steps are optional, however, and are not fundamental to the invention.

The final step in the invention is a treatment of these threads or films with a solution of a diazonium salt. This is usually accomplished in the cold or at ordinary temperatures and results in the formation of an azo dye within the cellulose structure. The time of treatment with the diazonium salt need be no longer than 1–10 minutes, and it is preferable that the solution of the diazonium salt be freshly prepared. It may be prepared by methods well known in the dye industry, such as treatment of a solution of an amine in dilute acid with sodium nitrite, or by dissolving a stabilized diazonium salt in water.

The polymeric compounds useful as addition agents in this invention are those containing multiple structural residues of the type requisite for coupling with diazonium salts. These compounds mostly contain aromatic nuclei directly bearing groups such as the amino or hydroxyl groups, or else they may contain reactive methylene groups. The coupling nuclei may be present in the viscose modifier as an integral part of the principal polymer chain, for example, the phenolic nuclei in a phenol-formaldehyde resin, or as side groups attached to the principal chain as in the case of J-acid (2-amino-5-naphthol-7-sulfonic acid) residues attached through amide linkages to an interpolymer formed from styrene and maleic anhydride. Another example in which the coupling nuclei are present as side groups is that of polymeric acetals such as that formed from salicylaldehyde and polyvinyl alcohol. The diazo bases which are used in the formation of the diazonium compounds for coupling with the polymeric modifying agents to form azo dyes in the cellulose structure may be any aromatic or heterocyclic primary amine capable of forming a diazonium salt and reacting with substituted aromatic or reactive methylene groups. The choice of particular polymeric dye coupling intermediates and of diazonium salts will, of course, depend on the color of the dye ultimately desired. However, in the case of the polymeric dye coupling intermediate, a single compound added in the viscose usually can give rise to a range of dyes simply by varying the character of the diazonium salt reacted with it. By way of illustrating this point further, there is given below a number of polymeric compounds and a table containing azo dye coupling residues and diazo bases suitable for use in this invention together with the colors of the resulting dyestuffs.

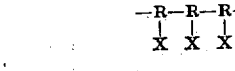
Typical polymeric materials suitable for use in this invention

(1) Polymers with the dye coupling aromatic nuclei in the chain:
- Phenol-formaldehyde polymers.
- Polymers of phenol, formaldehyde and amino or amido nitrogen compounds such as aliphatic primary or secondary amines, urea, thiourea, piperazine, etc.
- Polymers from active methylene compounds and aldehydes or ketones, e. g. those formed from 1-(m-aminophenyl)-3-methyl-5-pyrazolone or bis-aceto-acetbenzidide and formaldehyde, dimethylolurea, acetone, phthalaldehydic acid, etc.

(2) Polymers with the dye coupling aromatic nuclei in the form of side groups:
- Styrene-maleic anhydride interpolymers condensed with aromatic amino compounds, e. g. aminophenol.
- Ethylene-maleic anhydride interpolymers condensed with aromatic amino compounds, e. g. J-acid. (2-amino-5-naphthol-7-sulfonic acid)
- Propylene-maleic anhydride interpolymer condensed with aromatic amino compounds, e. g. H-acid. (1-amino-8-naphthol-3,6-disulfonic acid)
- Butylene-maleic anhydride interpolymers condensed with aromatic amino compounds, e. g. as above.
- Acrylic acid polymers or interpolymers condensed with aromatic amino compounds, e. g. as above.
- Methacrylic acid polymers condensed with aromatic amino compounds, e. g. as above.
- Polyvinyl alcohol condensed with aromatic aldehydes containing coupling groups.

From the above discussion, it will be apparent that the polymeric materials used in the process of this invention have one of the two general structures schematically represented below:

I —R—X—R—X—R—X—

II


wherein R—X is the divalent radical of a polymeric chain and —X— is the (either monovalent or divalent) residue capable of coupling with a diazonium compound to give an azo dye. To comply with this requirement, X must obviously be one of the following:

A. An aromatic nucleus bearing, directly attached thereto, an activating group such as a hydroxyl group or a primary, secondary or tertiary amino group, together with a "reactive position," i. e., a position ortho or para to said hydroxyl or amino group, which is either free or occupied by a group which is removed during the coupling reaction.

B. A radical containing at least one active methylene group. By the term "active methylene group" is meant herein a methylene group capable of coupling with a diazonium compound. Examples of such active methylene groups are those of the beta-diketones such as bis-acetoacetbenzidide and of the pyrazolones such as 1-phenyl-3-methyl-5-pyrazolone.

The above groups, A and B, are those which are known to couple with diazonium compounds,

and therefore both are grouped under the generic expressions "groups capable of reacting with a diazonium salt," or "coupling residues."

As examples of the colors which can be obtained from various coupling residues and various diazo bases may be mentioned the following:

Coupling residue	Diazo base	Color of the dye formed
Aminophenol	Aniline	Yellow.
	4-nitraniline	Yellow-orange.
	Naphthylamine	Orange.
1-(m-aminophenyl)-3-methyl-5-pyrazolone	3-aminobenzenesulfonic acid	Yellow.
	4-nitraniline	Yellow-orange.
	o-Anisidine	Orange.
Para-aminoacetoacetanilide	3-aminobenzenesulfonic acid	Yellow.
	4-nitraniline	Yellow-orange.
	o-Anisidine	Orange.
J-acid (2-amino-5-napthol-7-sulfonic acid)	Aminobenzenedisulfonic acid	Golden yellow.
	7-methoxyl-8-amino-3-naphthalenesulfonic acid	Cerise.
	1-amino-5-naphthalenesulfonic acid	Scarlet.
	o-Dianisidine	Purple.
	3-methoxy-4-amino-7-naphthalenesulfonic acid azo-meta-benzene sulfonic acid.	Blue-green.
H-acid (1-amino-8-naphthol-3, 6-disulfonic acid)	2, 4-dichloroaniline	Yellow-orange.
	1-amino-8-naphthalene-sulfonic acid	Red.
	o-Dianisidine	Blue.
N-aminophenoxyethyl M-acid (1-amino-5-naphthol-7-sulfonic acid).	3-aminobenzenesulfonic acid (alkaline)	Yellow-orange.
	1, 5-aminonaphthalene-sulfonic acid (alkaline)	Red.
	2, 4-dichloroaniline (acid)	Cerise.
	o-Dianisidine (acid)	Purple.
	2-chloro-4-nitraniline (acid)	Blue.
	2, 4-dinitroaniline (acid)	Blue-green.
N-beta-aminoethyl J-acid	3-aminobenzenesulfonic acid (alkaline)	Yellow-orange.
	1-amino-5-naphthalene-sulfonic acid (alkaline)	Red.
	2-chloro-4-nitroaniline (acid)	Magenta.
Phenol-formaldehyde	p-Nitraniline-o-sulfonic acid	Light orange.
Phenol-formaldehyde-methylamine	p-Nitraniline-o-sulfonic acid	Russet.
Phenol-formaldehyde-urea	p-Nitraniline-o-sulfonic acid	Dark orange.
Salicylaldehyde	p-Nitraniline	Orange red.

The methods by which polymers suitable for this invention are prepared vary with the type of polymeric material used. No claim is made to the novelty of these polymers and the basic polymers are generally well described in the patent and chemical literature. For example, methods suitable to the preparation of styrene-maleic anhydride interpolymers may be found in U. S. Patent 2,047,398. Methods for preparing acrylic acid, methacrylic acid, and vinyl alcohol polymers are described in Ellis "The Chemistry of Synthetic Resins" and also in patents. Various procedures may also be used for attaching azo dye coupling residues to these polymers and these have been described in the literature, notably in U. S. Patent 2,178,612. By way of illustration, however, there is outlined below a general method (Example A) for effecting condensation of an aminonaphtholsulfonic acid with a styrene-maleic anhydride interpolymer. This method may be used with such amino sulfonic acids as J-acid (2-amino-5-naphthol-7-sulfonic acid), M-acid (1-amino-5-naphthol-7-sulfonic acid), gamma-acid (2-amino-8-naphthol-6-sulfonic acid), and S-acid (1-amino-8-naphthol-4-sulfonic acid).

Example A

In a reaction vessel equipped with thermometer, sealed stirrer and short fractionating column there are placed 240 parts of aminonaphtholsulfonic acid and 1,000 parts of dimethylformamide. These are stirred and heated to 80° C. when 40 parts of sodium hydroxide in 40 parts of water are added. Heat is then applied until distillation starts. A slow distillation is maintained until the temperature at the head of the column reaches 147–149° C. at which point there is added to the vessel a solution of one molecular equivalent of the polymeric anhydride (202 parts of styrene-maleic anhydride, 126 parts of ethylene maleic-anhydride, etc.), in 200 parts of dimethylformamide. Heating is continued until a total of 800 parts of solvent have been removed and the total heating time elapsed is six hours. The reaction mass is cooled to 60° C. and diluted with 4,000 parts of acetone while being agitated. A solid precipitate is removed and dried to give a total recovery of about 95%. This material may then either be dialyzed in an alkaline solution to remove unreacted dye intermediate or it may be dissolved and added directly to the solution of the fiber-forming material.

The foregoing is a general reaction and may be applied to aminonaphtholdisulfonic acids in which case 320 parts of the intermediate is used and 80 parts of sodium hydroxide added. Intermediates suitable for use in this reaction include H-acid (1-amino-8-naphthol-3,6-disulfonic acid), K acid (1-amino-8-naphthol-4,6-disulfonic acid), 2R acid (2-amino-8-naphthol-3,6-disulfonic acid), and 2S acid (1-amino-8-naphthol-2,4-disulfonic acid).

Further examples of polymers suitable for use in this invention may be found in U. S. 2,186,734 describing various phenol-formaldehyde and cresol-formaldehyde type polymers, U. S. 2,098,869, describing phenol-formaldehyde-amine polymers, McQueen application, Serial No. 261,794, filed March 14, 1939 disclosing suitable acidic phenol-formaldehyde polymers, Woodward application, Serial No. 335,416, filed May 15, 1940 disclosing suitable polymers containing aromatic amino nuclei, and McQueen application, Serial No. 363,789, filed October 31, 1940 disclosing suitable polymers derived from pyrazolone and containing reactive methylene groups.

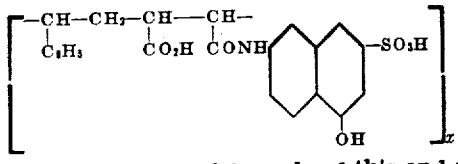
The more detailed practice of the invention is illustrated by the following examples, wherein parts given are by weight. There are of course many forms of the invention other than these specific embodiments.

Example I

To a commercial viscose containing 7% cellulose and 6% alkali there is added 1.4%, based on the cellulose, of a styrene-maleic acid interpolymer containing J-acid residues attached through amide linkages. The viscose is ripened to a salt index of 4.2 and forced through a 40-hole spinneret into an acid-salt coagulating bath comprising 11% sulfuric acid, 23% sodium sulfate, and

0.85% zinc sulfate. Temperature of the coagulating bath is 45° C., the bath travel 25 inches, and the spinning tension 20 g. for 150 denier thread. The thread is collected on a bobbin at a linear speed of 2500 inches per minute and the collected yarn is washed free of acid, desulfured by treating with an 0.3% sodium carbonate solution at 80° for 15 minutes, and is again thoroughly washed and dried. The yarn at this stage is colorless but can be dyed various colors by treating with solutions of diazonium salts. Thus, a golden yellow color is obtained by treating the yarn in the cold (0–5° C.) with a freshly prepared solution of diazotized meta-anilinesulfonic acid of pH about 6–8. If Laurent's acid (1-amino-5-naphthalenesulfonic acid) is used, a red color is obtained and if amino Schaeffer's monomethyl ether (1-amino-2-methoxynaphthalene-6-sulfonic acid) is used in the formation of the diazonium salt, a cerise color is obtained. A purple color is obtained by treatment with tetrazotized o-dianisidine and a blue color may be obtained by treating this yarn in a diazotized solution of a monoazo dye formed by coupling anilinedisulfonic acid with amino Schaeffer's monomethyl ether. An orange colored yarn is obtained by coupling with diazotized para-dodecylaniline.

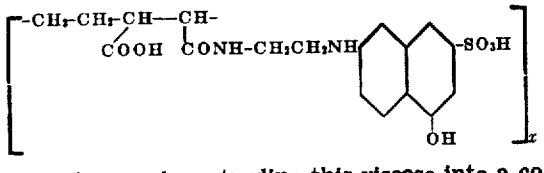
The styrene-maleic acid polymer containing J-acid nuclei is prepared by following the general method above outlined and has the probable structural formula:



The x in the structural formula of this and subsequent polymers represents the number of units in the polymer and is six or preferably an even larger integer. The dyed yarns prepared by the above procedure have excellent physical properties, and the colors are extremely fast to washing. The levelness of the shades obtained is also good.

Example II

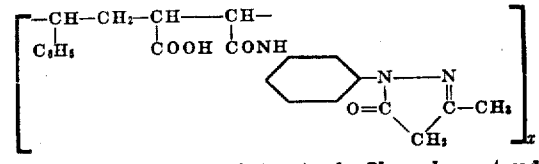
Viscose of the same initial composition as that of Example I is modified by dissolving in it 2%, based on the cellulose, of an ethylene-maleic acid interpolymer containing N-beta-aminoethyl J-acid residues connected through amide groups. This interpolymer is prepared as indicated above and has the following probable structural formula:



Yarn is spun by extruding this viscose into a coagulating bath comprising 9% sulfuric acid, 19% sodium sulfate, 4% glucose, and 0.85% zinc sulfate. The other spinning conditions, such as temperature of the bath, bath travel, tension, etc., are the same as in Example I. The washed and purified yarn is dyed a beautiful yellow-orange by treatment with a cold diazotized solution of 3-aminobenzenesulfonic acid at a pH of about 7. Some other colors which can be obtained from this yarn by treatment with diazo compounds are: red by treatment at a pH of about 6 with diazotized Laurent's acid (1-amino-5-naphthalenesulfonic acid) and magenta by treatment at a pH of about 1–6 with diazotized 2-chloro-4-nitroaniline. These dyeings, like those of Example I, are fast to washing and level in shade.

Example III

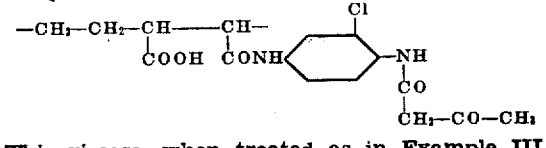
Viscose of low alkali content such as one containing 7% cellulose and 4% alkali is modified by adding to it 2% of a styrene-maleic anhydride interpolymer containing recurring residues of 1-(m-aminophenyl)-3-methyl-5-pyrazolone attached through amide groups. This polymer is prepared by stirring an aqueous 10% solution of the above pyrazolone with an equal molar portion of a styrene-maleic anhydride polymer for 24 hours at 20 to 50° C., while 20% aqueous sodium hydroxide is added to keep the solution mildly alkaline (pH 7–9). The polymer so produced has the following probable structural formula:



This viscose is spun into staple fibers by extruding through a spinneret containing 3600 holes into a regenerating bath comprising 8.5% sulfuric acid, 24% sodium sulfate, and 0.7% zinc sulfate. The large bundle or rope of fibers so produced is purified and cut into staple lengths of 1.5 inches. These fibers can be spun into yarn using either the cotton or woolen system and the yarns dyed by treating with appropriate diazonium salts in solution. A solution of diazotized meta-amino-benzene-sulfonic acid gives a beautiful yellow color while diazotized para-nitraniline produced an orange.

Example IV

Viscose of the same initial composition as that of Example III is modified by dissolving in it 2%, based on the cellulose, of an ethylene-maleic acid polymer containing acetoacetanilide residue. Such a polymer is prepared by boiling a dioxane solution containing equal molar portions of an ethylene-maleic anhydride polymer and 4-amino-2-chloroacetoacetanilide for six hours and precipitating by adding a liquid hydrocarbon, e. g., benzene, hexane, etc. The product obtained in this way probably contains the following structural units:



This viscose, when treated as in Example III, gives fibers which are converted to bright yellow azo dyes when treated with diazotized anilines.

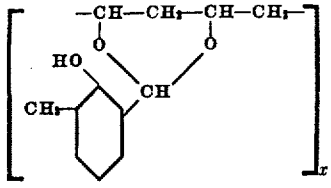
Example V

Viscose similar to that of Example III is modified by adding to it 2%, based on the cellulose, of a polymeric product containing active methylene groups as prepared in McQueen's application Serial No. 363,789, filed October 23, 1940. These products are obtained by the reaction of aldehydes and ketones with bifunctional compounds containing active methylene groups. Products described in the said application and found useful in this invention include, among others, the products obtained from: 1-(meta-aminophenyl)-

3-methyl-5-pyrazolone and formaldehyde, acetaldehyde or acetone; 5-bis-meta-(3-methyl-5-pyrazolone-1-yl) phenylurea with formaldehyde; 4-aminoaceto-acetanilide and benzaldehyde; 4,4'-bis-acetoacetaminodiphenyl with formaldehyde, acetaldehyde and benzaldehyde-o-sulfonic acid. In all cases, when the modified viscose is treated as in Example III, fibers are obtained which, on treatment with diazotized sulfanilic acid, give yellow to golden yellow colors.

Example VI

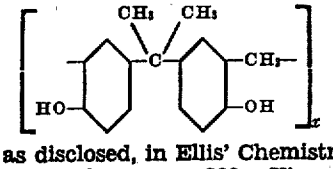
Viscose prepared from wood pulp and containing 8.5% cellulose and 6.5% alkali is modified by adding to it 1% of a polymer formed by condensation of polyvinyl alcohol with o-homosalicylaldehyde according to Dorough and McQueen, U. S. Patent 2,310,943. This polymer has the structural formula:



This viscose is ripened to an index of 2.0 and extruded as a film into a coagulating bath comprising 13% sulfuric acid and 19% sodium sulfate. The film of regenerated cellulose is purified by treating with hot solutions of sodium carbonate and then dyed by passing it through a cold solution of diazotized para-nitraniline. An orange-red dye is formed which is fast and will not bleed if the film is wet or comes in contact with alkaline materials such as soap.

Example VII

Viscose similar to that used in Example I is modified by addition of 5%, based on the cellulose, of a diphenylol-propane-formaldehyde resin of the probable formula:



prepared as disclosed, in Ellis' Chemistry of Synthetic Resins, vol. 1, page 389. Viscose is spun into fibers as described in Example I and after purifying the resulting threads are dyed a beautiful orange color by treating them with a cold solution of diazotized para-nitraniline-o-sulfonic acid.

Example VIII

A 15% solution of rayon grade cellulose acetate is prepared with acetone as solvent. To this is added 2% (based on the cellulose acetate) of the styrene-maleic anhydride interpolymer containing J-acid residues employed in Example I. Though this particular dye intermediate is not completely soluble in the acetone solution, the cloudy composition can be spun either in the conventional manner by extruding into the top of a hot tower or by the electrostatic method. By coupling the yarn with diazotized p-nitroaniline, the polymer within the fibers gives a bright orange color. The dyeing is fast to washing. In much the same manner, fibers or films from other organic solvent-soluble cellulose derivatives can be dyed.

In the process of this invention any polymeric high molecular weight material having a multiplicity of structural residues capable of coupling with a diazonium salt, and which may be dispersed in the solution of the cellulose derivative, may be employed. In the compounds of the present invention dye-forming or dye coupling nuclei are those capable of coupling with a diazonium salt. Thus, the dye forming nuclei may be aromatic, in which case it must have hydrogen or readily replaceable groups such as halogen, sulfonic acid or carboxyl groups in the ortho or para position to, i. e., separated by an even number, from two to four, of nuclear carbons from, amino or oxy oxygen substituent on the ring. In place of the foregoing, the coupling group may contain a reactive methylene group, or free aromatic primary amino group capable of diazotization, or oxidation and coupling. The pyrazolone compounds of Examples III, IV and V, illustrate the reactive methylene type of coupling group.

The preferred class of polymeric materials for use in this invention is that consisting of the styrene-maleic anhydride interpolymer derivatives. Another very useful class is that of phenol-formaldehyde resins.

Any cellulose derivative, preferably water-insoluble, capable of solution without essential chemical change whether in organic solvents as in the case of cellulose acetate or in aqueous alkali as in the case of cellulose xanthate or in aqueous alkali with the aid of low temperatures or dispersing agents or both as in the case of certain low substituted cellulose ethers may be employed in the process of this invention. Even a water-soluble cellulose derivative, e. g., water-soluble methylcellulose, which can subsequently be made into a film or fiber, or coated on a support, can be used.

The dyed yarns produced as a result of this invention may be put to any use in which ordinary textile rayons are adaptable. Since the dyes consist of a large number of azo units connected through covalent bonds into long chains which are, in fact, an integral part of the fiber, the colors obtained are extremely fast to washing and, because of this, the yarns are particularly useful in woven and knitted fabrics subjected to frequent launderings. A special use for these fibers is in the manufacture of cross dyed fabrics which can be produced by weaving together one or more of these special rayons with standard rayon, cotton, or other fibers and treating the fabric with a solution of a diazonium salt. Still another use is a simplified method of printing rayon fabrics in which two or more diazonium compounds are applied to the fabric composed of yarns containing polymeric dye coupling intermediates.

While regenerated cellulose sheeting, unlike a textile fiber, is not required to undergo laundry treatment, and therefore the advantage of a fast dye of the azo type over the dyes now used (mostly direct dyes and vegetable dyes) is not as great as in the case of textiles, nevertheless, a dyestuff firmly attached to a polymer incorporated in the sheet, according to this invention, positively avoids difficulties from bleeding of colors should the sheet come in contact with water or moist surfaces. The methods of incorporating the dye intermediate in the regenerated cellulose sheet and afterwards forming the dyestuff are, of course, strictly comparable to those already outlined for rayon.

This method of permanently coloring a shaped

object is not so advantageous in application to heavier, thicker objects as with fibers or thin films since penetration of the solution of diazonium salt into the object would necessarily be slow and possibly incomplete.

In the claims, the term "cellulosic material" is to be understood to include not only cellulose regenerated from viscose, cuprammonium, etc. solutions, but also cellulose organic acid esters and cellulose ethers.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

What is claimed is:

1. Process which comprises bringing an aqueous solution of a diazonium salt in contact with a regenerated cellulose structure having interspersed and coprecipitated therein a high molecular weight, macromolecular, polymeric material containing at least six structural groups having a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a hydroxyl group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said hydroxyl group, and an aromatic nucleus having an amino group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said amino group, whereby said structural groups are reactive with said diazonium salt to produce an azo dye.

2. Process which comprises bringing an aqueous solution of a diazonium salt in contact with a regenerated cellulose filament having interspersed and coprecipitated therein a high molecular weight, macromolecular polymeric material containing at least six structural groups having a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a hydroxyl group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said hydroxyl group, and an aromatic nucleus having an amino group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said amino group, whereby said structural groups are reactive with said diazonium salt to produce an azo dye.

3. A regenerated cellulose structure having intimately associated and interspersed therewith an azo dye condensation product of a diazonium salt with a high molecular weight, macromolecular, polymeric material at least six structural groups having a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a hydroxyl group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said hydroxyl group, and an aromatic nucleus having an amino group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said amino group, whereby said structural groups are reactive with said diazonium salt, said dyed structure being produced by the process of claim 1.

4. A regenerated cellulose filament having intimately associated and interspersed therewith an azo dye condensation product of a diazonium salt with a high molecular weight, macromolecular, polymeric material having at least six structural groups having a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a hydroxyl group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said hydroxyl group, and an aromatic nucleus having an amino group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said amino group, whereby said structural groups are reactive with said diazonium salt, said dyed filament being produced by the process of claim 2.

5. Process which comprises regenerating cellulose in shaped form from a viscose solution having dispersed therein a high molecular weight, macromolecular, polymeric material containing at least six structural groups having a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a hydroxyl group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said hydroxyl group, and an aromatic nucleus having an amino group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said amino group, whereby said structural groups are reactive with a diazonium salt to form a dye, and treating the resulting shaped object with a diazonium salt solution.

6. Process which comprises casting a film from a viscous solution having dispersed therein a high molecular weight, macromolecular, polymeric material containing at least six structural groups having a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a hydroxyl group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said hydroxyl group, and an aromatic nucleus having an amino group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said amino group, whereby said structural groups are reactive with a diazonium salt to form a dye, and treating said film with a solution of said diazonium salt.

7. Process which comprises spinning a filament from a viscose solution having dispersed therein a high molecular weight, macromolecular, polymeric material containing at least six structural groups having a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a hydroxyl group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said hydroxyl group, and an aromatic nucleus having an amino group on nuclear carbon and a reactive position separated by an even number, from two to four, of nuclear carbons from said amino group, whereby said structural groups are reactive with a diazonium salt to form a dye, and treating said filament with a solution of said diazonium salt.

8. A regenerated cellulose structure having intimately associated and interspersed therewith an azo dye condensation product of a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group.

9. A regenerated cellulose filament having intimately associated and interspersed therewith an azo dye condensation product of a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group.

10. A regenerated cellulose film having intimately associated and interspersed therewith an azo dye condensation product of a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group.

11. Process for preparing dyed shaped objects of superior dye fastness which comprises regenerating cellulose in shaped form from a viscose solution having dispersed therein a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group and treating the resulting shaped object with a diazonium salt solution.

12. Process for preparing dyed filaments of superior dye fastness which comprises spinning a filament from a viscose solution having dispersed therein a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group, and treating said filament with a solution of a diazonium salt.

13. Process for preparing dyed films of superior dye fastness which comprises casting a film from a viscose solution having dispersed therein a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group, and treating said film with a solution of a diazonium salt.

HAROLD EDWARD WOODWARD.

Certificate of Correction

Patent No. 2,397,454. March 26, 1946.

HAROLD EDWARD WOODWARD

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 6, first column, line 57, claim 3, after the word "material" insert *having*; and second column, line 33, claim 6, for "viscous" read *viscose*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of July, A. D. 1946.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.

9. A regenerated cellulose filament having intimately associated and interspersed therewith an azo dye condensation product of a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group.

10. A regenerated cellulose film having intimately associated and interspersed therewith an azo dye condensation product of a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group.

11. Process for preparing dyed shaped objects of superior dye fastness which comprises regenerating cellulose in shaped form from a viscose solution having dispersed therein a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group and treating the resulting shaped object with a diazonium salt solution.

12. Process for preparing dyed filaments of superior dye fastness which comprises spinning a filament from a viscose solution having dispersed therein a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group, and treating said filament with a solution of a diazonium salt.

13. Process for preparing dyed films of superior dye fastness which comprises casting a film from a viscose solution having dispersed therein a polyvinyl acetal of an aromatic aldehyde having on nuclear carbon a reactive position and, separated therefrom by an even number, from two to four, of nuclear carbons, an activating group selected from the class consisting of the hydroxyl group and the amino group, and treating said film with a solution of a diazonium salt.

HAROLD EDWARD WOODWARD.

Certificate of Correction

Patent No. 2,397,454. March 26, 1946.

HAROLD EDWARD WOODWARD

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 6, first column, line 57, claim 3, after the word "material" insert *having*; and second column, line 33, claim 6, for "viscous" read *viscose*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of July, A. D. 1946.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.