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PROCESS AND PRODUCTS THEREFROM

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11 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 condensation product of a maleic anhydride-olefin interpolymer with an aromatic amine, said condensation product being capable of reacting with a diazonium compound and having on the aromatic nucleus a hydroxyl group, or a primary, secondary or tertiary amino group or having reactive methylene groups, is dispersed in a solution of a cellulose derivative, the cellulosic material is regenerated from the solution, intimately associated and interspersed with said condensation product, in a suitable solid form and the shaped object thus produced is treated with an aqueous solution of a diazonium compound 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 celluloseglycollic 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 the condensation product of the maleic anhydride-olefin interpolymer containing at least six recurring aromatic nuclei bearing amino or hydroxyl groups or at least six recurring 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 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 on 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 so-

lution 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 contain aromatic nuclei or methylene groups capable of coupling with diazonium salts. These aromatic nuclei or methylene groups are present as side groups attached through amide linkages to an interpolymer formed from maleic anhydride and an olefin.

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 include 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 intermediate and of diazonium salt 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 are given below Table I tabulating a number of polymeric compounds, and Table II tabulating a number of azo dye coupling residues and diazo bases suitable for use in this invention together with the colors of the resulting dyestuffs.

TABLE I

Typical polymeric materials

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
Propylene-maleic anhydride interpolymer condensed with aromatic amino compounds, e. g.—	H-acid
Butylene-maleic anhydride interpolymers condensed with aromatic amino compounds, e. g.—	As above

The polymeric materials of this invention thus have the structure

$$\left(\begin{array}{c} -R-CH-\!\!-CH- \\ \quad\;\; | \qquad\;\; | \\ \quad COOH \;\; CONHX \end{array}\right)_x$$

wherein x is the number of such units in the polymer, R is the saturated divalent radical corresponding to an olefin the double bond of which is replaced by a single bond, i. e., a saturated linkage, between two carbons from which stem the two valences of the divalent radical, i. e. R is the vicinal alkylene, including substituted alkylene corresponding to the alkylene or olefine, and X is a monovalent residue capable of coupling with a diazonium compound to give an azo dye. In the case of ethylene polymer R is $-CH_2-CH_2-$, in the case of styrene

$$-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-$$

To be capable of coupling with a diazonium compound to give a dye, X must 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 (separated by an even number, from two to four, of nuclear carbons from) 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.

Examples of the colors obtainable with maleic anhydride-olefin condensation products of various amines coupled with various diazo bases, i. e., bases which are transformed into the corresponding diazonium salt are given in the following table.

TABLE II

Amine condensed	Diazo base	Color of the dye formed
Aminophenol	Aniline	Yellow.
	4-nitraniline	Yellow-orange.
	Naphthylaminesulfonic acids.	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-naphthol-7-sulfonic acid).	Aminobenzenedisulfonic acid.	Golden yellow.
	7-methoxy-8-amino-3-naphthalenesulfonic acid.	Cerise.
	1-amino-5-naphthalenesulfonic acid.	Scarlet.
	o-Dianisidine	Purple.
	7-methoxy-8-amino-3-naphthalenesulfonic acid azo-meta-benzenesulfonic acid.	Blue-green.
H-acid (1-amino-8-naphthol-3, 6-disulfonic acid.	2,4-dichloroaniline	Yellow-orange.
	1-amino-8-naphthalenesulfonic acid.	Red.
	o-Dianisidine	Blue.
N-aminophenoxyethyl M-acid (1-amino-5-naphthol-7-sulfonic acid).	3-aminobenzenesulfonic acid (alkaline).	Yellow-orange.
	1,5-aminonaphthalenesulfonic 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-naphthalenesulfonic acid (alkaline).	Red.
	2-chloro-4-nitroaniline (acid).	Magenta.

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 1,976,679 and U. S. Patent 2,047,398. By way of illustration 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), R-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-A acid (1-amino-5-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).

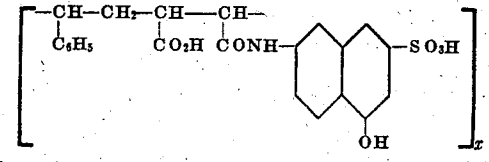
In another method the amino dye intermediate may be dissolved in an alkaline aqueous or dioxane-water solution and an equal molar amount of the olefin-maleic anhydride polymer added. The mixture is stirred at ordinary temperature for 24 hours while being kept at a pH of about 7 to 8 by addition of aqueous 20% sodium hydroxide. Such a solution may then be added directly to the viscose.

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 a 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 metanilinesulfonic 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 aniline disulfonic acid with amino Schaeffer's monomethyl ether. An orange colored yarn is obtained by coupling with diazotized para-dodecylaniline.

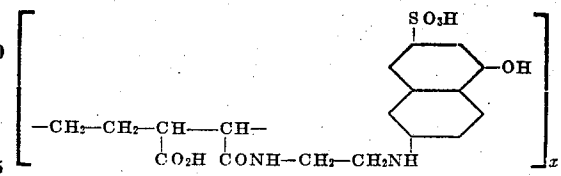
The styrene-maleic acid polymer condensation product with J-acid is prepared by the general method above outlined and has the probable structural formula:



The x in the structural formula of this and subsequent polymer represents the number of units in the polymer, is an integer and is at least six. It is usually even larger. 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:

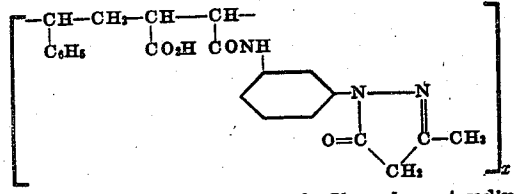


Yarn is spun by extruding this viscose into a coagulating bath comprising 9% sulfuric acid, 19% sodium sulfate, 4% glucose, and 0.85% zinc sulfate. The other spinning conditions, such as temperature of the bath, bath travel, tension, etc., are the same as in Example I. The washed and purified yarn is 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 ob-

tained from this yarn by treatment with diazo compounds are: red by treatment with Laurent's acid at pH of about 6 (1-amino-5-naphthalene-sulfonic acid) and magenta by treatment with 2-chloro-4-nitroaniline at pH of about 4–6. These dyeings, like those of Example I, are fast to washing and level in shade.

Example III

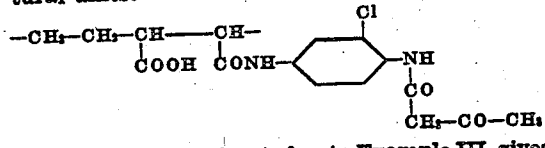
Viscose of low alkali content such as one containing 7% cellulose and 4% alkali is modified by adding to it 2% of a styrene-maleic anhydride interpolymer containing recurring residues of 1-(m-aminophenyl)3-methyl-5-pyrazolone attached through amide groups. This polymer is prepared by stirring an aqueous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



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-aminobenzene-sulfonic acid gives a beautiful yellow color while diazotized para-nitraniline produces 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

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 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 condensation product, having hydroxyl or amino groups on nuclear carbon and coupling positions thereby activated, or having reactive methylene groups, of an aromatic amine with a maleic anhydride-olefin interpolymer may be employed. The nucleus thus condensed is capable of coupling with a diazonium salt.

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 be subsequently 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 in-

tended 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 cellulosic structure having interspersed and coprecipitated therein a high molecular weight condensation product of an aromatic amine with a maleic acid-olefin hydrocarbon interpolymer, said condensation product being reactive with diazonium compounds and having, in a side group attached through an amide linkage to the polymer, a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from a hydroxyl group on nuclear carbon and an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from an amino group on nuclear carbon.

2. Process which comprises bringing an aqueous solution of a diazonium salt in contact with a cellulosic filament having interspersed and coprecipitated therein a high molecular weight condensation product of an aromatic amine with a maleic acid-olefin hydrocarbon interpolymer, said condensation product being reactive with diazonium compounds and having, in a side group attached through an amide linkage to the polymer, a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from a hydroxyl group on nuclear carbon and an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from an amino group on nuclear carbon.

3. A cellulosic structure having intimately associated and interspersed therewith an azo dye condensation product of a diazonium salt with a high molecular weight condensation product of an aromatic amine with a maleic acid-olefin hydrocarbon interpolymer, said condensation product having, in a side group attached through an amide linkage to the polymer, a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from a hydroxyl group on nuclear carbon and an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from an amino group on nuclear carbon.

4. A cellulosic filament having intimately associated and interspersed therewith an azo dye condensation product of a diazonium salt with a high molecular weight condensation product of an aromatic amine with a maleic acid-olefin hydrocarbon interpolymer, said condensation product having, in a side group attached through an amide linkage to the polymer, a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from a hydroxyl group on nuclear carbon and an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from an amino group on nuclear carbon.

5. Process which comprises regenerating a cellulosic material in shaped form from a solution, in an inert solvent, containing a cellulose derivative having a cellulose nucleus, said solution having dispersed therein a high molecular weight condensation product of an aromatic amine with a maleic acid-olefin hydrocarbon interpolymer, said condensation product having, in a side group attached through an amide linkage to the polymer, a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from a hydroxyl group on nuclear carbon and an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from an amino group on nuclear carbon, and bringing the shaped article thus formed in contact with an aqueous solution of a diazonium salt.

6. Process which comprises casting a film from a solution, in an inert solvent, containing a cellulose derivative having a cellulose nucleus, said solution having dispersed therein a high molecular weight condensation product of an aromatic amine with a maleic acid-olefin hydrocarbon interpolymer, said condensation product having, in a side group attached through an amide linkage to the polymer, a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from a hydroxyl group on nuclear carbon and an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from an amino group on nuclear carbon, and bringing the film thus formed in contact with an aqueous solution of a diazonium salt.

7. Process which comprises spinning a filament from a solution, in an inert solvent, containing a cellulose derivative having a cellulose nucleus, said solution having dispersed therein a high molecular weight condensation product of an aromatic amine with a maleic acid-olefin hydrocarbon interpolymer, said condensation product having, in a side group attached through an amide linkage to the polymer, a coupling group selected from the class consisting of an active methylene group, an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from a hydroxyl group on nuclear carbon and an aromatic nucleus having a reactive position separated by an even number, from two to four, of nuclear carbon atoms from an amino group on nuclear carbon, and bringing the filament thus formed in contact with an aqueous solution of a diazonium salt.

8. A cellulosic filament having intimately associated and interspersed therewith an azo dye condensation product of a diazonium salt with a high molecular weight condensation product of J-acid with a maleic acid-styrene interpolymer.

9. Process which comprises spinning a filament from a solution, in an inert solvent, containing a cellulose derivative having a cellulose nucleus, said solution having dispersed therein a high molecular weight condensation product of J-acid with a maleic acid-styrene interpolymer and bringing the filament thus formed in contact with an aqueous solution of a diazonium salt.

10. A cellulosic filament having intimately as-

sociated and interspersed therewith an azo dye condensation product of a diazonium salt with a high molecular weight condensation product of 1-(m-aminophenyl)-3-methyl-5-pyrazolone with a maleic acid-styrene interpolymer.

11. Process which comprises spinning a filament from a solution, in an inert solvent, containing a cellulose derivative having a cellulose nucleus, said solution having dispersed therein a high molecular weight condensation product of 1-(m-aminophenyl)-3-methyl-5-pyrazolone with a maleic acid-styrene interpolymer and bringing the filament thus formed in contact with an aqueous solution of a diazonium salt.

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