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CELLULOSIC STRUCTURE AND METHOD OF
PRODUCING SAMEWinfield Walter Heckert, Wilmington, Del., as-
signor to E. I. du Pont de Nemours & Company,
Wilmington, Del., a corporation of DelawareNo Drawing. Application May 20, 1937,
Serial No. 143,830

26 Claims. (Cl. 3-64)

This invention relates to the manufacture of cellulose derivative materials and especially cellulose acetate materials, such as yarns, threads, filaments, fibers and the like or fabrics made therefrom, or other structures such as films, pellicles, caps, bands or the like which will have improved affinity for dyestuffs.

This application is a divisional application of my copending application Serial No. 143,829 filed on even date herewith.

Cellulose derivative materials, and particularly materials made from cellulose esters such as cellulose acetate, have always presented dyeing difficulties. The dyestuffs and dyeing processes commonly used for coloring cellulose acetate products are very costly in comparison to the dyeing of other materials. Furthermore, a great many of the dyes which will dye other materials will not dye cellulose acetate. Likewise, the dyestuffs developed for cellulose acetate generally are not suitable for dyeing other fibers. In dyeing mixed fabrics or threads which contain both cellulose acetate fibers and fibers of other materials such as wool, cotton, regenerated cellulose, linen or silk, it has heretofore, therefore, been necessary to subject the thread to a plurality of dyeing operations in which the different fibers are separately dyed with different dyestuffs. Another phase of dyeing of cellulose acetate fabrics in which difficulty has frequently been encountered, particularly with respect to suitable ranges of color, is the discharge printing of these fabrics. For lack of a better solution, it has long been standard practice to overcome as much as possible these dyeing difficulties, by saponifying the cellulose acetate materials until a surface of regenerated cellulose is secured even though such saponification tended to impair the strength and handle of the cellulose acetate materials.

It has now been found that by treating cellulose derivatives particularly cellulose esters such as cellulose acetate with certain materials, the former will have an affinity with all known dyestuffs. Cellulose derivative materials can, due to this remarkable discovery, be dyed with cheaper dyes and with less expensive procedures. The present invention will furthermore permit the union dyeing of mixed fabrics with a single dye in a single dyeing procedure, and will permit the ready dyeing of cellulose derivatives with direct and other dischargeable dyes and the discharging of these dyes for the production of print goods without resorting to expensive and degrading saponification procedures.

It is therefore an object of the present invention to provide a method for the treatment of cellulose derivatives, particularly cellulose esters, which will impart thereto an affinity for all dyestuffs.

It is a further object of this invention to produce a treated cellulose derivative and more specifically a treated cellulose ester which will have an affinity for all dyestuffs.

It is another object of this invention to provide a process for the incorporation of certain materials in cellulose derivatives and more specifically cellulose esters whereby to impart to said derivative or ester an affinity for all dyestuffs.

It is still another object of this invention to produce a cellulose derivative and more specifically a cellulose ester having embodied therein a material which imparts thereto an affinity for all dyestuffs.

The objects of the invention may be accomplished in general by treating cellulose derivative structures or by incorporating in cellulose derivative solutions, preferably prior to the formation of said structures, a polymeric amino alcohol ester of acrylic acid or of alpha substituted acrylic acid of the type disclosed in the copending application of Jesse Harmon, Serial No. 21,810, filed May 16, 1935.

As examples of polymeric amino alcohol esters of acrylic acid or of alpha substituted acrylic acid suitable for use in accordance with the present invention may be mentioned:

Beta-dimethylaminoethyl methacrylate
Beta-diethylaminoethyl methacrylate
Beta-dicyclohexylaminoethyl methacrylate
Beta-di-n-butylaminoethyl methacrylate
2-aminocyclohexyl methacrylate
Triethanolamine monomethacrylate
2-(diethylamino) cyclohexyl methacrylate
1-(beta-methacryloxyethyl) piperidine
4-(beta-methacryloxyethyl) morpholine

The amino alcohol esters of acrylic acid or of alpha substituted acrylic acid may be prepared by treating the monomeric amino alcohol ester of acrylic acid or of alpha substituted acrylic acid with a stoichiometric equivalent amount of an acid, the salt thus formed being dissolved in water or other suitable solvent and the resulting solution subjected to polymerizing conditions in the presence or absence of polymerization catalysts as disclosed in detail in the above-identified Harmon application.

To further illustrate the preparation of a few

of these amino resins the following examples are given.

EXAMPLE A.—Beta-dimethylaminoethyl methacrylate

5 A. Synthesis of monomer: A solution of 89 grams (1 mol) of beta-dimethylaminoethanol and 400 grams (4 mols) of methyl methacrylate in 500 grams of dry benzene containing 30 grams of paraphenylenediamine is made up, heated in
10 an oil bath under a 48" fractionating column fitted with a distilling head arranged for controlled reflux, and distilled until the moisture present in the reagents is removed. As soon as all the
15 water is off, a solution of 2 grams of metallic sodium in 20 cc. of dry methanol is added dropwise to the refluxing reaction mixture during the course of 6 hours, during which time a benzene-methanol binary (boiling point 58° C.) is collected at the head of the column. The distillation and collection of binary is continued until
20 no more methanol is liberated, whereupon the reaction mixture is allowed to cool, filtered, and the excess methyl methacrylate removed by fractional distillation under reduced pressure through
25 a long column, and the product distilled through a short column under reduced pressure in an atmosphere of nitrogen. The yield of product boiling at 62–65° C. at 6 mm. pressure is 59% of the theoretical, and analyzes 8.2% nitrogen, whereas the calculated value for betadimethylaminoethyl methacrylate is 8.9%.

B. Polymerization of the monomer: Polymerization is effected by dissolving the monomer in an equivalent amount of dilute acetic acid, diluting with water to 10% monomer concentration, adding powdered benzoyl peroxide (1% based on the monomer), and heating at 100° C. for 21 hours. The viscous polymeric salt solution obtained is diluted to 1.5% resin concentration, the solution poured into five times its volume of acetone, and the polymeric salt that precipitates, filtered, and dried, is obtained as a white, water-soluble powder. The polymeric free base may be obtained by heating the polymeric salt at about 100° C. The product thus obtained is soluble in water, alcohol, acetone, etc., whereas the polymeric free base obtained by spontaneous polymerization of monomer at room temperature without catalyst is insoluble in common organic solvents.

EXAMPLE B.—Beta-diethylaminoethyl methacrylate

55 This compound is made by dissolving 117 grams (1 mol) of beta-diethylaminoethanol and 400 grams (4 mols) of methyl methacrylate in 300 grams of dry benzene containing 30 grams p-phenylene diamine, and heated in an oil bath
60 under a 48" fractionating column fitted with a distilling heat arranged for controlled reflux and distilled until all the moisture present in the reagent has been removed. Beta-diethylaminoethyl methacrylate is isolated by collecting the
65 fraction boiling at 85±3° C. at 5 mm. pressure, carefully washing 8 times with cold water to remove traces of p-phenylene diamine, drying with anhydrous magnesium sulfate, filtering, washing the drying agent with ether, combining the washings with the bulk of the product and then distilling the ether under reduced pressure in an
70 atmosphere of nitrogen. The monomeric ester is left in the distilling glass as an almost colorless liquid which polymerizes spontaneously to a
75 tough, transparent, pale amber polymer. When

allowed to stand at room temperature or even at a lower temperature, the polymer was insoluble in water and in the common oxygenated organic solvents, soluble in acetone.

EXAMPLE C.—Beta-dicyclohexylaminoethyl methacrylate

5 A. Beta-dicyclohexylamino ethanol: Eighty grams (1 mol) of ethylene chlorhydrin is added during 20 minutes to 185 grams (1.02 mols) of dicyclohexylamine maintained at 90° C. The mixture is stirred and heated in an oil bath at 130–140° C. for 14 hours, at the end of which time the reaction mixture is allowed to cool, and an excess of 20% sodium hydroxide solution added, the oil that forms is separated, washed with water, dried, and fractionally distilled in vacuo. The yield of product boiling at 156–163° C. at 6 mm. pressure is 48–50% of the theoretical. The product has a neutral equivalent of 228.5, whereas the calculated neutral equivalent of beta-dicyclohexylamino ethanol is 225.

B. Synthesis of monomer: Beta-dicyclohexylaminoethyl methacrylate monomer is made by ester interchange between methyl methacrylate and beta-dicyclohexylamino ethanol by the technique described under Example A, and purified by the method described under Example B. The yield of product boiling at 153–159° C. at 2 mm. pressure is 73% of the theoretical. Analysis of the product shows it to contain 4.87% nitrogen, whereas the theoretical nitrogen content of beta-dicyclohexylaminoethyl methacrylate is 4.8%.

C. Polymerization of monomer: Polymerization is effected by adding an equivalent amount of hydrochloric acid to a weighed sample of the monomer, warming to dissolve the monomer, diluting with water to 10% monomer concentration, adding powdered benzoyl peroxide (1% based on the monomer), and heating at 100° C. for 24 hours.

The free base polymer is recovered as an amorphous powder, from the polymeric salt solution by adding thereto an excess of sodium bicarbonate solution. The free base polymer thus obtained is soluble in benzene, toluene, mineral spirits, and in an excess of dilute hydrochloric or acetic acids, whereas free base polymer obtained by the spontaneous polymerization at or below room temperature without catalyst is insoluble in acids and organic solvents. The free base polymer obtained from the polymeric salt is compatible with oil modified polyhydric alcohol-polycarboxylic acid resins, nitrocellulose and China-wood oil.

55 Instead of simple polymers, interpolymers may be prepared, for instance by reacting methyl methacrylate and methyl vinyl ketone in the presence of ammonium hydroxide or reacting
60 beta-cyclohexylaminoethyl methacrylate monomer and beta-dimethylaminoethyl methacrylate monomer together under suitable conditions. Other equivalent polymeric materials such as copolymers may also be used.

65 In carrying out the instant invention, these polymers are incorporated in the cellulose derivative material, such as cellulose acetate in any suitable manner, as for instance by dissolving or dispersing the polymer in the cellulose acetate spinning solution, or by dissolving or dispersing
70 the polymer in a suitable solvent or dispersing medium, impregnating the cellulose acetate material with this solution or dispersion and removing the solvent or dispersing medium.

In accordance with the preferred embodiment 75

of the invention, it is desirable to have the amino polymer present in the cellulose derivative structure in the form of a salt prior to the dyeing thereof. This may be accomplished by formation of the amino polymer salt prior to the incorporation of the polymer in the cellulose derivative structure or by forming the salt thereof, for example, the acetate of the polymer after the incorporation thereof in the structure. This can be accomplished by adding a small amount of acetic, lactic, succinic, levulinic, or benzoic acid or other water-soluble mono-basic acid to the cellulose derivative solution together with the amino polymer, or by treating the cellulose derivative thread or other structure with a dilute solution of the acid before dyeing the same. The addition of an organic acid to the cellulose derivative solution modified with the amino polymer constitutes separate invention and accordingly is claimed in copending application to Izard Serial No. 146,440, filed June 4, 1937.

Cellulose derivatives and specifically cellulose esters which have been treated in accordance with the present invention are found to have a particularly improved affinity for the so-called "direct" dyes, "acid" dyes, "developed" color dyes, "chrome" dyes and "vat" dyes.

As illustrative examples of the above mentioned classes of dyes for which the cellulose derivatives of the present invention have a satisfactory affinity upon actual test may be mentioned:

Direct dyes

"Pontamine" Scarlet B, color index 382.

"Pontamine" Blue RW, color index 512.

Also direct dyes having color index Nos. 518, 278, 533, 415, 365, 598, 419, 326, 593 and 539.

Acid dyes

Milling Red R Conc., color index 430.

Brilliant Milling Green B Conc., color index 667.

Monophyl Fast Blue 5-R (color index not known).

Also acid dyes having color index Nos. 649, 31, 1088 and 307.

Developed color dyes (diazo dyes)

"Pontamine" Diazo Bordeaux RB color index 324A.

"Pontamine" Diazo Orange R (see 1934 Yearbook of American Association of Textile Chemists and Colorists, color index not given).

"Pontamine" Diazo Black BHSW Conc., color index 401.

"Pontamine" Diazo Blue BR (see above mentioned yearbook).

Also "Developed" dyes having color index Nos. 317, 654 and 552.

Chrome dyes

"Pontachrome" Blue R, color index 179.

"Pontachrome" Green G (see above mentioned yearbook).

"Du Pont" Chromate Brown EB, color index Pr. 12.

Also chrome dyes having color index Nos. 216, 40, 299 and 302.

Vat dyes

"Sulfanthrene" Scarlet G Paste (see above mentioned yearbook).

"Ponsol" Jade Green Double Paste, color index 1101.

"Ponsol" Blue GD Double Paste, color index 1113.

Also vat dyes having color index No. 1095, as well as "Sulfanthrene" Scarlet G Paste.

Basic dyes having color index Nos. 922 and 749.

Basic substituted anthraquinone dyestuffs, commonly used to dye unmodified cellulose acetate rayon, such as Celanthrene Red Y, Celanthrene Fast Light Yellow, Celanthrene Sky Blue B, Celanthrene Scarlet G, and Acetamine Orange GR.

The color index numbers cited in the present specification are all taken from Rowe's "Colour Index", Society of Dyers and Colorists, first edition, 1924.

The following examples are given to illustrate the principles of this invention, it being understood of course that the invention is not limited to these precise examples which are merely illustrative of the invention.

EXAMPLE I

The beta-diethylaminoethyl methacrylate prepared according to Example B is dissolved in acetone and to this solution sufficient cellulose acetate is added to form a spinning solution containing 20% cellulose acetate, 4% polymer and 76% acetone. The solution spun electrically, for example, in the method set forth in Formhals Patent No. 1,975,504.

The yarn to be dyed is soaked in an aqueous bath containing 0.5% sodium oleate soap and 0.5% sodium carbonate heated to from 70-80° C. for 15 minutes. The yarn is rinsed with water and permitted to drain for a few minutes, after which it is immersed in a dye bath. The aqueous dye bath is made up with 15 to 20% of Glauber's salt, 4% of acetic acid of 28% concentration, and with a sufficient quantity of a direct cotton dye, color index No. 382, to give the requisite depth of shade and a 40:1 ratio of liquor volume to the weight of the material. The yarn is entered into the lukewarm bath and turned frequently while the temperature of the dye bath is raised to 85-90° C. and maintained there for 15 minutes. Two further 4% additions of acetic acid (28% concentration) are now made, each followed by heating to 80-90° C. for 15 minutes, if necessary to obtain exhaustion of the dye bath. The dyed yarn is removed, rinsed and dried.

The yarn so produced has good physical properties and shows good affinity for the direct dyestuff above mentioned as well as other kinds and types of dyes.

EXAMPLE II

The resinous polymer prepared according to Example G above was dissolved in 5% acetic acid to the extent of 2% resin. The solution was heated to 60° C. and a small piece of cellulose acetate fabric immersed in a solution where it was allowed to remain for about 5 minutes. The fabric was removed, the excess solution drained therefrom and then placed in a 5% ammonium hydroxide water bath at room temperature for 5 minutes. At the end of this time the sample was removed, rinsed with water and dried at 40° C. The fabric so treated showed a remarkable improvement in affinity for direct dyestuffs as compared with cellulose acetate which had not been treated.

EXAMPLE III

An interpolymer prepared by the condensation of 65% dicyclohexyl amino ethyl methacrylate monomer and 35% dimethyl amino ethyl methacrylate monomer is dissolved in a mixture of ethylene dichloride and isopropyl alcohol and

into this solution cellulose acetate is dissolved to form a solution containing:

	Parts by weight
Cellulose acetate.....	15
5 Ethylene dichloride.....	70
Isopropyl alcohol.....	30
The interpolymers.....	3

The solution is spun electrically in the manner described in U. S. Patent No. 1,975,504. A sample of the fibers so produced when dyed in the manner described under Example I showed good affinity for direct dyes.

EXAMPLE IV

Cellulose acetate taffeta fabric woven from cellulose acetate threads modified with beta-diethylaminoethyl methacrylate is dyed in the following manner:

An aqueous dye bath is made up with 15 to 20% of Glauber's salt, 4% of acetic acid of 28% concentration, and with sufficient quantity of the developable dye, color index No. 317, to give the desired depth of shade. The modified cellulose acetate taffeta is entered into the lukewarm bath which has a 40:1 ratio of liquor volume to the weight of the material; the temperature is raised to 80-90° C. and maintained there for 15 minutes while frequently turning the taffeta. Then, two further 4% additions of acetic acid (28% concentration) are made, each followed by heating at 80-90° C. for 15 minutes if necessary, to obtain exhaustion of the dye bath. The fabric is next removed from the dye bath, rinsed well, and entered into a diazotizing bath at a temperature of 18-24° C. and containing 3% sodium nitrite and 4% sulfuric acid. After a treatment of 20 minutes with occasional turning, the fabric is quickly but thoroughly rinsed with water and entered into a developing bath cooled to a temperature of 15-18° C. and containing 1% of betanaphthol as the developer and 0.5% sodium hydroxide. The fabric is treated with the diazotizing bath for a period of 20 minutes, then is rinsed thoroughly, squeezed out, and dried. The fabric is found to have a good affinity for the developed color.

Depending on the particular "developed" color selected, the percentage of salt, acid, or other dye assistant added to the dye bath will, of course, be varied from the above to a certain extent. As is also well recognized, different developers may be chosen depending on the particular dyestuff employed and the color desired. Some dyes, when developed with beta-naphthol for example, give one color while with some other developer such as p-toluylene diamine, an entirely different color will result.

EXAMPLE V

Cellulose acetate fabric woven from cellulose acetate threads modified with beta-diethylaminoethyl methacrylate in accordance with the procedure outlined in Example I may be dyed with "Pontachrome" blue R, color index 179 as follows:

An aqueous dye bath is made up with 15 to 20% of Glauber's salt, 4% of acetic acid of 28% concentration, and with a sufficient quantity of chrome dye of color index No. 179 to give the desired shade and a 40:1 ratio of liquor volume to the weight of the material. The thoroughly wetted fabric is entered in this dye bath and turned for 10 minutes. During the course of the next 15 minutes, the temperature of the dye bath

is gradually raised to 85-90° C. and dyeing continued at that temperature for 30 minutes with frequent turning of the fabric. At the end of the 30 minutes, the fabric is lifted from the dye bath, 10% additional acetic acid is added to the dye liquid and the dyeing continued for 30 minutes. The fabric is then lifted from the dye bath and entered in a fresh aqueous bath containing 2% potassium dichromate and 4% formic acid. The fabric is entered into this bath at 70° C. which is then heated to 85-90° C. for 90 minutes. The dyed fabric is withdrawn, rinsed thoroughly, squeezed out, and dried.

EXAMPLE VIII

To print a red shade on a woven or knitted fabric containing the cellulose derivative yarn modified according to the invention, the following procedure may be followed:

Thickening

	Grams
Highly torrefied corn starch (British gum).....	600
Gum arabic (50% aqueous solution).....	600
Water.....	800
Total.....	2,000

The British gum, dissolved in a little water, is mixed with Gum arabic solution and more water added, after which the whole is boiled for 10 minutes and made up to bulk.

Printing color

	Grams
Acid dye, color index No. 430.....	4
Sodium carbonate.....	5
Ammonium thiocyanate.....	20
Water.....	45
Thickening (prepared as above).....	295
Total.....	364

After the sodium carbonate and dye have been dissolved separately in a little water, the solutions are poured together and intimately mixed with the thickening. The ammonium thiocyanate, dissolved in water, is now added and the whole is brought to the boil and bulked.

A knitted or woven fabric consisting of cellulose acetate yarn containing 10% by weight of the acetate salt of polymerized beta-diethylaminoethyl methacrylate is printed the desired colored design with the so prepared printing paste, using the roller printing method, although any recognized printing procedure may be employed. In the roller printing method, the printing roller consists of an iron mandrel having an outer copper shell bearing an intaglio engraving of the design to be printed. Below the printing roller is located a color box containing the printing paste. Between the color box and the printing roller is placed a revolving brush which picks up the printing paste and smears it in a promiscuous fashion over the surface of the printing roller. As the printing roller rotates, a doctor knife scrapes the printing paste cleanly from the plain surface portion, leaving only the engraved portions of the printing roller filled with the printing paste. A pressure drum having a springy surface is positioned above and in contact with the printing roller. The cellulose acetate fabric is passed between the printing roller and the pressure drum and becomes printed by being forced into the engraved portions of the printing roller carrying the printing paste.

The printed fabric is dried preferably with hot air, dry steamed for 15 to 20 minutes, soaped lightly at 60° C., washed in soft water, and dried. The printed portions of the fabric apparently are relatively fast to washing. In a similar fashion the fabrics may be printed with direct, basic and other dyestuffs.

EXAMPLE VI

Cellulose acetate fabric woven from cellulose acetate threads modified with beta-diethylaminoethyl methacrylate in accordance with the procedure outlined in Example I may be dyed with "Ponsol" Jade Green Double Paste, color index 1101 in the following manner:

20 parts of the dye paste is mixed with 80 parts of the following composition:

	Parts
A boiled mixture comprising 700 parts gum tragacanth (6%) and 300 parts British gum powder	550
190 parts Potassium carbonate	190
Dissolve at 170° F. cool to 140° F. and add:	

	Parts
Sodium sulfoxylate formaldehyde	160
Glycerine	50
Water	50

The dye mixture is printed on the fabric, dried, aged for 4 to 6 minutes at 214° F. to 220° F. in an air-free ager, after which it is oxidized for 2 to 3 minutes at 110° F. to 130° F. in the following bath:

	Parts
Sodium perborate	5
Water	1000

After oxidation the prints are rinsed, soaped lightly, rinsed and dried.

If desired this printing of the vat dye can be carried out on a modified cellulose acetate fabric, dyed with a readily dischargeable ground shade by the use of a developed dye as above described in Example IV.

The modified cellulose acetate fabric will be dyed readily to any desired depth in this manner and any developed color will be readily discharged.

If it is desired to get a white discharge of the developed color, or direct color, the following procedure can be used:

A printing paste is prepared as follows:

	Parts
Zinc sulfoxylate formaldehyde conc.	20
Diethylene glycol	15
Water	15
Gum tragacanth (6% solution)	50

The pastes are printed on the dischargeable ground of direct or developed dye, dried, aged for 4 to 6 minutes at 214°-220° F. in an air-free ager, rinsed, soaped lightly if desired rinsed and dried.

In discharge printing, it is distinctly preferred to apply the zinc or sodium formaldehyde sulfoxylate discharge agents in the presence of a solvent or softening agent for the organic derivative of cellulose. In this connection it is particularly advantageous to use a mixture of zinc or sodium formaldehyde sulfoxylate with zinc thiocyanate and optionally an additional solvent or swelling agent.

In all the above examples, unless otherwise specified, percentages are based on the weight of the material being treated.

It will be apparent from the foregoing examples that these polymeric amino nitrogen con-

taining bodies may be incorporated in the cellulose acetate structures in many ways. If the resin is incorporated in the solution from which the cellulose acetate structure is formed, which is the preferred method, it is generally desirable to add a higher concentration of resin to the solution, based on the cellulose acetate content, than is added to the bath in which the cellulose acetate materials are after-treated.

If the polymer is to be added to the spinning solution, concentrations as high as 30% or even more, based on the weight of the cellulose acetate present may be used. In general, however, I find that concentrations ranging from 5% up to about 20%, depending of course on the effectiveness of the specific materials chosen, are sufficient for most purposes. While it is possible to increase the depth of dyeing by the addition of still larger quantities of the polymer, the increased depth of dyeing is offset by weakening of the cellulose acetate structure, so that from the practical standpoint, it is advisable to use no more resin in the cellulose acetate structure than is necessary to obtain the depth of color desired.

Where the polymer is to be added to the cellulose acetate thread or the like by after-treatment, concentrations of polymer in the solution which is impregnated in the cellulose acetate structure need be no more than about 10%. Very good results have been secured with as little as 1% and generally, it is not necessary to increase the concentration over 5% or 6%. It is preferred to select a resin which, in a solution composed of 20% polymer, 10% water, and 70% acetone at 25° C. has a viscosity between 25 and 300 centipoises and it is particularly preferred to select a resin having a viscosity of between 50 and 125 centipoises.

It is preferred of course to select a resin which will be soluble in a suitable solvent according to the process to be used. For instance, if the material is to be incorporated in a cellulose acetate spinning solution, a resin should be selected which is soluble in acetone, acetone-alcohol mixtures, or other solvent or solvent mixture for cellulose acetate. In some cases, it is possible to use resins which are dispersed rather than dissolved in the spinning solution.

In some instances, it may be desirable to incorporate the resin forming material or the monomer in the cellulose acetate structure and to form the resin in situ. This is a desirable procedure, especially where the resin to be used is insoluble in a suitable solvent, but where the resin forming materials or the monomer is soluble in a suitable solvent.

If desired, the dye may be dissolved in the treating bath containing the amine polymer, the monomer or the resin forming materials and the cellulose derivative structure treated in a single bath. Also, the dye may be incorporated in the cellulose derivative solution along with the amino polymer or the like and colored structures produced therefrom.

This invention is of primary interest in connection with cellulose esters, and more particularly cellulose acetate although other cellulose esters, such as cellulose propionate, cellulose butyrate and the like can be produced of improved dyeing characteristics by incorporating therein one or more of the resins or polymers referred to in this case. Quite probably, cellulose ethers, such as benzyl cellulose, ethyl cellulose, methyl cellulose, glycol cellulose, etc., whether in the form of threads, films or other form may be en-

dowed with improved dyeing properties when treated in accordance with the teachings of this invention.

It is apparent that this invention considerably widens the range of dyestuffs available for use with cellulose acetate and other cellulose esters. It enables the dyer to use new classes of dyes which can be easily applied, which are relatively cheap and which will produce uniform colors fast to light, washing, and other factors tending to affect the color. Furthermore, since these resins are of high molecular weight, they are slow to diffuse from the fiber and since they are generally of film forming materials, they do not tend to weaken the fiber to the extent the fibers would be weakened by incorporating therein low molecular weight substances such as monomers. Also, these materials have a further advantage for this use in that they are definitely not volatile and water insoluble and therefore resist removal by heat or washing.

By means of this invention cellulose acetate threads may be mixed with wool, cotton, regenerated cellulose or the like and satisfactory dye results secured with the desired class of dyes. Furthermore, fabrics made from 100% cellulose acetate yarn are simply and inexpensively dyed with the desired dyestuff and dischargeable printing may be carried out with very good results.

Parts and proportions referred to are parts and proportions by weight unless otherwise specified.

Since it is obvious that many changes and modifications can be made in the above described processes and products without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited except as set forth in the appended claims.

I claim:

1. The process of imparting to an organic cellulose derivative structure an affinity for dyestuffs which comprises uniting the said structure with a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

2. The process of imparting to a cellulose ester structure an affinity for dyestuffs which comprises uniting the said structure with a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

3. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises uniting the said structure with a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

4. The process of imparting to an organic cellulose derivative structure an affinity for dyestuffs which comprises uniting the said structure with a salt of a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

5. The process of imparting to a cellulose ester structure an affinity for dyestuffs which comprises uniting the said structure with a salt of a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

6. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises uniting the said structure with a salt of a polymeric amino alcohol ester of an acid

taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

7. The process of imparting to an organic cellulose derivative structure an affinity for dyestuffs which comprises embodying in said structure a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

8. The process of imparting to a cellulose ester structure an affinity for dyestuffs which comprises embodying in said structure a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

9. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises embodying in said structure a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid.

10. In a process of forming an organic cellulose derivative article having an affinity for all dyestuffs the steps comprising embodying in a cellulose derivative composition a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, forming an article therefrom, and converting said polymer to a salt.

11. In a process of forming a cellulose ester article having an affinity for all dyestuffs the steps comprising embodying in a cellulose ester composition a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, forming an article therefrom, and converting said polymer to a salt.

12. In a process of forming a cellulose acetate article having an affinity for all dyestuffs the steps comprising embodying in a cellulose acetate composition a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, forming an article therefrom, and converting said polymer to a salt.

13. An organic cellulose derivative structure containing a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, and a dyestuff.

14. A cellulose ester structure containing a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, and a dyestuff.

15. A cellulose acetate structure containing a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, and a dyestuff.

16. An organic cellulose derivative structure containing a salt of a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, and a dyestuff.

17. A cellulose ester structure containing a salt of a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, and a dyestuff.

18. A cellulose acetate structure containing a salt of a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, and a dyestuff.

19. In a process for the discharge dyeing of an organic cellulose derivative structure the steps comprising uniting the said structure with a polymeric amino alcohol ester of an acid taken

from the group consisting of acrylic acid and alpha substituted acrylic acid, dyeing said structure with a dischargeable dye, and discharging said dye with a discharging agent.

5 20. In a process for the discharge dyeing of an organic cellulose derivative structure the steps comprising uniting the said structure with a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, dyeing said structure with a dischargeable dye, and discharging said dye with a discharging agent composed of a mixture of a sulfoxylate and a thiocyanate.

15 21. In a process for the discharge dyeing of an organic cellulose derivative structure the steps comprising uniting the said structure with a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, dyeing said structure with a dischargeable dye, and discharging said dye with a discharging agent composed of zinc formaldehyde sulfoxylate.

20 22. A discharge-dyed organic cellulose derivative structure containing a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, dyeing said structure with a dischargeable dye, and discharging said dye with a discharging agent composed of zinc formaldehyde sulfoxylate.

sisting of acrylic acid and alpha substituted acrylic acid and a dischargeable dye.

23. A discharge-dyed organic cellulose derivative structure containing a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, a ground color comprising a dischargeable dye, and a design of contrasting color.

24. A discharge-dyed organic cellulose derivative structure containing a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, a ground color comprising a dischargeable dye, and a colorless design.

25. An organic cellulose derivative structure containing a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid, and a vat dyestuff.

26. An organic cellulosic derivative structure containing a polymeric amino alcohol ester of an acid taken from the group consisting of acrylic acid and alpha substituted acrylic acid and a developed dyestuff.

WINFIELD WALTER HECKERT.