Patented Feb. 27, 1940 2,191,887

UNITED STATES PATENT OFFICE

2,191,887

CELLULOSIC STRUCTURE AND PROCESS OF MAKING THE SAME

Winfield Walter Heckert, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application May 20, 1937, Serial No. 143,829

34 Claims. (Cl. 8—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 continuation-in-part of my copending application Serial No. 85,816 filed June 17, 1936.

Cellulose derivative materials, and particularly materials made from cellulose organic 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 consequently heretofore 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, prior to formation of structures, a non-cellulosic, non-proteinous, polymeric compound containing amino nitrogen. Such amino nitrogen may be primary, secondary or tertiary, part of an open chain or of a cyclic molecular structure.

The polymeric compounds which may be introduced into the cellulose derivative structures to improve their affinity for dyestuffs may be subdivided into several groups as follows:

1. The first group may be considered as hexose amine polymers, or more broadly as carbohydrate amine polymers which have, where necessary, been purified and converted into the acid soluble type. With or without such treatments, the highly polymeric molecule is built up by nature and the amino nitrogen, as a rule is present in the natural product. Those in which the nitrogen is present in the substance as it exists naturally may be of marine or insect origin on the one hand, or vegetable origin on the other. Deacetylated chitin, which is an example of a non-cellulosic hexose amine polymer is of marine origin, and the polymers obtained from fungi such as aspergillus niger are of vegetable origin. Regardless of the source of the nitrogen, this first group also includes various reaction products and chemical derivatives of carbohydrate amine polymers.

2. The second group of polymeric compounds comprises that group of synthetic resins, in the making of which ammonia in some instances

and monomeric amino nitrogen containing bodies in others have been employed. This group is distinct in that the highly polymeric molecules are built up synthetically wholly by artificial means, i. e., they are not synthesized by nature. The resins of this group may be considered broadly as those which contain amino nitrogen. The following types of resins are illustrative of the classes among which highly polymeric amino nitrogen containing bodies falling in this classification may be found. (*a*) Resinous polymeric amino alcohol esters of acrylic acid and of its homologues substituted in the alpha position by a hydrocarbon radical, (*b*) resinous reaction products of phenols, aldehydes and ammonia or primary or secondary amines, and (*c*) resinous condensation polymers of amino dihydric alcohols with dibasic acids.

(*a*) Examples of the first of the above sub-classes of resins are beta-diethylaminoethyl alpha-methacrylate, beta-piperidyl-N - ethyl-alpha-methacrylate, and beta-dicyclo-hexylamino-ethyl alpha-methacrylate. These resins may be prepared by spontaneous polymerization of the monomeric compounds, but for the purposes of the present invention, advantage can be taken of a unique property of the monomers, namely their ability to form polymerizable salts with aqueous acids. The monomer as prepared may simply be dissolved in the stoichiometrical amount or more of aqueous acid and the solution heated with a polymerization catalyst such as benzoyl peroxide until polymerization of the salt is effected.

(*b*) An example of the second of the above sub-classes of resins having amino nitrogen and the requisite solubilities is the reaction product of meta-cresol, formaldehyde and dimethylamine. Other phenols such as phenol itself or p-tertiary amyl phenol may be substituted for the cresol, and the ammonia or various primary or secondary amines for the dimethylamine. It is desirable in most cases, possible in all cases, and necessary in some cases, to react the amine or ammonia with a part of the formaldehyde before adding the remainder. These resins are to be sharply distinguished from the phenol-aldehyde resins prepared in the presence of only catalytic amounts of ammonia or amines, which resins cannot be employed in accordance with the methods of this invention because they lack the preponderance of amino nitrogen which induces the proper solubility characteristics. The molal ratio of amine to phenol which is used in making the resins with which the present invention is concerned is on the order of 1:2.

(*c*) As examples of the third of the above sub-classes of resins may be mentioned the resinous condensation polymers, diethanol methylamine succinate and diethanol methylamine phthalate.

Example A

Crude chitin (e. g. crab shells) was first purified by alternate treatment with 1% soda ash at boiling temperature and with 5% hydrochloric acid at ordinary temperature until the material was free from lime salts and adherent protein. The pure chitin thereby obtained was then digested with 40% sodium hydroxide at 110° C. for about 4 hours under conditions which substantially exclude oxidation. The deacetylated chitin thus produced was soluble in aqueous acetic acid, for example, in the proportion of 161 grams of deacetylated chitin to 48 grams of acetic acid, dissolved in the amount of water required to give the desired viscosity.

Since deacetylated chitin is essentially a substance which, although highly polymeric, contains a large percentage of its nitrogen in the form of primary amino groups, it would be expected to form salts with acids, and this presumably is what occurs when acids are employed for conversion of the product to the form in which it is to be used in making the coating compositions of the present invention. Evidence for salt formation is that the product requires the stoichiometrical amount of acetic acid, for example, before complete solution takes place. While reference will be made hereinafter to these solutions in acid as acid solutions of the polymeric amino nitrogen containing body or as solutions of the acetate, propionate, etc., depending on the acid employed, it is not desired to be confined in the appended claims to a theory of salt formation. Most of the "salts" described herein (which may if desired be prepared with more than a stoichiometrical amount of acid and thus may contain an excess thereof) are water soluble. Thus, the acetate, benzoate, formate, lactate, maleate, adipate, citrate, glutamate, isobutyrate, and under certain circumstances the hydrochloride of deacetylated chitin are readily soluble; the succinate, phthalate and hypochlorite are, however, only slightly soluble; others such as the oxalate, salicylate, and linoleate, are even less soluble; and the sulfate is relatively insoluble.

The preparation of various polymeric compounds is fully discussed in a number of patents and copending applications, such as for instance, the U. S. patent to Rigby No. 2,040,879 granted May 19, 1936, relating to the preparation of deacetylated chitin; Graves application Serial No. 21,807, filed May 16, 1935, relating to polymeric amino alcohol esters of alpha substituted acrylic acid; Harman application Serial No. 21,810, filed May 16, 1935, relating to polymeric salts of amino alcoholic esters of alpha substituted acrylic acid; Balthus application Serial No. 69,725, filed March 19, 1936, now Patent 2,122,707 of July 5, 1938, relating to the resin prepared by reacting vinyl ketone polymers such as methyl vinyl ketone with ammonia or a primary amine; and U. S. Letters Patent to Greenewalt No. 2,063,158 granted December 8, 1936, relating to hydrogenating ketone resins in the presence of ammonia or a primary or secondary amine; reference is also made to U. S. Letters Patent to Bruson No. 2,031,557, granted February 18, 1936, relating to amine phenol formaldehyde resins.

To further illustrate the preparation of a few of these amino resins the following examples are given.

Example B

Beta-diethylaminoethyl methacrylate

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 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 fraction boiling at 85±5° 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 atmosphere of nitrogen. The monomeric ester is left in the distilling glass as an almost colorless liquid which polymerizes spontaneously to a 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

Fifty grams of polymeric methyl vinyl ketone are dissolved in 250 grams of dioxan and agitated overnight with 50 grams of cyclohexylamine. A test showed that the resin was not readily soluble in dilute acids; hence, the reaction mixture was heated in a steam bath for 5 hours. The resin was then precipitated. By pouring the reaction mixture in water and after standing 12 hours in fresh water, it was filtered and dried in vacuo. The yield was 55 grams. The pulverized resin was soluble to the extent of 4 grams in 96 grams of 5% aqueous solution of acetic acid.

EXAMPLE D

A solution of 18 grams (0.4 mol) of dimethylamine in 32.4 grams (0.4 mol) of 37% aqueous formaldehyde was added with mechanical stirring and cooling to 53.5 grams (0.5 mol) of 88% phenol. To the above mixture, a solution of 81 grams (1 mol) of 37% aqueous formaldehyde and 30.4 grams (0.5 mol) of 28% aqueous ammonia was added with cooling. The resulting solution was gradually heated in a water bath to 90° C. and held at that temperature for 5 hours. The resulting resin was purified by grinding it to a uniform slurry in the presence of a little water in an ice cold mortar, followed by filtration and washing with ice cold water. After drying, it weighed 74 grams. It was a yellow material which softened slightly above room temperature. It was soluble in acetone, ethyl acetate, dioxan, 10% aqueous sodium hydroxide, 1.5% aqueous acetic acid, 3% formic acid, and 90% toluene-10% ethanol mixture.

There are of course numerous other non-cellulosic, non-proteinous amino polymers that can be prepared in much the same way as will be apparent from a study of the applications specifically referred to above, such as for instance beta-dimethylaminoethyl methacrylate; beta-dicyclohexylaminoethyl methacrylate; beta-di-N-butylaminoethyl methacrylate; beta-morpholine-N-ethyl methacrylate; piperidyl aminoethyl methacrylate; triethanolamine monomethacrylate; the polymerization product resulting by reacting polymeric methyl vinyl ketone with concentrated ammonium hydroxide or with amines such as cyclohexylamine; glucamine, ethanolamine, ethylene diamine; the reaction product between phenol, formaldehyde, ammonia and dimethylamine; between phenol, lignin, formaldehyde and dimethylamine; between phenol, formaldehyde and dimethylaminomethanol; between phenol, formaldehyde and dimethylol cyclohexanolamine; between phenol, formaldehyde, ammonia and aniline; and many others.

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 beta-cyclohexylaminoethyl methacrylate monomer and beta-dimethylaminoethyl methacrylate monomer together under suitable conditions. Other equivalent polymeric materials such as copolymers may also be used, provided their solubility characteristics are as previously set forth.

The particularly preferred non-cellulosic, non-proteinous polymeric compounds of the present invention are those which are substantially insoluble in water and in 5% aqueous ammonia solutions, and which are soluble in 2% aqueous acetic acid solutions.

It is preferred that the non-cellulosic, non-proteinous polymeric compounds of the present invention be substantially colorless, odorless, acetone soluble compounds containing at least 2% amino nitrogen.

It is furthermore preferred that the non-cellulosic, non-proteinous polymeric compounds are resinous.

It has also been found that non-cellulosic, non-proteinous polymeric compounds containing a basic tertiary amino nitrogen group are particularly suitable for use in the improvement in affinity for dyes of cellulose derivative structures.

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 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 of the invention, it is desirable to have the polymeric compound 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 polymeric 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 polymeric compound, 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 polymeric compound constitutes a 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

Monophyll 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 324 A

"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

Deacetylated chitin prepared according to Example A is dissolved in a 5% acetic acid to form a solution containing 3% deacetylated chitin and this solution heated to 50° C. A small skein of cellulose acetate yarn is soaked in this solution for 5 minutes, then removed, the excess solution drained therefrom and the yarn placed in 5% aqueous ammonium hydroxide at room temperature for 5 minutes and then dried at room temperature. The yarn so treated, when dyed in the manner described immediately below, showed good affinity for direct dyestuffs. If desired, the drying of the deacetylated chitin treated yarn may precede the ammonia treatment. Yarn treated in this manner has also been found to have an affinity for all of numerous other types and kinds of dyes.

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 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.

EXAMPLE II

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 and the yarn so produced dyed in the same manner as described under Example I, using either Pontamine Scarlet B, color index 382 or Pontamine Blue RW, color index 512. The yarn so produced has good physical properties and shows good affinity for the direct dyestuffs above mentioned as well as other kinds and types of dyes.

EXAMPLE III

The resin prepared according to Example D was dissolved in a cellulose acetate spinning solution to the extent of 10%, based on the cellulose acetate present. The cellulose acetate solution prior to the addition of the resin comprises 15% cellulose acetate in a solvent composed of 97% acetone and 3% water. The spinning solution containing the resin dissolved therein was dry spun in the usual manner. A skein of this yarn, when dyed in the manner described under Example I, showed a decided affinity for direct dyes and was comparable in uniformity and depth of color to wool yarn dyed in the same manner.

EXAMPLE IV

The resinous polymer prepared according to Example C 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 V

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:

15 parts (by weight) of cellulose acetate
70 parts (by weight) of ethylene dichloride
30 parts (by weight) of isopropyl alcohol
3 parts (by weight) of the interpolymer

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 VI

Cellulose acetate taffeta fabric woven from cellulose acetate threads modified with beta-diethylaminoethyl methacrylate in accordance with the procedure outlined in Example II was dyed with a developable dye having a color index number of 317 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 beta-naphthol 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 VII

Cellulose acetate fabric woven from cellulose acetate threads modified with beta-diethylaminoethyl methacrylate in accordance with the procedure outlined in Example II 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-diethylamino-ethyl 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 engravure 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 IX

Cellulose acetate fabric woven from cellulose acetate threads modified with beta-diethylaminoethyl methacrylate in accordance with the procedure outlined in Example II 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:

550 parts of a boiled mixture comprising
700 parts gum tragacanth (6%) and
300 parts British gum powder
190 parts potassium carbonate
Dissolve at 170° F. cool to 140° F. and add:
160 parts sodium sulfoxylate formaldehyde
50 parts glycerine
50 parts water

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 VI.

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 containing 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 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 polymeric compound, 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 polymeric compound 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 endowed 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 non-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 non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen.

2. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises uniting the said structure with a non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen.

3. The process of imparting to an organic cellulose derivative structure an affinity for dyestuffs which comprises uniting the said structure with a non-cellulosic, non-proteinous polymeric salt containing amino nitrogen.

4. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises uniting the said structure with a non-cellulosic, non-proteinous polymeric salt containing amino nitrogen.

5. The process of imparting to an organic cellulose derivative structure an affinity for dyestuffs which comprises uniting the said structure with a non-cellulosic, polymeric compound containing a basic tertiary amino nitrogen group.

6. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises uniting the said structure with a non-cellulosic, polymeric compound containing a basic tertiary amino nitrogen group.

7. The process of imparting to an organic cellulose derivative structure an affinity for dyestuffs which comprises uniting the said structure with a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen which is insoluble in water and in 5% aqueous ammonia and soluble in 2% aqueous acetic acid.

8. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises uniting the said structure with a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen which is insoluble in water and in 5% aqueous ammonia and soluble in 2% aqueous acetic acid.

9. The process of imparting to an organic cellulose derivative structure an affinity for dyestuffs which comprises uniting the said structure with a resinous, non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen.

10. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises uniting the said structure with a resinous, non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen.

11. The process of imparting to an organic cellulose derivative structure an affinity for dyestuffs which comprises embodying in said structure a non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen.

12. The process of imparting to a cellulose acetate structure an affinity for dyestuffs which comprises embodying in said structure a non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen.

13. The process of forming an organic cellulose derivative article having an affinity for all dyestuffs which comprises incorporating in a cellulose derivative composition a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen, forming an article therefrom and converting said compound to a salt.

14. The process of forming a cellulose acetate article having an affinity for all dyestuffs which comprises incorporating in a cellulose acetate composition a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen, forming an article therefrom, and converting said compound to a salt.

15. An organic cellulose derivative structure containing a non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen and a dyestuff.

16. A cellulose acetate structure containing a non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen and a dyestuff.

17. An organic cellulose derivative structure containing a non-cellulosic, non-proteinous polymeric salt containing amino nitrogen and a dyestuff.

18. A cellulose acetate structure containing a non-cellulosic, non-proteinous polymeric salt containing amino nitrogen and a dyestuff.

19. An organic cellulose derivative structure containing a non-cellulosic polymeric compound containing a basic tertiary amino nitrogen group and a dyestuff.

20. A cellulose acetate structure containing a non-cellulosic polymeric compound containing a basic tertiary amino nitrogen group and a dyestuff.

21. An organic cellulose derivative structure containing a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen which is insoluble in water and in 5% aqueous ammonia and soluble in 2% aqueous acetic acid and a dyestuff.

22. A cellulose acetate structure containing a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen which is insoluble in water and in 5% aqueous ammonia and soluble in 2% aqueous acetic acid and a dyestuff.

23. An organic cellulose derivative structure containing a resinous non-cellulosic, non-pro-

teinous polymeric compound containing at least 2% amino nitrogen and a dyestuff.

24. A cellulose acetate structure containing a resinous non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen and a dyestuff.

25. An organic cellulose derivative structure having embodied therein a non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen and a dyestuff.

26. A cellulose acetate structure having embodied therein a non-cellulosic, non-proteinous polymeric compound containing at least 2% amino nitrogen and a dyestuff.

27. In a process for the discharge dyeing of an organic cellulose derivative structure the steps comprising uniting the said structure with a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen, dyeing said structure with a dischargeable dye, and discharging said dye with a discharging agent.

28. In a process for the discharge dyeing of an organic cellulose derivative structure the steps comprising uniting the said structure with a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen, 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.

29. In a process for the discharge dyeing of an organic cellulose derivative structure the steps comprising uniting the said structure with a non-cellulosic, non-proteinous polymeric compound, containing amino nitrogen, dyeing said structure with a dischargeable dye, and discharging said dye with a discharging agent composed of zinc formaldehyde sulfoxylate.

30. A discharge-printed organic cellulose derivative structure containing a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen and a dischargeable dye.

31. A discharge-printed organic cellulose derivative structure containing a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen, a ground color comprising a dischargeable dye, and a design of contrasting color.

32. A discharge-printed organic cellulose derivative structure containing a non-cellulosic, non-proteinous polymeric compound containing amino nitrogen, a ground color comprising a dischargeable dye, and a colorless design.

33. An organic cellulose derivative structure having in combination therewith a polymeric compound containing amino nitrogen and a vat dye.

34. An organic cellulose derivative structure having in combination therewith a polymeric compound containing amino nitrogen and a developed dyestuff.

WINFIELD WALTER HECKERT.