

UNITED STATES PATENT OFFICE

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CELLULOSIC MATERIAL AND METHOD FOR
PREPARING SAME

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This invention relates to the manufacture of cellulosic materials such as cords, threads, yarns, filaments, fibers and the like or fabrics made therefrom and films, pellicles, caps, bands and the like which have improved affinity for acid or direct dyestuffs.

Direct dyes possess the property of dyeing cotton, linen and regenerated cellulose as well as wool and silk and form a very important class of coloring matter. Direct dyes in general are dischargeable, which is an important characteristic and is necessary for the manufacture of an important class of textile fabrics known as print goods. Acid dyes are used almost exclusively for dyeing wool, silk and other animal fibers and are also extremely valuable.

Regenerated cellulose structures are readily dyed with direct colors. Regenerated cellulose, however, has practically no affinity for acid dyestuffs and when regenerated cellulose fibers are mixed with wool to produce composite threads or yarns or when regenerated cellulose yarns are fabricated with woolen yarns to produce a mixed fabric, the product cannot be dyed to a uniform color with acid dyestuffs. Although the mixed fabric might be fairly uniformly dyed with a direct dye, it is at times desirable and preferable to use acid dyestuffs because of differences in light fastness, laundry fastness, etc., between direct dyes and acid dyestuffs.

Cellulose derivative structures and especially the cellulose esters, such as cellulose acetate, can only be dyed with expensive dyestuffs and by means of special, expensive and difficult procedures. For the most part, none of the cellulose acetate dyes are satisfactorily dischargeable and consequently cellulose acetate fabrics cannot be subjected to discharge printing as are fabrics of wool, cotton, regenerated cellulose rayon, or the like. Furthermore, cellulose acetate has no affinity for either the acid or direct dyes. It is because of this that cellulose acetate has been used to a considerable extent where cross dyeing effects are desired, but on the other hand, when cellulose acetate is mixed with regenerated cellulose, cotton, wool or natural silk, and uniform, solid color is desired, it has been necessary to go through a long, expensive procedure attended by undesirable changes in the yarn or fabric properties.

It is known that the affinity of regenerated cellulose yarn for acid dyes may be considerably enhanced by incorporating proteins in the spinning solution. Furthermore, it has been proposed to harden the protein contained in the

regenerated cellulose thread with formaldehyde to render it resistant to chemicals which, unfortunately, decreases the affinity of the added protein for acid dyestuffs. More recently, it has been proposed to treat the protein with a material to insolubilize it, for instance to form reaction products, which are not easily removed from the fibers.

It is therefore an object of this invention to improve the affinity of cellulosic structures for dyestuffs.

Another object of this invention is to improve the affinity of cellulosic structures for direct acid dyestuffs.

Another object of this invention is to improve the affinity of regenerated cellulose structures for acid dyestuffs.

Still another object of this invention is to improve the affinity of cellulose esters, such as cellulose acetate, for direct acid dyestuffs.

Other objects will be apparent from the description that follows.

The objects of this invention are accomplished in general by incorporating in the cellulosic material in any suitable manner an amine-phenol-aldehyde resin prepared by reacting a phenol having at least two free reactive positions, i. e., positions ortho and para to the phenolic hydroxyl, and containing only organic groups as ring constituents, an aldehyde (particularly formaldehyde) and an organic compound, preferably of not over six carbon atoms which has at least one amino nitrogen atom joined to an aliphatic carbon atom, i. e., a carbon atom which is not a part of an aromatic ring, and to at least one hydrogen atom, and isolating the resulting resinous reaction product.

It is preferred that these resins be insoluble in water and soluble in dilute aqueous mineral or organic acids when used in cellulose derivative structures. Some of these resins are soluble in dilute aqueous caustic solutions, in acetone and in certain other solvents as set forth hereinafter.

The preparation of certain of these resins is described in United States Patent No. 2,031,557 to Bruson and certain others in United States Letters Patent of Harmon and Meigs, No. 2,098,869. To illustrate the preparation of certain of these amino phenol aldehyde resins, the following examples are given:

EXAMPLE A.—*Phenol-formaldehyde-dimethylamine-ammonia resin*

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.

EXAMPLE B.—Phenol lignin - formaldehyde - dimethylamine resin

The crude phenol lignin used in this preparation was made as follows:

A 3-liter 3-necked flask was equipped with a hook-type mechanical stirrer, wide bore air reflux condenser and thermometer and mounted in an oil bath. The flask was charged with 900 grams of phenol, the stirrer started and 190 grams of a fine grade of spruce wood flour (100 mesh or better) were added through the condenser while the temperature of the phenol was increased from 65° to 116° C. Then 25 grams of concentrated hydrochloric acid were added all at once. After the reaction mixture had become homogeneous (about 15 minutes), 190 grams more of wood flour were added during the course of about one hour. Heating at 116-120° C. and stirring were continued for 4 hours, at which time the reaction mixture was viscous and black. It was allowed to cool, diluted with 2 liters of 95% ethanol, heated with stirring until the alcohol refluxed, filtered with suction, and the cellulosic residue was washed well with hot alcohol. The alcohol and 200 grams of phenol were removed from the filtrate by heating in a hot water bath in vacuo (2.5 mm. to take off the phenol). The remaining uncombined phenol was removed from the product by steam distilling until 6.5 liters of distillate had collected. The flask was allowed to cool, the water layer (about 1 liter) was decanted from the tarry product, about 500 cc. of distilled water was added and steam distillation was continued until test samples of the distillate were free from phenol (FeCl₃ test). The water which had collected in the flask was decanted and the residual product of crude phenol lignin was allowed to cool. It was a fused, hard, brittle, black mass and weighed 560 grams. It probably did not contain more than 5% of its weight of water.

The amine resin was made as follows from the crude phenol lignin described above:

The 560 grams of crude phenol lignin prepared as described above was dissolved in 1,900 cc. of 95% ethanol. The solution was cooled to 8° C. and an aqueous solution of 3.8 mols of dimethylaminomethanol was added with mechanical stirring at 8° C. during the course of 15 minutes. The dimethylaminomethanol solution was made by bubbling 171 grams of dimethylamine into 308 grams of aqueous 37% formaldehyde solution while the temperature was kept below 30° C. After the addition of dimethylaminomethanol was completed the ice bath was removed and the solution was warmed to 36° C., at which temperature a mild exothermic reaction set in. Heating

was discontinued. The reaction temperature stayed at 36-38° C. for 1.25 hours and then started to drop. The reaction was next heated in a water bath at 65-70° C. for 3 hours. The alcohol solution was allowed to cool and then added slowly to 12.5 liters of efficiently stirred distilled water. The resin was precipitated as a finely divided light brown, amorphous solid. It was filtered, washed well with water and dried first in the air and then in a vacuum desiccator. The dry product was light brown in color and weighed 459 grams. It was soluble in acetone, ethanol, dioxan, chloroform, hot ethyl acetate, 1.5% aqueous acetic acid, and 5% aqueous sodium hydroxide solution.

EXAMPLE C.—Phenol - formaldehyde - dimethylamine resin

To a solution of 564 grams (6 mols) of phenol in 680 grams (8.4 mols) of aqueous 37% formaldehyde was added, with stirring and cooling at such a rate that the temperature remained below 10° C., an aqueous solution of 3 mols of dimethylaminomethanol made by bubbling 135 grams (3 mols) of dimethylamine into 243 grams (3 mols) of cold aqueous 37% formaldehyde. The addition of this solution to the phenol solution required about an hour. The cooling bath was then removed and the temperature of the reaction mixture was allowed to rise spontaneously to 40° C., where it was held by means of a cooling bath until the exothermic reaction was over. The reaction mixture was then heated in a boiling water bath until the resinous mass which was formed was too thick to stir mechanically. It was transferred, while hot, to a large nickel plate, cooled, and the brittle resin was ground in a cold mortar with a little cold water to a uniform slurry. The resin was filtered, washed thoroughly with water, and dried in vacuo at room temperature. After drying, the weight of light yellow, granular, resin was 900 grams. Analysis showed that the product contained 4.94% nitrogen. It was soluble in dilute (1.5%) acetic acid to the extent of at least 1 gram of resin in 99 grams of acid solution, in 5% sodium hydroxide solution, and in benzyl alcohol and pyridine. It was insoluble in aromatic hydrocarbons. A film flowed from the acetic acid was, after being baked at 100° C. for 15 hours, clear, colorless, hard, and insoluble in dilute acids. The resin was also soluble to the extent of at least 1% in 1.5% aqueous solutions of the following acids: formic, glycollic, lactic, tartaric, phosphoric, and maleic. It was soluble in 0.6% aqueous hydrochloric acid to the extent of 4.5 grams in 95.5 grams of the acid solution. Mineral acids in concentrations of 1.5% or more appear to catalyze hardening of the resin. Consequently they do not dissolve in it. The resin was insoluble in 1.5% aqueous sulfuric acid, n-caprylic acid, and hydrochloric acid.

EXAMPLE D.—Phenol - formaldehyde - dimethylamine resin

The above procedure was repeated except that the ratios of reactants were phenol, 1 mol; formaldehyde 1.4 mols; dimethylaminomethanol, 1 mol. The resulting resin was a yellow amorphous powder. It was insoluble in all of the common organic solvents except methyl Cellosolve. It was soluble in the theoretical amount of 1.5% aqueous acetic acid and was also soluble in 5% sodium hydroxide solution. A suspension of this resin in ice cold water was dissolved when the water was saturated with carbon dioxide. A film flowed from a dilute (1.5%) acetic acid solution

of this resin remained clear and was soluble in dilute acetic acid after prolonged baking at 100° C.

5 **EXAMPLE E.—Phenol-aniline-ammonia-formaldehyde resin**

A mixture of 94 grams (1 mol) of phenol, 18.6 grams (0.2 mol) of aniline, and 61 grams (1 mol) of 28% aqueous ammonia was cooled in an ice bath and stirred mechanically. To this, 97 grams (1.2 mols) of 37% aqueous formaldehyde were added all at once. The mixture cleared up at first, then quickly became turbid and warmed up to 60° C. The temperature soon dropped to 10 40° C. The ice bath was removed and 49 grams (0.6 mol) of 37% aqueous formaldehyde were added. The temperature rose immediately to 15 50° C. After the exothermic reaction had subsided, the mixture was heated in a water bath at 70–90° C. for 2 hours, at the end of which time a thick resin had formed. The resin was purified by the method outlined under Example C above. It was a light yellow, amorphous powder and weighed 135 grams. It was soluble in acetone, ethyl acetate, dioxan, chloroform, 5% aqueous sodium hydroxide solution, and 25% aqueous acetic acid.

20 **EXAMPLE F.—Phenol-formaldehyde-cyclohexylamine resin**

A mixture of 85.5 grams (0.8 mol) of 88% phenol and 91 grams (1.12 mols) of 37% formaldehyde was stirred mechanically and cooled in an ice bath. To this mixture at 5° C., there was added a solution made from 54.5 grams (0.55 mol) of cyclohexylamine and 65.5 grams (0.64 mol) of 37% aqueous formaldehyde. The ice bath was removed and the stirred reaction mixture was allowed to warm to room temperature and it was then heated gradually on a water bath up to 90° C. and was held there for 3.5 hours. The resin which formed was purified by the method outlined under Example C. It was a light yellow, granular solid and weighed 143 grams. It was soluble in 45% acetic acid, ethyl acetate, dioxan, pyridine, and 90% toluene—10% ethanol mixture.

40 **EXAMPLE G.—Phenol-formaldehyde-ammonia resin**

To a solution of 94 grams (1 mol) of phenol in 140 grams of water, there was added 61 grams (1 mol) of 28% aqueous ammonia. The solution was stirred and cooled in an ice bath while 162 grams (2 mols) of 37% aqueous formaldehyde were added. During this time a solid formed. The mixture was next gradually brought to the temperature of a boiling water bath and held there for 1.5 hours during which time a fused mass of resin formed. The resin was purified by the method outlined under Example C above. It weighed 107 grams, contained 5.07% nitrogen, was soluble in acetone and dioxan, but was not completely soluble in acetic acid of concentrations lower than 50%. It was also soluble in 5% aqueous sodium hydroxide solution.

There are, of course, numerous other amine phenol formaldehyde resins which are prepared in much the same manner as described in these specific examples which may be used with good results in improving the dyeing qualities of cellulose structures, as for example resins prepared from symmetrical xylenol, formaldehyde and methylamine; phenol, lignin, formaldehyde and methylamine; phenol, formaldehyde and cyclo-

hexanolamine; p-toluene sulfonamide, phenol, formaldehyde and methylamine; diphenylol cyclohexanone, formaldehyde and dimethylamino-methanol; diphenylguanidine and formaldehyde; phenol, formaldehyde and dimethylamine; m-cresol, formaldehyde and di-methylamine; xylenol, formaldehyde and dimethylaminomethanol; phenol, formaldehyde, ammonia and diethanolamine, etc.

The resins described above may be incorporated in the cellulosic structure in any suitable manner, as for instance by dissolving or dispersing the resin in the cellulosic spinning solutions or by dissolving or dispersing the resin in a suitable solvent or dispersing agent, impregnating the cellulosic structure in the form of threads, fabric or the like with the solution or dispersion of the resin and removing the solvent or dispersing medium by evaporation.

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.

25 **EXAMPLE I**

The resin prepared according to Example A from phenol formaldehyde, ammonia and dimethylamine is 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 and uniformly incorporated therein is spun electrically, for example, in the manner set forth in the United States patent to Formhals No. 1,975,504, into a cellulose acetate thread. A skein of this thread or yarn, when dyed in the manner described immediately below is uniformly colored to substantially the same shade as wool dyed in a like bath.

Milling Red R Conc. (color index 430) (see 1932 Yearbook of the American Association of Textile Chemists and Colorists) is dissolved in water to form a dye solution containing 0.2% dye. Twenty-five ccs. of this dye solution, and 0.5 gram of acetic acid are dissolved in 175 ccs. of water. The solution is heated to 40° C. and a 5-gram sample of the yarn introduced, whereupon the solution is heated to boiling and boiled for ½ hour, and then 0.5 cc. of 10% acetic acid is added to the dye bath and the boiling continued for another ½ hour. At the end of that time the sample is removed from the bath, rinsed with water and dried.

50 **EXAMPLE II**

A resin prepared according to Example B from phenol, lignin, formaldehyde and dimethylamine is dissolved in acetone and to this solution sufficient cellulose acetate added to form a spinning solution containing 20% cellulose acetate, 4% resin and 76% acetone. The solution is dry spun in the usual manner and the yarn so produced is dyed in a neutral solution in much the same manner as disclosed under Example I, except no acid is added. This yarn dyes a deep red similar in shade and depth to a sample of wool dyed in a bath prepared and used in the same way.

55 **EXAMPLE III**

A resin prepared according to Example C from phenol, formaldehyde and dimethylamine

is dissolved in a 5% aqueous caustic solution to the extent of 3% resin in the final solution. A piece of cellulose acetate fabric is immersed in this solution which is heated to 50° C., and allowed to remain there for 5 minutes. The fabric is removed, the excess solution drained therefrom and then immersed in a 5% acetic acid solution at 25° C. for 5 minutes, after which it is removed, rinsed with water and dried at room temperature. This fabric, when dyed with Brilliant Milling Green B Conc. as in the preceding example is as deeply colored as a standard sample of wool dyed with the same dye in the same manner.

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EXAMPLE IV

A resin prepared according to Example D from phenol, formaldehyde and dimethylaminomethanol is dissolved in 2% aqueous caustic to form a solution containing 1% of the resin. After heating to 80° C., cellulose acetate staple fibers are immersed in the solution for 5 minutes, whereupon the fibers are removed from the bath, the excess solution drained therefrom and the fibers then placed in a 5% acetic acid bath at 25° C. for 5 minutes. Upon removal of the fibers from the bath, they are rinsed in water and dried at 80° C. When dyed with Brilliant Milling Green B Conc. according to the method described under Example I, it is observed that the fibers take the acid dye to substantially the same extent as does wool.

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EXAMPLE V

The resin prepared in the manner described in Example A from phenol, formaldehyde, ammonia and dimethylamine is dissolved in 4% acetic acid to form a solution containing 2% resin and this solution heated to 50° C. A 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 a 5% ammonium hydroxide water solution at room temperature for 5 minutes, removed, rinsed and dried at room temperature. The yarn so treated is tested in the same manner as described in any of the preceding examples and is found to have taken the acid dye exceedingly well.

While the preceding examples have been directed more specifically to processes that would show a decided improved affinity of cellulose acetate for acid dyes, it should be noted that in all these cases the material exhibited substantial improvement in affinity for direct dyes as well. On the other hand, if it is desired primarily to improve the affinity of cellulose acetate material to direct dyes, I prefer to use certain other resins such as those set forth in the two examples that follow. Likewise, while these two examples are given to illustrate the improvement in cellulose acetate structures for direct dyes, it should also be understood that in these cases there is a decided improvement in the affinity of cellulose acetate structures for acid dyes.

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EXAMPLE VI

The resin prepared in accordance with Example E from phenol, formaldehyde, ammonia and aniline is added to a cellulose acetate spinning solution comprising 15% cellulose acetate dissolved in a solvent made up of 97% acetone and 3% water to the extent that the solution contains 15% of the resin based on the cellulose acetate present. After thoroughly incorporating the resin in the cellulose acetate solution, the

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solution is dry spun in the usual manner and the yarn so produced is tested with a direct dye in the manner described below.

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 removed and rinsed with water and permitted to drain for a few minutes, after which it is immersed in a dye bath. The dye bath is made up by dissolving a direct color such as Pontamine Scarlet B (color index 382) in water to form a 0.2% solution of dye and then 25 ccs. of this solution, 0.75 gram of sodium sulfate and 2 grams of 10% acetic acid are dissolved in 175 ccs. of water, the solution heated to 40° C. and a 5-gram sample of yarn immersed therein. The temperature of the solution is raised to boiling and boiled for 15 minutes, at which time 2 grams of 10% acetic acid are added and then the boiling continued for another 15 minutes, when 2 grams of 10% acetic acid are again added. The boiling is continued another 15 minutes, the yarn sample removed, rinsed and dried.

The sample of yarn is found to be colored as deeply as wool which is dyed in a like manner and in a like dye bath.

EXAMPLE VII

A resin prepared according to the procedure given in Example F from phenol, formaldehyde, dimethylol cyclohexanolamine is dissolved in a 4% acetic acid solution to the extent of 2%. The solution is heated to 50° C., a sample of normal cellulose acetate yarn immersed therein for 5 minutes, then removed, drained and next placed in a 5% ammonium hydroxide water bath at room temperature for 5 minutes. At the end of this time the sample is removed, rinsed with water and dried. The dried yarn is scoured and dyed in the dye bath described under Example VI, using however in place of the Pontamine Scarlet B, Pontamine Blue RW (color index 512). It is observed that the yarn so treated was dyed to a relatively deep shade, showing an improvement many times over that of untreated cellulose acetate yarn and comparable in uniformity and depth of color to wool yarn dyed in the same manner.

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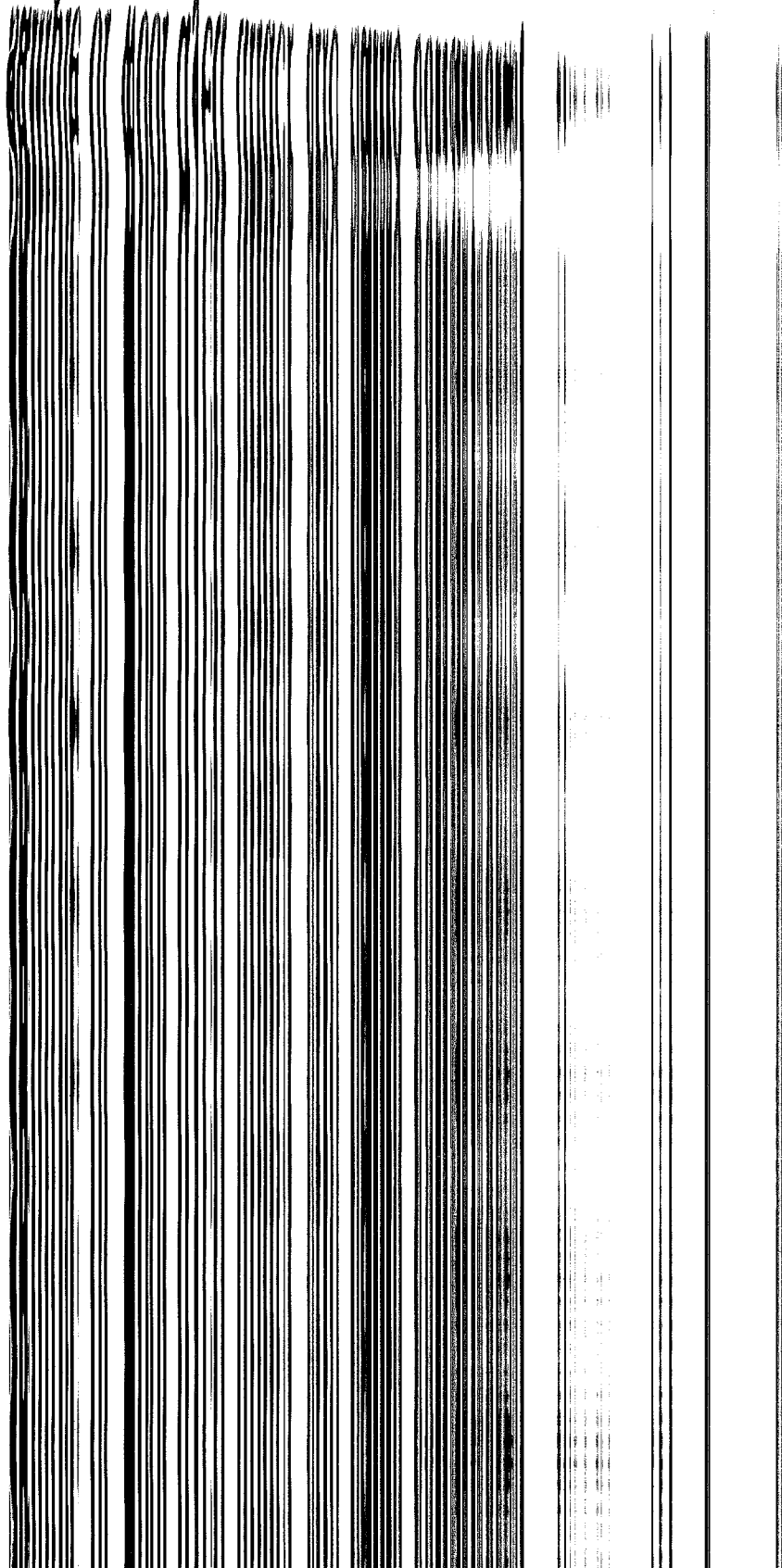
EXAMPLE VIII

The resin prepared according to Example C from phenol, formaldehyde and dimethylaminomethanol is added to a viscose solution containing 7% cellulose and 6% NaOH to the extent of 10% resin, based on the cellulose in the viscose solution. The viscose is stirred until the resin is dissolved, which takes about 30 minutes, then evacuated for several hours and spun into the usual sulfuric acid-sodium sulfate spinning bath. The yarn is collected on a bobbin or other suitable device and when a cake of the desired size is formed, the bobbin or the like containing the yarn is removed from the spinning machine, washed acid free with water, desulfured (with sodium sulfide solution) and bleached, preferably with hydrogen peroxide. Following bleaching, the yarn is again washed with soft water and dried at 60° C. or at any other suitable temperature. The yarn so produced is dyed in a bath in accordance with the procedure set forth under Example I, using for instance Milling Red R Conc. and is found to acquire a very good depth of color, being substantially equal to a comparable

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sample of wool dyed under the same conditions,

about 20%, depending on the effectiveness of the



The dyes which have been disclosed hereinbefore are merely illustrative of the class of dyes, either acid or direct, and any other dyes generally classified as acid or direct dyes may be substituted therefor.

It is apparent that this invention considerably widens the range of dyestuffs available for use in cellulose acetate and/or regenerated cellulose threads and fibers. 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 soluble and therefore resist removal by heat and washing. The invention is particularly useful for improving the dyeing properties of cellulose acetate yarn which has been spun electrically as, for instance, by the method disclosed in United States Patent No. 1,975,504.

By means of this invention regenerated cellulose fibers may be mixed with wool and dyed satisfactorily with acid dyes. Also, regenerated cellulose may be mixed with cellulose acetate yarn and dyed with either acid or direct dyes. Furthermore, fabrics made from 100% cellulose acetate are simply and inexpensively dyed. As the result of this invention direct dyes can be used with cellulose acetate fabrics for producing print goods and also with cellulose acetate-cotton mixed goods either for print work where a dischargeable dye is very desirable or where the goods are dyed in a dye bath. It is also possible by means of this invention to mix cellulose acetate materials with wool and secure satisfactory dye results with either acid or direct colors.

While this invention has been described in connection with textile threads, fabrics, etc., it is also useful in connection with other types of structures. For instance film, sheeting, bands, caps, ribbons, horsehair, straw or the like of cellulosic material may be readily dyed with good results.

Parts and proportions of materials as set forth in the specification and claims refer to 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 which comprises dyeing a cellulosic structure containing a phenol-aldehyde-amine resin with a dyestuff taken from the group consisting of acid and direct dyestuffs.

2. The process which comprises dyeing a cellulosic thread composed of artificial fibers and containing a phenol-aldehyde-amine resin with a

dyestuff taken from the group consisting of acid and direct dyestuffs.

3. The process which comprises dyeing an organic cellulose derivative structure containing a phenol-aldehyde-amine resin with a dyestuff taken from the group consisting of acid and direct dyestuffs.

4. The process which comprises dyeing a cellulosic structure containing a phenol-aldehyde-amine resin with an acid dyestuff.

5. The process which comprises dyeing an organic cellulose derivative structure containing a phenol-aldehyde-amine resin with an acid dyestuff.

6. The process which comprises dyeing an organic cellulose derivative structure containing a phenol-aldehyde-amine resin with a direct dyestuff.

7. The process which comprises dyeing an organic cellulose derivative structure containing phenol-formaldehyde-dimethylamine-ammonia resin with a dyestuff taken from the group consisting of acid and direct dyestuffs.

8. The process which comprises dyeing an organic cellulose derivative structure containing phenol-formaldehyde-dimethylamine resin with a dyestuff taken from the group consisting of acid and direct dyestuffs.

9. The process which comprises dyeing an organic cellulose derivative structure containing m-cresol-formaldehyde-dimethylamine resin with a dyestuff taken from the group consisting of acid and direct dyestuffs.

10. As a new article of manufacture, a cellulosic thread comprised of artificial fibers containing a phenol-aldehyde-amine resin and a dyestuff taken from the group consisting of acid and direct dyestuffs.

11. As a new article of manufacture, an organic cellulose derivative structure containing a phenol-aldehyde-amine resin and a dyestuff taken from the group consisting of acid and direct dyestuffs.

12. As a new article of manufacture, an organic cellulose derivative structure containing a phenol-aldehyde-amine resin and an acid dyestuff.

13. As a new article of manufacture, an organic cellulose derivative structure containing a phenol-aldehyde-amine resin and a direct dyestuff.

14. As a new article of manufacture, an organic cellulose derivative structure containing phenol-formaldehyde-dimethylamine resin and a dyestuff taken from the group consisting of acid and direct dyestuff.

15. A new article of manufacture comprising an organic cellulose derivative structure containing phenol-formaldehyde-dimethylamine-ammonia resin and a dyestuff taken from the group of acid and direct dyestuffs.

16. A new article of manufacture comprising an organic cellulose derivative structure containing a m-cresol-formaldehyde-dimethylamine resin and a dyestuff taken from the group consisting of acid and direct dyestuffs.

WINFIELD WALTER HECKERT.

CERTIFICATE OF CORRECTION.

Patent No. 2,168,335.

August 8, 1939.

WINFIELD WALTER HECKERT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 21, for "apaprent" read apparent; page 2, second column, line 66, for "dimethylaminomethanol" read dimethylaminomethanol; page 3, second column, line 17, for "fobric" read fabric; page 5, first column, line 6, for "90%" read 95%; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 26th day of September, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.