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DYED REGENERATED CELLULOSE CONTAINING A POLYAMIDE

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This invention relates to the manufacture of artificial filaments, yarns, fibers, films, caps, bands, sponges, or similar structures having an improved affinity for dyestuffs. More particularly, the invention relates to the manufacture of such structures from cellulosic or synthetic resinous compositions which have film- or filament-forming properties.

Artificial filaments, fibers, films, and similar structures have been produced by spinning or casting operations. Thus, structures have been produced comprising or consisting of regenerated cellulose, as obtained by the viscose or cuprammonium processes; cellulose derivatives including cellulose esters such as cellulose acetate, formate or propionate and cellulose ethers such as methyl, ethyl or benzyl cellulose, as well as mixed esters, mixed ethers, mixed ether-esters or even mixtures of these; or synthetic resinous materials including polymeric vinyl compounds, such as polyvinyl chloride, polyvinyl acetate, chlorinated polyvinyl chloride, interpolymers of polyvinyl chloride and polyvinyl acetate as well as the polymers of acrylic or methacrylic acid and their esters, such as methyl methacrylate and even interpolymers of methacrylate and vinyl chloride or the like.

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 materials. 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 mixed fabrics, 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 special 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 the 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 a uniform solid color is desired, it has been necessary to subject the same to several dyeing operations in separate dye baths or to go through a long expensive procedure attended by undesirable changes in the yarn or fabric properties. In the same way, structures prepared from synthetic resinous materials having film- or filament-forming properties have been found to be highly resistant to the action of certain well known dyes. These resinous materials have little or no affinity for either direct or acid dyes and, consequently, it has been impossible to secure suitable dyeing of film, filaments, yarns and the like prepared therefrom.

In some cases the elevated temperatures necessary for dyeing with such dyes as have been found useful, cause the materials to shrink or deteriorate so that use of such dyes is impractical.

It is, therefore, an object of this invention to improve the affinity of artificial films, filaments, and the like for dyestuffs.

It is another object of this invention to improve the affinity of these artificial structures for direct or acid dyestuffs.

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

It is still another object of this invention to improve the affinity of cellulose derivative structures, such as cellulose acetate, for direct or acid dyestuffs.

It is still another object of this invention to improve the affinity of synthetic resinous film- or filament-forming materials for either direct or acid dyestuffs.

Other objects will be apparent from the accompanying description and examples.

Generally speaking, the objects of this invention can be accomplished by adding to the structure-forming composition as the case may be, discrete particles of non-cellulosic, non-proteinous, linear polymeric compounds containing

amido nitrogen (i. e., linear polymers containing recurring —CONH— groups in their molecule).

The polymeric compounds which may be introduced into the film- or filament-forming composition in accordance with this invention to improve the dyeing affinity of pellicular or filamentary structures prepared therefrom are selected from the class of synthetic linear polymers and particularly synthetic linear polyamides such as are described in Carothers U. S. Patent No. 2,071,250. These synthetic linear polyamides are of two types: those obtainable from polymerizable monoaminomonocarboxylic acids and those obtainable from the reaction of suitable diamines and dibasic carboxylic acids. In the polyamides the amide groups form an integral part of the main chain of atoms in the polymer. These synthetic linear polyamides may be prepared, for example, by a process of condensation polymerization such as is described in Carothers U. S. Patents Nos. 2,130,948, 2,130,523 and 2,071,253.

It has been found that a large variety of synthetic polyamides can be used to accomplish the objects of this invention depending on the type of film- or filament-forming compositions from which the desired structures are to be produced. Generally speaking, a synthetic polyamide will be chosen which will be insoluble or substantially so in the liquid vehicle used to make up the film- or filament-forming composition. Thus, for example, in the case of a regenerated cellulose structure obtained by the viscose process, the synthetic polyamide chosen will be one which is insoluble in water as well as in the caustic solutions used to make up the viscose, and the acid baths or the like subsequently used in the regeneration process. In the case of a cellulose acetate structure, however, which is to be prepared by dry spinning or dry casting from a volatile solvent vehicle, the synthetic polyamide chosen may be one which is water-soluble so long as it is insoluble in the solvent or solvent mixture which is chosen as the vehicle for the film- or filament-forming composition. Similarly, in the case of a synthetic resinous structure, such as a filament of an interpolymer of polyvinyl chloride and polyvinyl acetate which can be spun by a dry spinning process, the synthetic polyamide will be chosen as one insoluble in the solvent used to make up the spinning solution.

The following examples illustrate certain typical synthetic linear polyamides which can be used in the practice of this invention. These examples are, of course, to be considered as illustrative and not limitative.

Example I

A quantity of the monomeric salt obtained by the reaction of hexamethylene diamine with adipic acid such as is described in Carothers U. S. Patent No. 2,130,947 was heated with 15% of its weight of water in an autoclave for a period of two hours at a temperature of 225° C. The reaction product was allowed to cool and solidify whereupon it was ground up, yielding a white, micro-crystalline solid having an intrinsic viscosity of 0.3 as defined in Corothers U. S. Patent No. 2,130,948.

Example II

Three mols of hexamethylene diamine and two mols of adipic acid were dissolved in cresol using a weight of cresol equal to the weight of the reactant material. The mixture was heated in a nitrogen atmosphere for 6½ hours at 200° C. after which the mixture was poured quickly into a relatively large volume of ethyl acetate. A flocculent, colorless, solid separated from the mixture which was filtered off and washed with more ethyl acetate. The synthetic linear polyamide so obtained exhibited and intrinsic viscosity of 0.15. It was soluble in phenol and in formic or acetic acid, although it was substantially insoluble in the usual organic solvents.

Instead of the simple polymeric type illustrated by the above examples, numerous other synthetic polyamides can be used for the practice of this invention. Interpolymers can be used, as, for example, the interpolymer obtained by the co-polymerization of hexamethylene diammonium adipate and decamethylene diammonium sebacate or an esteramide interpolymer; e. g., one derived from a diamine, a glycol, and a dibasic acid. Likewise, polyamides obtainable from the reaction of adipic acid with diethylene triamine or from the reaction of diglycolic acid with diethylene triamine or from the reaction of tartaric acid with hexamethylene diamine or from the reaction of maleic acid with hexamethylene diamine may be used successfully.

Particularly desirable results are obtainable by the use of linear polyamides having a sufficiently low molecular weight to have an intrinsic viscosity not in excess of 0.6. It has also been found that very desirable results are obtainable by the use of that class of linear polyamides which have a low molecular weight and are non-fiber forming.

The molecular weight of synthetic linear polyamides may be controlled in a number of ways. If a diamine and a dibasic acid are allowed to react in equivalent amounts, the molecular weight of the resulting polymer may be controlled by adjusting the time of reaction, the temperature of reaction, or, more conveniently, by adjusting the amount of water which is present in the reaction vessel. It has been found that the presence of a small amount of excess water in the reaction vessel, along with the diamine and dicarboxylic acid, represses the polymerization sufficiently to give a polymer of the desired mechanical properties. The polymer prepared in this way may be readily ground to suitable particle size, and the incorporation of such polymer in films and filaments will permit the dyeing of the latter with any number of the common silk and wool dyes.

Another and very convenient method of controlling the molecular weight is by the use of an excess of diamine or dicarboxylic acid, or other monofunctional or difunctional acid or introgenous base. Thus, the reaction of 3 mols of diamine and 2 mols of dicarboxylic acid gives a polymer in the desired molecular weight range. The nature of the polymer produced by this method may be quite different from that produced by the use of equimolecular proportions of reactants; they are, however, very suitable for use in accordance with the present invention. Not only is such a polymer satisfactory in its solubility and grinding characteristics, but the acid dyestuffs are especially substantive thereto. Likewise, basic dyes are very substantive to a polymer prepared using excess dibasic acid. No solvent is necessary in conducting the polymerization but, if desired, the phenols or cresols may advantageously be used; when the reaction is completed, the product may be precipitated by the addition of a non-solvent, such as ethyl acetate and further ground up if necessary.

While it is preferred that the synthetic polyamide employed shall be insoluble in the liquid vehicle used to disperse or dissolve the film- or filament-forming material, it is possible to use polyamides which show appreciable solubility. This is particularly true in those cases where a dry spinning or dry casting process is to be employed because here, regardless of the solubility, when the liquid vehicle is removed by the evaporation step in the process, the synthetic polyamide will be left associated with the film- or filament-forming material. In the case where it is desired to modify a regenerated cellulose structure, however, a water-insoluble synthetic polyamide is to be preferred because the normal processing of the regenerated cellulose structure will usually subject it to numerous washing actions and a water-soluble synthetic polyamide might be removed at least in part during these operations resulting in a structure which would not dye uniformly.

The following example is illustrative of the practice of the invention in improving the dye affinity of a regenerated cellulose structure:

Example III

Thirty-six grams of the polyhexamethylene adipamide described in Carothers U. S. Patent No. 2,130,948, together with 60 cc. of water and 5 grams of Monopole Oil were placed in a one-quart ball mill and ground for 6 hours. The contents were then washed out of the ball mill with 257 cc. of water giving a slurry containing about 10% of the synthetic linear polyamide with an average particle size of some 3 to 5 microns. One hundred seventeen grams of this slurry were then stirred into 1500 grams of viscose using a high speed mixer. The viscose was then deaerated whereupon it was spun in the usual manner using a conventional acid coagulating bath. The resulting regenerated cellulose yarn was processed in the usual way including desulfuring, bleaching, and washing operations and then dried.

The finished yarn was dyed by immersing it in a bath maintained at 45° C. and containing 1% of Du Pont Anthraquinone Blue SKY (Color Index 1088), 10% Glauber's salt and 4% acetic acid, the proportions of the ingredients of the dye bath being calculated on the dry weight of the yarn. The temperature of the bath was slowly raised to about 85° C. and held at that temperature for 45 minutes, the yarn being turned frequently during the dyeing operation. The yarn was found to dye quite deeply and uniformly with this acid dye for which unmodified regenerated cellulose has little or no affinity whatsoever.

Example IV

A slurry of the synthetic polyamide described in Example II was prepared and added to viscose in the same way as described in Example III. The modified viscose was spun in the customary way into a saturated ammonium sulfate bath from which bath the coagulated but unregenerated yarn was conducted to a hot glycerin bath (temperature 125° C.) wherein regeneration was effected. The resulting regenerated cellulose yarn was washed, processed, and dried in the usual fashion and when subsequently dyed with an acid dye in the manner described in Example III, the yarn was found to dye to highly satisfactory depth and uniformity.

Example V

To a solution consisting of 0.25 gram of a vinyl chloride-methyl methacrylate interpolymer, 10 cc. of chloroform and 2 cc. of methanol, were added 0.05 gram of the interpolymer obtained by co-polymerization of equal parts of hexamethylene diammonium adipate and decamethylene diammonium sebacate. The mixture was poured onto the surface of a heated glass slide and baked for 10 minutes in an oven 130° C. The thin film of modified synthetic resinous material was stripped from the palte easily.

A dye bath consisting of 2 cc. of 20% aqueous sodium chloride, 50 cc. of 0.2% aqueous dye solution, and 50 cc. of distilled water was heated to 90° C. and the resinous film material immersed therein for several minutes. After dyeing, the film material was washed with hot and cold distilled water and dried. The film material modified with the synthetic polyamide exhibited marked dye receptivity whereas a similar film, unmodified, gave no indications of dye receptivity. Acid dyes such as "Pontacyl" Fast Blue 5R Conc. (Color Index 289) and "Pontacyl" Fast Red A. S. (Color Index 176), while direct dyes such as "Pontamine" Blue RW (Color Index 512) and the red dye obtained by Example I of U. S. Patent No. 1,940,683 were used, the dyeing time being 5 minutes for acid dyes and 7 minutes for direct dyes.

Example VI

An aqueous slurry containing about 40% of the synthetic polyamide described in Example I was prepared in the manner described in Example III. Ten grams of this slurry were then thoroughly mixed with 240 grams of a 15% solution of cellulose acetate (acetic acid content 54.5%) in acetone. The mixture was then spun by an electrical spinning process, such as described in Formhals U. S. Patent No. 1,975,504, into filaments of modified cellulose acetate yarn.

The finished yarn was dyed according to the procedure set forth in Example III, using "Pontamine" Fast Red 8 BL (Color Index 278). The yarn was found to be quite receptive to this dye for which normal cellulose acetate yarn had no affinity whatsoever.

In order to effectively improve the dye affinity of the structure-forming material, the synthetic polyamide may be added to the spinning or casting composition in concentrations as high as 30% or even more, based on the weight of the structure-forming material present. In general, however, it has been found that concentrations ranging from 5% 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 synthetic polyamide, increased depth of dyeing is frequently offset by weakening of the structure so that from the practical standpoint, it is advisable to use no more of the synthetic polyamide than is necessary to obtain the depth of color desired.

Film or filament structures of the type described which have been prepared in accordance with the present invention have been found to have particularly improved affinity for so-called "direct" dyes, "acid" dyes, "developed" color dyes, "chrome" dyes and "vat" dyes. The affinity of structures for other dyes will also be improved.

As illustrative examples of the above-mentioned classes of dyes for which the structures of the present invention have a satisfactory affinity may be mentioned:

Direct dyes

Name	Color index
"Pontamine" Blue RW	512
"Pontamine" Sky Blue 6BX	518
"Pontamine" Yellow CH	365
"Pontamine" Green BX	593
"Pontamine" Orange R	415
The red dye obtained by Example I of U. S. Patent No. 1,940,683	

Acid dyes

Name	Color index
"Pontacyl" Wool Blue BL	833
"Pontacyl" Fast Red AS	176
"Pontacyl" Violet C4B	698
"Pontacyl" Fast Blue 5R Conc	289
"Pontacyl" Green NV Conc	735
Du Pont Anthraquinone Blue SKY	1088
Du Pont Anthraquinone Blue B	1054
Du Pont Anthraquinone Rubine R Conc	1091

Developed color dyes (diazo dyes)

"Pontamine" Diazo Black BHSW Conc. (Color Index 401).

The blue trisazo dye disclosed in U. S. Patent No. 648,623.

Also "Developed" dyes having Color Index Nos. 317, 654, and 552.

Chrome dyes

"Pontachrome" Blue R (Color Index 179).

Du Pont Chromate Brown EB (Color Index Pr 12).

Also chrome dyes having Color Index Nos. 216, 40, 299, and 302.

Vat dyes

"Sulfanthrene" Orange R (Color Index 1217).

"Ponsol" Jade Green Double Paste (Color Index 1101).

"Ponsol" Blue GD Double Paste (Color Index 1113).

"Sulfogene" Carbon (Color Index 978).

"Sulfogene" Direct Blue, BN (Color Index 956).

"Sulfogene" Brilliant Blue 2G (Color Index 951).

"Sulfogene" Navy Blue 4RCS (Color Index 959).

"Sulfogene" Bordeaux 5B (Color Index 1012).

Also vat dyes having Color Index 1095.

Other dyes

Basic dyes such as Methylene Blue (Color Index 922) and Rhodamine B (Color Index 749) may be used.

Basic substituted anthraquinone dyestuffs, commonly used to dye unmodified cellulose acetate rayon, such as the red dye 1-methylamino-anthraquinone, the yellow dye 1-nitro acridone, the blue dye 1.4.5.8-tetra-amino-anthraquinone, the red-violet dye 1.4-diamino-anthraquinone, as well as such dyes as the orange dye 4-nitro-4'-amino-azobenzene may be used. Likewise, dyes of the type of 1-amino-4-arylamino anthraquinone-2-sulphonic acid may be useful.

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.

It is understood, of course, that the structures provided by this invention may be dyed in accordance with any of the customary procedures employed in the dyeing art for the particular type of dye chosen.

In those cases where the film or filament structure comprises a substantially water-insensitive material such as cellulose acetate or a conjoint polymer of vinyl chloride and vinyl acetate or an interpolymer of vinyl chloride and methyl methacrylate, the dyeing process can be expedited by including in the dye bath a small amount of a solvent or swelling agent for the structure-forming material. Thus, for example, a small amount of methyl Cellosolve or acetone added to the aqueous dye bath will facilitate the dyeing of a cellulose acetate structure modified in accordance with the present invention. It is readily understood, of course, that this is not a question of the effectiveness of the dye modifying ingredient, but obviously since the cellulose acetate, for example, is water-insensitive and since the dye bath is an aqueous medium, the ability of the dye to enter the film or filament structure is probably of a low degree. The addition of the solvent or swelling agent serves to facilitate the entry of the dye into the structure so that the color can be retained by the dye modifying agent described herein.

It is apparent that this invention considerably widens the range of dyestuffs available for use with regenerated cellulose and with cellulose derivative structures. It enables the dyeing of structures comprising synthetic resinous film- or filament-forming materials, such as the polymerized vinyl compounds, methacrylic acid esters and the like with dyestuffs which have comparatively little or no affinity for materials in their unmodified form. It enables the dyers to use 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. The materials are definitely non-volatile and, therefore, resist removal by heat as in ironing operations. The synthetic linear polyamides are of relatively high molecular weight so that they are slow to diffuse from the fiber thus offering stability and fastness.

By means of this invention synthetic filaments and yarns may be made into threads which can be mixed with wool, cotton, regenerated cellulose and the like and satisfactory dye results secured with any desired class of dye. Fabrics made from 100% cellulose derivative yarns or synthetic resinous yarns may be simply and inexpensively dyed with the desired dyestuff. In artificial structures such as sponges, for example, those made from viscose, the invention finds particular application. In such structures, properties of luster, transparency, etc., are very much subordinate to dye receptivity and this invention offers opportunity for use of a large variety of dyes.

Since it is obvious that many changes and modifications can be made in the above-described procedures 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. Regenerated cellulose films and filaments dyed with an acid dyestuff and containing, as an agent for promoting the affinity of said films and filaments for said acid dyestuff, 5% to 20% of finely divided discrete particles of a synthetic linear polyamide, taken from the class consisting of amino acid polyamides which, upon prolonged heating with a dilute mineral acid, are hydrolyzed yielding the monomeric amino-acid from which

they were derived, and diamine-dibasic acid polyamides which, upon heating with a strong mineral acid, are hydrolyzed to the dibasic acids and diamines from which they were derived, said polyamide having recurring structural units containing amide groups, the structural units having a unit length of at least 7, said films and filaments exhibiting a uniform coloration throughout the body thereof.

2. Regenerated cellulose films and filaments dyed with an acid dyestuff and containing, as an agent for promoting the affinity of said films and filaments for said dyestuff, 5% to 20% of finely divided discrete particles of a synthetic linear polyamide having an intrinsic viscosity not to exceed 0.6, said polyamide taken from the class consisting of amino acid polyamides and which upon prolonged heating with a dilute mineral acid, are hydrolyzed yielding the monomeric amino-acid from which they were derived, and diamine-dibasic acid polyamides which, upon heating with a strong mineral acid, are hydrolyzed to the dibasic acids and diamines from which they were derived, said polyamide having recurring structural units containing amide groups, the structural units having a unit length of at least 7, said films and filaments exhibiting a uniform coloration throughout the body thereof.

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