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DRY SPUN AND DRY CAST STRUCTURES OF
SYNTHETIC MATERIALS

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This invention relates to the manufacture of products such as filaments, yarns, ribbons, and films comprised of synthetic polymeric material. More particularly, it relates to the improvement in the dyeing characteristics of filaments, yarns, ribbons, films and the like made by the dry or evaporative spinning or casting of synthetic film- and filament-forming, water-insensitive, synthetic polymeric materials such as cellulose esters, cellulose ethers, polyvinyl acetals, polystyrenes, methacrylate polymers, etc.

Products resulting from the dry spinning or dry casting of synthetic polymeric materials, particularly the cellulose organic derivatives such as cellulose acetate, cellulose propionate, cellulose butyrate, methyl cellulose, ethyl cellulose, and mixed cellulose esters, ethers and ester-ethers, which are water-insensitive, i. e. do not swell appreciably in water, have little or no affinity for direct dyes commonly used in dyeing cotton and regenerated cellulose, or for acid and chrome dyes commonly used to dye wool.

This fact is of especial concern in the textile field because the dyes which do satisfactorily dye these synthetic polymer materials do not dye cotton, wool or regenerated cellulose, and where, as is often the case, one of the water-insensitive synthetic polymer materials is combined with wool, cotton or regenerated cellulose to form a mixed fabric, uniform dyeing of such fabric is a desideratum difficult to realize even by using two dye baths, one for dyeing the water-insensitive synthetic polymeric material and one for the natural fibers. Furthermore, the dyes and dyeing processes useful in the coloring of the water-insensitive synthetic polymers are very costly in comparison with the acid, direct, and chrome dyeing of natural and artificial textile materials.

It is therefore desirable that the dyeing affinities of organic derivatives of cellulose and like film- and filament-forming materials be modified to render them susceptible to satisfactory dyeing with acid, direct and chrome dyes. A great number of expedients for the purpose, heretofore employed, involve chemical modification of the polymer to a point where wanted characteristics are often sacrificed. Other expedients effect only physical modification and are based on the well known fact that the yarn, e. g. cellulose acetate yarn, is readily dyed while in the gel state, i. e. before the cell walls of the filaments thereof have collapsed and formed a barrier against penetration of the dye solution. Of these latter proposals those which involve incorporation in the filament structure of soluble inert substances

which operate to prevent collapse of the cell walls, and those which involve incorporation in the filament structure of substances such as basic nitrogen-containing compounds which operate as dye acceptors, have shown considerable promise. In practice these substances are added to the filament- or film-forming solutions. However, experience has shown that in yarns formed by the dry spinning technique, inert substances in amounts of the order of 75% to 100% or more, based on the weight of cellulose acetate, must be contained in the formed filaments in order to achieve satisfactory dye receptivity. Such a high percentage of inert material serves to so weaken the yarn during processing that it is of reduced commercial value. Dry spun yarns of cellulose acetate containing only basic nitrogen-containing compounds in amounts of the order of 5 to 20% may be dyed deeply and uniformly but the fastness of such dyeings to light is generally poor.

In order to overcome to some extent the limitation attending dry spun yarns containing a very high percentage of a water-soluble substance, it has been further proposed to after-treat the yarn in one or more aqueous baths to dissolve out the inert substance and to replace it by a very much smaller amount of a material that acts as a dye acceptor. Suitable replacement materials are the protein-like compounds or synthetic polymeric compounds containing amino nitrogen and other compounds containing basic nitrogen groups. By this procedure, it is possible to produce a yarn which, instead of consisting of only 50% of the polymeric filament- or film-forming substance, consists in the neighborhood of 90 or 95% of the polymeric product and because of this substantial replacement of the bulk agent and condensation of the structure prior to forming it into fabrics, generally improved fabrics can thus be produced. The carrying out of this process, however, is necessarily expensive in view of the time and equipment needed to satisfactorily after-treat the formed filaments.

I have now found that, in spite of all the difficulties arising from prior methods of altering the affinity for water-insensitive synthetic polymeric structures to accept acid, direct and chrome dyestuffs, a certain combination of these prior proposals, when properly combined, will enable cellulose organic derivative yarns, ribbons, films and the like, and structures of other water-insensitive synthetic polymers to be produced which have good affinity for acid, direct and chrome dyestuffs, which dyeings will be reasonably fast to washing and light fading.

An object of this invention, therefore, is to provide dry spun or cast structures of water-insensitive filament- or film-forming synthetic polymers which have good affinity for acid, direct, and chrome dyestuffs.

A further object is to provide a process for conferring on dry spun or cast structures of water-insensitive filament- or film-forming synthetic polymers, affinity for acid, direct and chrome dyes.

A still further object is to form dry spun yarns of cellulose organic derivatives which can be dyed with acid, direct and chrome dyes.

These and other objects will more clearly appear hereinafter.

These objects are accomplished by my invention which comprises incorporating in a spinning or casting liquid from which structures of water-insensitive filament- or film-forming synthetic polymers are formed, mutually compatible constituents comprising (1) a bulk agent soluble in the spinning or casting liquid and also soluble in a convenient after-treating liquid which is not a solvent for said polymers, and (2) a substance containing basic trivalent nitrogen, also soluble in the spinning or casting liquid. The filament or film is formed in the usual way by the dry or evaporative method, and the bulk agent is subsequently removed just prior to or during the dyeing operation, by the action of the after-treating liquid in which the bulk agent is soluble.

By the term "bulk agent" is meant any relatively nonvolatile inert impregnant which can fill the capillaries or spaces between molecules or crystallites of the synthetic polymer and prevent substantial collapse of the walls enclosing these spaces on drying of the filament or film.

As a matter of convenience, the invention will be further described with specific reference to cellulose acetate as the water-insensitive filament- or film-forming synthetic polymer, it being understood that the invention is applicable as well to all members of the broad class heretofore described.

Glycol polyformal (molecular weight from 400 to 1000) constitutes the preferred bulk agent for purposes of this invention.

Representative suitable compounds containing basic trivalent nitrogen for combining with the bulk agent in the solution are tetraethylene pentamine, "Hyamine H" (a nitrogenous basic substance marketed by Röhm and Haas Co.), phenol-formaldehyde-aminocaproic acid resin, dimethylaminoethyl methacrylate polymer, diethylaminoethyl methacrylate polymer, hexose amine polymers such as deacetylated chitin, piperidyl-N-ethyl methacrylate polymer, dicyclohexylaminoethyl methacrylate polymer, the reaction product of meta-cresol, formaldehyde and dimethylamine, the reaction product of tertiary amyl phenol, formaldehyde and dimethylamine, diethanol methylamine succinate condensation polymer and diethanol methylamine phthalate condensation polymer. While most of these compounds are water-insoluble, some few of them, e. g. tetraethylene pentamine, are water-soluble, and where a water-soluble basic trivalent nitrogen-containing compound is employed for purposes of this invention prolonged soaking of the dried yarn containing such a compound in water or in aqueous scouring liquid prior to dyeing must of course be avoided, since prolonged soaking or scouring before dyeing would result in leaching out of the dye acceptor compound from the yarn, before the dye acceptor has reacted with the dye

whereby to form an insoluble color compound within the filament structure.

The amount of bulk agent incorporated in the spinning or casting liquid may range from about 10% to about 60% of the amount of the cellulose acetate in the spinning liquid. In itself, this amount of agent would not give to the yarn or other structure produced from such a solution any substantial affinity for acid, direct or chrome dyestuffs. However, when used in combination with from about 0.5% to about 10% of a basic trivalent nitrogen-containing compound, based on the cellulose acetate, such as a compound containing amino nitrogen, the structure formed therefrom by the dry or evaporative method may subsequently be dyed to full shade with any of the common acid, direct or chrome dyestuffs. Again, if the basic trivalent nitrogen compound were used alone and only in the concentrations needed for the purposes of this invention, then the structure produced therefrom would also lack sufficient affinity for direct, acid and chrome dyestuffs to permit dyeing to full shades.

The following examples further illustrate the invention. Parts are by weight.

Example I

A cellulose acetate spinning solution was prepared by dissolving 12 parts of cellulose acetate (containing about 54.5% combined acetic acid) in 90 parts of acetone and to this solution was added 0.10 part of tetraethylene pentamine and 3.0 parts of glycol polyformal (molecular weight 463). After thoroughly mixing, deaerating and filtering, the solution was spun by an electrical spinning process such as described in U. S. Patent No. 1,975,504 (Formhals) to produce discontinuous fibers. These fibers were of good quality and contained about 0.8% tetraethylene pentamine and about 25% glycol polyformal, based on the cellulose acetate. Deep, uniform and fast dyeings were obtained with a number of direct, acid and chrome dyestuffs including "Pontamine" Fast Red 8BL, "Pontacyl" Carmine 2G, "Pontacyl" Light Yellow GX, "Pontacyl" Violet RL, "Pontacyl" Carmine 2B, Du Pont Anthraquinone Blue SWF, Du Pont Orange G, Du Pont Brilliant Milling Blue B, Du Pont Brilliant Milling Green B, Du Pont Milling Yellow GN, and "Pontachrome" Azure Blue B.

Example II

A solution comprised of 22.2 parts of acetone-soluble cellulose acetate, 80 parts of acetone, 7.5 parts of glycol polyformal (425 molecular weight), and 0.3 part of dimethylaminoethyl methacrylate polymer was dry cast on a plate to form a film. This film had good affinity for typical acid and direct dyestuffs. When the amount of dimethylaminoethyl methacrylate polymer was increased to 0.6 part, the other ingredients of the solution remaining the same, a film which dyed to full deep shades with acid and direct dyestuffs was obtained. In the absence of glycol polyformal in the film and even though the concentration of dimethylaminoethyl methacrylate polymer therein was 2%, films thus produced showed very little dye affinity for the acid and direct dyestuffs. Likewise films containing 1 part of glycol polyformal to 3 parts of cellulose acetate and no dye acceptor showed very little dye affinity, and not until the amount of glycol polyformal was increased to equal parts with the cellulose acetate (without a dye acceptor) could excellent dye

affinity for acid, direct and chrome dyestuffs be obtained.

Although this invention has been specifically described in terms of producing cellulose acetate structures of the acetone-soluble type, it is also applicable to the modification of cellulose acetates of other combined acetic acid values, such as substantially completely acetylated cellulose, commonly termed "cellulose triacetate." The invention is also applicable to other cellulose esters, such as cellulose propionate, cellulose butyrate, mixed esters such as cellulose acetate butyrate, cellulose acetate propionate and the like; cellulose ethers such as methyl cellulose, ethyl cellulose, benzyl cellulose, mixed ethers such as methyl benzyl cellulose, mixed ether esters such as ethyl cellulose acetate, and other similar organic derivatives of cellulose which are organic solvent-soluble. Furthermore, other water-insensitive polymeric filament- or film-forming materials may be modified in accordance with this invention; for instance, polyvinyl acetals and other polyvinyl products, polystyrene, methacrylate polymers and the like.

In addition to improving the dye receptivity of dry spun or dry cast structures of water-insensitive synthetic polymers, the present invention can be employed with advantage to facilitate incorporation in such structures of plasticizers, resins, resin-forming ingredients, lubricants or any other of the agents commonly employed to improve and modify the characteristics of yarns, films and the like. For example, the desired agent is most conveniently and effectively introduced into the structure while it is still in a porous condition, i. e. immediately after the bulk agent has been removed and before the resultant porosity is substantially reduced by drying.

Structures of water-insensitive filament- and film-forming synthetic polymers are modified in accordance with this invention without substantial sacrifice of essential physical properties; tenacity, for instance, being at least one gram per denier in the case of modified filaments and fibers of cellulose acetate. Also, the volume shrinkage due to the elimination of the bulk agent by after-treatment prior to dyeing is not excessive as in the case of prior art treatments involving the use of bulk agents. Furthermore, because of the relatively small amount of basic trivalent nitrogen compounds present, the dyed structures are not subject to excessive fading when exposed to sunlight and yet have excellent affinity for acid, direct and chrome dyes.

I claim:

1. In the process wherein filaments, yarns, ribbons, films, and like structures are formed by the dry or evaporative method from a liquid containing a water-insensitive filament- and film-forming synthetic polymeric material and thereafter

dyed, the improvement which comprises adding to said liquid (1) from about 10% to about 60% by weight, based on the weight of said polymer, of glycol polyformal (molecular weight from 400 to 1000), and (2) from about 0.5% to about 10% by weight of a basic trivalent nitrogen-containing compound soluble in said liquid, whereby said structures are rendered receptive to direct, acid and chrome dyes.

2. In the process wherein filaments, yarns, ribbons, films, and like structures are formed by the dry or evaporative method from a liquid containing a cellulose organic ester and thereafter dyed, the improvement which comprises adding to said liquid (1) from about 10% to about 60% by weight, based on the weight of said cellulose organic ester, of glycol polyformal (molecular weight from 400 to 1000), and (2) from about 0.5% to about 10% by weight of a basic trivalent nitrogen-containing compound soluble in said liquid, whereby said structures are rendered receptive to direct, acid and chrome dyes.

3. In the process wherein filaments, yarns, ribbons, films, and like structures of cellulose acetate are formed by the dry or evaporative method from a solution of cellulose acetate in an organic solvent, the improvement which comprises adding to said solution from about 10% to about 60% by weight, based on the weight of cellulose acetate, of glycol polyformal (molecular weight from 400 to 1000), and from about 0.5% to about 10% by weight of a basic trivalent nitrogen-containing compound soluble in said solvent whereby said structures are rendered receptive to direct, acid and chrome dyes.

4. The process of claim 3 wherein the basic trivalent nitrogen-containing compound is tetraethylene pentamine.

5. As new articles of manufacture filaments, yarns, ribbons, films, and like structures comprised essentially of (1) water-insensitive filament- and film-forming synthetic polymeric material, (2) from about 10% to about 60% by weight, based on the weight of said polymer, of glycol polyformal (molecular weight from 400 to 1000), and (3) from about 0.5% to about 10% by weight of a basic trivalent nitrogen-containing compound, said structures having an affinity for acid, direct and chrome dyes.

6. As new articles of manufacture filaments, yarns, ribbons, films, and like structures comprised essentially of (1) cellulose acetate, (2) about 10% to about 60% by weight, based on the weight of cellulose acetate, of glycol polyformal (molecular weight from 400 to 1000), and (3) from about 0.5% to about 10% by weight of tetraethylene pentamine, said structures having an affinity for acid, direct and chrome dyes.

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