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DYEING OF ACRYLIC FIBERS WITH VAT DYESTUFFS

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This invention relates to the dyeing of polyacrylic fibers and more particularly to a process of dyeing fibers having a basis of polyacrylonitrile with vat dyestuffs and to the products produced thereby.

Synthetic fibers of the acrylonitrile type cannot be colored by conventional methods by vat dyestuffs from an alkaline vat as is used for cotton and other cellulosic materials. The yields produced thereby are negligible or so low as to make such methods uneconomical. It has been proposed to dye acrylonitrile yarns with a limited range of vat colors of the indigoid type in a special pressure machine operating at temperatures of 270 to 275° F. However, such a method involves complicated and expensive apparatus and procedures and is, therefore, to that extent undesirable.

It is an object of this invention to produce colorations of vat dyestuffs on polyacrylonitrile fibers in a full range from light to dark shades having excellent light fastness, wash fastness, crock fastness and the like. Another object is to provide a new process for dyeing polyacrylonitrile fibrous material with vat dyestuffs. A further object is to provide polyacrylonitrile fibrous material dyed with vat dyestuffs in good shades having excellent fastness and other properties. Other objects and advantages will appear as the description proceeds.

The accomplishment of these objects is made possible by the instant invention which broadly comprises impregnating the fiber with an acidified vat (i. e., an acid reacting aqueous colloidal dispersion of the leuco compound of a vat dyestuff, as produced, for example, by acidifying an aqueous alkaline vat as ordinarily applied for producing vat colorations on cellulosic fibers and containing a dispersing agent which is effective in the presence of acids), drying the fiber thus impregnated and then subjecting the fiber to a dry heat treatment for a short period of time. Shades may thus be obtained of any desired depth having excellent light fastness, wash fastness, and crock fastness.

The heat treatment of the fiber padded with an acid leuco vat dye dispersion in accordance with this invention can be carried out by radiation (e. g., by exposing the material to infrared rays), by convection (e. g., by exposure of the material to circulating hot air or other gases), or by conduction (e. g., by passage over a heated surface or immersion in a heated water-immiscible liquid) or by any combination thereof. Advantageously, the fiber is subject to heat treatment at a suitable temperature employing infrared rays, circulating hot gasses or heated rollers or by temporarily immersing the fibers in or passing them through a molten oil or metal bath maintained at the desired temperature. The impregnating or padding operation and the drying and heating treatments can be conveniently carried out in a continuous manner on piece goods, warps, slubbing, yarns, filaments, fibers, and the like, by progressively passing such material through padding equipment and a heating zone or apparatus.

The drying operation after the impregnation or padding may be carried out as a separate operation or may be effected in the same operation as in the heat treatment, in which case, of course, the fibers are first dried in the initial stage of the heat treatment for a suitable time and at a suitable temperature range. The duration of the dry heat treatment will, of course, be dependent upon the particular temperature employed, the nature of the fiber being treated (heat resistance, melting point, sticking temperature, etc.) and the like. In general, temperatures

of about 300° F. to about 400° F. are operative and durations of treatment may range from about ten seconds to about two minutes. Where the fiber contains other components besides the polyacrylonitrile which may tend to lower its heat resistance, lower temperatures should be utilized for longer periods of time.

The instant invention is applicable to fibrous materials having a basis of polyacrylonitrile in any suitable form as, for example, in the form of staple or continuous filaments, yarns, slubbings, warps, fabrics, and the like. The fiber content may be composed principally of acrylonitrile homopolymer, or of heteropolymers of acrylonitrile and up to about 5 to 15 per cent by weight of other polymeric material such as vinyl chloride or acetate, styrene, methacrylic acid, chloracrylic acid, and their amides, chlorides, nitriles and the like. Various modifying agents such as plasticizers, stabilizers, pigments, and the like may be present for their known functions. Suitable fibrous material may be obtained under the designation of Orlon, Chemstrand and the like.

Almost any vat dye (e. g., of the quinoid or indigoid series) can be used in the process of this invention. Acid aqueous dispersions of the corresponding leuco compounds, as employed for padding the acrylonitrile fiber in accordance with the invention, are prepared by vatting the dyestuff in an aqueous alkaline solution with an alkali metal hydrosulfite or equivalent reducing agent, incorporating therein a dispersing agent effective in acid solution, and acidifying the resulting alkaline vat to adjust the pH to a range of 2 to 5. Suitable dispersing agents are, especially, surface-active water-soluble sulfonic acids such as alkyl aryl sulfonates, e. g., higher alkyl benzene sulfonates, sulfonated condensation products of naphthalene and formaldehyde or their homologues, isopropyl- and isobutyl-naphthalene sulfonates, and aliphatic or alicyclic sulfonates such as N-oleyl-N-methyl taurine, higher alkyl esters (e. g., the dioctyl ester) of sulfosuccinic acid, sulfonated rosin or its derivatives, and lignin sulfonates. Generally, about 20 to 50% or more of the dispersing agent is employed by weight of the dyestuff paste. Acids employed for acidification of the alkaline vat are preferably organic acids such as acetic or formic acids, although other acids can be used to adjust the pH to the aforesaid range.

When the padded material is heat treated by immersion in, or passage through, a molten bath, metals or alloys suitable for use are those liquid at the temperature of the heat treatment. The latter metals and alloys can be used without difficulty from local solidification of the metal, not only in the treatment of predried materials but also with moist padded materials. A suitable alloy for this purpose is Wood's metal, composed of 50% bismuth, 25% lead, and 12.5% each of tin and cadmium. Other bismuth-lead alloys containing tin and/or cadmium are also known which are liquid at the temperatures to be employed herein, and can be used in place of Wood's metal.

Peculiarly enough, the instant process does not require separate or subsequent reducing or oxidizing treatments. The oxidation may here be considered as in the nature of a dehydrogenation of the free leuco form of the dyestuff and the vat dyestuff is oxidized and fixed by the dry heat treatment described above. Inasmuch as a vat acid padded liquor can be only of a limited concentration varying with the particular dyestuff employed, heavy shades can be obtained by padding through the same liquor two or more times with intermediate drying.

The following examples are illustrative of the instant invention and are not to be regarded as limitative:

Example 1

10.0 g. of Indanthrene Black BBN double paste (C. I. 1102) were vatted with 2.75 g. NaOH and 3.0 g. $Na_2S_2O_4$ in the presence of 5.0 g. of a dispersing agent such as naphthalene sodium sulfonate condensate (Blancol) in a volume of 200 ml. H_2O for five minutes at 130–140° F. The resulting alkaline vat was converted to the acid vat with 17 ml. CH_3COOH 28% diluted to 50 ml. with H_2O.

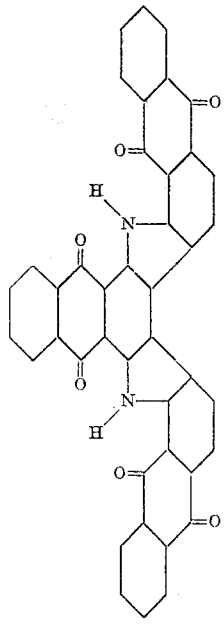
This vat was then heated to 150–160° F. and padded onto a fabric constructed of 100% polyacrylonitrile filament containing the usual modifying agents, dried and

subjected in an oven to a dry heat setting operation of one minute at 350° F.

The dyeing was then scoured with synthetic detergent. The finished product exhibited good light, wash and crock fastness.

Example 2

10.0 g. 2,3'-3,2''-trianthraquinonyl-1,4'-4,1''-diimid of the formula



were vatted in the same manner as in Example 1. Subsequent operations also were identical.

The finished dyeing possessed good light, wash and crock fastness.

Example 3

5.0 g. of the vat dyestuff in Example 1, 4.0 g. dimethoxy Violanthrone (Schultz No. 1269) and 2.0 g. Indanthrene Golden Orange G double paste (C. I. 1096) were vatted with 2.75 g. NaOH and 3.0 g. $Na_2S_2O_4$ in the presence of 5.0 g. of a dispersing agent as in Example 1. Subsequent operations to obtain the acid vat were also the same. The resulting vat acid pad liquor was padded onto a polyacrylonitrile Taffeta fabric twice with intermediate drying. The dyeing was heat set in an oven at 350° F. for one minute and then scoured with synthetic detergent. A heavy shade was obtained of good wash fastness.

Various modifications and variations of this invention will be obvious to a person skilled in the art, and such variations and modifications are to be regarded as within the purview of this application and the spirit and scope of the appended claims.

I claim:

1. A process for dyeing fibrous materials which comprises impregnating said material, the fiber content of which is composed of at least 85 per cent by weight of polyacrylonitrile, with an acid reacting aqueous dispersion of a pH of 2 to 5 of the leuco compound of a vat dye and subjecting the impregnated material to dry heat at a temperature of about 300 to 400° F. for a period ranging from about ten seconds to two minutes.

2. A process for dyeing fibrous material which comprises impregnating said material, the fiber content of which is composed of at least 85 per cent by weight of polyacrylonitrile, with an acid reacting aqueous dispersion of a pH of 2 to 5 of the leuco compound of a vat dye, drying the impregnated material and then subjecting said dried material to dry heat at a temperature of about 300 to 400° F. for a period ranging from about ten seconds to two minutes.

3. The process of claim 2 wherein the said aqueous dispersion is prepared by acidifying an aqueous alkaline vat of the vat dyestuff containing an aromatic sulfonate dispersing agent with an organic acid in sufficient amount to yield a pH of from 2 to 5.

4. A process for dyeing fibrous material which comprises impregnating said material, the fiber content of which is composed of at least 85 per cent by weight of polyacrylonitrile, with an acid reacting aqueous dispersion of a pH of 2 to 5 of a leuco compound of a vat dye, drying the impregnated material and then subjecting said material to a dry heat treatment at about 350° F. for about one minute.

5. The process of claim 4 in which before said drying step said fibrous material is twice impregnated with said dispersion with intermediate drying.

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