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DYEING SYNTHETIC FIBERS WITH VAT DYESTUFFS

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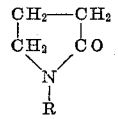
This invention relates to the dyeing of synthetic fibrous materials, and more particularly to the dyeing of polyacrylonitrile and synthetic linear polyester fibers with vat dyestuffs.

The dyeing of fibrous materials having a basis of polyacrylonitrile or synthetic linear polyesters has for some time been a problem encountered by workers skilled in the art. Various methods and expedients have been proposed for producing dyeings on such fibrous material but the results have not been completely satisfactory. This has been particularly true with respect to attempts made to dye such fibrous material with vat dyestuffs. These fibers are well known for their relatively hydrophobic nature whereby an aqueous treatment bath may wet the fibers superficially but has difficulty penetrating the inside of the fiber. Accordingly, conventional methods for dyeing cotton and other cellulosic materials with vat dyestuffs from an alkaline vat cannot be employed.

It is an object of this invention to produce acceptable dyeings with vat dyestuffs on fibrous material having a basis of polyacrylonitrile or synthetic linear polyesters. Another object of this invention is the provision of a vat dyestuff composition useful for dyeing such fibrous material. Other objects and advantages will appear as the description proceeds.

The above objects are attained by the instant invention which is based upon the discovery that an aqueous dyebath containing a member of the group consisting of sulfuric acid ester salts of leuco vat dyestuffs and vat dyestuffs in free anthrol (acid vat) form, and about 5 to 20% by weight (of the dyebath) of an N-lower alkyl-2-pyrrolidone produces commercially acceptable and highly improved pad dyeings on the aforementioned fibrous material. Accordingly, in addition to the aforementioned aqueous dyebath, the instant invention includes the improvement comprising employing such a dyebath for pad dyeing in known manner fibrous material composed of at least 75% by weight of a member of the group consisting of polyacrylonitrile and synthetic linear polyesters.

The n-lower alkyl-2-pyrrolidones employed in the dyebaths of the instant invention have the formula



wherein R is an alkyl radical of from 1 to 4 carbon atoms such as ethyl, propyl, isopropyl, butyl, isobutyl and especially methyl. Such pyrrolidones and their methods of production are well known in the art and no claim is made thereto per se. The use of these compounds in the instant invention enables the attainment of more uniform and stable dyebaths, of higher concentrations, in addition to more uniform and level dyeings in pastel to medium light shades of high quality, as determined by such properties as fastness to light, washing and dry cleaning. While the exact mechanism of their function in achieving these improved results is not fully understood, it is believed that such results are attributable to the hydrotropic character of such compounds and their plasticizing action on the fibers during the dyeing operation.

The sulfuric acid ester salts of leuco vat dyestuffs employed in the instant invention are also well known in the art, being in general available on the market under, for example, the trade mark "Algosol" (General Aniline & Film Corporation). They may be made by various methods and with the use of various assistants disclosed in the prior art. The alkali metal salts, such as those of sodium and potassium, are usually preferred, although other water soluble or readily water dispersible salts may be employed such as those with triethanolamine and the like. Illustratively, the sulfuric acid ester salts of the following vat dyestuffs, indentified in A.A.T.C.C. 1953, may be employed in accordance with this invention. The term "A.A.T.C.C." refers to the Technical Manual and Year Book of the American Association of Textile Chemists and Colorists.

	Prototype No.	C.I. No.
Algosol Olive IT	547	
Algosol Olive Green IB	293	
Algosol Brown IBR	118	
Algosol Blue IBC Paste		1113
Algosol Golden Orange IRR		1098
Algosol Brilliant Orange IRKL	1116	
Algosol Red IFBB	296	
Algosol Green IBW Paste		1101
Algosol Yellow GCA	9	

Similarly, the free anthrol or acid vat form of vat dyestuff employed in the instant invention may be made in a manner well known in the art. As with Algosols, almost any vat dye (e.g. of the quinoid or indigoid series) can be employed for their production. Thus, acid aqueous dispersions of the corresponding leuco compounds may be 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 adjusting with acid to a neutral or acid pH. Suitable dispersing agents are, especially surface active water-soluble sulfonic acids such as alkylaryl sulfonates, e.g. higher alkylbenzene sulfonates, sulfonated condensation products of naphthalene and formaldehyde or their homologs, 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 of the aforesaid range.

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, fibers, and the like. The fiber content may be composed principally of acrylonitrile homopolymer or of heteropolymers of acrylonitrile and up to 25% by weight of other polymeric material such as vinyl chloride or acetate, styrene, methacrylic acid, chloroacrylic acid, and their amides, chlorides, nitriles and the like. Other modifying agents may of course be present in the fiber. Such materials, and their methods of production are disclosed for example in U.S. Patents 2,527,863, 2,548,282, 2,558,735, 2,595,848, etc. Exceptionally good results are obtained in dyeing fibrous

materials having a basis of polyacrylonitrile as available on the market under the trade marks Acrilan (Chemstrand Corporation) and Orlon (du Pont). Exceptional results are attained with Orlon 81 fiber.

Fibrous materials having a basis of synthetic linear polyesters which may be dyed in accordance with the instant invention, and their methods of production are also well known in the art. Such polyester fibers are generally linear condensation polymers of terephthalic acid (or an ester-forming functional derivative thereof) with a polymethylene glycol (preferably ethylene glycol) having up to 10 methylene groups in a chain interconnected to terminal hydroxy groups. Modified or plasticized variations of these fibers may of course also be employed which contain up to 25% of other substances or copolymerized materials, e.g., linear polyesters of ethylene glycol and terephthalic acid (polyethylene terephthalate) which have been modified by the addition of up to 10% of other glycols and/or dibasic acids or which have been mixed with other materials such as plasticizers, modifiers, etc. Such fibrous materials are available on the market under the trade marks Terylene, Dacron, Fiber V (du Pont), etc.

As stated above, the improved aqueous dyebaths containing the N-lower alkyl-2-pyrrolidone are employed in dyeing the aforementioned fibrous materials in accordance with the known pad dyeing processes used in applying the aforementioned forms of vat dyestuffs. In preparing the pad liquor, the N-lower alkyl-2-pyrrolidone is generally introduced into the aqueous dyebath after the leuco ester salt has been dissolved therein or the acid vat has been made, as the case may be. Alternatively, a previously prepared concentrate of suitable leuco ester salt and N-lower alkyl-2-pyrrolidone, with or without water and/or solubilizing or dispersing assistants, may be employed for producing the pad liquor. Since the process does not operate by exhaustion and the rate of pickup after the squeeze rolls is relatively low being of the order of from about 25 to 60% of liquor by weight of fiber, the concentration of the dyestuff in the dyebath must be selected accordingly to give the desired depths of shade. In general, from about 1 to 8 oz. of dyestuff (as commercially available) per gallon (about 0.75–6.0% by weight) of pad liquor is sufficient to achieve the desired results. Within the above-mentioned range of about 5 to 20% by weight of N-lower alkyl-2-pyrrolidone, lower proportions are usually necessary when employing pad liquors containing the acid vats as compared with pad liquors containing the leuco ester salts. In general, about 5 to 15% is sufficient for pad dyeing with the acid vat form of dyestuff, while about 12 to 20% is usually desirable for pad dyeing with the leuco ester salt. Oxidizing agents effective for converting the above-mentioned dyestuffs to the final keto form may be added to the above-mentioned pad liquors or may be applied in a subsequent developing step. It will accordingly be understood that the process of the instant invention is based solely upon the use, in the known processes, of a pad liquor containing the above-mentioned forms of vat dyestuffs and an N-lower alkyl-2-pyrrolidone for dyeing the above-mentioned fibrous materials, and that such invention may be employed in conjunction with known dye and development assistants, manipulative procedures, and the like. Highly advantages results have for example been obtained by employing the pad liquors of the instant invention in the processes disclosed and claimed in U. S. Patents 2,627,449 and 2,695,832.

The following examples, in which parts are by weight unless otherwise indicated are illustrative of the instant invention and are not to be regarded as limitative.

Example 1

An aqueous pad liquor is prepared by dissolving Algosol Red IFBB in hot water in proportions of 1.5 oz. per gallon. N-methyl-2-pyrrolidone is then mixed into the dyebath in proportions of about 1.3 lbs. per gallon. Sodium nitrite in proportions of about 1 oz. per gallon is then dissolved in the dyebath and a strip of polyacrylonitrile fabric (Orlon 81) is padded with the resulting dye liquor at 140 to 150° F., and dried. The dyeing is then developed by passing the fabric through a 2% sulfuric acid solution (by volume) at 140° F., rinsed with hot water, and scoured in the presence of soda ash at 140 to 150° F., for 10 minutes. A uniform, level, reddish-pink dyeing is produced having good light fastness, excellent resistance to A.A.T.C.C. Wash Test Nos. 2 and 3, and good resistance to dry cleaning at room temperature.

A uniform, level, light blue dyeing having similar fastness properties is produced when the above process is repeated employing Algosol Blue IBC Paste instead of Algosol Red IFBB.

A uniform, level, light green dyeing having similar fastness properties is produced when the above process is repeated using Algosol Green IBW Paste instead of Algosol Red IFBB.

A uniform, level, medium blue dyeing having good to excellent fastness properties when subjected to A.A.T.C.C. Wash Tests Nos. 2 and 3, an acid perspiration test, an alkaline perspiration test, dry cleaning three times in carbon tetrachloride, and 40 hours in the Fadeometer is obtained when the above process is repeated using 2½ oz. per gallon of Algosol Blue IPC Paste and ⅜ oz. per gallon of Algosol Brown IBR instead of Algosol Red IFBB.

Example 2

An aqueous pad liquor is prepared by dispersing Indanthrene Navy Blue BRP Paste in water in proportions of 4 oz. per gallon and dissolving therein sodium dodecylbenzene sulfonate at the rate of 2.0 oz. per gallon. N-methyl-2-pyrrolidone is then mixed into the dyebath in proportions of about 6 oz. per gallon, and the dyestuff vatted by treatment with 1.5 oz. per gallon of caustic soda and 1.5 oz. per gallon of sodium hydrosulfite. Acetic acid (56%) at the rate of 4.5 oz. per gallon is then added to the dyebath to acidify same and convert the dyestuff to the free anthrol (acid vat) form. The dye bath is strained and a strip of synthetic linear polyester fabric (Dacron) is padded with the resulting dye liquor at 130 to 160° F., air-dried, heated in a curing range at 350–400° F. for 2–5 minutes and scoured at the boil with an aqueous detergent composition containing soda ash. A uniform, level, fairly deep shade of violet is produced having good to excellent fastness properties.

A uniform, level, pink dyeing having similar fastness properties is produced when the above process is repeated using 2 oz. per gallon of Indanthrene Brilliant Pink RN Paste instead of the 4 oz. per gallon of Indanthrene Navy Blue BRP Paste.

A uniform, level, yellow dyeing having similar fastness properties is produced when the above process is repeated using Algol Yellow GCA Paste instead of Indanthrene Navy Blue BRP Paste.

Similar results are obtained when the above described process of this example are applied to Acrilan and Orlon.

This invention has been disclosed with respect to certain preferred embodiments, and various modifications and variations thereof will become obvious to those skilled in the art. It is to be understood that such modifications and variations are to be included within the spirit and purview of this application and the scope of the appended claims.

I claim:

1. In a process wherein fibers composed of at least 75% by weight of a member of the group consisting of polyacrylonitrile and synthetic linear polyesters of terephthalic acid with a polymethylene glycol are dyed by padding with an aqueous dyebath containing a member of the group consisting of sulfuric acid ester salts of leuco vat dyestuffs and vat dyestuffs in free anthrol form, the

improvement comprising including in said dyebath about 5 to 20% by weight of an N-lower alkyl-2-pyrrolidone.

2. A process as defined in claim 1 wherein said N-lower alkyl-2-pyrrolidone is N-methyl-2-pyrrolidone.

3. A process as defined in claim 2 wherein said fibers are composed of at least 75% by weight of polyacrylonitrile.

4. A process as defined in claim 3 wherein the dyebath contains a sulfuric acid ester salt of a lauco vat dyestuff.

5. A process as defined in claim 3 wherein said dyebath contains a vat dyestuff in free anthrol form.

6. A process as defined in claim 2 wherein said fibers are composed of at least 75% by weight of said synthetic linear polyester.

7. A process as defined in claim 6 wherein said dyebath contains a vat dyestuff in free anthrol form.

8. A process as defined in claim 2 wherein said fibers are composed of at least 75% by weight of polyethylene terephthalate.

9. A process as defined in claim 8 wherein said dyebath contains a vat dyestuff in free anthrol form.

10. An aqueous dyebath containing a member of the group consisting of sulfuric acid ester salts of leuco vat dyestuffs and vat dyestuffs in free anthrol form and about 5 to 20% by weight of an N-lower alkyl-2-pyrrolidone.

11. A dyebath as defined in claim 10 wherein said N-lower alkyl-2-pyrrolidone is N-methyl-2-pyrrolidone.

12. A dyebath as defined in claim 11 containing a sulfuric acid ester salt of a leuco vat dyestuff.

13. A dyebath as defined in claim 11 containing a vat dyestuff in free anthrol form.

References Cited in the file of this patent

UNITED STATES PATENTS

2,569,470	Hagemeyer et al.	Oct. 2, 1951
2,646,339	Ward et al.	July 12, 1953
2,670,263	Luttringhaus et al.	Feb. 23, 1954

OTHER REFERENCES

Am. Dyestuff Reporter, November 13, 1950, p. 790.