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2,989,360

CONTINUOUS DYEING PROCESS

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This invention relates to a continuous dyeing process, and more particularly to a process for the continuous dyeing of running lengths of polyacrylonitrile materials with acid dyestuffs.

The use of acid dyestuffs for dyeing fibrous materials is well known, but the use of such dyestuffs for continuously dyeing running lengths of sheet or fibrous polyacrylonitrile materials under mill conditions has not heretofore met with success. Relatively long periods of time have been required in batch processes for impregnating such fibrous materials with sufficient amounts of dyestuff to attain good penetration and fixation and heavy shades. The problem is particularly serious in the dyeing of thick and bulky materials, for example, meltons, ducks, blanket felts, automobile safety straps, upholstery and drapery fabrics and the like.

Attempts have heretofore been made to increase the dye affinity of materials having a basis of polyacrylonitrile by copolymerization in the presence of other monomeric materials, incorporation of various auxiliary agents, and the like. Thus, in Australian Patent No. 167,575, there is disclosed the production of readily dyeable oriented products made from polyacrylonitrile by incorporating various types of dye assistants in the spun article during the course of its manufacture and before it is dried and reduced to its final dimensions. Such products have, however, not proved capable of being satisfactorily dyed by a continuous process with acid dyestuffs.

It is an object of this invention to provide a continuous process for dyeing running lengths of sheet or fibrous polyacrylonitrile materials in heavy shades with acid dyestuffs. It is another object of this invention to provide such a process which will enable the production of dyeings have good fixation and/or penetration, level shades and/or good hand and/or fastness properties. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant invention, which includes a process comprising continuously treating a running length of material consisting essentially of a polymer containing at least 85% of acrylonitrile in the polymer molecule and from about 1 to 40% by weight of said material of a water-soluble dye assistant selected from the group consisting of water soluble amine salts, quaternary ammonium salts, sulfonium salts, phosphonium halides, polymeric N-vinyl fatty acid amides and polymeric N-vinyl lactams in an aqueous dye solution having a pH not exceeding about 7 and a temperature of about 175–212° F. and containing per gallon about 0.25–8 oz. of an acid dyestuff and about 2–16 oz. of a water-miscible, acid-stable, high-boiling organic solvent for said dyestuff for about 20–90 seconds, removing excess solution from the dyed running length and then steaming the dyed running length at a temperature of about 212–225° F. It has been found that the process of the instant invention enables the attainment of heavy shades of dyeings having good to excellent properties with respect to penetration, fixation, solidity, levelness, hand and/or fastness (e.g. perspiration, light, rubbing, etc.). It will be understood that even where the properties of the dyeings produced by the instant process do not have improved properties as com-

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pared with dyeings produced with the conventional batch processes, the instant invention enables the attainment of the high dyeing speeds required by the high production rates necessary to the successful operation of most present-day mills.

The process of the instant invention is applicable for the continuous dyeing of running lengths of polymeric sheet and fibrous materials containing at least 85% acrylonitrile in the polymer molecule and about 1 to 40% by weight of the material of a dye assistant as described above. Such materials are produced in accordance with the processes disclosed in Australian Patent 167,575, mentioned above. In general, the dye assistant must be incorporated into the spun material during the course of its manufacture and before it is dried and reduced to its final dimensions. In other words, such assistant may be introduced into the spinning dope or into the coagulated and still swollen spun material before or after partial orientation. Although the material may be made by dry-spinning or wet-spinning from organic solutions of the polymer, the instant process is particularly applicable to materials made by wet-spinning of aqueous saline solutions of the polymer. The material should be oriented following coagulation by stretching sufficiently to give a product having a yield point when dried of at least 0.8 gram per denier, when dealing with salt spun polyacrylonitrile, as less fully oriented products, those with yield points near 0.6 gram per denier or less, may be dyed relatively easily. When incorporated after spinning, the water-soluble dye assistant is applied to and absorbed by the aquagel material, i.e., before it has been dried irreversibly, in an amount of at least 1.0% of the dry weight of the material. The product is thereafter dried while still retaining the dye assistant. The dye assistant may be applied to the spun material before, during and/or after the stretching operation.

The dye assistants which are contained in the polyacrylonitriles dyed in accordance with the instant invention in general contain at least 10 carbon atoms and may contain aliphatic, aromatic, alicyclic and/or heterocyclic radicals. The water-soluble amine salts are in general hydrochlorides of primary, secondary or tertiary amines, as for example octadecyl ammonium chloride, di-n-amyl ammonium chloride, tri-n-amyl ammonium chloride, N-2-[2-(2,2,3,3-tetramethylbutyl phenoxy)ethoxy] ethyl-N,N-dimethyl ammonium chloride, N-2-(heptoxy)ethyl-N,N-dimethyl ammonium chloride, N-dodecyl-N,N-di(2-hydroxyethyl)ammonium chloride, 5-ethyl-2-n-nonylpyridine hydrochloride, N-n-octadecylpyridine hydrochloride, and 2-heptadecyl-3-butyl glyoxalidine hydrochloride and the like.

Representative water-soluble quaternary ammonium salts include n-nonyltrimethyl ammonium bromide, n-dodecylbenzyl trimethyl ammonium chloride, n-dodecyltolylmethyltrimethyl ammonium chloride, n-decyloxyethyltrimethyl ammonium iodide, n-[2-(2,2,3,3-tetramethylbutyl phenoxy)ethoxy] ethyltrimethyl ammonium iodide, carboxymethyl dimethyl tetradecyl ammonium chloride, 2-hydroxyethyl-n-octadecyl dimethyl ammonium bromide, benzyl - 2 - [2 - (2,3,4,6 - tetrachlorophenoxy)ethoxy]ethyl morpholinium chloride, n-dodecyl pyridinium chloride, n-dodecyl isoquinolinium bromide, bis-(polyoxyethylene oleate)ethyl methyl ammonium ethosulfate, trimethylene bis(dimethyl-n-tetradecyl ammonium bromide), D - methyl - 2 - hydroxyethyl stearamidopropyl ammonium chloride and the like.

Representative water-soluble sulfonium salt dye assistants include n-dodecyl dimethyl sulfonium chloride or methosulfate, 2[2 - (2 - biphenyloxy)ethoxy] ethylbutyl methyl sulfonium methosulfate, di - (2 - hydroxyethyl)-methyl sulfonium methosulfate, di-capric ester, cetyl-p-

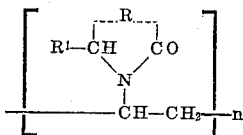
tolyl methyl sulfonium methosulfate, n-dodecyl-2-chloroethyl methyl sulfonium 2-chloroethyl sulfate, and 2[2-(4-cyclohexylphenoxy)ethoxy] ethyl diethyl sulfonium ethosulfate and the like.

Representative water-soluble phosphonium halide dye assistants include triethyl-n-octyl phosphonium iodide, benzyl-n-dodecyl dimethyl phosphonium bromide, and dichlorobenzyl triphenyl phosphonium chloride, and the like.

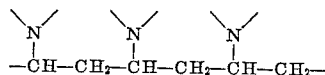
Representative water-soluble polymers of N-vinyl fatty acid amides are preferably N-vinyl N-lower alkyl lower fatty acid amides such as N-vinyl N-ethyl formamide, N-vinyl N-methyl acetamide, and the like.

The preferred dye assistants employed in the materials which may be dyed in accordance with this invention are the water-soluble polymers of N-vinyl lactams; such polymer may be a homopolymer, a copolymer of an N-vinyl lactam and one or more other polymerizable monomers or a mixture of a polymerized N-vinyl lactam and at least one other polymer, it being understood that in the case of copolymers and mixtures of polymers, there must be present in the dye assistant at least about 20% by weight of a polymerized N-vinyl lactam.

Polymeric N-vinyl lactams, as exemplified by polyvinyl-pyrrolidone (PVP, poly-1-vinyl-2-pyrrolidone, poly-N-vinyl-2-pyrrolidone, poly-N-vinyl-alpha-pyrrolidone), are by this time well known as extremely versatile chemicals which have found many uses in a variety of fields. They are white powders or colorless, horn-like or glass-like materials with a high softening point and have the highly desirable property of being soluble in water. They are characterized by the following recurring structural formula:



wherein R represents an alkylene bridge group e.g. ethylene, propylene, butylene, necessary to complete a 5, 6 or 7-membered heterocyclic ring system; R¹ represents hydrogen or a lower alkyl group such as methyl or ethyl; and n represents a number indicative of the extent of polymerization and is usually at least about 25. They are obtained by polymerizing organic 5, 6, or 7-membered ring compounds containing in their rings the —NH—CO— group such as, for example, N-vinyl-2-pyrrolidone, N-vinyl-5-, -4, and -3-methyl-2-pyrrolidones, N-vinyl-3,3-dimethyl-2-pyrrolidone, N-vinyl-5-ethyl-2-pyrrolidone, N-vinyl-ε-caprolactam, N-vinyl-hexahydrophthalimidine and the like. Depending upon the extent of polymerization, they may have molecular weights ranging from at least about 5,000 up to 80,000 or more, and preferably from about 25,000 to about 40,000. Viscosity measurements are commonly used as an indication of the average molecular weight of polymeric compositions, the instant polymers being characterized by a chain of carbon atoms to which the lactam rings are attached through their nitrogen atoms, as follows:



The K value (Fikentscher) of any particular mixture of polymers is calculated from viscosity data and is useful as an indication of the average molecular weight of such mixture. Its determination is fully described in "Modern Plastics," 23, No. 3, 157-61, 212, 214, 216, 218 (1945) and is defined as 1000 times k in the empirical relative viscosity equation:

$$\frac{\log_{10} \eta_{rel}}{C} = \frac{75k^2}{1 + 1.5kC} + k$$

wherein C is the concentration in grams per hundred cc. of polymer solution and η_{rel} is the ratio of the viscosity of the solution to that of pure solvent. The K values are reported as 1000 times the calculated viscosity coefficient in order to avoid the use of decimals. For the purpose of the present invention, there may be employed those polymeric N-vinyl lactams having a K value of about 10 to 200, and preferably of about 15 to 100.

K values and specific viscosities (η_{sp}) are interconvertible and are related through relative viscosity (η_{rel}). Thus, when viscosity measurements are taken on solutions which have a concentration of 1.00 gram of polymer per deciliter of solution at 25° C. (C=1), the relationships are as follows:

$$\eta_{rel} = \eta_{sp} + 1$$

Relative viscosity = specific viscosity plus one.

$$\text{Relative viscosity} = 10[0.001K + 0.000075K^2/(1 - 0.0015K)]$$

Hence,

$$\eta_{sp} = -1 + 10[0.001K + 0.000075K^2/(1 + 0.0015K)]$$

dimensionless, whereas inherent viscosity

$$\frac{(\log_e \eta_{rel})}{C}$$

and intrinsic viscosity (the limit of inherent viscosity as C approaches zero) have the dimensions of dilution, i.e., the reciprocal of concentration. Intrinsic viscosity and K are intended to be independent of concentration.

The number of recurring polymer units enclosed by brackets in the foregoing general structural formula, indicated by "n," or the extent or degree of polymerization, corresponds to a chain of roughly 25 to 1,000 monomer units or more. In actual practice the mixture of polymeric molecules each containing a different number (n) of monomer units is always produced. These homopolymers are readily prepared by the procedural steps given in U.S. Patents 2,265,450, 2,317,804 and 2,335,454 in which working examples of species included within the above formula are given and which are incorporated herein by reference thereto.

Watersoluble copolymers operative in the instant invention are derived from polymerizable monomeric compositions containing at least about 20% by weight of an N-vinyl lactam. The proportional of N-vinyl lactam present in such polymerizable monomeric compositions will depend upon the amount and nature of the other monomer or monomers, but should in all cases be at least sufficient to impart to the final copolymer the desired water soluble property. By way of example, the following list gives the maximum limit of representative monomers which may be copolymerized with the N-vinyl lactam for the production of operable copolymers:

	Percent		Percent
Allyl alcohol	50	Vinyl acetate	40
Diallyl phthalate	20	Vinyl chloride	35
Isobutyl vinyl ether	20	Acrylic acid	75
Ethyl vinyl ether	50	Vinyl laurate	20
Methyl vinyl ether	80	Vinyl stearate	15
Maleic anhydride	80		

The following table lists some monomeric compositions useful in the production of suitable water-soluble copolymers.

	Table	Percent
N-vinyl-2-pyrrolidone	-----	70
+		
Allyl alcohol	-----	30
N-vinyl-2-pyrrolidone	-----	85
+		
Diallyl phthalate	-----	15

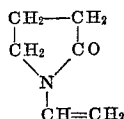
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	Percent
N-vinyl-2-pyrrolidone -----	60
+ Vinyl ethyl ether -----	40
N-vinyl-2-pyrrolidone -----	30
+ Vinyl methyl ether -----	70
N-vinyl-2-pyrrolidone -----	75
+ Vinyl acetate -----	25
N-vinyl-2-pyrrolidone -----	50
+ Acrylic acid -----	50
N-vinyl-2-pyrrolidone -----	20
+ Maleic anhydride -----	80
N-vinyl-2-pyrrolidone -----	94
+ Vinyl stearate -----	6
3-methyl-N-vinyl-2-pyrrolidone -----	87
+ Vinyl bromide -----	13
3-methyl-N-vinyl-2-pyrrolidone -----	87
+ Vinyl chloride -----	13
4-methyl-N-vinyl-2-pyrrolidone -----	88
+ Vinyl chloride -----	12
3,3-dimethyl-N-vinyl-2-pyrrolidone -----	91
+ Vinyl chloride -----	9

It will be understood that the above-described copolymers are generally prepared in the same manner as the homo-polymers of the N-vinyl lactams and have similar properties with respect to water-solubility, K values and the like.

Instead of copolymers prepared from mixtures of monomers as described above, a water-soluble polymeric material may be employed which is produced by mixing the polymerized N-vinyl lactam with one or more of the polymerized monomeric unsaturated compounds employed in producing such copolymers provided of course that the mixture contains at least 20% of polymerized N-vinyl lactam, is water-soluble, and has the above-described properties with respect to K values and the like.

The preferred N-vinyl lactams for use in the compositions of the instant invention are N-vinyl-2-pyrrolidone and its lower alkyl substituted derivatives, which may be characterized by the formula:



in which one or more of the hydrogen atoms in the cyclic methylene groups may be substituted by the lower alkyl radical such as methyl, ethyl or the like.

Within the above ranges, a polymerized N-vinyl lactam such as polyvinylpyrrolidone is preferred having a K value of from about 50 to 60 and is preferably employed in the form of a concentrated aqueous solution having a concentration of 40 to 50% and a pH on the acid side, preferably about 5, obtainable by addition of an acidic material as for example formic acid, acetic acid, or the like. It will be understood that the above discussion relative to K values and specific values and their ranges is also applicable to the polymerized N-vinyl fatty acid amides.

The polymer in the running length of sheet or fibrous material dyed in accordance with the process of the instant invention may be principally or entirely acryloni-

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trile homopolymer or a copolymer of acrylonitrile and up to 15% by weight of one or more polymerizable monomers containing at least 1 carbon to carbon double or triple bond, such as vinyl chloride, vinyl acetate, styrene, acrylic acid, methacrylic acid, chloroacrylic acid, and their amides, chlorides, esters and the like. Fibrous material dyed in accordance with the instant invention may be in any suitable form, as for example staple or continuous filaments, yarns, slubbings, warps, ribbons, woven or filtered fabrics, and the like, and may contain, in addition to the modified polyacrylonitrile fibers or filaments of the above-described composition, fibers or filaments having a different chemical constitution. Depending upon the nature of such hetero-fibers or filaments, level dyeings or decorative effects may be obtained.

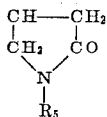
Excellent dyeing results are also obtained when fibrous materials containing polyacrylonitrile fibers of the type described above are admixed with protein fibers in any proportions prior to treatment by the instant process since such protein fibers are dyed equally well thereby. Uniform, level dyeings may thereby be obtained on such mixed fibers. The admixed protein fibers may be of natural origin, such as silk, goat and other animal hair, and particularly wool, or they may be artificially regenerated protein fibers such as derived from casein, zein, or soyabean or the like, preferably of the hardened type as obtainable for example by acetylation or treatment with formaldehyde.

The dyestuffs employed in the instant process are likewise readily available and well known in the art and descriptions thereof are readily available in the literature or patent fields. In general, the acid dyestuffs suitable for use herein are those water soluble dyes commonly employed for dyeing wool, contain at least one carboxylic, sulfonic, sulfone or sulfonamide group or a substituted derivative thereof and are applied from a neutral to acid aqueous medium. A great number of them are of the azo type (mono-, di-, polyazo dyestuffs). However, other groups of acid dyes are known which are operative herein, including, for example, the quinoline, pyrazolone, and di- or triphenylmethane colors, the acid anthraquinones, the dyes derived from xanthene such as the eosines, phthaleins, and sulfo rhodamines, and the chromoxan dyes derived from oxytrimellitic acid. The dyestuff may be premetalized, such dyestuffs being generally described as metallized acid or metallized azo dyestuffs. Such dyestuffs are available under such trademarks as Palatine Fast Colors, Neolans, Inochromes, Chromacys, Chromolans, Vitrolans, Glycolans, Supralans and the like. The mordant acid dyestuffs are also operative herein, such dyestuffs being metallized on the fiber in the usual manner subsequent to treatment in accordance with the above-defined process of the instant invention. As metallized and mordant acid dyestuffs employed herein, those preferred contain in o,o'-positions relative to an azo linkage well known groups (e.g. OH, COOH, etc.), capable of forming complexes with metals. The aqueous dye solution employed in the instant process must be adjusted to the optimum pH (not exceeding about 7) in each instance, depending upon the fibrous material being dyed and the dyestuffs employed.

The water-miscible, acid-stable, high-boiling organic solvent for the dyestuff employed in the instant process not only aids in enabling the solubilization of increased amounts of dyestuff in the solution, necessary for the attainment of heavier shades, but also increases penetration and/or fixation of the dyestuff in and on the fiber, perhaps by some form of swelling or plasticizing action. By the term "water-miscible" is meant the property of the solvent to dissolve in water under the conditions required herein. The high-boiling property is necessary to prevent volatilization and to maintain the dyed fibrous material in wet condition during the subsequent steaming operation. As representative of suitable water-miscible, acid-stable, high-boiling organic solvents for use in the instant

invention, there may be broadly mentioned the N-lower alkyl-2-pyrrolidones, N,N-di-substituted formamides, γ -lactones such as γ -butyrolactone, and lower aliphatic polyhydric alcohols and the partial alkyl ethers thereof.

The N-lower alkyl-2-pyrrolidones which may be employed in the dyebaths of the instant invention have the formula:



wherein R^3 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 N,N-di-lower alkyl- and di-lower hydroxy-alkyl formamides which may be employed in the dyebaths of the instant invention are likewise well known in the art and no claim is made thereto per se. N,N-dihydroxyethyl-formamide may be readily produced by the amidation of formic acid with diethanolamine in known manner. The N,N-dimethyl- and diethyl-formamides may, of course, also be employed.

Suitable polyhydric alcohols or lower alkyl ethers thereof are, for example, 1,6-hexanediol, 1,7-heptanediol, 1,4-butanediol, 1,2,4-butanetriol, glycerol, ethylene glycol, propylene glycol, diethylene glycol, and suitable cello-solves and carbitols, such as the mono-methyl, -ethyl, and -butyl ethers of ethylene glycol and diethylene glycol.

The aqueous dye solutions of the instant invention may in some instances contain dissolved therein an acid-reacting salt to enable better pH control and the like. They are in general water soluble salts of weak bases with relatively strong acids, such as the acetates, sulfates, sulfocyanides, nitrates and the like of ammonium, aluminum and the like, amounts of about 2 to 7 ounces per gallon being usually employed.

Improved results are also obtained in some instances by including in the dye solution about $\frac{1}{2}$ to 2 ounces per gallon of an acid stable, high boiling organic ester water-miscible at that concentration under the required impregnating conditions herein. As representative of such esters, there may be mentioned the propyl, butyl and isobutyl acetates and the butyl, isobutyl, amyl, and hexyl formates. These esters apparently aid in solubilizing the dyes and/or achieving improved penetration, levelness and/or the like.

In carrying out the process of the invention, the running length of modified polyacrylonitrile material is passed through the above-described aqueous solution, maintained at a temperature of about 175° F. up to just below its boiling point, preferably about 200 to 211° F., at such a rate that the fibers are subjected to treatment in the solution for from about 20 to 90 and preferably about 30 to 40 seconds. This rate will, of course, depend upon the size of the dyebath. Excellent results have been obtained when the process of the instant invention is carried out in the apparatus disclosed in U.S. Patent Nos. 2,364,838 and 2,552,078, issued to Sumner H. Williams. In the use of such apparatus, the aqueous solution containing the dyestuff and high-boiling solvent may be passed in concurrent or counter-current direction relative to the running length of material and recycled if desired. It will be understood that when mixtures of dyes are employed to obtain a desired shade, the dye solution must be properly replenished to maintain uniform shades end to end, having in mind the differences in substantivity of the dyes.

Following treatment of the material with the aqueous dye solution as above described, the running length of material is then, desirably after removing excess solution therefrom, as by squeezing, vacuum, blowing, centrifugation, etc., submitted to a steaming operation at a

temperature of about 212–225° F. In the case of fibrous materials, the liquor pick-up after removal of excess and before steaming may range from about 50 to 100% of the weight of the fiber, depending upon the construction of the fibrous material and the like. The duration of steam treatment will in general depend upon the particular dyestuff employed and the amounts in which it is used, the material being dyed, and the temperature of steaming, the latter varying inversely with the duration.

Duration of about 15 seconds up to 1 minute are usually sufficient. In some instances, in fact, acceptable shades may be obtained without any subsequent steaming operation, but in all such instances, substantially deeper, heavier, and more solid shades are obtained with steaming.

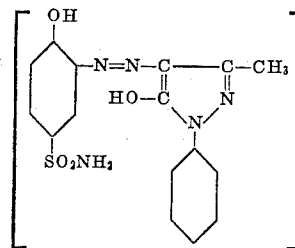
It will of course be understood that the material may be continuously subjected to two or even more successive treatments with the above-described aqueous dye solutions, each preferably followed by a squeezing or similar operation to remove excess solution prior to the final steam treatment. The apparatus disclosed in the above-mentioned Williams patents are particularly adapted for such tandem operation.

Following the steaming operation, the dyed material is preferably rinsed and washed or scoured in known manner with soap and/or synthetic detergents (e.g. 0.1–2% solutions), usually at elevated temperatures of about 120–130° F. Synthetic detergents for this purpose are preferably of the nonionic surface-active type such as the polyoxyethylenated alkyl phenols and higher aliphatic alcohols and carboxylic acids, or the anionic type such as the higher alkyl sulfates, higher acyl taurides, sulfate esters of the above-mentioned polyoxyethylenated derivatives, and the like. These and other similar synthetic detergents are well known in the art and need no further description. As representative thereof, there may be mentioned the condensation product of 8 moles of ethylene oxide with one mole of nonyl phenol, sodium-N-methyl-N-palmitoyl taurate, and the like.

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

A pad liquor is prepared containing per gallon
3 oz. of dyestuff II having the formula



Chromium Complex

10 oz. N-methylpyrrolidone.

2 oz. butyl acetate.

Water to make up the balance

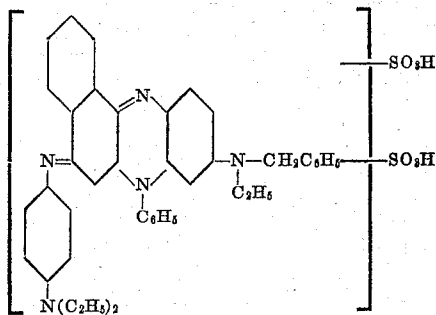
The above pad liquor, heated to 200° F., is placed in a Williams unit of the type described in U.S. Patent 2,364,838 and maintained at that temperature therein while a roll of lawn fabric formed from fibers of polyacrylonitrile containing 10% by weight thereof of polymerized N-vinyl pyrrolidone ($K=55$) and produced as described in Example 5 of Australian Patent No. 167,575 is continuously fed therethrough. The rate of feed of the material is adjusted to subject the fibers to treatment in the concurrently flowing pad liquor for about 40 seconds. The running length of material is then passed through squeeze rolls to remove excess pad liquor and continuously steamed for about 1 minute at 215° F., after which

it is continuously rinsed and washed or scoured at the boil for one minute in an 0.1% aqueous solution of sodium-N-methyl-N-palmitoyl taurate. The resulting dyeing is a bright, level shade of orange having good to excellent fastness properties with respect to acid perspiration, alkaline perspiration, crocking and light.

Example 2

The procedure of Example 1 is repeated, except that the pad liquor contains per gallon.

4.0 oz. Indocyanine B. conc., of the formula



10.0 oz. N-methylpyrrolidone.

2.0 oz. butyl acetate.

Water to make up the balance

and the duration of steaming is about 1.5 minutes. The resulting blue dyeing has improved properties similar to those obtained in Example 1.

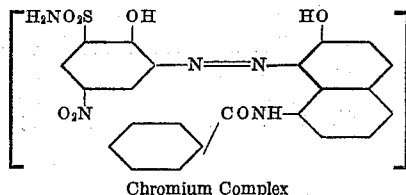
Example 3

The procedure of Example 2 is repeated, except that instead of 10 ounces of N-methylpyrrolidone, the pad liquor contains 12 ounces of γ -butyrolactone per gallon. The resulting blue dyeing is slightly different in shade from that obtained in Example 2, but otherwise has the same improved properties.

Example 4

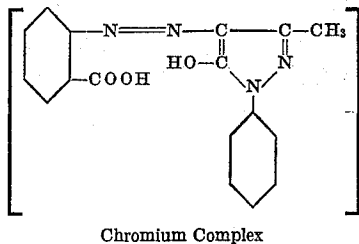
The procedure of Example 1 is repeated, except that the pad liquor contains per gallon

2.10 oz. of dyestuff I having the formula



0.42 oz. of dyestuff II above

0.14 oz. of dyestuff III having the formula



12.0 oz. N-methylpyrrolidone

Water to make up the balance

and the material dyed is a twill fabric formed from the same fibers. The resulting greyish-black dyeing has improved properties similar to those obtained in Example 1.

Example 5

The procedure of Example 4 is repeated, except that the pad liquor contains per gallon

- 5 2.0 oz. of dyestuff I
- .36 oz. of dyestuff II
- .20 oz. of dyestuff III
- 8.0 oz. of N-methylpyrrolidone
- 1.0 oz. of butyl acetate
- 10 Water to make up the balance

and the pad liquor is applied to a twill fabric of similar fiber content but containing only 3% of the PVP by weight of the polyacrylonitrile. The resulting greyish-black dyeing has improved properties similar to those obtained in Example 1.

Example 6

The procedure of Example 4 is repeated, except that the pad liquor contains per gallon

- 20 2.0 oz. of dyestuff I
- .36 oz. of dyestuff II
- .20 oz. of dyestuff III
- 16.0 oz. of N,N-dimethyl formamide
- Water to make up the balance

25 The resulting greyish-black dyeing has improved properties similar to those obtained in Example 1.

Example 7

The procedure of Example 4 is repeated, except that the pad liquor contains per gallon

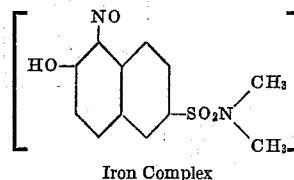
- 2.0 oz. of dyestuff I
- 0.36 oz. of dyestuff II
- 0.20 oz. of dyestuff III
- 35 16.0 oz. of 1,6-hexanediol
- Water to make up the balance

The resulting greyish-black dyeing has improved properties similar to those obtained in Example 1.

Example 8

The procedure of Example 4 is repeated, except that the pad liquor contains per gallon

2.0 oz. of dyestuff IV having the formula



10.0 oz. N-methylpyrrolidone

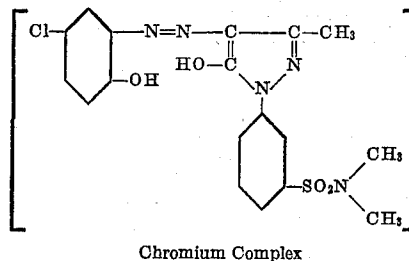
Water to make up the balance

55 The resulting bright green dyeing has improved properties similar to those obtained in Example 1.

Example 9

The procedure of Example 4 is repeated, except that the pad liquor contains per gallon

2.0 oz. of dyestuff V having the formula



10.0 oz. N-methylpyrrolidone

75 Water to make up the balance

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The resulting deep red dyeing has improved properties similar to those obtained in Example 1.

Example 10

The procedure of Example 9 is repeated, but applied to a twill fabric formed from fibers of polyacrylonitrile containing 3% by weight thereof of polymerized N-vinylpyrrolidone (K=56), produced as described in Example 7 of said Australian patent. Similar results are obtained.

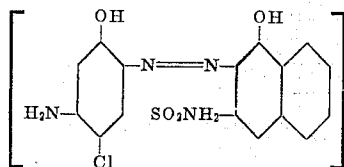
Example 11

The procedure of Example 10 is repeated, except that the fibers contain 10% of the PVP by weight of the polyacrylonitrile. Similar results are obtained except for a somewhat deeper shade.

Example 12

The procedure of Example 4 is repeated, except that the pad liquor contains per gallon

2.0 oz. of dyestuff VI having the formula



Chromium Complex

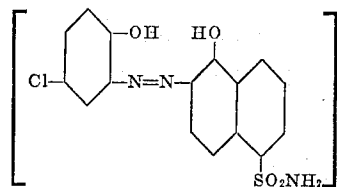
10.0 oz. N-methylpyrrolidone
Water to make up the balance

The resulting deep blue dyeing has improved properties similar to those obtained in Example 1.

Example 13

The procedure of Example 1 is repeated, except that the pad liquor contains per gallon

1.20 oz. of dyestuff II above
0.60 oz. of dyestuff III above
0.25 oz. of dyestuff VII having the formula



Chromium Complex

12.0 oz. N-methylpyrrolidone
Water to make up the balance

and the material dyed is a tropical worsted type fabric containing 60% by weight of the fibers described in Example 1 and 40% wool. The resulting dyeing is a level shade of medium brown having improved properties similar to those obtained in Example 1.

Example 14

The procedure of Example 13 is repeated except that the pad liquor contains per gallon

2.0 oz. of dyestuff VII above
12.0 oz. N-methylpyrrolidone
Water to make up the balance

12

The resulting dyeing is a level shade of violet having improved properties similar to those obtained in Example 1.

This invention has been disclosed with respect to certain preferred embodiments, and there will become obvious to persons skilled in the art various modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

I claim:

1. A process comprising continuously treating a running length of material, said material consisting essentially of (1) a polymer containing at least 85% of acrylonitrile in the polymer molecule and (2) from about 1 to 40% by weight of said material of a water-soluble dye assistant selected from the group consisting of water soluble amine salts, quaternary ammonium salts, sulfonium salts, phosphonium halides, polymeric N-vinyl fatty acid amides and polymeric N-vinyl lactams, in an aqueous dye solution having a pH not exceeding about 7 and a temperature of about 175–212° F. and containing per gallon about 0.25–8 oz. of an acid dyestuff and about 2–16 oz. of a water-miscible, acid-stable, high boiling organic solvent for said dyestuff for about 20–90 seconds, removing excess solution from the dyed running length and then steaming the dyed running length at a temperature of about 212–225° F. said solvent being selected from the group consisting of N-lower alkyl-2-pyrrolidones, N,N-di-substituted formamides, gamma-lactones, and lower aliphatic polyhydric alcohols and partial alkyl ethers of such alcohols.
2. A process as defined in claim 1 wherein said dye assistant is a polymeric N-vinyl lactam.
3. A process as defined in claim 1 wherein said dye assistant is a polymeric N-vinyl pyrrolidone.
4. A process as defined in claim 1 wherein said solvent is N-methyl pyrrolidone.
5. A process as defined in claim 1 wherein said solvent is 1,6-hexanediol.
6. A process as defined in claim 1 wherein said solvent is γ -butyrolactone.
7. A process as defined in claim 1 wherein said solvent is N,N-dimethylformamide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

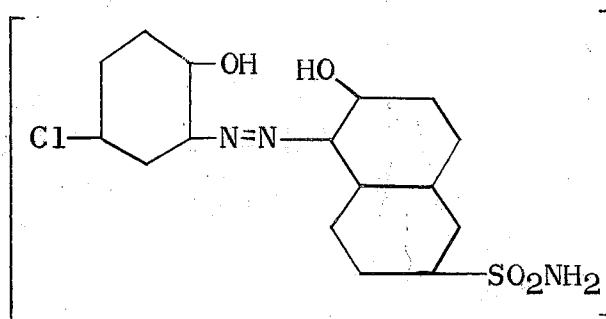
Patent No. 2,989,360

June 20, 1961

Henry R. Mautner

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 44, for "have" read -- having --; column 9, line 37, for "-methylpyrrolidone" read -- N-methylpyrrolidone --; column 11, lines 42 to 49, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 10th day of April 1962.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents