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2,888,313

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 fibrous material with acid dyestuffs.

The use of acid dyestuffs for dyeing proteinaceous and nylon fibrous materials is well known, but the use of such dyestuffs for continuously dyeing running lengths of such fibrous material 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.

It is an object of this invention to provide a continuous process for dyeing running lengths of polyamide fibrous 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 having 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 polyamide fibrous material 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 compared 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 polyamide fibrous material in any desired form, as for example, loose stock, slubbings, warps, ribbons, yarns, felted and woven fabrics, and the like. The process is applicable for the dyeing of any of the known artificial superpolyamide fibers presently available, such as nylon, Perlon L and T, Silon, Steelon, Furon, and the like. For example, the nylon may be derived from adipic acid and hexamethylenediamine (Nylon 66), ω -aminocaproic acid

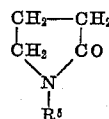
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(Nylon 6), sebacic acid and hexamethylenediamine (Nylon 610), or mixtures or copolymers thereof. Natural protein fibers such as silk, goat and other animal hair, and particularly wool are readily dyed by the process of the instant invention. Artificial regenerated protein fibers such as derived from casein, zein, or soyabean or the like, may also be dyed by the process of the instant invention. Such regenerated protein fibers are 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 premetallized, 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, Chromacyls, 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-disubstituted 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 R⁵ is an alkyl radical of from 1 to 4 carbon atoms such as ethyl, propyl, isopropyl, butyl, isobutyl and

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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 hydroxyalkyl-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 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 Cellosolves 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 fibrous 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 fibrous 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 fibrous material with the aqueous dye solution as above described, the running length of fibrous 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. 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, the fibrous material being dyed, and the temperature of steaming, the latter varying inversely with the duration. In general, nylon fibers should be given a longer steam treatment than protein fibers to obtain the desired heavy shades. Durations of steam treatment of from about 15 seconds to 5 minutes are usually employed for obtaining optimum results, durations of about 15 seconds up to 1 minute being usually sufficient in the treatment of protein fibrous material, and about 45 sec-

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onds to 5 minutes for nylon fibers. In some instances, in fact, acceptable shades may be obtained on protein fibers 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 fibrous 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 fibrous 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 polyoxethylenated 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:

- 4 oz. Sulphon Cyanine 5RA (C.I. 289)
- 2 oz. Wool Fast Orange GA-CF (C.I. 274)
- 1 oz. Anthralan Red BA-CF (Pr. 210)
- 10 oz. N-methylpyrrolidone
- 3 oz. ammonium 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 automobile safety strap material formed from nylon fibers derived from adipic acid and hexamethylenediamine 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 30 seconds. The running length of material is then passed through squeeze rolls to remove excess pad liquor and continuously steamed for 3 minutes 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 deep, level shade of black having excellent penetration throughout, and 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:

- 1.5 oz. Wool Fast Orange GA-CF
- 1.5 oz. Anthralan Red BA-CF
- 5.0 oz. N-methylpyrrolidone
- 3.0 oz. ammonium acetate
- Water to make up the balance

A reddish orange dyeing is obtained having improved properties similar to those obtained in Example 1.

Example 3

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

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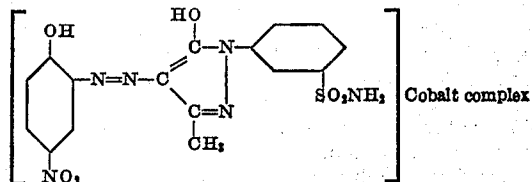
3.6 oz. Anthralan Red BA-CF
1.2 oz. Wool Fast Orange GA-CF
0.07 oz. Alizarine Fast Grey BLN New CF (Pr. 206)
10.00 oz. N-methylpyrrolidone
3.00 oz. ammonium acetate
Water to make up the balance

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

Example 4

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

3.0 oz. of the dyestuff having the formula



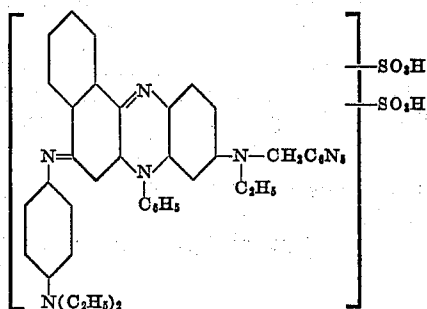
1.0 oz. Anthraquinone Violet 3RA (C.I. 1080)
0.2 oz. Alizarine Fast Grey BLN New CF
10.0 oz. N-methylpyrrolidone
3.0 ammonium acetate
Water to make up the balance

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

Example 5

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

The material dyed is a wool gabardine, the duration of treatment in the pad liquor is about 40 seconds, and the duration of steaming is about one minute. The resulting blue dyeing has improved properties similar to those obtained in Example 1.

Example 6

The procedure of Example 5 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 5, but otherwise has the same improved properties.

Example 7

The procedure of Example 5 is repeated, except that the pad liquor contains per gallon:

3.0 oz. of Indocyanine B conc.
3.0 oz. Sulfone Cyanine 5RA
16.0 oz. N-methylpyrrolidone
5.0 oz. ammonium acetate
Water to make up the balance

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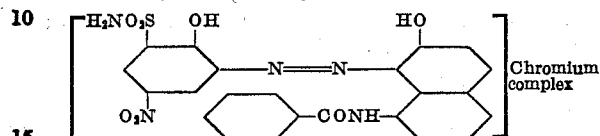
and the liquor is applied to a melton-type wool fabric and a tropical worsted fabric. The resulting navy blue dyeings have improved properties similar to those obtained in Example 1.

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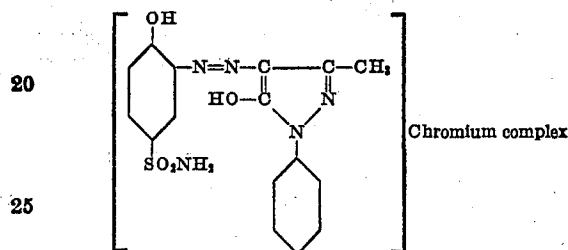
Example 8

The procedure of Example 5 is repeated, except that the pad liquor contains per gallon:

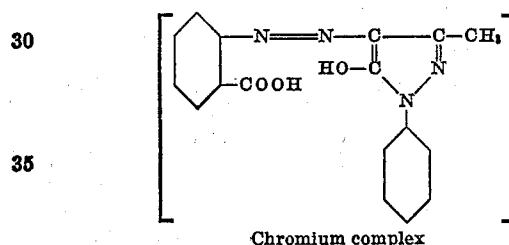
2.0 oz. of dyestuff I having the formula



0.36 oz. of dyestuff II having the formula



0.2 oz. dyestuff III having the formula



12.0 oz. N-methylpyrrolidone

1.0 oz. butyl acetate
Water to make up the balance,

and the material dyed is a tropical worsted. The resulting olive green dyeing has improved properties similar to those obtained in Example 1.

Example 9

The procedure of Example 5 is repeated, except that the pad liquor contains per gallon:

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
Water to make up the balance,

and the pad liquor is applied to a wool serge and a hard-finished gabardine. The resulting olive green dyeings have improved properties similar to those obtained in Example 1.

Example 10

The procedure of Example 9 is repeated, except that a Williams stock dyeing unit is employed of the type disclosed in U.S. Patent No. 2,552,078, the material dyed being raw wool stock. A crock-fast light olive green dyeing is obtained.

Example 11

The procedure of Example 8 is repeated, except that the pad liquor does not contain any butyl acetate. The resulting dyeing is somewhat lighter in shade than that obtained in Example 8.

Example 12

The procedure of Example 5 is repeated, except that the pad liquor contains per gallon:

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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.

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

Example 13

The procedure of Example 5 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
 16.0 oz. of 1,6-hexanediol
 Water to make up the balance,

and the material dyed is a wool serge. The resulting dark olive green dyeing has improved properties similar to those obtained in Example 1.

Example 14

A pad liquor is prepared containing per gallon:

0.64 oz. Monochrome Black Blue GA (Pr. 299)
 0.50 oz. Alizarine Fast Grey BBLW (Pr. 206)
 0.05 oz. Chrome Fast Orange 3RLA (Pr. 247)
 0.30 oz. Acid Alizarine Flavine RA (Pr. 1)
 12.0 oz. N-methyl pyrrolidone
 0.5 oz. butyl acetate,
 Water to make up the balance.

The above pad liquor, heated to 210° 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 length of wool gabardine fabric is continuously fed there-through. 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 one minute at about 212° F. The dyed material is then chromed by treatment for five minutes at the boil in an 0.2-0.4% aqueous solution of ammonium bichromate, after which it is rinsed and washed. The resulting dyeing is a level green shade of black having excellent penetration throughout, and having good to excellent fastness properties with respect to acid and alkaline perspiration,

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crocking, light and drycleaning. Similar results are obtained in dyeing a wool flannel fabric.

This invention has been disclosed with respect to certain preferred embodiments, and various modifications and variations thereof will become obvious to the person 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. A process comprising continuously treating a running length of fibrous material containing polyamide fibers selected from the group consisting of protein and artificial linear condensation superpolyamide fibers 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 ounces of an acid dyestuff and about 2-16 ounces of a water-miscible, organic solvent for said dyestuff selected from the group consisting of N-lower alkyl-2-pyrrolidones and gamma-lactones boiling above 225° F. 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. for about 15 seconds to 5 minutes.
2. A process as defined in claim 1 wherein said fibrous material contains nylon fibers.
3. A process as defined in claim 1 wherein said fibrous material contains protein fibers.
4. A process as defined in claim 1 wherein said fibrous material contains wool fibers.
5. A process as defined in claim 1 wherein said solvent is N-methylpyrrolidone.
6. A process as defined in claim 1 wherein said solvent is γ -butyrolactone.

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