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PROCESS FOR DYEING DRAWN FILAMENTS OF AROMATIC POLYAMIDES WITH BASIC DYESTUFFS IN THE PRESENCE OF AN ORGANIC DYE CARRIER

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ABSTRACT OF THE DISCLOSURE

A process for dyeing a textile formed from an aromatic polyamide containing a dye-associable copolymeric unit wherein a drawn filament of the said polyamide, e.g., poly(m-phenyleneisophthalamide) and poly[N,N'-m-phenylene bis(meta amino benzamide)isophthalamide], is heat-relaxed prior to dyeing the textile in a dye-bath containing (1) a dye to which the copolymeric unit is associable and (2) a dye carrier, e.g., an equal weight mixture of dimethyl terephthalate and benzilide.

BACKGROUND OF THE INVENTION

Field of the invention

Aromatic polyamides have been found well-suited for a broad range of utility where exposure to high temperatures is involved. Such polymers and shaped structures derived therefrom are shown, for example, in the Kwolek et al. U.S. Patent 3,063,966, which teaches process for their manufacture. Consistent with their excellent utility at high temperature there is a strong tendency for members of this class to crystallize or, by some mechanism not yet defined, to develop a highly consolidated, dense structure. The closely packed molecular configuration of shaped structures comprising aromatic polyamides known heretofore is not penetrated by dyes in the processes normally in use. The structures, therefore, are classified as "non-dyeable." While many of the uses for such high-temperature-resistant polymers are adequately served by structures which have not been colored (for uses such as electrical insulation for motors, transformers and the like and other industrial uses such as filter bags, heating ducts, etc.), it would be highly desirable to provide commercially practical means for dyeing textiles formed from aromatic polyamides. Such a means is described in the present application.

Description of the prior art

While the various manipulative steps are individually known in the art, their combination in order to obtain the highly desirable result of the present invention is not known to be suggested by the art.

SUMMARY OF THE INVENTION

In accordance with the present invention a process is provided for dyeing textiles formed from synthetic meta or para oriented, wholly aromatic polyamides containing from 2 to about 15 molar percentage of an aromatic dye associable copolymeric unit which comprises heating the drawn filaments of the said textile while the said filaments are free to relax to a temperature between about 150 to 280° C. for a period between about 1 minute (at the upper temperature) and about 45 minutes (at the lower temperature) and thereafter dyeing the said textile in a dye-bath containing (1) a dye with which the said copolymeric unit is associable and (2) a dye assistant.

DEFINITIONS AND STANDARDS

By a "dye assistant" is meant any organic substance which is substantially inert to the dyebath under the conditions employed and capable of being absorbed by the shaped aromatic polyamide structure to the indicated extent under the conditions of dyeing specified. The substance may be a pure compound or a mixture of compounds.

In the examples *K/S* refers to the ratio of absorbed light to scattered light as measured in the usual manner, using a photometer for measuring incident and reflected light. *K/S* values are related to apparent depth of dyeing attained; "percent dye on fiber" is no more complex than implied for the expression, being merely an indication of the quantity of dye in or on the fiber which is not removed by a simple scour. Dye yield is calculated as the ratio of *K/S* value to the percent dye-on-fiber and is an indication of the effectiveness of the dye taken up by the fiber in producing visible coloration. "Dye yield" and "percent-exhaust" are closely allied to economy of the dyeing operation and therefore of great practical importance. It will be obvious that a very high dye yield is of no commercial importance in a dyeing which gives unacceptably poor percent-exhaust, since the dye bath normally is discarded following a dyeing operation. Likewise, a high percent-exhaust can occur in a dyeing coincidentally with a very low dye yield as, for example, in cases where the fiber has been delustered by taut annealing at high temperature. Thus, to be acceptable economically a dyeing process must be considered on the basis of all of the listed criteria and no single criterion may be used in determining adequacy of a dyeing operation.

The invention is illustrated by the following examples, which are not limitative. In the examples parts are by weight unless otherwise noted. Inherent viscosity is measured in the usual manner at 25° C., using dimethyl acetamide, containing 4% lithium chloride, as solvent.

EXAMPLES

Example 1

A series of aromatic copolyamides is prepared by a process as taught in the Kwolek et al. U.S. Patent 3,063,966 to comprise as the major constituent metaphenylene isophthalamide (MPD-I) and as copolymeric constituent up to 10 mol percent of NaSMPD-I (where "NaSMPD" is the sodium salt of 2,4-diaminobenzene sulfonic acid) as indicated in Table I. The polymers are dry-spun from a solution in dimethyl acetamide (DMAc), containing calcium chloride, to multifilament tows. The spun yarn is drawn to the indicated percent of spun length in hot water while simultaneously being extracted to reduce the residual solvent and salt to an acceptable level. In some instances, the tow is exposed for about one second to rolls heated to the indicated temperature while being restrained from shrinking (indicated in Table I as "taut"). In others, it is heated at 260° C. for 20 or 30 minutes (as indicated in Table I) under no restraint (indicated in Table I as "relaxed").

The tows are then cut to about a 2-inch staple length, and hand-carded pads are prepared from each lot for dyeing. The pads are dyed individually under a pressure of 20 p.s.i.g. in 40 times their weight of a dye-bath of the following parts by weight composition:

	Parts
C.I. Basic Blue 22	0.16
Dye assistant (where used)	0.8
Wetting agent	0.1
Acetic acid (to pH 2.9).	
Water (to 80 parts total).	

Yarn identity and treatment history are reported in Table I.

TABLE I

Item No.	Mole percent NaSMPD-I	Polymer inh. Visc.	Percent drawn	Heating conditions, min. (° C.)	Denier per filament
1	0	1.57	438	Taut, 20 (320)	2
2	0	1.57	438	Relaxed, 20 (260)	2.6
3	2.5	1.71	438	Taut, 20 (320)	2.1
4	2.5	1.62	450	Relaxed, 20 (260)	2.4
5	6.0	1.68	450	Taut, 20 (320)	1.3
6	6.0	1.68	450	Relaxed, 30 (260)	2.2
7	10.0	1.48	447	Relaxed, 20 (260)	2.7

A total of 13 dyeings is made, six without a dye assistant and seven with an equal weight mixture of dimethyl terephthalate and benzanilide as a dye assistant. The dyeing periods and results obtained are summarized in Table II. The *a* items each were dyed with the dye assistant, the *b* items contained no dye assistant.

TABLE II

	2 hours				3 hours			
Item No.	K/S	Percent on fiber	Percent exhaust	Dye yield	K/S	Percent on fiber	Percent exhaust	Dye yield
1*a*	0.3	0.1	1.1		0.4	0.1	1.4	
1*b*	0.2				0.2			
2*a*	2.5	1.1	14.3	2.27	2.8	1.5	19.0	1.93
2*b*	0.2				0.2			
3*a*	0.7	0.5	6.7		0.9	0.2	2.6	
3*b*	0.2				0.3			
4*a*	6.4	3.9	50.8	1.63	6.8	4.4	57.3	1.54
4*b*	0.4	0.1	1.3		0.5	0.2	2.0	
5*a*	4.8	4.8	62.4	1.00	4.9	5.2	67.8	0.95
5*b*	0.6	0.3	4.3		0.6	0.3	4.1	
6*a*	8.4	5.7	74.2	1.47	8.9	6.1	79.8	1.45
6*b*	0.8	0.3	4.1		1.0	0.4	4.9	
7*a*	8.5	7.1	88.8	1.19	8.3	6.7	83.2	1.24

As can be seen from Table II (comparing the various *a* and *b* items) use of the dye assistant is critical. Furthermore, comparing the 3*a* versus the 4*a* and the 5*a* versus the 6*a* sample (each pair with identical and comparable copolymeric modification) substantial improvement of the "relaxed" versus the "taut" samples can be observed. (Note that although sample 5*a* shows a relatively high dye exhaust, it shows a poor dye yield.) Samples 1*a*, 1*b*, 2*a* and 2*b* which contained no copolymeric modifying unit are very poor in dyeing performance.

Without use of superatmospheric pressure, dye pickup by the polymer of this example is so low as to be completely unattractive commercially even with the highest level of modification by NaSMPD. It will be apparent from the tabulated data that when, in addition to pressure, both a dye assistant and appreciable modification by NaSMPD are employed, an attractive increase in dyeability results only in those yarns which have not been heated, while taut. Use of 1 part of salicylanilide for the dye assistant of this example provides 100% more dye exhaust in a similar dyeing.

Example 2

This example illustrates application of the process of this invention to the acid-dyeing of aromatic polyamide structures.

To a nitrogen-blanketed solution of 100 parts metaphenylenediamine (MPD) in 985 parts DMAc which has been cooled to −20° C. is slowly added 189 parts of a .94/.06 molar mixture of isophthaloyl chloride/pyridine 2,5-dicarbonyl chloride (I/2,5-Py). The resulting viscous solution is neutralized by the addition of 69 parts dry lime slurried in an additional 117 parts of DMAc. The solution is vacuum-deaerated with elimination of 180 parts of DMAc containing a small amount of water, after which it contains 19.5% of a copolymer of MPD-I/MPD-2,5-Py in a 94/6 molar ratio having an inherent viscosity of 1.58.

The solution is dry-spun by means available in the art to 160 denier. 18-filament yarn which subsequently is drawn to 316% of its as-spun length in hot water, which also extracts the residual solvent and salt, and dried for 5.7 seconds over rolls heated to 100° C.

The yarn is knitted on a stoll-knitting machine and the resulting knitted fabric is relaxed at 240° C. for 30 minutes under conditions of no restraint. The relaxed fabric is dyed with an acid dye under a pressure of 15 p.s.i.g. for two hours, the dye bath having the following composition and the ratio of bath to tubing being 50/1.

	Pt.
CI Index 68215	0.1
Dye Assistant as in Ex. 1	1.0
Wetting agent	0.1
Sulfuric acid (to pH 1.6).	
Water (to 100 pts.).	

Dye exhaust is nearly quantitative. In a comparison with an unmodified MPD-I polymer yarn, it is found that less than 50% of the dye was taken up by the fiber.

Example 3

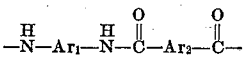
This example illustrates suitability of the process of this invention for dyeing of ordered copolymers such as disclosed in U.S. 3,232,910.

N,N′-m-phenylene bis(meta amino benzamide), abbreviated MPBB hereinafter, is prepared by reacting two mol-parts of meta nitro benzoyl chloride with one mol-part of MPD in DMAc and reduction of the resulting dinitro intermediate to the diamine by atmospheric pressure by hydrogenation, using Pd-on-carbon as catalyst

To the diamine (154 parts) and 11.4 parts of CaSMPD in 1420 parts of DMAc cooled to −20° C. is slowly added 101 parts isophthaloyl chloride with good agitation. The resulting viscous solution is neutralized by addition of 37 parts dry lime slurried in an additional 100 parts DMAc. After vacuum deaeration with elimination of a portion of the DMAc and a small amount of water, the solution is found to contain a copolymer of MPBB-I/CaSMPD-I in a molar ratio of 89/11, suitable for dry-spinning to useful fibers. The solution is dry spun in a manner equivalent to that of Example 1 and the filaments so obtained are extraction-drawn to 450% of their spun length in hot water. The filaments are heated at 260° C. for 20–30 minutes under conditions of no restraint.

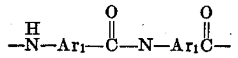
The filaments are cut to about 2″ (about 5 cm.) staple and hand carded pads made therefrom. The pads are dyed at 15 p.s.i.g. for 2 hours at a pH 45, otherwise using the procedure and formulation of Example 1 The fiber is found to dye satisfactorily to deep shades.

While the invention has been described with particlar reference to copolymers of MPD-I, it will be obvious that the process may be advantageously applied to any aromatic copolyamide (including terpolymers). The amides which may occur at the major constituent in the aromatic polyamides used in the process of this invention are exemplified by those disclosed in the Kwolek et al., U.S. Patent 3,063,966. Suitable as major constituents are those based on aromatic diamines and aromatic diacyl compounds as well as those based on aromatic amino-acyl compounds. The former yield polymers having the repeating structure



$$-\overset{H}{N}-Ar_1-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-Ar_2-\overset{O}{\overset{\|}{C}}-$$

while the latter yields polymers having the repeating structure



$$-\overset{H}{N}-Ar_1-\overset{O}{\overset{\|}{C}}-N-Ar_1\overset{O}{\overset{\|}{C}}-$$

wherein Ar_1 and Ar_2 represent divalent aromatic residues and may be the same or different. Also useful in the practice of this invention are the various combinations, ordered or random, of both types of structures. Ordered copolymers are illustrated in the Preston U.S. Patent 3,232,910. The minor amide constituents are exemplified by those derived from

sodium-2,4- (or 3,5) diamino benzensulfonate,
disodium-4,4′-diamino biphenyl-2,2′-disulfonate,
5-sulfo isophthaloyl chloride (or of sulfoterephthaloyl chloride),
pyridine 2,5-dicarbonyl chloride,
4,4′-diamino stilbene-2,2′-di(sodium sulfonate),
4,4′-diamino diphenyl methane-2,2′-di(sodium sulfonate),
4,4′-diamino diphenyl methane-3,3′-di(sodium sulfonate),
4,4′-diamino diphenyl sulfone-3,3′-di(sodium sulfonate),
4,4′-diamino diphenyl sulfide-2,2′-di(sodium sulfonate),
sodium-2,6-naphthalene diamino-8-sulfonate,
4,4′-diaminodiphenyl ether-2,2′-di(sodium sulfonate),
4,4′-diaminodiphenyl ether-3,3′-di(sodium sulfonate),
2,4-quinoline dicarbonyl chloride,

and the like.

In addition to copolyamides, blends of polyamides where a minor component of the lend is a polyamide containing a dye associable substituent may be used in the process of the present invention, the minor component constituting from about 2 to about 15 weight percentage of the blend. A typical blend for such a purpose can be formed by mixing 2400 parts of an 18.4% MPD-I polymer solution in DMAc/calcium chloride with 272 parts of a 20% solution of a CaSMPD-I polymer in DMAc. The solution can then be dry spun to a filament.

As pointed out above, the process of this invention is generally applicable to aromatic polyamide structures. It is especially useful for aromatic polyamides which strongly tend to consolidate to highly dense structures at high temperature; these are characterized as those having a well-ordered molecular structure and/or unsubstituted amide hydrogens. When highly consolidated by heat, structures of polyamides are not penetrated by dyes available in the trade to a useful extent. The utility of this invention in process for dyeing of such structures is subject only to three limitations: (1) the polymer must carry functional groups which tend to yield stable associations with a dyestuff, (2) high temperature exposure in the process for preparation of the shaped structure must be encountered only when the structure is free to relax, and not exceed 280° C., and (3) a dye assistant

is required which is, under the conditions of dyeing, absorbed by the structure to the extent of at least 5%. Typical useful dye assistants are B-napthol; diphenyl sulfone; salicyl aldehyde; salicylic acid, salicylanilide; dimethyl isophthalate; benzyl alcohol; pelargonic acid; benzoic acid; o-phenyl phenol; dimethyl terephthalate; benzanilide; isopropylidene 4,4′-di-phenol; hexamethyl phosphoramide; dimethyl acetamide; or other members of the homologous series, wherein the acyl residue comprises 1–10 carbon atoms, formic acid and the lower homologues thereof, methylene chloride, dimethyl cyanamide, tetramethylene sulfone, 2,4-dimethyltetramethylene sulfone, ethylene diamine, triethylene tetramine, pyrrolidine, pyridine, piperidine, cyclohexylamine, and the like, it being required only that the compound or mixture employed as a dye assistant must have sufficient affinity for the aromatic polyamide structure that it is absorbed by said structure to the indicated extent despite the tendency of many of the materials to form a stable solution in water under the conditions employed. It is recognized that not all of the materials which are suitable for use as a dye-carrier of a shaped structure comprising a given aromatic polymer will be suitable for use as a dye carrier for structures of all other polymers. The requirements are less severe in selection of a carrier for dyeing of a structure comprising a highly modified polymer, and a broader range of carriers is found suitable.

The use of autogenous superatmospheric pressure (5–30 p.s.i.g.) with its attendant higher temperature is of distinct advantage to this process. In addition, the presence of up to about 15 molar percentage of a second copolymeric constituent in addition to the one bearing the dye sensitive substituent will tend to break up the well ordered structure of the main polyamide chain and further enhance its susceptibility to dyeing. Use of such terpolymers in the copolymeric structure and/or presence of a larger quantity of carrier therein may permit dyeing to a practical degree without use of superatmospheric pressure.

In processing the fibers of the present invention it is important that they not be exposed to temperatures as high as about 200° C. while taut prior to high-temperature relaxation. Heating of the drawn filaments while relaxed for as little as 1 min. at the upper range of tempeature treatment is usually adequate for purposes of the present invention. Longer periods are required if lower temperatures are used. Generally a draw of about 4½ times extruded length is used to develop good textile properties in the yarn, and relaxed heating is provided until an effective draw of about 3½ times is reached due to shrinkage in the heat treatment step. The heat relaxation step can be performed upon the yarn, staple or fabric. It is often advantageous to steam the drawn yarn (or staple or fabric) prior to heat relaxation in order to reduce residual shrinkage in boiling water in the final structure. Such steaming does not affect dyeability.

Although only the sodium and calcium salts of the anionic-active minor constituent of the copolymeric structure have been exemplified, other neutralizing cations may conveniently and advantageously be employed. Among these are the magnesium, manganese, bismuth, triethyl ammonium, aluminum zinc, ammonium, cadmium, potassium and lithium salts.

The invention is not limited to the exemplified anionic-active or cationic-active copolymeric constituents. It will be apparent to one skilled in this art that the only criterion of such a constituent is that it comprise an aromatic-ring substituent of the desired functionality in combination with bifunctional, polyamide-forming capability. Such a compound may comprise one or more aromatic rings and where two or more are involved may comprise additionally alkylene, cycloalkylene or heterocyclic groups therebetween with the limitation that the chain-extending, amide-precursive groups must, in each case, be directly attached to carbon of aromatic rings.

Other bifunctional radicals which may bridge between aromatic moieties of the starting materials are oxo, sulfide, disulfide, methylene, propylene, dimethyl methylene, carbonyl, sulfo, hexafluoroisopropylidene and the like. It is within the scope of this invention to employ an amino carbonyl halide bearing a functional group capable of stable association with a dyestuff, as exemplified by 3-amino chlorobenzoyl 5-sulfonic acid.

Since many departures from the specifically exemplified embodiments may be made which are within the spirit and scope of this invention, limitations are to be regarded only as set out in the claims which follow.

What is claimed is:

1. A process for dyeing drawn filaments of a copolymer of repeat units selected from the group consisting of m-phenyleneisophthalamide and N,N′-m-phenylene bis (meta amino benzamide)isophthalamide, and from 2 to 15 molar percent of repeat units consisting of the isophthalamide of a metallic salt of 2,4-diaminobenzene sulfonic acid, said process comprising heating said drawn filaments, while they are free to relax, at a temperature between about 150° to 280° C. for a period of from about 1 minute at the upper temperature to about 45 minutes at the lower temperature and thereafter dyeing said filaments under superatmospheric pressure in an aqueous dyebath containing a basic dye and an organic dye carrier which is substantially inert to the dyebath under the conditions employed and is capable of being absorbed by said filaments to the extent of at least 5% by weight of said filaments under the conditions employed.

2. The process of claim **1** wherein said organic dye carrier is an equal weight mixture of dimethyl terephthalate and benzilide.

References Cited

UNITED STATES PATENTS

3,184,436 5/1965 Magat -------------- 260—78

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U.S. Cl. X.R.

8—173, 174, 178; 260—78