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PROCESS FOR ADJUSTING THE DYE RECEPTIVITY OF ACRYLIC FIBERS

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ABSTRACT OF THE DISCLOSURE

A process for adjusting the dye receptivity of dry-spun acrylic fiber is provided by changing the temperature of the wash-draw liquid based upon a deviation in dyeability of the product from that of a standardized range of dyeability. The temperature of the liquid is changed inversely with the direction of change to be made in the fiber dyeability.

This invention is concerned with the production of acrylic staple and tow which is conveniently dyeable by means available in the textile art, and more particularly to a novel method for the production of acrylic staple and tow having more uniform dye receptivity from one lot of production to another.

It is recognized in the art that many, if not most, end uses for textile fiber require that the fiber be dyeable by means available in the textile trade. Further, it is essential that the textile processor be able to duplicate reliably the dye shade desired in all lots of a given fiber. Preferably, this uniform depth of dyeing should be achieved without deviation from some standard dyeing procedure.

In the production of synthetic textile fibers, therefore, control of lot-to-lot variations in dye receptivity is an important objective. In U.S. Patents 2,837,500 and 2,837,501, for example, copolymers and terpolymers, respectively, are described which comprise chemically combined anionic groups (derived from a copolymerizable sulfonate) capable of reacting with and retaining in a shaped structure thereof any of a large group of cation-active, or basic, dyes. The primary control of dyeability in manufacturing fibers from such polymers is careful control of anionic-function content. Similarly, acid, or anionic, dyeability may be conferred by the inclusion in the polymer of cationic function such as is represented by a variety of vinyl pyridines; such copolymers are described, for example, in U.S. Patent 2,491,471. Also, disperse dyeability (with dyes which do not depend on chemical bonding for retention by the fiber) is enhanced, for example, by the inclusion in the polymer of a second copolymerizable monomer which alters molecular structure in such a way as to encourage entry of the dispersed dye into the fine structure of the fiber. An example of such a copolymer is disclosed in U.S. Patent 2,325,454. As in the case of the polymers having anionic-active substituents, the primary control of acid- and disperse-dyeability resides in the amount of the modifier added.

It has long been recognized, however, that factors other than modifier content are present in the manufacture of synthetic fibers which can exert small, but important, influences on the dyeability of the product fiber. Such factors are incompletely defined and thus are not amenable to the degree of control necessary to maintain consistently the required uniformity of dye-receptivity in the product fiber. Compensating variations in modifier content of the polymer which the fiber comprises has been found a useful expedient, but this approach is severely limited in value because of the slow response inherent in any commercial operation having a large mass of fiber-forming solution in process at any given time. The need for a compensating control late in the process of manufacture has long been recognized.

This invention provides an improved means for control of dye receptivity in synthetic fibers. It more particularly provides a means for controlling the dye receptivity of acrylic fiber which is independent of polymer composition. Further advantages will be recognized as the description of invention proceeds.

In accordance with the present discovery, uniformity or adjustment of dye receptivity in acrylic staple or tow is achieved by adjusting the temperature of the wash solution conventionally employed in the wash-draw zone used in the production of such products. It has been discovered that a change in dye receptivity of acrylic fiber can be brought about by changing the temperature of the wash solution inversely with the direction of change to be made in dyeability. Thus, if in operation of the process with say 95° C. wash liquid, a sustained decrease in dye receptivity is noted, compared with a standardized level of dye receptivity for the fiber being produced, dye receptivity is returned or increased to the standardized or specification range by lowering the temperature of the wash liquid and continuing operation with that lower temperature. The converse of the foregoing also can be carried out. With any given polymer and wash liquid, the proportional effect of temperature change on dye receptivity can be determined whereupon a simplified control chart can be provided to guide operators in the practice of the invention.

The application of the invention to a typical process is as follows: acrylic fiber is dry spun from a solution of the polymer in an organic solvent. The spun fibers are drawn 150 to 600% of their as-spun length in a bath of water and the spinning solvent. This solution serves to extract the spinning solvent from the fibers to a level of 1.5% or less and is passed counter-current to the passage of fibers. Normally its temperature is in the range of 90 to 10° C. The tow from the wash-draw zone is then dried and if staple is to be produced, cut to the desired length. From time-to-time, dye receptivity of the product is determined and when it deviates from a specification level, the level is reestablished by adjusting the wash liquid temperature as determined from previously established empirical relationship between wash-water temperature and product dyeability to either maintain the existing level of dyeability (i.e. prevent further deviation) or to make an appropriate change toward the desired level. In general, an increase in wash water temperature results in a decrease in dyeability. It has been found that the lowest dependence of dye receptivity on wash water temperature occurs in the range of 94–96° C. It is advantageous, therefore, to operate at about 95° C. routinely to minimize the effect of small variations in wash water temperature on dye receptivity. It will also be apparent that temperature adjustments may be made from this middle-ground to

compensate for adventitious variations in dye receptivity in either direction.

The substantial advantages of adjustment for dye receptivity variations as late in the process of manufacture as wash-drawing will readily be recognized by one skilled in this art. It is not understood why small changes in temperature at this stage have an effect on dye receptivity, but it is believed that the fine structure of the fiber may be altered in some manner by variations in temperature during wash-drawing.

The invention may more readily be understood by reference to the following examples.

In the examples, "Percent Dye" is a measure of dye receptivity expressed as percentage of an arbitrary standard represented by a lot of retained fiber. Each laboratory test of dyeability includes samples of this retained lot so that variables in lot-to-lot dye testing are blanked out. The procedure employed is as follows:

A bath consisting of approximately 400 ml. per gm. of fiber to be dyed is prepared to contain the following ingredients (in terms of gms. per gram of fiber to be dyed).

	Grams
Cationic dye stripper commonly used for stripping azoic dyes	0.025
Glacial acetic acid	0.005
Sodium acetate	0.005
Sodium sulfate (calc. as anhydrous)	0.10
Non-ionic surfactant commonly used as a dyeing assistant	0.01
CI Basic Red 18	0.05

A three-gram sample of each test fiber, in the form of approximately 2" staple, and samples of the standard fiber mentioned above, are hand-carded to pads which are then placed in a basket designed to rotate slowly in the above bath.

The bath is heated to 70° C. and the samples are added. Agitation by slow rotation of the basket is begun immediately. The bath is rapidly brought to a boil, by admission of steam to immersed heating coils, and is boiled for 20 minutes. The bath is then drained away and the samples rinsed twice with water. The vessel is then filled with pure water to which is added .01 gm./gm. of fiber being dyed of the surfactant employed in the dyeing step. The bath is boiled for 30 minutes then drained away, and the samples are then rinsed thoroughly and centrifuged to thoroughly remove adherent water. They are then recarded to 3" x 6" pads and examined for dye pick-up by the method of Glasser, J. Op. Soc. Am., vol. 42, No. 9, pp. 652–660, September 1956. In this method, each sample is analyzed in a differential colorimeter for blue reflectance, using a standard 4% gray plate as reference. Each test sample is reported in terms of the percentage of blue light absorbed by it relative to the average of the pads of standard fiber, which are arbitrarily rated as 100%.

EXAMPLE I

An acrylic tow of 470,000 total final denier, of filaments of 3 denier each, is prepared by dry-spinning a solution in dimethyl formamide of a terpolymer of 1.5 intrinsic viscosity comprising, by weight, 93.8% acrylonitrile, 6% methyl acrylate and 0.2% sodium styrene sulfonate through multi-orifice spinnerets; combining into a single rope sufficient ends of the spun filaments to provide the desired denier after drawing; washing and drawing the rope 4.5× (to 450% of its as-spun length) by directing it sequentially under driven rolls immersed in each of a series of ten tanks of wash liquor maintained at the temperature specified below; and drying the washed and drawn rope to less than 1% moisture on a continuous, foraminous-belt dryer using circulated, heated air.

In Test A, the wash-liquor temperature in each tank is controlled at 98° ±0.5° C. In Test B, the wash liquor is maintained at 85° ± 0.5° C. In these, as in all tests described herein, temperature is instrumentally controlled

and heat is provided by means of immersed steam coils. All other process factors are identical for the two tests.

Three samples of dried tow from each test are analyzed. Average values obtained are reported in Table 1.

TABLE 1

Test	Wash Temp. (° C.)	Avg. Dye (Percent)	Tenacity (g.p.d.)	Elongation at break (Percent)	Residual DMF (Percent)
A	98	91.0	2.1	35.1	0.6
B	85	108.6	1.9	35.5	0.7

A significant different is seen only in dye receptivity.

EXAMPLE II

Following the procedure of Example I, twelve additional lots of two are prepared, four in each of 3 d.p.f., 4.5 d.p.f. and 6 d.p.f. One lot of each denier is wash-drawn in wash liquor maintained at each of the following temperatures: 92° C., 94° C., 96° C., 98° C. Table 2 presents the results obtained by analyzing these lots.

TABLE 2

Tow identify (d.p.f.)	Wash Temp. (° C.)	Avg. Dye (Percent)	Tenacity (g.p.d.)	Elongation at break (Percent)	Residual DMF (Percent)
3	92	102.3	2.4	34	0.4
3	94	100.7	2.3	34	0.5
3	96	100.7	2.5	34	0.4
3	98	97.7	2.4	34	0.5
4.5	92	94.7	2.6	37	0.5
4.5	94	91.7	2.6	32	0.7
4.5	96	91.7	2.7	37	0.4
4.5	98	91.3	2.6	37	0.6
6	92	96.3	2.6	44	0.8
6	94	90.7	2.7	41	1.1
6	96	90.3	2.6	39	0.7
6	98	87.3	2.8	41	1.0

Again, it is seen that in no case is any property of a lot excepting dye receptivity affected significantly. The low dependence of dye receptivity on wash-liquor tempeature in the range of 94–96° C. is clearly evident in each of the three filament sizes tested.

The discovery that wash liquor temperature is related to dye receptivity of the fiber could not have been predicted from the published art. It will become apparent that this invention represents a significant advance in the art of acrylic fiber manufacture when it is considered that a 10% change in percent dyeability on the scale employed herein represents a change of 2 to 2.5 standard shades in dyed fabrics.

EXAMPLE III

This example illustrates the practical utility of the process of this invention in continuous production of an acrylic fiber.

The process of Example I is repeated on a continuous production basis. Wash-draw liquor temperature is set at a value based on experience in earlier production which indicates that the temperature will generally yield a product having the desired level of dyeability. After a period of controlled operation it becomes evident that some undefined factor in the process is leading to a downward trend in dyeability. By the 10th day of test, an out-of-limits dyeability value is obtained. Thereupon the wash liquor temperature is lowered to 95° C., a change determined from previous tests to be effective to bring the dyeability well within the specification limits desired. Table 3 records the daily values obtained and illustrates the immediate response in level of dyeability resulting from the change in wash-liquor temperature.

TABLE 3

Day of test	Wash liquor temp. (° C.)	Anionic substituent, milliequivalents/kg.[1]	Dyeability (Percent)
1	97	52.8	93.5
2	97	51.5	94
3	97	52	91.3
4	97	51.5	90.8
5	97	51.5	90.6
6	97	51.8	89.2
7	97	51.5	88.8
8	97	51.0	88.2
9	97	51.5	88.5
10	97	51.2	87
11	97→95	51.5	85.8
12	95	51.5	97.4
13	95	51.5	93.3
14	95	51.2	93.5
15	95	51.5	95.2
16	95	50.7	93.2
17	95	50.7	95.5

[1] From analysis of the polymer representative of that which the fiber sample for that day comprises. This figure is obtained by (1) dissolving a sample of the polymer in a suitable solvent such as dimethylformamide, (2) dionization of the solution by passage in sequence through beds of (a) mixed strong cationic- and strong anionic-exchange resins and, (b) strong cationic exchange resin, such that all anionic function in the polymer is converted to the free acid form and all ionic impurities are removed and (3) titration of the combined acid with standardized alcoholic potassium hydroxide. (The ion-exchange resins must have been thoroughly dehydrated by washing with the solvent before use. They are stored under the same solvent between uses.) The first and last appearance of the sample in the effluent from the ion-exchange columns can be determined by use of a suitable indicator for acid such as a mixture of equal parts of neutral red and xylene cyanol FF which can serve as an end-point indicator in the titration which follows. Alternatively, an electrometric titration may be employed. Results are calculated in the usual way after subtracting the amount of excess of standardized potassium hydroxide required to reach the same color or E.M.F. end point in an equal-volume sample of pure solvent which has been passed through the same columns and to which subsequently has been added a known amount of standardized hydrochloric acid. The weight of polymer in the sample is conveniently obtained by evaporation of an aliquot portion to constant weight. Alternatively, the solids content may be determined by measurement of viscosity of the effluent solution, taking into account the known intrinsic viscosity of the polymer.

It will be obvious that any of the recognized methods of process regulation based on statistical and inferential evaluation of performance may be employed in this process. For example, the method of the cumulative sum of variance may quickly establish any long-term drift of the mean and thus lead to smaller excursions from the aim. In this method, the variance from the aim (or mean) is summed over an arbitrary period of time, say for 6–10 days; on succeeding days the oldest value is dropped and the newest value added. Whenever the sum of variance reaches an arbitrary limit either above or below the aim, a change is made. Regardless of the method employed, it must be considered as subject to adjustment as required by the process until it provides the optimum in response to the indicated corrections.

It is not intended, therefore, that this invention be limited to any specific method of determining that the operation or process needs adjustment. The heart of the invention is the unexpected discovery that a practical regulation of dyeability can be realized through small changes in wash liquor temperature. The fact that dyeability dependence on wash liquor temperature is at a minimum near the center of the useful range of temperature is fortuitous and highly advantageous, particularly in so-called normal operation when no adjustment in temperature is required. It will also be apparent that process control in accordance with the present discovery can be made essentially automatic, if desired.

While this invention has been exemplified with fibers produced from a particular process and a particular acrylonitrile terpolymer, it should be apparent that it is applicable to production of any acrylic fiber by the dry-spinning process. By acrylic fiber is meant any fiber comprising a polymer of at least 85% acrylonitrile and 0 t 15% of at least one other ethylenically unsaturate monomer copolymerizable with acrylonitrile.

What is claimed is:

1. In the processing of tow of dry-spun acrylic fibers which tow is passed to a wash-draw zone where it drawn and washed with an aqueous solution maintaine at an elevated temperature and the drawn tow then dried and its dyeability is determined and compared wi a standardized range of dyeability, that method of chan ing the dyeability of tow being produced to move it to t standardized range comprising changing the temperatu of the liquid in contact with tow in the wash-draw zor inversely with the direction of change to be made in to dyeability.

2. In the processing of tow of dry-spun acrylic fibers i which the tow is passed to a wash-draw zone where it drawn and washed with an aqueous solution maintaine at an elevated temperature within the range of about 90 to 100° C. and the drawn tow then is dried and its dye ability is determined and compared with a standardize range of dyeability, that method of increasing the level o dyeability of tow being produced when it has decrease to a level below the standardized range comprising de creasing the temperature of the liquid in contact with to in the wash-draw zone.

3. In the processing of tow of dry-spun acrylic fibers i which the tow is passed to a wash-draw zone where it i drawn and washed with an aqueous solution maintaine at an elevated temperature and the drawn tow then i dried, a dyeability control procedure comprising con tinuously determining dyeability of the tow product an comparing it with a standard, noting deviations from sai standard, and when a plurality of dyeability deviations ar uniformly removed from specification dyeability, the ste of restoring dyeability of the tow to the specification level comprising changing the temperature of said wash liquic in contact with tow in the draw zone proportional to the deviation and inversely with the direction of change tc be made in tow dyeability to return it to specification dyeability.

4. In the processing of tow of dry-spun acrylic fibers in which the tow is passed to a wash-draw zone where it is drawn and washed with an aqueous solution at a temperature of about 90° to 100° C. and the drawn tow then is dried, a dyeability control procedure comprising continuously determining dyeability of the tow product and comparing it with a standard, noting dyeability decreases from said standard, and when a plurality of dyeability decreases are uniformly removed from specification dyeability, the step of increasing dyeability of the tow to the specification level comprising decreasing the temperature of said wash lqiuid in contact with tow in the draw zone proportional to the deviation to return tow dyeability to specification dyeability.

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