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PROCESS OF DYEING NYLON WITH DILUTE SOLUTIONS OF ACID DYES

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4 Claims. (Cl. 8—55)

1

This invention relates to the dyeing of textile fabrics and more particularly to dyeing nylon fibers and fabrics.

The synthetic linear polyamides known as nylon and the production of fibers and fabrics therefrom have been described in a number of United States patents in particular in 2,071,250, 2,071,253 and 2,130,948. These fiber-forming polycarbonamides described in the previously mentioned patents are obtained by several methods, for example, by self-polymerization of a monoaminomonohydric alcohol, e. g., monoethacaproic acid or 12-aminostearic acid, by reacting in substantially equimolecular proportions a dibasic acid, e. g., adipic or sebacic acid with a diamine, e. g., hexamethylenediamine or with a monoaminomonohydric alcohol, e. g., monethanolamine, it being understood that these reactants can be replaced by their equivalent amide-forming derivatives. These linear polyamides also include polyesteramides, for example, those obtained by admixture with other linear polymer-forming reactants, such as glycol-dibasic acid mixtures, or mixtures of hydroxy acids, with the previously mentioned polyamide-forming reactants. On hydrolysis with hydrochloric acid the amino acid polymers yield the amino acid hydrochloride, the diamine-dibasic acid polymers yield the diamine hydrochloride and the dibasic carboxylic acid, and the amino alcohol-dibasic acid polymers yield the amino alcohol hydrochloride and the dibasic carboxylic acid. In these polyamides the average number of carbon atoms separating the amide groups is at least 2. The preferred polyamides have an intrinsic viscosity of at least 0.4 (defined as in Patent 2,130,948) and a unit length (defined in Patents 2,071,253 and 2,130,948) of at least 7.

The filaments, yarns, fibers, fabrics and the like, made from the nylon polymers described above, which may be referred to more briefly as nylon textile articles, when dyed with certain types of colors, and particularly with the class known as acid dyes, are characterized by unevenness of color application, and depth of shade differences due to variation of dye affinity over the fiber. Yarns from different bobbins, i. e., spun at different times or from different lots of polymer show this effect most clearly. In practically every case, yarns treated exactly alike in manufacture but from different bobbins are colored to a different extent with acid colors when dyed by standard dyeing procedures. These variations in yarn dyeing properties are responsible for streaks and shade depth variations in knitted goods and

2

for barré effects and warp streaks in woven goods. Non-uniformity in dyeing behavior of the yarn is due to slight variations in chemical composition which cannot be completely controlled by present manufacturing processes and to variation in orientation (draw ratio) arising either in the spinning and processing of the yarn or in mechanical action of the textile machinery used in knitting or weaving of the yarn into fabrics, although other as yet unrecognized causes may also be contributing factors. In spite of these disadvantages, it is desirable to use these acid dyes as they are fast to washing on nylon. In contrast the acetate dyes, which are used extensively in commercial practice, are fugitive to washing but they are not highly sensitive to normal variations found in the yarn as described above.

This invention has as an object a method for the acid dyeing of nylon with evenness of color application and without the resulting streaks and shade depth variations that have previously characterized the acid dyeing of nylon fabrics. Other objects will appear hereinafter.

The above objects are accomplished by a controlled-rate dyeing method wherein the concentration of the dyestuff is so extremely dilute that the dyebath is practically colorless, this method comprising dyeing the nylon by immersion in an aqueous dye bath in which the concentration of the acid dye in the liquid phase of the bath is maintained between 0.1 and 50 parts per million based on the aqueous medium throughout the dyeing operation.

I have discovered that nylon fibers can be dyed in the above described manner and that when they are so dyed they are uniformly colored without the variations in shade that normally occurs in acid dyeing of nylon yarns because of differences in dye affinity over the fiber length by reason of variation in orientation, or because of variation in chemical constitution of the nylon composing the yarn being dyed.

In one method for carrying out the invention the nylon is immersed in water and the acid dyestuff is added with good agitation at a rate equal to, or less than, the rate at which the dyestuff is taken up by the nylon. In a preferred procedure embodying this method a section of nylon fabric is placed in a bath containing 5% of acetic acid based on the weight of nylon present. To this is added a dilute solution of dyestuff with vigorous agitation at a rate such that the nylon absorbs the color as fast at it is added, i. e., the bath remains visually colorless at all

times. With most acid dyestuffs, this addition can be carried out to obtain a hosiery shade in about one hour. The nylon fabric is then lifted from the dyebath, rinsed with hot water and dried. Dyestuff is applied evenly over the surface by this method even though draw ratio of the yarn used in preparation of the fabrics differs by as much as 4%, or if the fabric is prepared from yarns spun from different lots of nylon which, under normal dyeing conditions, show wide variation in depth of shade.

Another method of accomplishing the same result is by first applying the color to a medium capable of absorbing the dye, such as wool or other polymer containing amine groups, and then heating the dyed medium and nylon fabric together in a dyebath. The dyestuff comes off the medium at a very slow rate and is taken up by the nylon as fast as it is made available. Heating is continued until the desired depth of shade is obtained on the nylon. The time required for this operation varies with the type of the dyestuff applied, and upon the depth of shade desired, being generally from about one hour to about 12 hours.

The invention is further illustrated by the following examples in which the parts given are by weight unless otherwise stated.

Example I

This example illustrates the use of dyed wool as a source of dyestuff in the coloration of nylon.

Two parts of wool are washed with alcohol followed by an ether wash to remove spinning and processing oils and the wool is then dried. The dried wool is placed in a bath containing 3% of Du Pont Anthraquinone Green G, Rowe Color Index No. 1078, and 1% of acetic acid (all percentages based on the weight of wool present). The bath is heated to 100° C. slowly and kept at that temperature for 45 minutes at which time a further 2% portion of acetic acid is added and heating continued for 15 minutes longer. The wool is then washed and dried.

The above sample of wool is placed in 300 parts of water with 2.4 parts of a section of knitted nylon fabric prepared from yarns drawn respectively 3.82 and 3.99 (a difference of 4%) times its length as spun from the molten polymer. To this is added 5% of acetic acid and 10% of sodium sulfate with percentages based on the weight of nylon present. This bath is brought up to 100° C. and kept at that temperature for 1 hour. During this time color slowly leaves the wool and is taken up by the nylon. The percent color in the bath is determined by spectrophotometric methods to be about 0.8 part per million based on the aqueous medium. The amount of color on the nylon at the end of one hour of heating was about 0.5%. This dyed nylon fabric is uniformly colored over the entire section and shows no change in depth of shade where the two yarns were spliced together in the knitting of the fabric. A similar section of nylon fabric knitted from the same yarns is dyed in a bath containing 300 parts of water, 0.5% Du Pont Anthraquinone Green G, Rowe color index No. 1078, 5% of acetic acid and 10% sodium sulfate (percentages based on the weight of nylon present) for 1 hour at 100° C. The resulting dyed section shows a marked increase in shade depth at the point where the yarn of draw ratio 3.99 was spliced to the yarn of draw ratio 3.82 during knitting.

Example II

This example illustrates use of dyed wool as a source of dyestuff coloration of nylon fabric, knitted from yarns differing 4% in draw ratio, with a range of acid dyes.

Two parts of wool are dyed with acid colors according to the method described in Example I. In each case the wool sample is heated together with a section of nylon fabric half of which is knitted from a yarn of draw ratio 3.82 and the other half knitted from a yarn of draw ratio 3.99 (a difference of 4%), in a bath buffered to pH 7 or 4 as shown in the accompanying table. In each case the nylon fabric is evenly colored and does not show any difference in shade depth where the two yarns were spliced together. Dyeing of similar nylon sections with these acid dyes by the conventional method as described in Example I, results in fabric that is distinctly more deeply colored on the side knit from yarn of draw ratio 3.82 than on the side knit from yarn of draw ratio 3.99.

Rowe Color Index No.	Name	Parts Wool	Percent Dye on Wool	Parts Nylon	pH of Transfer Bath	Hours Heating of Transfer Bath	Percent Color on Nylon
430	Du Pont Milling Red SWB	2	5	2.5	7	12	1.5
430	Du Pont Milling Red SWB	2	10	2.5	7	1.5	0.25
1054	Du Pont Anthraquinone Blue B	2	2.8	1.7	4	3	0.5
1080	Du Pont Anthraquinone Violet R	2	3	1.5	4	3	0.1

Example III

This example illustrates the advantages of dyeing from a very dilute solution by mechanically regulating the rate of dyestuff addition slower than the rate of dye take-up by nylon.

Two parts of a piece of nylon fabric similar to that described in Examples I and II is put in a bath containing 0.04 part of acetic acid. To this is added a mixture of dye dissolved in 100 parts of water consisting of 0.0024 part of the product obtained by diazotization of 4-nitro-4'-aminodiphenylamine-2-sulfonic acid and coupling with O-cresol followed by condensation with p-toluenesulfonic acid, 0.0044 part of the product obtained by diazotization of 4-nitro-4'-aminodiphenylamine-2-sulfonic acid and coupling to 1-aminonaphthalene-7 sulfonic acid diazotized and coupled to phenol and subsequently condensing with p-toluenesulfonyl chloride, and 0.0007 part of the product obtained by coupling diazotized 4-amino-4'-methyldiphenylamine-2-sulfonic acid to α-naphthylamine followed by diazotization and coupling to 2-naphthol-6-sulfonic acid over a period of 5 hours dropwise with the goods being agitated well during the addition of dyestuff. The dyebath remains visually colorless throughout the addition of the dyestuff. After rinsing, the nylon goods is found to be dyed evenly with no blotches and no variation in shade depth due to change in draw ratio of the nylon yarn.

Dyeing a similar section of nylon with the same colors in the same amounts in the normal procedure, i. e., dissolving the colors in water,

adding acid and then introducing the nylon, followed by heating to the boiling point, and keeping it at that temperature for 1 hour, leads to a piece of dyed nylon fabric that is spotty and that shows sharp differences in shade depth where draw ratio is changed.

Example IV

This example illustrates uniform application of acid dyes on nylon fabric knitted from yarns that show bobbin-to-bobbin shade depth differences in conventional dyeing procedures which are due mainly to effects other than orientation (draw ratio) variation.

Two parts of a section of nylon fabric knit from two yarns spun at different times, each of which was drawn 3.99 times its original length on the same machinery and otherwise processed alike in coning and knitting, are placed in a bath consisting of 170 parts of water and 0.1 part of acetic acid. The bath is heated to 90° C. and the same dyestuff mixture described in Example III dissolved in 100 parts of water is added dropwise over a three hour period with vigorous agitation of the dyebath. The dyebath remains visually colorless throughout the addition of the dyestuff and the concentration of dye was in the range of 1 to 10 parts per million. The nylon piece is then rinsed and dried. Examination of the piece shows that it is evenly colored and contains no light shaded areas or spots.

For comparison, a dyeing is made on a similar section (2 parts) of fabric knit from the same yarns as used above and dyed in the conventional manner with the same dyestuff mixture. The nylon section is introduced into a dyebath consisting of the dyestuff dissolved in 100 parts of water and 0.1 part of acetic acid. The temperature is gradually raised to 100° C. and heating at that temperature continued for 1 hour. After rinsing and drying the fabric is colored in two sections, one side being much more deeply colored than the other with the line of demarcation corresponding to the point at which the two yarns were spliced together during knitting.

The most important factors to be considered in dyeing by the method of this invention are concentration of dyestuff in the dyebath and agitation of the nylon goods during dyeing. Unless dyestuff concentration is kept very low throughout the dyeing period, variation in dyeing properties in nylon yarn are not equalized and streaks and shade depth difference become apparent. Also unless the nylon fabric being dyed is vigorously agitated, spotty dyed pieces are obtained.

A marked improvement in the dyed nylon is obtained with a concentration of the dyestuff as high as 100 parts per million. However, in order to obtain the best dyeings, in which the dyeing differences in the yarn are completely eliminated, concentrations of from 0.1 to 50 parts per million and preferably 0.1 to 25 parts per million, based on the weight of the water in which the nylon is being dyed, are used.

The dyestuff concentration can be regulated in several ways. As has been mentioned previously, one method is slow addition of very small increments of dyestuff so that nylon absorbs one increment before the next is added, and another consists in applying dye on a medium capable of absorbing dyestuffs which then will slowly liberate the color in a heated water bath, and heating the medium in such a bath with the nylon. Suitable mediums for this purpose are wool, polymers containing amino groups and basic ion-exchange resins. Examples of polymers containing amino groups that are suitable for this purpose are polymers and interpolymers of vinyl pyridine, 5-ethyl-2-vinylpyridine, etc., e. g. acrylonitrile/5 - ethyl-2-vinylpyridine. Still another method is to compress the dyestuff into pellets which dissolve slowly in the bath so that color is made available for dyeing at a slow or controlled rate.

In carrying out the method of this invention, the pH of the bath, temperature, character of the dyestuff used, rate of dyestuff addition, and rate at which dyestuff is absorbed by the nylon are factors, as will be understood by those skilled in the dyeing art, which affect the concentration of dyestuff that is attained in the bath. These factors are interrelated as will be explained in the following discussion.

The range of pH at which the dyeing is best carried out is from 2 to 7. As pH is decreased the rate of absorption by the nylon increases. Therefore, at low pH, the rate of dyestuff concentration can be maintained sufficiently low. On the other hand at high pH, rate of absorption of dyestuff by the nylon is very much slower, so that rate of dyestuff addition must be decreased accordingly to maintain satisfactory dyestuff dilution. For example, at a pH of from 3 to 4 with most acid dyestuffs as much as 1% based on fabric weight can be added in 1–3 hours at temperatures of 50–100° C., whereas at a pH of from 5 to 7 a much longer dyeing period is required to achieve the same results.

Similarly a wide temperature range, as in conventional dyeing practice, can be employed in carrying out these dyeings. The preferred range is from 50 to 100° C., and more advantageously from 75 to 100° C. As temperature is increased, rate of dye absorption by nylon increases, although not nearly to the same extent as that caused by pH change. Accordingly, the higher dyeing temperatures allow more rapid rate of dyestuff addition to the bath. Although temperatures below 50° C. can be employed, the rate of dyestuff absorption by the nylon becomes so slow that the dyestuff addition must be slowed down very greatly to maintain dyestuff concentration in the bath within the desired limits.

All of the types of the colors known as acid dyes are applicable to this invention. However, the members of this class vary widely in dyeing properties. For example, those known as acid leveling acid dyes, of which Du Pont Anthraquinone Blue AB (Rowe color index number 1075) is an example, are absorbed very slowly by nylon at high pH, although absorption is very rapid at low pH such as 3 to 4. For this reason it is preferred to employ baths of low pH when dyeing with these colors. On the other hand, the milling colors, of which Du Pont Milling Red SWB (Rowe color index number 430) is an example, are absorbed by nylon at a relatively rapid rate in dye baths of high pH. With these colors dyebaths of either high or low pH are satisfactory.

The amount of dyestuff that may be applied by the method of this invention is limited to substantially the same quantities that may be applied by conventional methods. However, as dye is applied to the nylon, the rate of further dye absorption begins to decrease. For this reason, if relatively large amounts of dyestuff, e. g., 1 to 2% based on the weight of the nylon with most colors, are to be applied to the nylon the rate of dyestuff addition must be decreased during the latter stages of dyeing to keep dyestuff

dilution in the bath within the limits prescribed in the earlier part of this discussion.

The nylon fabric used in the foregoing examples was prepared from hexamethylene adipamide. The nylon can, however, be any of the synthetic linear polyamides and interpolyamides previously referred to. The nylon fabric can, for example, be woven from yarn prepared from such polymers as polyhexamethylene sebacamide, polydecamethylene sebacamide, poly-omega caproamide, etc., and interpolymers. The polymer from which the fabric is prepared has an intrinsic viscosity of at least 0.4 and can be defined as a synthetic linear polycarbonamide wherein the average number of carbons in the segments of the chain separating the amide groups is at least two.

Additives which tend to reduce nonuniformity due to variation in yarn dyeing properties in conventional dyeing procedures may be added in the process of this invention. These include p-aminobenzoic acid, amylene/maleic anhydride adduct, isoamyl oxalate, and aniline sulfamate.

The invention can be readily carried out in various forms of available apparatus. The apparatus should be designed to allow free movement of the fabric to be dyed and good agitation of the bath. Further, arrangements should be made for heating the dyebath and for addition of the dyestuff at a controlled rate.

The present invention presents a valuable advance in the dyeing of nylon fabrics and particularly of hosiery since heretofore it has not been feasible commercially, despite the excellent wash-fastness of acid colors, to dye nylon hosiery with these colors because of the extreme differences in dyeing properties that acid colors show on yarn from different packages, that is from different lots of polymer. The method described herein eliminates the effects of these package to package differences in the dyed products and yields wash-fast dyed nylon fabrics that are remarkably even in color.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for obtaining by dyeing with acid dyestuff evenly dyed nylon textile articles, said process comprising immersing the nylon article in an aqueous dyebath containing the acid dyestuff in the liquid phase in a concentration at which the dyestuff is present in amount of from 0.1 to 50 parts per million based on the weight of the aqueous medium, and at which the dyebath is without appreciable visual color, adding to the dyebath during the dyeing a dilute solution of the acid dyestuff at a rate which is less than

the rate of absorption of the dyestuff by the nylon, and which maintains the dyebath throughout the dyeing without appreciable visual color, and continuing the addition of the dye solution at said rate until the desired depth of shade in the nylon article is obtained.

2. A process for obtaining by dyeing with acid dyestuff evenly dyed nylon textile articles, said process comprising immersing the nylon article in an aqueous dyebath which is without appreciable visual color and which contains a medium having acid dyestuff absorbed therein, heating the bath containing the nylon article and said medium immersed therein to cause transfer of the dyestuff from the dyed medium into the bath at a rate which maintains the concentration of the acid dyestuff in the bath within the range of from 0.1 to 50 parts per million based on the weight of the aqueous medium, and which is less than the rate of absorption of the acid dyestuff by the nylon, and which maintains the bath during the dyeing without appreciable visual color, agitating the bath during the dyeing, and continuing the heating with transfer of the dyestuff from said medium into the dyebath at said rate until the desired depth of shade in the nylon article is obtained.

3. The process set forth in claim 1 in which the concentration of the acid dyestuff in the liquid phase of the bath is from 0.1 to 25 parts per million based on the weight of the aqueous medium.

4. The process set forth in claim 2 in which the concentration of the acid dyestuff in the liquid phase of the bath is from 0.1 to 25 parts per million based on the weight of the aqueous medium.

WILLIAM H. SHARKEY.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,499,787 March 7, 1950

WILLIAM H. SHARKEY

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 1, lines 12 and 13, for the words "monoaminomonohydric alcohol, e. g., monoethacaprioc acid" read *monoaminomonocarboxylic acid e. g., 6-aminocaproic acid;*

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of July, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.