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DYEING NYLON HOSIERY

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This invention relates to the dyeing of nylon, and more particularly to an improvement in the process of dyeing nylon hosiery in which monofilament and multifilament yarns of different denier are employed in their fabrication, such as in the manufacture of sheer nylon hosiery for ladies' wear.

The term "nylon" is used in this specification to designate the new synthetic, fiber-forming, linear polyamides generally referred to in the trade today as nylon and which are described in the patents of W. H. Carothers U. S. 2,071,250, 2,071,253, 2,130,523, 2,130,948, 2,174,527 and 2,195,166. The nylon to which the present invention relates more particularly is that synthetic, fiber-forming linear polyamide produced by the condensation of adipic acid and hexamethylene diamine, as described in the above-mentioned patents.

The dyeing of nylon fibers with the various types of dyes was early considered in a paper by P. H. Stott, published in American Dyestuff Reporter, vol. 28, No. 20, October 2, 1939. Up to the present time it has been found that the acetate rayon colors which are water-insoluble, dispersed dyes give the most satisfactory results in the dyeing of nylon fibers, particularly in the dyeing of nylon hosiery. Under ordinary conditions in the dyeing of nylon multifilament yarns of varying denier, the same or closely similar tones are obtained as distinguished from the different shades or tones which are obtained when nylon yarn of varying denier is dyed with other types of dyes.

More recently, however, there has been introduced in the hosiery trade new types of sheer nylon hosiery for ladies' wear which are constructed of from 10 to 20 denier monofilament yarn in the leg or boot and of 30 to 60 denier plied nylon multifilament yarn in the welt. In the initial attempts to dye this new type of hosiery the acetate colors were used, for experience over a number of years has shown that this type of dyestuff gives far superior results in the dyeing of nylon than any other type of dye. These water-insoluble cellulose acetate dispersed colors have been found to give good dye union at junctions between nylon fibers having slightly different physical or chemical properties, such as "draw ratio," acidic or basic end groups, etc., as well as junctions of nylon multifilament yarns of somewhat different deniers.

It was found, however, that this type of dye, when employed on hose made from 10 to 20 denier monofilament in the leg and from 30 to 60

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denier multifilament in the welt, did not give a satisfactory union. Various expedients were tried to improve the union, such as by increasing the dyeing time or by increasing the dyeing temperature, but these expedients did not give the necessary improvement, or, if some improvement was obtained, other difficulties were experienced such as creasing of the hosiery, etc. The hosiery dyed with the acetate dispersed colors had more color in the leg of the hose than in the welt, and this effect detracted from the salability of the product because of the psychological block apparently set up in the minds of those persons who had not accepted hosiery dyed in contrasting strength in their various portions. It was, therefore, necessary to find some method for dyeing such hosiery with a good color union between the monofilament and the multifilament of varying deniers.

It is therefore an object of this invention to provide a process for dyeing nylon hosiery composed in part of monofilament and in part of multifilament, which filaments are of different denier, in substantially the same shade by a simple and economical procedure and one that can be satisfactorily employed in the dyeing of this fiber without producing other undesirable effects. A more specific object of this invention is to dye nylon hose, constructed of from 10 to 20 denier nylon monofilaments in the leg and of 30 to 60 denier nylon multifilaments in the welt, with cellulose acetate colors by a method which will give good color union between the welt and the leg.

I have found that nylon hosiery constructed of monofilaments and multifilaments of varying denier can be dyed with dispersed cellulose acetate dyes in much more uniform shades where the dyeing is carried out in the presence of from 2% to 10% of tannic acid, based on the weight of the nylon being dyed. The dyeing in the presence of the tannic acid is preferably carried out in the presence of a weak organic acid, such as acetic acid or formic acid, although the use of the auxiliary acid may be omitted, where desired. Wetting and dispersing agents, such as the higher fatty alcohol sulfates, may also be employed in treating the nylon material with the tannic acid solution. In carrying out the dye process, the hose are preferably scoured in the usual manner, rinsed free from the scouring assistants and then treated at temperatures of from 110° to 130° F. with a solution of tannic acid and acetic acid, with or without the addition in that solution of a higher fatty alcohol sulfate. The fiber so treated may then be dyed in the usual

manner with the cellulose acetate dyes at the temperatures ordinarily employed. Where it is found to be desired, the dispersed cellulose acetate dyes may be added directly to the tannic acid treating bath after the textile has been thoroughly wetted with the acid solution.

The tannic acid-acetic acid combination has been found to give best results when used to pretreat the hose before dyeing. However, improved results can be obtained when the tannic acid-acetic acid combination is added simultaneously with the acetate color at the start of the dyeing operation. In general, the dyeing of the nylon with the cellulose acetate colors is carried out under conditions normally used in dyeing nylon with this type of dye. The preferred temperature for the dye operation is within the range of 155° to 165° F., for below 155° F. the dye absorption is too slow and above 165° F. the tendency toward the formation of creases in the nylon hose is increased so that higher temperatures are preferably avoided. The time required in carrying out the dyeing process is substantially that employed in conventional nylon hosiery dyeing methods.

The following examples are given to illustrate the invention. The parts used are by weight, unless otherwise specified. Where percentages are employed, they are based on the weight of the nylon being treated, unless otherwise designated.

Example 1.—A 15 lb. capacity drum rotary dyeing machine was charged with 19 gallons (40 parts based on the weight of the hose) of softened water and 4 lbs. (dry weight) of scoured and rinsed women's nylon hosiery with a 15 denier monofilament boot and a 40 denier multifilament twisted welt. There was added 0.193 lb. of tannic acid and 0.11 lb. of acetic acid (28% strength) with continuous agitation of the hose at 90° F. The temperature was raised to 125°–130° F. and agitation continued for 15 minutes. Thereafter, a mixture of the following acetate rayon colors, which had been previously dispersed in water with 0.05 lb of a long chain aliphatic alcohol sulfate (such as prepared from commercial alcohols of from 10 to 18 carbon atoms, such as cetyl, lauryl, oleyl, etc., and which will be referred to hereinafter generally as "Duponol"), was added. The colors used in this example are dye powders prepared in readily dispersible form suitable for the dyeing of cellulose acetate rayon and which contain the usual dispersing agents.

0.0252 lb.—Yellow azo dye, containing 40% color solids, which dye was prepared from p-nitroaniline and p-chlorophenol according to the process of Example 1 of U. S. P. 2,366,034

0.0198 lb.—Acetamine scarlet B (containing 30% color solids) (prototype No. 244)

0.0170 lb.—Celanthrene brilliant blue FFS, containing 36% color solids (prototype No. 228)

The temperature was raised to 160° F. and held for two hours while the dyeing proceeded. The dye bath was then drained and the hose given a rinse, followed by drying in the normal manner.

By this method the hose was dyed a shade similar to the Bronzeskin shade given in 1947 Fall Season Hosiery Color Card of America. An excellent color balance between the boot and the welt resulted. This balance was much superior to that obtained when the hose was dyed with the above dye formula by the usual hosiery dyeing method in which the acetate colors are applied in the usual manner from a soap and detergent dye dispersion.

Example 2.—Sixty-two pounds (62 lbs.) of women's nylon hosiery with a 15 denier monofilament boot and a 40 denier multifilament welt was dyed as follows:

The hose was scoured in a rotary dyeing machine at 160° F. for ¾ hour with a bath containing, in 200 gallons of water:

	Pounds
"Duponol"	0.48
Soap	1.9
Trisodium phosphate	1.9

The scour bath was dropped and the hose rinsed well with water.

There was then charged into the rotary dyeing machine, at 90° F.:

Softened water	gallons	200
Tannic acid	pounds	4.0
Acetic acid (56%)	do	3.0
"Duponol"	do	0.75

The temperature was raised to 125°–130° F. and held for 15 minutes.

The same colors employed in Example 1, and which were dispersed in water with 0.25 lb. of "Duponol," were added:

0.171 lb.—Yellow azo dye (40% color solids)

0.171 lb.—Acetamine scarlet B (30% color solids)

0.235 lb.—Celanthrene brilliant blue FFS (36% color solids)

The temperature was raised to 160° F. and the dyeing run for one hour at this temperature.

The bath was dropped, the hose well rinsed with water, and finally dried.

By the above process, a "Mistique" shade (1947 Fall Season Hosiery Color Card of America) was obtained with an excellent color union between the boot and the welt.

To demonstrate the wash fastness of the nylon hosiery dyed by the above method a series of twenty-five wash tests, with drying of the hose between each test, was run. The wash tests were run for one-half hour each at 105° F. with a 30:1 volume (based on the weight of the hose) of a 0.5% soap solution. The average loss in tinctorial strength over the entire series of tests was about 20% in the boot and 40% in the welt. Hence, the tannic acid method of dyeing yields an improved color balance or uniformity between the welt and the leg, and at the same time the hose so dyed have wash fastness equal or superior to that dyed by conventional methods.

Example 3.—A 15 lb. drum rotary dyeing machine was charged with:

Soft water	gallons	18
Women's nylon hose as described in Ex. 1	pounds	1.5

With agitation, there was added:

	Pounds
Tannic acid	0.157
Acetic acid (56%)	0.110

The temperature was raised to 125°–130° F. and agitation continued for 15 minutes. Thereafter, a dispersion of:

0.04 lb.—"Duponol"

0.0192 lb.—Yellow azo dye used in Ex. 1 (40% color solids)

0.0128 lb.—Acetamine scarlet B (30% color solids)

0.0315 lb.—Celanthrene brilliant blue FFS (36% color solids)

in 2 quarts of water was added while continually agitating. The temperature was raised to 160° F. over 15 minutes and then held at 160° F. while agitating. After rinsing and drying, the hosiery was dyed with excellent balance between the boot and the welt to the "Black beauty" shade of the 1947 Fall Season Hosiery Color Card of America.

Example 4.—Three pounds (equivalent to about 9 dozen pairs women's hose of the above described type) of nylon hose were scoured with a conventional alkaline soap scour, and rinsed with running water. The lot was treated with:

	Pounds
Tannic acid	0.3
Formic acid (87%)	0.15
Zinc chloride	0.15

in about 30 gallons of soft water, by warming from 80°–90° F. to 160° F. and holding with continual agitation at 160° F. for one-quarter hour. The bath was then discharged and the rotary dyeing machine was partially filled with cold water again and agitated while adding:

0.24 lb. trisodium phosphate

and the following colors:

0.0193 lb.—Yellow azo dye used in Ex. 1 (40% color solids)
0.0186 lb.—Acetamine scarlet B (30% color solids)
0.0265 lb.—Celanthrene brilliant blue FFS (36% color solids)

dispersed in one gallon of warm water containing:

	Pounds
Soap	0.06
"Duponol"	0.015

The temperature was gradually raised over 15 minutes to 160° F. and held for three-quarters of an hour. The hose were dyed a dark brown shade with good union between the leg and the welt.

For light hosiery shades, it is recommended that a combination of 5% of tannic acid and 3% of acetic acid (28% strength) be used. For dark hosiery shades, 10% of tannic acid and 5% of acetic acid (28% strength) has been found suitable. For very light shades, as little as 2% of tannic acid will be sufficient, and even less acetic acid. As stated above, when desired the acetic acid may be omitted, but in general it is found advantageous to use at least small amounts. The percentage figures represent the percentage based on the dry weight of the hose.

The tannic acid in which the nylon hosiery is to be treated may be of any desired volume, preferably from 20 to 40 parts of water per part of nylon to be treated, which volumes are similar to those normally employed in the dyeing of the nylon with water insoluble dispersed cellulose acetate dyes.

While "Duponol" has been employed in illustrating the invention, any detergent, wetting and dispersing agent (preferably one that is insensitive to calcareous water) which operates in acid solutions, may be employed. The present invention is not dependent upon any specific detergent or wetting agent.

I claim:

1. A process of dyeing nylon hosiery composed in part of monofilament and in part of multifilament yarns of different denier with water insoluble dispersed cellulose acetate dyes, which comprises treating the nylon in an aqueous bath containing from 5% to 10% of tannic acid and from 3% to 5% of an acid of the group consisting of acetic and formic acids, both percentages being based on the weight of the nylon, and applying the water insoluble dispersed dyes by heating the nylon in the aqueous dispersion thereof.

2. A process of dyeing nylon hosiery composed in part of monofilament and in part of multifilament yarns of different denier with water insoluble dispersed cellulose acetate dyes, which comprises treating the nylon in an aqueous bath containing from 5% to 10% of tannic acid based on the weight of the nylon, and thereafter applying to the nylon containing the tannic acid the water insoluble dispersed dyes by heating the nylon in the aqueous dispersion of the dye.

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REFERENCES CITED

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

"Nylon Dyeing," by Clapham, article in American Dyestuff Reporter for May 3, 1948, pages P299, P300.