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PROCESS OF DYEING MODIFIED POLY-
ACRYLONITRILE STAPLE FABRIC

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This invention relates to a process of dyeing modified polyacrylonitrile staple fabric in rope form. It is an object of this invention to improve the process of dyeing fabric of the aforesaid nature with acid colors. Other important objects of this invention will appear as the description proceeds.

Modified polyacrylonitrile material as used herein refers to copolymers of acrylonitrile and vinyl pyridines or vinyl picolines, as disclosed in Arnold, U. S. P. 2,491,471. Modified polyacrylonitrile staple fabric is fabric woven or knitted from yarns spun from staple fibers of modified polyacrylonitrile material. Such fabric is generally dyed in rope form. In this system of dyeing, one or more bolts of fabric are run side-by-side over the reel of a beck machine, the two ends of each bolt of fabric being sewn together to form a continuous band of fabric. As the fabric falls off the reel into the beck it forms a folded pile in the beck, and as the reel rotates, each portion of the band of fabric is continuously dipped in and drawn out of the dye bath. A handy description of this method, with sketches of the apparatus, occurs in the American Wool Handbook, 2nd ed. (1948), at pages 748-751.

Modified polyacrylonitrile material is specially suited for dyeing with acid dyestuffs, whereas unmodified acrylonitrile polymers have no affinity for this type of dye. In the case of staple fabric, however, when dyed in rope form, the longitudinal creases formed by the roping of the fabric band on the reel as well as the horizontal folds formed in the beck interfere with the production of level dyeings. Uneven dye streaks appear in the fabric, probably due to improper penetration of the dye bath at the creases and folds.

We have now found that the above defect can be corrected if the dyeing is effected in the presence of a small quantity of a phenyl-carboxylic acid, such as benzoic acid or salicylic acid. By small quantity, we mean a concentration of 0.5 to 2% (i. e. 5 gm./l. to 20 gm./l.). Furthermore, we find that dyeing can be achieved at a somewhat lower temperature (180°-200° F.) than in the absence of the mentioned auxiliary agents (which requires 205°-212° F.).

Apart from the above detail, the dyeing may proceed along conventional lines, or may follow the special details devised in the art for polyacrylonitrile or modified polyacrylonitrile material. Thus, the dye may be any desirable acid dye which is applicable to modified polyacrylonitrile material. Its concentration in the dye bath may vary within wide limits depending on the strength

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of shade desired. Sulfuric acid in quantity usually not exceeding 0.1 part for each part by weight of fabric being dyed, may be added as dyeing proceeds, to assist in exhausting the dye bath.

Without limiting our invention, the following examples are given to illustrate our preferred mode of procedure. Parts mentioned are by weight. "C. I." numbers refer to the well known Colour Index numbers. "Pr." numbers are the Prototype numbers assigned to colors in the Yearbook of A. A. T. C. C. for 1949.

Example 1

One part of staple fabric woven of modified polyacrylonitrile fiber was dyed in rope form in a beck in 60 parts of liquor containing 0.3 part (5 g./l.) of salicylic acid and 0.01 part of the red dye listed as #430 in the Colour Index. After dyeing for 30 minutes at 200° F., 0.09 part of sulfuric acid was added and the dyeing was continued for an additional 30 minutes at 200° F. A level and well penetrated dyeing was obtained.

Example 2

A staple fabric of modified polyacrylonitrile fabric was dyed for one hour at 200° F. with 0.01 part of the red dye referred to in Example 1, using 20 grams per liter of salicylic acid. In this case no sulfuric acid was added. A bright, level and completely penetrated dyeing was obtained.

Example 3

A thirty-two yard length of staple fabric of modified polyacrylonitrile, weighing fifteen pounds, was worked for 15 minutes at 170° F. in 250 gallons of a bath containing 5.0 g./l. of salicylic acid. 118 grams of the navy blue dye, C. I. #304 and 43.5 grams of the blue dye, Pr. #12, previously dissolved in water, were then added. The temperature of the bath was raised to 200° F., during one hour, and dyeing was continued at this temperature for 1½ hours, during which period 2 pints of sulfuric acid were added in small portions. The bath was then flooded and the fabric was scoured for 20 minutes at 200° F. in 250 gallons of water, to which had been added 50 grams of the sodium salt of oleylmethyl taurine (a synthetic detergent) and 1 quart of concentrated ammonium hydroxide. The fabric was then rinsed thoroughly and dried. It exhibited good levelness, being substantially free from rope creases.

Example 4

Thirty-two yards of staple fabric made of

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modified polyacrylonitrile and weighing fifteen pounds was treated in rope form on a beck in 200 gallons of water to which 8 lbs. of salicylic acid had been added. After the goods had been worked in this bath for 30 minutes at 170° F., 71 grams of the brown dye described in Example 1 of U. S. 2,093,355 and 18 grams of 4,4'-diamino-1,1'-dianthrime disulfonic acid disodium salt (a gray dye), were added. The temperature was raised to 180° F., and dyeing was continued at this temperature for one hour. One pine of sulfuric acid was added over a period of 30 minutes, during which the temperature was raised to 200° F., and dyeing was continued at this temperature for one hour longer. The bath was then flooded and the fabric was washed for 20 minutes at 200° F. In 200 gallons of water containing 50 grams of the synthetic detergent mentioned in Example 3, and 1 quart of concentrated ammonium hydroxide. The goods were then rinsed thoroughly and dried. A level, well penetrated dyeing was obtained.

Example 5

One piece of a modified polyacrylonitrile fabric weighing 9.4 kg. was entered into 100 gallons of water containing 1.9 kg. of salicylic acid (5 g./l.) at a temperature of 180° F., and worked therein for 20 minutes. To this bath, 365 grams of the brown dyestuff, C. I. #105, and 94 grams of the yellow dyestuff, C. I. #40, were added portionwise over a period of 20 minutes. The bath was raised to a temperature of 200° F. over a period of 20 minutes, and the goods were worked therein at 200° F. for 45 minutes. Dyeing was then continued at the same temperature for two hours longer, during which period 300 cc. of concentrated sulfuric acid were added in three portions. The goods were then washed well and subjected to chroming in a fresh bath of 200 gallons of water containing 200 grams of sodium dichromate and 200 cc. of concentrated sulfuric acid. This operation was carried out for one hour at 205° F. and for one hour longer at 210° F. The goods were then washed thoroughly, hydro-extracted, and dried on a tenter. A level, dark brown dyeing was obtained.

Example 6

A fabric of modified polyacrylonitrile staple fabric was dyed on a beck in a dye bath containing a combination of dyestuffs as follows:

- 3% (on weight of fabric) sodium salt of benzene-azo-beta-naphthol-6:8-disulfonic acid (C. I. #252)
- 0.4% (on weight of fabric) sulfonic acid of dialkylamino - phenylamino - phenylnaphtho-phenazonium-chloride (C. I. #833)
- 0.6% (on weight of fabric) sodium salt of 1:4 di-o-sulpho-p-tolylaminoanthraquinone (C. I. #1078)

Salicylic acid in quantity of five grams per liter was added to the dye bath, and the fabric was dyed for thirty minutes at 200° F. An addition of 6 per cent sulfuric acid (on weight of fabric) was made and dyeing continued for 30 minutes at 200° F. A level, well penetrated dyeing was obtained.

It will be understood that the details of the above examples may be varied within the skill of those engaged in this art. Thus, the ratio of dye bath to fiber may be several fold the ratios used in the above examples, provided the concen-

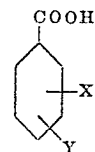
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tration of salicylic acid is kept within the limits indicated (i. e. 5 to 20 g./l.).

Instead of adding salicylic acid directly to the bath, the fabric may be pretreated with a salicylic acid bath of the indicated concentration range prior to dyeing.

For best light fastness results, it is recommended that the dyed fabric be scoured with soap and alkali, such as NH_4OH , to remove excess acid.

In lieu of salicylic acid, benzoic acid may be employed. Homologs and halogen derivatives of these acids are also useful. In general, the auxiliary agents recommended by this invention may be defined by the formula



wherein X and Y each stand for hydrogen, methyl, hydroxy or chlorine. The preferred auxiliary agents are those which are soluble in water to the extent of at least 5 grams per liter at temperatures of 180° to 200° F. However, this is not an absolute condition, inasmuch as dispersing agents may be employed where the auxiliary agent selected does not possess sufficient solubility.

Chrome dyes are merely a branch of the acid dye family, differing from the other members only in the fact that they require an after-chroming treatment. In agreement with this general proposition, we find that our invention may be practiced to advantage also with chrome dyes, the procedure being essentially the same as in the foregoing examples, except that the dyed fabric is given an after-chroming treatment with sodium or potassium dichromate and sulfuric acid.

Furthermore, although direct colors are not generally classed as acid dyes, they seem to behave like acid dyes when applied to modified polyacrylonitrile fiber. In any event, we find that our invention, substantially as outlined in the above examples (including exhaustion of the bath by the aid of sulfuric acid), may be applied to advantage in the case of many colors which are normally classified as direct colors.

As additional illustrations of dyes coming within the above classes and actually tested by us with good results, the following may be mentioned:

- Chrysophenine, C. I. 365
- Diamine Fast Red F, C. I. 419
- Benzo Fast Red 8BL, C. I. 278
- Benzo Fast Heliotrope, C. I. 319
- Polar Yellow, C. I. 642
- Brilliant Crocein M, C. I. 252
- Alizarin Supra Blue A, Pr. 12
- Alizarin Sky Blue B, C. I. 1088
- Alizarin Cyanine Green, C. I. 1078
- Polar Red, C. I. 430
- Fast Red A, C. I. 176
- Acid Anthracine Brown R, C. I. 105
- Alizarin Yellow R, C. I. 40
- Alizarin Yellow 2G, C. I. 36
- Eriochrome Black T, C. I. 203

We are aware of Richards, U. S. P. 2,512,969, wherein it is recommended to dye polyacrylonitrile with acetate and basic dyes, using metacresol as special assistant. The differences be-

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tween said patent and our invention are obvious. The material being dyed, the colors employed and the assistant found useful are all different in the two cases.

The said patent contains also a reference to copending application Serial No. 771,243 (Webb, U. S. P. 2,527,863), which discloses that blends of acrylonitrile polymers and polyvinyl pyridines may be dyed with acid colors using metacresol as assistant.

This disclosure, however, is still not relevant to our invention. In the first place, a blend of the two polymers mentioned is not the same material as a copolymer prepared according to Arnold, U. S. P. 2,491,471. In the second place, the copending application seems to be concerned with dyeing structures at random made from said blend, and is not concerned with the particular trouble of streaking effects obtained in the special case of dyeing staple fabric, due to the creasing of the material in the process. And finally, the auxiliary agent which we found useful to solve our special problem is not suggested in said copending application.

We claim as our invention:

1. A process for dyeing modified polyacrylonitrile staple fabric, which comprises treating said fabric in rope form with an aqueous solution of an acid dye in the presence of salicylic acid.

2. A process as in claim 1, the concentration of the salicylic acid in the dye bath being from 0.5% to 2% by weight.

3. A process for dyeing modified polyacrylonitrile staple fabric, which comprises treating said

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fabric in rope form with an aqueous solution of an acid dye at a temperature between 180° F. and 200° F., said aqueous dye bath containing salicylic acid in a concentration between 0.5% and 2% by weight.

4. A process as in claim 3, the dyeing being finished in the presence of sulfuric acid, in quantity not exceeding 0.1 part for each part by weight of fabric being dyed, to assist in exhausting the dye bath.

5. A process as in claim 4, the fabric being scoured after dyeing, with a detergent and dilute alkali, to remove loosely adhering coloring material and absorbed acid.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,491,471	Arnold	Dec. 20, 1949
2,527,863	Webb	Oct. 31, 1950

FOREIGN PATENTS

Number	Country	Date
616,385	Great Britain	Jan. 20, 1949

OTHER REFERENCES

American Dyestuff Reporter for December 12, 1949, pages P925 to P927.