

## UNITED STATES PATENT OFFICE

2,543,994

VAT DYEING OF ACRYLONITRILE  
POLYMERSRobert Joseph Thomas, Carney's Point, N. J., as-  
signor to E. I. du Pont de Nemours & Company,  
Wilmington, Del., a corporation of DelawareNo Drawing. Application August 29, 1947,  
Serial No. 771,379

11 Claims. (Cl. 8—34)

1

This invention relates to the modification of polymers of acrylonitrile. More particularly, it relates to new methods of dyeing structures comprising acrylonitrile polymers.

By "structures" is meant shaped articles, such as yarns, films, bristles, fabrics, tubings, molded articles and the like, and by "acrylonitrile polymers" is meant those polymers containing at least 85% by weight of acrylonitrile.

Acrylonitrile polymers containing a major portion of acrylonitrile are relatively insoluble, unreactive and hydrophobic materials. These characteristics make the dyeing of structures prepared from such polymers a difficult problem. Indeed, standard commercial dyeing techniques can not be used satisfactorily. For example, only light shades are obtained on dyeing structures of polyacrylonitrile with acetate, basic and certain vat colors. This is true for copolymers of acrylonitrile prepared using up to 15% of other vinyl type monomers. These copolymers retain the desirable properties of polyacrylonitrile and show only a slightly enhanced dye receptivity. Since the physical and chemical properties of shaped articles prepared from acrylonitrile polymers make the articles of considerable commercial interest, solutions of the difficult dyeing problems are highly desirable.

Accordingly, it is an object of this invention to provide a satisfactory process for dyeing structures prepared from acrylonitrile polymers. A still further object is the provision of a method for readily dyeing articles shaped from acrylonitrile polymers. Other objects are described hereinafter.

The objects of this invention are accomplished by treating the structures of this invention with an aqueous dye bath containing a vat dyestuff of the indigo, thioindigo or related types, alkali, 0.5% to 5.0% of an aromatic amine and a reducing agent and then oxidizing the leuco dyestuff on the article.

The invention will be more clearly understood by referring to the examples and discussion which follow. The examples are given for illustrative purposes and are not to be construed in any sense as limitative. Parts, proportions and percentages are by weight unless otherwise indicated.

*Example I*

A dye bath was prepared using 4000 parts of water, 20 parts of 6,6'-dibromo-4,4'-dimethyl-2,2'-bis-thionaphthen-indigo, 100 parts of sodium hydrosulfite, 40 parts of sodium hydroxide, 100 parts of sodium carbonate, and 40 parts of p-

2

aminodiphenyl. 100 parts of acrylonitrile yarn was kept immersed in the bath for one hour, the bath being heated to 97–98° C. After this time the yarn was rinsed in cold water and immersed in a bath containing 4000 parts of water and 40 parts of nitric acid. This oxidation bath was heated from 97 to 98° C. and the treatment lasted for one hour. The yarn was rinsed in cold water, soaped well, and dried. It was found to be dyed a strong pink shade.

*Example II*

100 parts of polyacrylonitrile yarn was immersed in a dye bath containing 4000 parts of water, 20 parts of 5,5'-dichloro-6,6'-dimethyl-2,2'-bis-thionaphthen-indigo, 100 parts of sodium hydrosulfite, 40 parts of sodium hydroxide, 100 parts of sodium carbonate, and 20 parts of betanaphthylamine, at 97° to 98° C. for one hour. After rinsing, oxidizing, and soaping as described in the previous example, the yarn was a strong red-violet shade.

*Example III*

100 parts of a film prepared from a copolymer of 95% acrylonitrile with 5% of 2-vinylpyridine was immersed in a dye bath containing 4000 parts of water, 20 parts of bis-2,1-naphthioindigo, 100 parts of sodium hydrosulfite, 40 parts of sodium hydroxide, 100 parts of sodium carbonate, and 80 parts of meta-toluidine at 97° to 98° C. for one hour. After rinsing, oxidizing, and soaping as described in the previous examples, the yarn was a strong brown shade.

*Example IV*

100 parts of a yarn prepared from a copolymer of 95% acrylonitrile with 5% of 2-vinylpyridine was immersed in a dye bath containing 4000 parts of water, 20 parts of 5,5', 7,7'-tetrabromoindigo, 100 parts of sodium hydrosulfite, 40 parts of sodium hydroxide, 100 parts of sodium carbonate and 160 parts of N-methyl aniline at 97° to 98° C. for one hour. After rinsing, oxidizing, and soaping as described in the previous examples the yarn was a strong blue shade.

*Example V*

100 parts of a fabric prepared from a 95/5 copolymer of acrylonitrile and methacrylic acid was immersed in a dye bath containing 4000 parts of water, 20 parts of indigo, 100 parts of sodium hydrosulfite, 40 parts of sodium hydroxide, 110 parts of sodium carbonate and 40 parts of p-aminodiphenyl. The treatment at 97° to 98° C.



3

lasted for one hour. The fabric was then oxidized in the manner described in Example I. The purified and dried fabric was dyed to a strong blue shade.

#### Example VI

100 parts of a knit tubing prepared from a 90/10 copolymer of acrylonitrile and acrylic acid was immersed in a dye bath containing 4000 parts of water, 20 parts of thioindigo, 100 parts of sodium hydrosulfite, 40 parts of sodium hydroxide, 100 parts of sodium carbonate and 20 parts of beta-naphthylamine. The bath was heated to boiling and the tubing was immersed in the bath at that temperature for one hour. After rinsing, oxidizing, and scouring with a dilute soap solution, the yarn was found to be dried to a strong red shade.

#### Example VII

A dye bath was prepared as described in Example IV except that the dye used was 2-thionaphthene-2'-acenaphthylene-indigo. A flat fabric composed of a 95/5 copolymer of acrylonitrile and styrene was immersed in the bath for one hour, the bath temperature being 97° to 98° C. After rinsing, oxidizing and purifying in the normal manner, the flat fabric retained a strong scarlet shade.

#### Example VIII

Three different dyebaths, each containing a different dye, were prepared using 6000 parts of water, 40 parts of dye, 20 parts of sodium hydroxide, 40 parts of sodium hydrosulfite and 40 parts of sodium formaldehyde sulfoxylate. The three dyes used were 6,6'-dibromo-4,4'-dimethyl-2,2'-bis-thionaphthen-indigo, 5,5'-dichloro-7,7'-dibromo indigo and 6,6'-diethoxy-2,2'-bisthionaphthen-indigo. After vatting, each dye bath was divided into two equal portions. One of each set was used as a control and to the other of each set was added 300 parts of aniline (5% based on the water). The six baths were then heated to about 100° C. and to each was added 100 parts of polyacrylonitrile yarn which was left immersed in the bath for one hour. The dyed structure was rinsed, oxidized, soaped, rinsed and dried in that order. In each instance strong shades resulted on the structures dyed in the aniline modified baths, whereas in the controls no or at most only light dyeing occurred.

The acrylonitrile polymers which are generally used commercially for the preparation of the shaped articles described in this invention must, of course, be of a sufficiently high molecular weight to possess film- or filament-forming properties. The polymers employed possess an average molecular weight within the range of 25,000 to 750,000 or even higher and preferably between the range of 40,000 to 250,000 as calculated from viscosity measurements by the Staudinger equation.

$$\text{Molecular weight} = \frac{N_{sp}}{K_m C}$$

wherein:

$$K_m = 1.5 \times 10^{-4}$$

$$N_{sp} =$$

$$\text{specific viscosity} = \frac{\text{viscosity of solution}}{\text{viscosity of solvent}} - 1$$

and

C = concentration of the solution expressed as the number of moles of the monomer (calculated) per liter of solution.

4

It is to be understood, however, that acrylonitrile polymers having molecular weights below or above the range indicated may be subjected successfully to the process of this invention.

5 The acrylonitrile polymers of commercial interest are those containing 85% by weight of the polymer of acrylonitrile. These polymers include polyacrylonitrile and copolymers and interpolymers of acrylonitrile with other polymerizable monomers. These monomers include, among others, vinyl acetate, vinyl chloride, acrylic and methacrylic acids and their derivatives or homologues, methyl vinyl ketone, vinyl pyridine and homologues thereof, and isobutylene or other  
10 polymerizable hydrocarbons. Polymers containing less than 85% of acrylonitrile can usually be dyed by standard processes, since inclusion of greater amounts of such materials as acrylic acid, methyl vinyl ketone and the like, leads to better  
15 dye receptivity. If desired, the process of this invention can be used to dye such polymers. However, since it is preferred to use polymers having at least 85% acrylonitrile to get the benefit of superior properties, such as toughness and chemical inertness, the process of this invention is chiefly of interest in the dyeing of structures prepared from polymers containing a major portion of acrylonitrile.

The yarns described herein are prepared by  
20 conventional wet or dry spinning techniques from solutions of polyacrylonitrile or copolymers containing 85% or more acrylonitrile in dimethyl formamide, tetramethylene sulfone or other known volatile solvents for these polymers as described in U. S. Patents Nos. 2,404,714 to 2,404,727 inclusive. On leaving the spinning cell the yarn is collected in a suitable package and this yarn package may then be washed free of residual solvent. In order to obtain full benefit of the  
35 properties of these yarns, it is desirable to draw the yarn from 2 to 10 times its original length. Moreover, when heated under tension for extended periods of time, the yarns show a remarkable retention of tenacity; while, on the other hand, if the yarns after drawing are heated in the relaxed state at temperatures in the order of 130° to 200° C., the yarns tend to shrink somewhat and such an after-treatment can be used to increase the elongation of the yarn to a point where they are satisfactory for use in the textile art.

The structures such as yarns, films, fabrics and the like may be prepared by the usual techniques, for example, yarns or fibers may be prepared as described above by dry spinning or wet spinning according to such procedures described in copending applications Serial Nos. 496,376, 735,666, and 746,651, now Patents 2,426,719; 2,451,420; 2,467,553 respectively. Films may be prepared in similar  
45 ways, or by casting techniques. Fabrics of the new compositions of matter of this invention may be prepared by any of the well known knitting or weaving techniques.

In addition to the dyes described in the above examples, it is possible to use 2-(5,7'-dibromoindole)-5'-bromo-2'-thionaphthen-indigo, 6,6'-diethoxy-2,2'-bis-thionaphthen-indigo and similar indigo and thioindigo vat colors. An appreciable improvement in dyeing with anthraquinone vat colors is also obtained upon using the amine assistants but the effect is much less marked than that obtained with the indigo and thioindigo dyes. It is preferred to use an indigo or a thioindigo dye in any desired amount. By the use  
50 of any of the above or other indigo and thio-



indigo vat colors, strong shades that are fast to washing and crocking are obtained.

The other ingredients of the dye bath and the conditions of dyeing may be varied widely. Any of the commercial techniques in respect to these factors may be employed herein. Standard commercial dyeing processes employ 30:1 to 50:1 ratios of bath to structure. These ratios may be used in this invention. The common vat dyeing procedure employs a bath having a relatively high pH, that is above 10. Any suitable alkali capable of producing this pH is satisfactory for use in this invention. It has been found that surprisingly deeper shades are obtained if part of the alkali is derived from a potassium compound such as potassium hydroxide or potassium carbonate. Good dyeing can be obtained in the absence of carriers if potassium ions are present in the alkaline bath at a pH of between 10 to 12.5. These highly alkaline baths exert no adverse effect on the acrylonitrile polymer structures of this invention. In general, any of the commercial dyeing apparatus and procedures, such as purification and oxidation and the like, may be used herein.

The oxidation of the vat dyestuff on the structure may be carried out in other ways. Instead of using nitric acid other agents for oxidation may be employed, such as, aqueous solutions of sodium dichromate, hydrogen peroxide, sodium perborate and the like.

While the temperature of the dye bath may be varied widely, it is preferred to use temperatures above 85° C. Below these temperatures the rate of dyeing is too slow to be commercially practical. This rate increases rapidly with higher temperatures and in the interest of economy, it is preferred to carry out the dyeing at a bath temperature between 95 and 100° C.

The dye assistants used in the process of this invention may be used in a concentration ranging from 0.5% to 5% by weight of the water in the dye bath. Generally, the concentration of approximately 2% is preferred. The dye assistant may be selected from a large number of aromatic amines including aniline, ortho-, meta-, and para-toluidine, N-methyl aniline, N,N-dimethyl aniline, alpha-naphthylamine, beta-naphthylamine, ortho-, meta-, and para-aminodiphenyl, phenyl - alpha - naphthylamine, phenyl - beta-naphthylamine, diphenylamine and anilines which are substituted on the ring by halogen, nitro, and aldehyde or keto carbonyl groups. Certain aromatic amines such as phenylene diamines and aminophenols, show slight improvement under the normal vat procedure in the dyeing of acrylonitrile polymer structures. The more soluble types, such as anthranilic acid and sulfanilic acid are not effective in the practice of this invention. Accordingly, it is preferred to use aromatic amines containing no solubilizing groups, such as carboxyl or sulfonic acid groups. Normally, structures prepared from acrylonitrile polymers can not be dyed satisfactorily with any dye, such as acid, direct, sulfur, acetate, basic or vat colors. At best only light shades are obtained with acetate, basic and certain vat dyes in standard processes. By the process of this invention, it is possible to obtain satisfactory dyeing with a vat dyestuff of the indigo, thioindigo or related dyes.

The effectiveness of a dye assistant is probably related to the solubility of the dye assistant in the polymer yarn. Other factors, such as the nature of the polymer and the nature of the dye

are also important factors. The best dye assistant for a particular synthetic fiber is not always the most efficient assistant for all classes of dye stuffs on that same fiber. Nor can it be predicted that an assistant effective in the dyeing of one class of structures will be effective in the dyeing of other classes of synthetic structures. It is not possible to predict which class and in turn which member of a class of so-called dye assistants will be most effective for a new synthetic fiber. Thus, the aromatic amine carriers, which, as described herein, are effective assistants in the vat dyeing of structures of acrylonitrile polymers, are unsatisfactory assistants in the dyeing of the structures with acetate colors because they cause a very noticeable, uncontrolled darkening of the structures. On the other hand, m-cresol, which, as described in co-pending application Serial No. 771,381, now Patent 2,512,969, is an effective assistant with dispersed acetate or basic dyes, does not satisfactorily assist the vat dyeing of the structures. The relative insoluble and unreactive characteristics of acrylonitrile polymers makes the dyeing of structures prepared from such polymers exceedingly difficult.

This invention provides a convenient and valuable method for dyeing structures prepared from acrylonitrile polymers. By the novel process of this invention difficultly dyed structures of acrylonitrile polymers can be dyed effectively at a rapid rate using standard commercial equipment. By the use of the preferred aromatic amine assistants described herein, vat dyeing procedures, which when normally applied to acrylonitrile polymer structures give no coloring or at most only light shades, are capable of rapidly dyeing the structures to level shades of satisfactory strengths. The dye bath exhaust is greatly increased and the colored products produced have excessively good resistance to washing and crocking. Furthermore, the physical and chemical properties of the dyed structures are comparable to the desirable properties of the undyed structures.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

I claim:

1. A process of vat dyeing structures prepared from acrylonitrile polymers containing at least 85% acrylonitrile which comprises treating said structures with an aqueous dye bath containing 0.5% to 5% of an aromatic monoamine containing no other solubilizing group and an alkaline solution of a reduced vat dye selected from the group consisting of indigo and thioindigo vat dyes.

2. A process for vat dyeing structures of acrylonitrile polymer containing at least 85% acrylonitrile which comprises treating said structures at a temperature above 85° C. with an aqueous dye bath containing 0.5% to 5% of an aromatic monoamine containing no other solubilizing group and an alkaline solution of a reduced vat dye selected from the group consisting of indigo and thioindigo vat dyes.

3. A process for vat dyeing polyacrylonitrile structures which comprises treating said structures with an aqueous dye bath containing 0.5% to 5% of an aromatic monoamine containing no other solubilizing group and an alkaline solution of a reduced vat dye selected from the group consisting of indigo and thioindigo vat dyes.

4. A process for vat dyeing structures prepared



7

from an acrylonitrile/methacrylic acid polymer containing at least 85% of acrylonitrile which comprises treating said structures with an aqueous dye bath containing 0.5% to 5% of an aromatic monoamine containing no other solubilizing group and an alkaline solution of a reduced vat dye selected from the group consisting of indigo and thioindigo vat dyes.

5. A process for vat dyeing structures prepared from acrylonitrile/styrene polymer containing at least 85% of acrylonitrile which comprises treating said structures with an aqueous dye bath containing 0.5% to 5% of an aromatic monoamine containing no other solubilizing group and an alkaline solution of a reduced vat dye selected from the group consisting of indigo and thioindigo vat dyes.

6. A process in accordance with claim 1 wherein the ratio of the said bath to the said structures is from 30:1 to 50:1.

7. A process in accordance with claim 1 wherein the pH of the said bath is above 10.

8. A process in accordance with claim 2 wherein the ratio of the said bath to the said structures is from 30:1 to 50:1.

9. A process in accordance with claim 2 wherein the pH of the said bath is above 10.

10. A process in accordance with claim 2 wherein the dye bath temperature is from 95° to 100° C.,

8

the ratio of said bath to the said structures is from 30:1 to 50:1 and the pH of the said bath is above 10.

11. A process in accordance with claim 2 in which the said monoamine is aniline.

ROBERT JOSEPH THOMAS.

#### REFERENCES CITED

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

#### UNITED STATES PATENTS

Number	Name	Date
2,257,076	Petke	Sept. 23, 1941
2,347,508	Rugeley	Apr. 25, 1944
2,362,375	Heymann	Nov. 7, 1944
2,404,727	Houtz	July 23, 1946
2,431,956	Moody	Dec. 2, 1947

#### FOREIGN PATENTS

Number	Country	Date
479,867	Great Britain	Feb. 14, 1938
847,107	France	June 26, 1939
583,939	Great Britain	Jan. 2, 1947

#### OTHER REFERENCES

Woodruff: "Dyeing of Vinyon," Amer. Dyes. Rep. for Apr. 22, 1946, pages 194-197.