

UNITED STATES PATENT OFFICE

2,512,969

DYEING OF ACRYLONITRILE POLYMERS
USING ACETATE DYES AND M-CRESOL AS
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mington, Del., a corporation of DelawareNo Drawing. Application August 29, 1947,
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7 Claims. (Cl. 8-4)

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This invention relates to the modification of polymers of acrylonitrile. More particularly, it relates to the dyeing of 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 35% 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 which 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 to 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 further object is the provision of methods for uniformly dyeing structures of acrylonitrile polymers. A still further object is the provision of dyed structures of such polymers which are deeply and uniformly dyed and which are fast to light and to washing. Other objects will appear hereinafter.

The objects of this invention are accomplished by treating the structures of this invention with an aqueous dye bath containing 1% to 5%, by weight of the bath, of meta-cresol and a dispersed acetate of basic dye.

The invention will be more clearly understood by referring to the examples and discussion which follow. These 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 5000 parts of water, 5 parts of 1,4,5,8-tetra-aminoanthraquinone and 50 parts of meta-cresol. 100 parts of polyacrylonitrile yarn was immersed in the bath. The immersion time was one hour and the bath temperature was 95° C. The yarn was then

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rinsed in water, scoured in 0.5% soap solution and finally dried. The yarn was dyed a strong shade of blue. Upon examination of cross-sections of the dyed yarn it was found that the dye penetrated the fiber completely. In comparison, similar yarn treated with a control dye bath, that is, one containing no meta-cresol, was colored only to a very light shade.

EXAMPLE II

To a dye bath containing 2000 parts of water, 5 parts of 1-hydroxy-4-aminoanthraquinone and 60 parts of meta-cresol and heated to 95° C. was added 100 parts of a fabric prepared from a 90/10 copolymer of acrylonitrile and methacrylic acid. The fabric was allowed to remain in the bath for one hour. After rinsing, scouring and drying, the fabric retained a deep shade of red. In comparison, a similar dye bath containing no meta-cresol had very little coloring effect on another sample of the fabric.

EXAMPLE III

10 parts of the dye p-nitroaniline→aniline was added to 10,000 parts of water containing 500 parts of meta-cresol. The dye bath so formed was heated to 90° C. and 100 parts of a polyacrylonitrile knit tubing was immersed in the bath for one hour. After purification the knit tubing was colored a deep orange. The dyed product was fast to washing and crocking.

EXAMPLE IV

A film was prepared from a 90/10 copolymer of acrylonitrile/acrylic acid using the usual casting technique. 100 parts of this film was dyed by immersion for one hour at 95° C. in a dye bath containing 5000 parts of water, 5 parts of a basic dyestuff, namely, fuchsin, and 50 parts of meta-cresol. After purification, the film was found to be thoroughly dyed to a strong red shade.

EXAMPLE V

A dye bath was prepared using 5 parts of malachite green, 2000 parts of water and 60 parts of meta-cresol. 100 parts of a flat fabric prepared from polyacrylonitrile yarn was kept in the bath for one hour, the bath being at a temperature of 95° C. The fabric was then rinsed, scoured and dried in the usual manner. A good strong, green shade was obtained. Like the other dyed structures, this had very good resistance to washing, crocking and wear by buffing or scratching.

EXAMPLE VI

A dye bath was prepared using 3300 parts of water, 5 parts of 1,4,5,8-tetraaminoanthraquinone and 66 parts of m-cresol. 100 parts of yarn prepared from a 95/5 acrylonitrile/styrene polymer was kept immersed in the bath (96° C.) for one hour. The yarn was then rinsed in water, scoured with 0.5% soap solution and finally dried. It was dyed to a strong blue shade. Under similar conditions using no m-cresol the yarn was dyed only to a very light shade.

EXAMPLE VII

To determine the effect of varying the amount of meta-cresol, unit weight samples of polyacrylonitrile yarns were dyed at 95° C. to 100° C. in baths containing 10%, based on the weight of yarn, of 1,4,5,8-tetra-aminoanthraquinone using a 50:1 bath to yarn ratio. The baths contained various amounts of meta-cresol. The dyed samples were rinsed free of surface color, were then dissolved in dimethyl formamide and the resultant solutions were analyzed spectrophotometrically for dye content. The results are given in Table I.

Table I

Sample	Per Cent Cresol in Bath	Relative Dye Content
1	0	1
2	2	3.7
3	3	4.5
4	5	ca. 2.8

From the above figures it can be seen that the deepest shades are obtained using about 3% of meta-cresol. Use of baths containing 5% or more meta-cresol resulted in lighter dyeing than that obtained with 2% meta-cresol. The dyeing obtained using from 1% to 5%, based on the bath, is satisfactory and while lower and higher amounts can be used, this is the preferred range. Standard commercial dyeing processes usually employ 30:1 to 50:1 ratios of bath to fabric and these ratios may be used in this invention.

Other phenolic compounds can be used as assistants in the dyeing of acrylonitrile polymer structures with dispersed acetate and basic colors. For example, phenol, ortho-cresol, para-cresol and homologues of these various phenols may be employed in the process of this invention. However, meta-cresol is by far the most effective of the phenolic compounds. For example, while beta-naphthol in 0.5% concentrations is equivalent to 2% phenol, beta-naphthol is not a satisfactory assistant. Its insolubility results in its crystallizing out of the dye bath and makes its removal from the dyed structures difficult. Further, it exerts a serious, deleterious effect on the light fastness of the dyeings. Meta-cresol has none of these faults and in addition, has the advantage that it is very effective. It is preferred to phenol, beta-naphthol, p-phenylphenol and other phenols which either do not as effectively assist the dyeing or exert adverse effects on the dyeings. The reason for the outstanding effectiveness of meta-cresol over the other phenolic materials is not known. Since only light shades are obtained with phenolic materials other than meta-cresol, it is preferred for commercial purposes to use meta-cresol for the dyeing of structures prepared from acrylonitrile polymers.

The rate of dyeing depends to some extent upon the temperature of the bath. At temperatures below 85° C. the rate of dyeing is too slow to be practical. Accordingly, it is preferred to carry out the dyeings in accordance with the process of this invention at a temperature above 85° C. The use of higher temperatures such as 95° C. and above leads to faster dyeing rates. Usually the dyeing will be effected at the boiling temperature of the bath. Temperatures above the boiling point may be used but since these require the use of relatively complicated apparatus they will not be used for the most part.

The dyeing may be carried out in any conventional manner using any dye, in any desired amount, selected from a number of classes such as dispersed acetate and basic dyestuffs. For example, the following dyes may be used in this invention: p-nitroaniline→aniline, 4-aminoazobenzene, 4,4'-diaminoazobenzene, 1,4,5,8-tetra-aminoanthraquinone, 1-amino-2-methylantraquinone, 1-hydroxy-4-aminoanthraquinone, fuchsin, malachite green, 4-aminoacetanilide→4-chlorophenol, 4-aminoacetophenone→aniline, and methyl violet may be added to the dye bath beside those indicated in the above examples. Further, the purification techniques may be varied to suit the objective desired. In general, conventional dyeing apparatus and procedures, such as purification methods may be used herein.

The acrylonitrile polymers which are generally used commercially to form the shaped articles described in this invention are those having 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 and 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.

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

The acrylonitrile polymers of commercial interest are those containing at least 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 or derivatives and homologues thereof, styrene, methyl vinyl ketone, and isobutylene or other similar polymerizable hydrocarbons. Polymers containing less than 85% of acrylonitrile can usually be dyed by the standard processes, since inclusion of greater amounts of such materials as acrylic acid, methyl vinyl ketone and the like leads to better 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% of 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 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, such as those described in Patents U. S. 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 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., they 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.

Any of the structures, such as yarns, films, fabrics and the like, may be prepared by the usual techniques. For example, yarns and fibers may be prepared by dry or wet spinning, as described for example, in copending applications Serial Nos. 496,376, 735,666 or 746,651, now respectively U. S. Patents 2,426,719, 2,451,420 and 2,467,553. Films may be prepared in similar ways, or by casting techniques. Fabrics may be prepared by any of the well-known knitting or weaving techniques.

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 dispersed acetate and basic dyes. Further, as disclosed in copending application Serial No. 771,243, m-cresol can be used effectively as an assistant in the dyeing of blends of acrylonitrile polymers and polyvinyl pyridines with acid and direct colors.

The effectiveness of meta-cresol is surprising. While the solubility of the assistant in the polymer is important, this is only one factor. For example, other phenolic materials, such as phenol, which have solubility characteristics similar to meta-cresol are relatively ineffective in the process of this invention when compared to meta-cresol. 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 synthetic structures will be effective in the dyeing of other classes of synthetic structures. For example, assistants effective in the dyeing of polymers of vinyl chloride containing chiefly vinyl chloride or assistants effective in the dyeing of other polymers, such as the phenolaldehyde resins, are not necessarily effective in the dyeing of acrylonitrile polymers. It is impossible to predict which class and in turn which mem-

ber of a class of so called dye assistants will be most effective for a new synthetic fiber. Thus, aromatic amine carriers, such as aniline, which are effective assistants in the vat dyeing of structures of acrylonitrile polymers as described in copending application Serial No. 771,379, are unsatisfactory as 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 herein, is an exceedingly effective assistant with dispersed acetate or basic dyes, does not satisfactorily assist the vat dyeing of the structures. The relative insoluble and unreactive character 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 readily at a rapid rate using standard commercial equipment. The dye bath exhaust is greatly increased and the colored products produced are dyed to deeper shades than hitherto obtainable. Further, the dyed products have exceptionally good resistance to washing and crocking. The structures are colored throughout and have excellent resistance to wear by scratching or scuffing. Furthermore, the physical and chemical properties of the dyed structures are comparable to the desired 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 for dyeing structures prepared from acrylonitrile polymers which comprises treating said structures with an aqueous dye bath containing 1% to 5% by weight of the bath of meta-cresol and a dispersed acetate dye.

2. A process for dyeing structures prepared from acrylonitrile polymers which comprises treating said structures at a temperature above 35° C. with an aqueous dye bath containing 1% to 5% based on the weight of the bath of meta-cresol and a dispersed acetate dye.

3. A process for dyeing structures prepared from polyacrylonitrile which comprises treating said structures with an aqueous dye bath containing 1% to 5% based on the weight of the bath of meta-cresol and a dispersed acetate dye.

4. A process for dyeing structures prepared from an acrylonitrile/methacrylic acid polymer containing at least 85% acrylonitrile which comprises treating said structures with an aqueous dye bath containing 1% to 5% based on the weight of the bath of meta-cresol and a dispersed acetate dye.

5. A process for dyeing structures prepared from an acrylonitrile/styrene polymer containing at least 85% of acrylonitrile which comprises treating said structures with an aqueous dye bath containing 1% to 5% based on the weight of the bath of meta-cresol and a dispersed acetate dye.

6. A process for dyeing structures prepared from acrylonitrile polymers which comprises immersing said structures in an aqueous dye bath containing 1,4,5,8-tetraaminoanthraquinone and 1% to 5%, based on the weight of the bath, of meta-cresol, the said bath being heated to a temperature of from 85° C. to 95° C.

7. A process in accordance with claim 6 in

which the said structures are yarns prepared from polyacrylonitrile.

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Number	Name	Date
2,362,375	Heymann	Nov. 7, 1944
2,431,956	Moody	Dec. 2, 1947

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date	10
2,347,508	Rugeley	Apr. 25, 1944	

OTHER REFERENCES

"Dyeing of Vinyon" by J. A. Woodruff, pages 194-197, 204, 205 of Amer. Dyes. Reporter for Apr. 22, 1946.