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COLOR REMOVAL FROM ACRYLONITRILE POLYMERS

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1

This invention relates to the removal of color from shaped articles comprising a polymer of acrylonitrile and is particularly concerned with the bleaching of yarn composed of acrylonitrile polymer.

Polymers of acrylonitrile such as acrylonitrile polymers in which the polymers are composed entirely of acrylonitrile, and interpolymers and copolymers of acrylonitrile with other materials such as vinyl chloride, vinyl acetate, acrylic acid, its esters and homologues, styrene, butadiene, isobutylene and other polymerizable substances, especially those containing olefinic and diolefinic linkages, although potentially of great value on account of their highly desirable properties, are insoluble in ordinary organic solvents when the polymers contain at least 85% by weight of acrylonitrile (vinyl cyanide) in the polymer molecule. Solutions of such polymers in organic solvents such as dimethyl formamide and other organic solvents, as well as their conversion by "wet" and "dry" or evaporative processes into various articles such as filaments, films, etc., are described and claimed in the copending applications of George Henry Latham, Serial No. 447,466, filed June 17, 1942, and Ray Clyde Houtz, Serial No. 447,446, filed June 17, 1942. This invention is broadly concerned with polymers of acrylonitrile containing at least 85% by weight of acrylonitrile in the polymer molecule although it is most particularly concerned with and will be specifically described in connection with polyacrylonitrile, i. e. the polymer which is composed substantially entirely of acrylonitrile in the polymer molecule.

One method which may be used to produce polyacrylonitrile yarn is the so-called "dry" or evaporative spinning process which comprises extruding a solution of polyacrylonitrile through a nozzle into air or other gas inert to the polymer, maintained at such a temperature and under such other conditions as will cause the complete vaporization of the solvent contained in the polymer solution. The yarn may be subjected, if desired, to a stretching operation in order to increase tenacity as well as otherwise to improve physical properties by orienting the micelles of which the yarn is composed. The stretching may be effected by subjecting the yarn at an elevated temperature of the order of 100° and above, to a tension adequate to effect the desired degree of stretching, this stretching procedure being described and claimed in the copending application of Daniel T. Meloon Serial No. 496,397, filed July 28, 1943.

Another method which may be used to produce polyacrylonitrile yarn is the so-called "wet" spinning process which comprises extruding a solution of polyacrylonitrile through a perforated nozzle (spinneret) into a bath composed of a liquid which will readily leach out the solvent from

2

the polymer solution and coagulate or precipitate the polymer from its solution, the yarn being carried through the bath for a period of time sufficient to solidify the polymer to the desired extent and being subjected, if desired, to a stretching operation, preferably while it is in the gel state, in order to increase tenacity as well as otherwise to improve physical properties by orienting the micelles of which the filaments are composed, the yarn being washed, if desired, to remove the coagulating bath liquid and dried.

Yarn produced by the dry and wet spinning processes described above has excellent physical properties, but does not possess that degree of freedom from color which is required by the exacting standards of the textile industry. Moreover, the customary methods utilized in the textile art for the bleaching of color from filaments, fibers and the like do not effect the desired elimination of color from polyacrylonitrile yarn. The yellowish or golden-brown color present in polyacrylonitrile articles occurs either during polymerization or processing of the polymer prior to or during shaping of the polymer to the desired form and may be caused by prolonged treatment of the polymer at high temperature, e. g. 100° C. and above.

The invention will be described most particularly with reference to yarn composed of continuous filaments, but it will be understood that this is merely by way of illustration since the invention may also be applied to staple fibers, thin transparent films such as may be used as wrapping tissue, monofils, artificial straw, hollow pellicles such as tubing and other industrial products composed of acrylonitrile polymer.

It is an object of this invention to provide a process for removing color from articles composed of acrylonitrile polymer. It is a particular object to produce color-free acrylonitrile polymer filaments, fibers and yarns, without substantially impairing the physical properties of the products. Other objects will appear hereinafter.

The objects of the invention are accomplished in general by spinning polyacrylonitrile yarn by a dry or by a wet spinning process, preferably collecting the dry yarn on a bobbin or other suitable collecting device and soaking the dry yarn for a short period of time in an aqueous solution of hypochlorous acid at a temperature of at least 90° C., the solution when temperatures above the boiling point at atmospheric pressure are used, i. e. temperatures of 100° C. or above, being maintained in the liquid state by the use of superatmospheric pressure, e. g. in an autoclave. Objectionable coloring present in the yarn is removed by the bleaching treatment with no substantial impairment of the desired physical properties of the yarn.

The following examples in which parts, per-

centages and proportions are by weight unless otherwise specified and which are intended to be illustrative instead of limitative, set forth preferred forms of the invention.

Example A

Yarn to be treated in accordance with the present invention may be prepared as follows:

A solution of 100 parts of polyacrylonitrile possessing an average molecular weight of 60,000 as determined from viscosity measurements by the Staudinger formula, in 300 parts of dimethylformamide, is extruded at the rate of 10.1 grams per minute and at a temperature of 130° C. downwardly through a spinneret having ten holes 0.125 mm. in diameter, into a tubular cell through which heated air is circulated in an upward direction. The walls of the cell are maintained at a temperature of approximately 400° C. The fresh air enters the lower portion of the chamber at a temperature of about 100° C. while the waste air leaving the upper portion of the cell is at a temperature of about 200° C. The cell has a length of 8 feet, sufficient for the evaporation of the dimethyl formamide from the extruded solution. The solidified, multifilament polyacrylonitrile yarn issuing from the bottom of the cell is collected on a rotating bobbin at a speed of 100 yards per minute. The yarn, which has a denier of 248, is soft and pliable and has a dry tenacity of 0.62 gram per denier and a wet tenacity of 0.53 gram per denier. Its elementary analysis corresponds to that of the polymer of acrylonitrile originally dissolved in the dimethyl formamide. The collected yarn is then unwound from the collecting bobbin, passed without slippage about a positively driven roller, heated to a temperature of 140° C. and wound upon a rotating bobbin, the peripheral speed of which is eight times that of the heated roller. The resulting yarn which has been permanently stretched by this treatment has a dry tenacity of 3.4 grams per denier.

Example I

A solution of sodium hypochlorite containing 0.25% available chlorine was acidified with sulfuric acid to a pH of 2.1. Three hundred (300) cc. of this solution were placed in an autoclave and a skein containing 45 yards of polyacrylonitrile yarn prepared by a dry spinning process such as that described in Example A was immersed in the bath. The autoclave was closed and steam was introduced, the autoclave being bled to remove air. The steam pressure was allowed ultimately to build up to 25 pounds, at which pressure it was maintained for one half hour (at a temperature of approximately 130° C.). At the end of that time, the autoclave was bled off, the skein was removed, washed with cold distilled water and dried. Physical properties were measured as follows: Before treatment, the yarn showed a dry tenacity of 3.3 grams per denier and a dry elongation of 14.7%, but after treatment, the dry tenacity was 3.3 grams per denier and the dry elongation 16%. The bleach rating was 1 on an arbitrary scale in which zero would represent perfect bleaching, as compared with a color rating of 4 for the same yarn which was not subjected to the bleaching treatment.

By comparison, gel polyacrylonitrile yarn which was wet-spun by extrusion of the solution through a nozzle into a coagulating liquid was collected, subjected to the same bleaching treatment, but with only 0.125% available chlorine present and after being dried, showed a decrease in dry tenacity of about 28%, compared with the dried, wet-spun yarn which had not been subjected to the bleaching treatment, and showed a color rating of 3.

Example II

A 50-yard skein of polyacrylonitrile yarn prepared by a dry-spinning process such as that described in Example A was placed in 300 ml. of a bleaching solution made from sodium hypochlorite (0.25% available chlorine) and acidified with sulfuric acid to a pH of 2.0. The solution contained in a 400 ml. beaker covered with a watch glass was placed in a steam bath and was heated to 97° C. Bleaching action first became pronounced when the temperature rose to about 90° C. After about a thirty minute treatment, no further bleaching took place. The yarn was then washed and dried as in Example I. The degree of freedom from color was at least as good as in Example I. The bleached yarn had a dry tenacity of 4.24 grams per denier and a dry elongation of 14.8% as compared with a dry tenacity of 4.21 grams per denier and a dry elongation of 14.5% for the same yarn before the bleaching treatment, this comparison showing that the bleaching treatment did not impair the physical properties of the yarn.

While the invention is particularly applicable to the bleaching of dry-spun polyacrylonitrile yarn, it may also be applied with corresponding benefit to the bleaching of wet-spun polyacrylonitrile yarn which has been dried as shown in the following example.

Example III

Dried polyacrylonitrile yarn obtained by a wet-spinning process, exhibiting a dry tenacity of 4.49 grams per denier and a dry elongation of 16.9% and having a color rating of 10 was treated in a covered beaker at 97° C. and at atmospheric pressure as was the yarn of Example II with the same bleaching solution of Example II having 0.25% available chlorine and a pH of 2.0, followed by washing with cold distilled water and drying, the periods of bleaching being respectively five minutes and thirty minutes. Two other experiments were run under the same conditions except that the bleaching solution contained 0.125% available chlorine with a pH of about 2.0 for respective periods of five and thirty minutes. The results of these experiments are tabulated as follows:

Concentration of Bleach Per cent Available Chlorine	Time of Bleaching	pH of Solution	Dry Tenacity	Dry Elongation	Color Rating
	Min.				
0.25	5	2.0	4.56	19.8	2
0.25	30	2.0	4.06	18.5	0
0.125	5	2.0	4.54	19.7	2
0.125	30	2.0	4.54	20.2	0

Example IV

Dried polyacrylonitrile yarn obtained by a wet-spinning process was treated in an autoclave under 10 pounds steam pressure with bleaching solutions such as those described in Example III containing respectively 0.25% and 0.125% available chlorine in separate experiments for thirty minutes, the pH of the solutions being 2.0. As compared with the dried yarn prior to the bleaching treatment which had a color rating of 10, the yarn so bleached showed a color rating of zero.

The acrylonitrile polymer for use with this invention is preferably prepared by the ammonium persulfate catalyzed polymerization of monomeric acrylonitrile dissolved or emulsified in water. It can, however, be prepared by any other suitable type of polymerization reaction, such as for example the emulsion type reaction disclosed by U. S. Patent No. 2,160,054 to Bauer et al. The polymer preferably possesses a molecular weight within the range 15,000 to 250,000 or even higher, as calculated from viscosity measurements by the Staudinger equation:

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

wherein:

$K_m=1.5\times10^{-4}$

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

and

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

The molecular weight of the polymer obtained is dependent on such factors as the concentration of the monomer in the water, the amount and type of catalyst present, the temperature of the reaction, etc. When the monomer is present in 5% aqueous solution maintained at a temperature of from 3° to 5° C., it is found that the use of 4% of ammonium persulfate catalyst (based on the weight of the acrylonitrile) results in the formation of a polymer having a molecular weight (as calculated by the above equation) of approximately 60,000. Increasing or decreasing the amount of the catalyst, while maintaining the other conditions constant, decreases or increases the molecular weight of the polymer.

The aqueous, hypochlorous acid solutions used in accordance with the present invention will contain 0.05% to 1.0% available chlorine and preferably 0.1% to 0.5%, with the most preferred concentration being in the neighborhood of 0.25%; hypochlorous acid solution may readily be prepared by dissolving a material such as sodium hypochlorite or calcium hypochlorite, or other soluble hypochlorite, in water, acidifying with a mineral acid such as hydrochloric or sulfuric acid to a pH of less than 7.0 and preferably 2.0 to 5.0, the term "available chlorine" signifying the chlorine present as hypochlorous acid. An excess of mineral acid added to the hypochlorite solution does no harm and the pH can be lower than 2.0 or even close to 0.0, if desired.

The temperature for the bleaching treatment should be within the range 90° to 150° C., and preferably 90° to 140° C., with the pressure being sufficiently high to maintain the treating solution liquid. The time of treatment will be short and preferably thirty minutes or less, but will depend on the temperature and the available chlorine concentration. It is preferred that the vessel in which the bleaching treatment is carried on be covered; for example, as in the case of an autoclave where the treatment is carried out under pressure as in Example I, or by the use of a watch glass or its equivalent as is described in Example II where the treatment is not carried out under pressure.

Sodium hypochlorite has been used in very dilute concentrations for the treatment of textile fibers such as cotton and rayon, but it has no useful effect, in the customary concentrations and at temperatures below those used in the practice of the present invention, as far as acrylonitrile polymer yarn is concerned. Alternatively, the use of the relatively concentrated solutions of bleaching agent used in accordance with this invention would so degrade the said textile materials as to make them practically useless.

The bleaching treatment of this invention may be applied to the yarn after the removal of the solvent (when the yarn is dry-spun), or after drying (when the yarn is wet-spun) and before collection of the yarn although the treatment is preferably applied after the dry yarn is wound on a bobbin which should be perforated to allow easy permeation of the yarn, or when the yarn is in the form of skeins.

By the process of the present invention, polyacrylonitrile yarn, filaments, fibers, film, monofilaments, artificial straw, hollow tubing and other structures can be bleached to a satisfactory colorless or white character without deleterious action on the structure. The bleached polyacrylonitrile structures of the present invention, except for improved color, exhibit substantially the same physical characteristics as the unbleached structures.

Since it is obvious that many changes and modifications can be made in the above described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to the details described herein except as set forth in the appended claims.

I claim:

1. In the process of removing color from an article composed of a polymer of acrylonitrile containing at least 85% acrylonitrile in the polymer molecule, the step which comprises subjecting said article after it has been dried to treatment with an aqueous solution containing hypochlorous acid corresponding to 0.05% to 1.0% by weight of said solution of available chlorine and at a temperature of 90° to 150° C., and for a period not exceeding thirty minutes.

2. In the process of removing color from a yarn composed of a polymer of acrylonitrile containing at least 85% acrylonitrile in the polymer molecule, the step which comprises subjecting said yarn after it has been dried to treatment with an aqueous solution containing hypochlorous acid corresponding to 0.05% to 1.0% by weight of said solution of available chlorine at a temperature of 90° to 150° C. and for a period not exceeding thirty minutes.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,021,763	Bauer	Nov. 19, 1935
2,226,356	McCarthy	Dec. 24, 1940
2,292,737	Blomer	Aug. 11, 1942
2,295,660	Hubert	Sept. 15, 1942

FOREIGN PATENTS

Number	Country	Date
437,271	Great Britain	Oct. 28, 1935
518,970	Great Britain	Mar. 13, 1940
802,840	France	Sept. 16, 1936