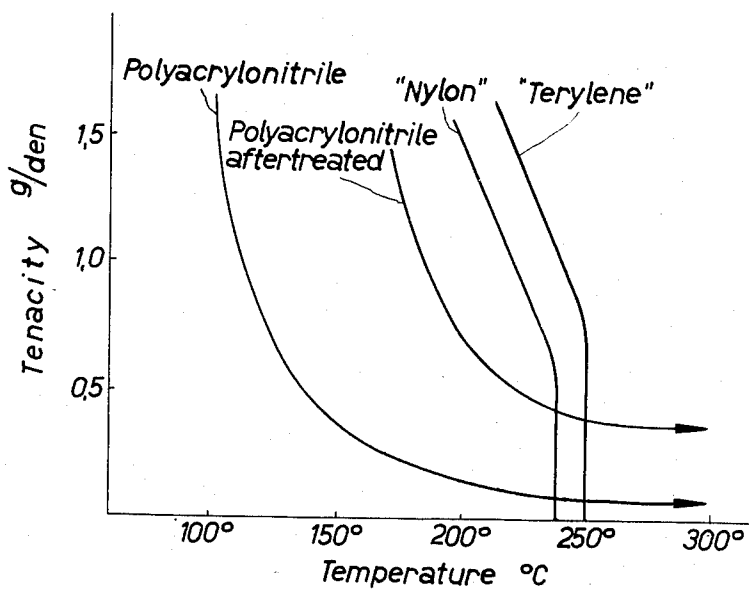


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TREATMENT OF POLYACRYLONITRILE FIBER WITH ETHYLENE
DIAMINE AND PRODUCT RESULTING THEREFROM
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TREATMENT OF POLYACRYLONITRILE FIBER WITH ETHYLENE DIAMINE AND PRODUCT RESULTING THEREFROM

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The present invention relates to acrylonitrile polymers or polymers consisting substantially or preponderantly of acrylonitrile. These polymers find application as fibers, foils or molded articles. They possess a very marked stability against chemical influences, also insolubility in nearly all solvents and infusibility. They have, however, certain disadvantages. Thus for instance their tenacity in the hot state is slight, and they possess a poor capacity for being dyed with the usual dyestuffs.

It is a characteristic feature of these polymers that they can stand a heat treatment up to 300° C. without damage and without any alteration of their shape as a fiber or foil, but that their tensile strength at such elevated temperatures is substantially decreased. At 100° C. the tenacity is about one half of the tenacity at normal temperatures, while at 170° C. it amounts to $\frac{1}{2}$ and at 300° C. only to $\frac{1}{60}$ thereof. In all cases, where a certain minimum tenacity in the heat is desired, for instance in hot-ironing of fabrics or in the employment of threads as tire cord, these properties are exceedingly undesirable. A further disadvantage of these polymers is their poor capacity for being dyed, which renders impossible their application as filaments or fibers in many textile fields.

It is an object of the invention to overcome the above named draw-backs of acrylonitrile polymers. A further object is to provide a process by which the tenacity in the heat of objects consisting of polyacrylonitrile or its copolymers or interpolymers with a preponderant amount of acrylonitrile, is substantially increased. Another object consists in the provision of a process by which the acrylonitrile polymers may be rendered capable of being dyed with the usual dyestuffs and according to the usual methods.

Still further objects will become apparent as the following specification proceeds.

The objects of the invention are accomplished by treating acrylonitrile polymers, copolymers, or interpolymers thereof, with aliphatic mono- or polyamines or even with ammonia. According to the invention the polymers may be treated at any stage of their working up. The process may be carried out for instance by treating fibers or foils or other shaped articles for some period of time with the liquid amine, preferably in the heat. The time and temperature of the treatment must be so selected that sufficient amine is taken up. The speed with which this can be performed, depends upon the physical structure of the polymer and the thickness of the layers to be penetrated. Thus, in spun fibers of a diameter of 20 den. which contain 3-8 per cent solvent or plasticizer remaining from the spinning process, a treatment of 1-2 hour at room temperature is sufficient. In contrast thereto, a filament which has been stretched and tempered and which has a diameter of three deniers, requires the employment of hot baths.

The effect observed may be also brought about by treating the unshaped polymer, for instance in the form of powder, with the amines. This process can be effected wherever the treatment does not impair the sub-

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sequent shaping process, for instance in the production of molded products. In such cases where the powders are still soluble after treatment, it is also possible to spin the dissolved polymer.

Primary aliphatic di- and polyamines are preferred. However monoamines can also be employed with good success. Even ammonia has some effect.

As aliphatic amines which may be used according to the invention, the following are named as examples: Lower aliphatic monoamines, such as methyl-, ethyl-, propyl- and n-butylamine, diamines, such as ethylene-, propylene-, butylenediamine, N-methyl-trimethylenediamine, ass. N-dimethyl-trimethylenediamin N-cyclohexyltrimethylenediamine, and N-phenylethylene diamine, also diethylenetriamine, di-(γ -aminopropyl)-amine, N,N'-bis-(γ -aminopropyl)-trimethylenediamine, N,N'-bis-(γ -aminopropyl)-tetramethylenediamine (Spermin), N,N'-dibutylpropylenediamine and others. Higher molecular amines may also be employed, such as for instance those obtained by reacting ammonia on ethylenechloride.

The aliphatic amines may be employed as such in the liquid or vapor phase, as well as diluted with water or organic solvents. Ammonia is preferably used in the liquid form in a pressure vessel.

The improvement of the tenacity in the heat is particularly noticeable, if the shaped polymer treated with the amine is exposed for some seconds to temperatures above 170° C. up to 240° C. This heat treatment, after the treatment with the amine, is of greater importance for the polymers treated with monoamines than for those treated with di- or polyamines.

The process of the invention can be applied to polyacrylonitrile fibers in various ways. The process may be carried out immediately following the spinning process with the unstretched fiber or it may follow the stretching process which is essential for obtaining good mechanical properties. It is important to state that the stretchability of the yarns is not impaired by the treatment in the unstretched state nor is the effect of the amine treatment lost by subsequent stretching in the heat.

The amine treatment in the unstretched state does not materially influence the subsequent stretching process. The maximum elongation is generally decreased from a ratio of 1:8 to 1:6, no disadvantages being incurred thereby. The heat treatment mentioned above, which is of particular importance if monoamines are employed, for obtaining an improved tenacity in the heat, is preferably carried out when the yarns are already stretched.

The improvement of the tenacity in the heat of fibers amounts to about six times that of the untreated fiber above 150° C., or generally speaking the heat tenacity is improved by 80-100° C.

In the self-explanatory diagram attached the tenacity of filaments at raised temperatures is shown. It appears from this diagram that filaments of crystalline superpolymers, such as nylon (superpolyamide from hexamethylenediamine and adipic acid), or Terylene (superpolyester from terephthalic acid and ethylene glycol), display a tenacity which suddenly drops to zero in the neighborhood of their melting point, while polyacrylonitrile fibers which are not treated according to the invention still have a very slight tenacity at 200° C. that slowly decreases up to temperatures of 300° C. A polyacrylonitrile filament aftertreated according to the invention has a tenacity at for instance 210° C. equal to that of an untreated filament at 130° C.

Example 1

Stretched fibers from polyacrylonitrile (K-value 90) having a diameter of 2, 5 den. are treated for one hour in boiling ethylene diamine, washed with water and dried at 50° C. The tensile strength at 200° C. of the fiber

thus treated is increased to four times that of the untreated fiber and amounts to 0, 7 g/den. at 200° C. Additionally the fiber may be dyed in acid baths in strong tints fast to washing and light with three per cent of an acid dyestuff, for instance that obtained according to the process of German Patent 280,646 from 1-amino-bromanthraquinone-2-sulfonic acid and acetophenylene-diamine.

Example 2

An interpolymer of 95 parts of acrylonitrile and five parts of vinylacetate having a K-value of 110 is spun from a 20 per cent solution in dimethylformamide, the fibers having a diameter of 20 den. The fibers which contain a residual amount of solvent of 5-10 per cent are immersed in the unstretched state for three hours at room temperature in ethylenediamine. After washing with water and drying at 40° C., the yarn is stretched to six times its original length over a piece of iron heated to 200° C., the yarn being kept at this temperature for three seconds. The yarn so obtained shows good affinity to acid dyes and has a tenacity at 200° C. six times as high as that of the untreated fiber. The tenacity at 180° C. for instance amounts to 1, 25 g/den.

Example 3

An interpolymer of 95 parts of acrylonitrile and five parts of vinylacetate having a K-value of 102 is spun from a 22 per cent solution in dimethylformamide to yield a yarn, whose individual fibers have a diameter of 15 den. The filaments which contain a residual 5-10 per cent of solvent are treated for one hour in a 30 per cent aqueous solution of ethylamine at 70° C., rinsed with water and dried at 40° C. They are then stretched to six times their original length over a piece of metal heated to 190° C. and kept at this temperature for two seconds. The yarn exhibits a tenacity which is 3-4 times that of an untreated fiber in the temperature range of between 150 and 300° C.

Example 4

Ten parts of powdered polyacrylonitrile (K-value 100) are heated for 18 hours in boiling n-butylamine. The

powder is sucked off, washed with water, acidified, washed again and dried. In contrast to the untreated powder it may now be dyed in strong tints with acid dyes, for instance Ponceau R (Schultz No. 95) or substantive dyes, for instance Chrysophenin G (Schultz No. 726).

Example 5

Powdered polyacrylonitrile of the K-value 100 is stirred for 18 hours in ten times the amount of n-butylamine at the boiling point of the solution (77° C.). The powder is then sucked off, washed and dried and dissolved in dimethyl-formamide to yield a 20 per cent paste which is spun in the usual manner. The filament thus obtained may be dyed with acid dyes, for instance Ponceau R, in tints which are resistant to washing and light. The tenacity of the filament is between 3.6 and 4 g/den.

We claim:

1. A process for improving the tensile strength at elevated temperatures of a stretched polyacrylonitrile fiber, which comprises immersing said fiber in a bath consisting essentially of boiling ethylene diamine for a period of approximately one hour, and then heating said fibers to a temperature of from about 170° to about 240° C. for a short period.
2. The improved polyacrylonitrile fiber obtained by the process defined in claim 1, said fiber having a tensile strength at 200° C. approximately 4 times that of the untreated fiber.

References Cited in the file of this patent

UNITED STATES PATENTS

1,984,417	Mark et al.	Dec. 18, 1934
2,404,720	Houtz	July 23, 1946
2,420,565	Rugeley et al.	May 13, 1947
2,445,042	Silverman	July 13, 1948
2,497,526	Arnold	Feb. 14, 1950
2,563,662	Rothrock	Aug. 7, 1951

FOREIGN PATENTS

613,817	Great Britain	Dec. 3, 1948
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