

March 5, 1963

YOSHISATO FUJISAKI ET AL
METHOD FOR PRODUCING ACRYLONITRILE POLYMER FIBERS
AND FILAMENTS BY WET SPINNING PROCESS
Filed Oct. 12, 1961

3,080,209

Fig. 1

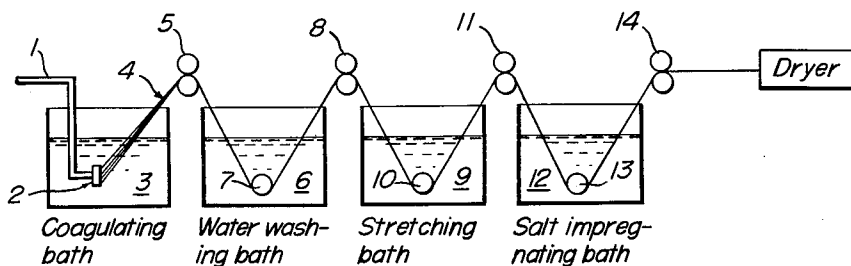


Fig. 2

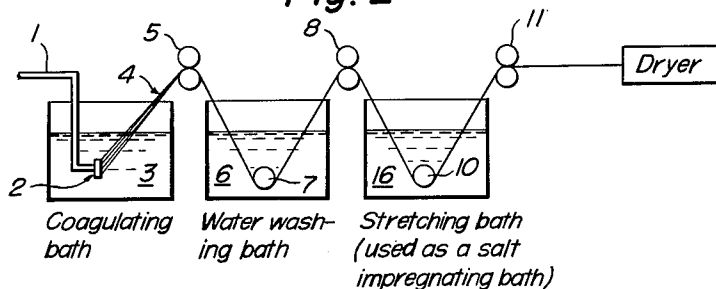
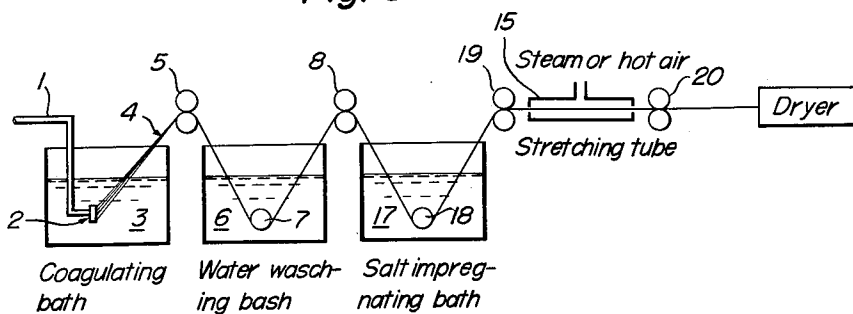


Fig. 3



1

3,080,209

METHOD FOR PRODUCING ACRYLONITRILE POLYMER FIBERS AND FILAMENTS BY WET SPINNING PROCESS

Yoshisato Fujisaki, Numazu-shi, and Toshio Ohfuka, Fuji-shi, Japan, assignors to Asahi Kasei Kogyo Kabushiki Kaisha, Osaka, Japan, a corporation of Japan
Filed Oct. 12, 1961, Ser. No. 144,533
6 Claims. (Cl. 18—54)

This invention relates to the preparation of fibers and filaments from acrylonitrile polymers by extruding a solution thereof in nitric acid into an aqueous nitric acid medium and drying the coagulated fibers or filaments. More particularly, this invention relates to a production of acrylonitrile fibers and filaments having superior dyeability for basic dyestuffs by incorporating univalent cations consisting of ammonium or alkali metal ions in the fibers and filaments.

In a well known method for preparing fibers and filaments of acrylonitrile polymers acrylonitrile polymer is dissolved in nitric acid at a temperature of below 5° C., extruded into dilute nitric acid at a lower temperature and stretched at a high temperature. Although it may be possible to produce fibers and filaments having excellent quality according to such method using nitric acid as a solvent, in many cases fibers and filaments having homogeneous and high affinity for the basic dyestuffs are hardly obtainable depending upon the properties of the initial polymer.

It is, therefore, an object of the present invention to provide a method for improving dyeability of acrylonitrile fibers and filaments for the basic dyestuffs.

It is another object to provide acrylonitrile fibers and filaments having superior dyeability for basic dyestuffs.

In the present specification, acrylonitrile polymers include polyacrylonitrile and polymers or copolymers containing at least 85% by weight of acrylonitrile and not more than 15% by weight of monoethylenically unsaturated compounds copolymerizable therewith. The monoethylenically unsaturated compounds comprise, for instance, esters such as methyl acrylate, ethyl methacrylate, vinyl acetate and the like; amides such as acrylamide, methacrylamide and the like; alcohols such as allyl alcohol and the like; ketones such as methyl vinyl ketone and the like; acids such as acrylic acid, methacrylic acid, itaconic acid and the like; sulfonic acids such as para-styrene sulfonic acid, vinyl sulfonic acid, sulfoethyl acrylate, sulfo-propyl methacrylate and the like; vinyl chloride and vinylidene chloride, but basic comonomers such as vinyl-pyridine and the like are not included.

Any basic dyestuffs may be used in the present process. Typical examples are Sevron Yellow L, Sevron Yellow R, Sevron Orange L, Sevron Brilliant Red 4G, Sevron Red L, Sevron Red GL, Sevron Blue B, Sevron Blue 2G, Sevron Blue 5G, Sevron Green B, Du Pont Fuchsine Conc., Du Pont Brilliant Green Crystals, Du Pont Victoria Green Small Crystals, Basacryl Yellow 3GLH, Basacryl Red 6BH, Basacryl Yellow 5GL, Basacryl Blue GL, Basacryl Violet RL, Astrazon Blue FGL, Astrazon Orange R, Astrazon Yellow 7GL, Astrazon Blue 3RN, Astrazon Red BBL, Astrazon Red 6B, Astrazon Pink FG, Astrazon Yellow 3G, Maxilon 3GL, Maxilon Blue GL, Maxilon Red BL, Genacryl Yellow 5GF, Genacryl Yellow 3G, Genacryl Red 6B, Genacryl Blue 6G, Deorline Yellow 5GL, Deorline Red 5B, Deorline Blue 5G, Cathilon Yellow 5GLH, Cathilon Orange GLH, Cathilon Blue BLH, Bismark Brown and Magenta.

Acrylonitrile polymer is first dissolved at lower temperature in nitric acid solvent (63% by weight or higher), extruded into a 25 to 45 weight percent nitric acid coagulation bath, washed with water, stretched to 4 to 20 times in hot water, superheated (unsaturated) steam, superat-

2

mospheric (saturated) steam or atmospheric pressure (100° C.) steam or hot air, and is then dried in the conventional way.

According to the present invention, the fiber after leaving the coagulation bath is treated with a solution containing univalent cations before drying in order to incorporate the cations in the fiber. Cations contained in the polymer or in the spinning solution are removed in the coagulation bath from the fibers, so that they are no longer active. Even when a large amount of cations is added to the coagulation bath to incorporate it into the fibers, the cations are still washed off in the final washing with water and are not active. The univalent cations are lithium, sodium, potassium and ammonium. They are used in the form of an aqueous solution of water soluble inorganic salts of such acids as nitric acid, sulfuric acid, hydrochloric acid, phosphoric acid, boric acid and the like. Salts with organic substances such as sodium lauryl sulfate are not desirable, since after being dyed with the basic dyestuff there occur defects in either fastness to washing or to light.

It is preferable to immerse the coagulated fibers and filaments in a bath of said aqueous solution of water soluble inorganic salts, at any stage after leaving the coagulating bath and before entering a drying step. In some cases, before drying, the coagulated fibers and filaments may be dehydrated by passing between rollers. However it is essential that the fibers and filaments must not have undergone drying before the immersion to an extent that the water content is less than 15% by weight based on the swelled gel and, preferably, the water content should not be less than 45%. The aqueous solution of inorganic salts may be poured or sprayed onto the filament or fiber.

Incorporation of the univalent cations in the fiber helps to prevent the loss of groups active to basic dyes from the acrylonitrile polymer and to improve the penetration velocity or diffusion velocity of the dyes into the fiber, thus to improving dyeability of the fibers.

Univalent cation is incorporated in the fibers preferably in a concentration range about from 0.003 to 0.02 mol/100 g. fibers, based on the dry weight of fibers. Dyeability of the fibers increases to a certain extent in proportion to the increase in the concentration of the univalent cations in the fibers. However, above the stated limitation, the increase in dyeability becomes very slow and also various defects are caused to arise, such as the decrease in whiteness or the loss of transparency of the fibers.

The polymers used in the present invention can be produced by any of the general methods which are well known and there is no particular limitation.

The accompanying drawings, FIGS. 1-3, show outlines of methods for impregnating coagulated filaments with salt in accordance with the present invention.

A spinning solution after cooling is filtered, introduced to a spinneret 2 through a conduit 1, and extruded at a fixed rate into a coagulating bath 3 to produce a coagulated filament 4.

As the coagulating bath, 25-40% (weight) nitric acid is ordinarily employed. The coagulated filament is introduced into a water washing bath 6 through rollers 5 wherein the acid content thereof is removed upon passing of the filament over rollers 7 and 8 before the filament is subjected to the salt-impregnating operation of the present invention. For example, the most convenient process is to apply the treatment of the present invention after the coagulated filament has been hot-stretched. This is shown in FIG. 1, wherein a salt-impregnating bath 12 is provided next to a hot-stretching bath 9 (10, 11, 13 and 14 are guide rollers). Generally the coagulated filament is stretched to 4 to 20 times in the hot-stretching bath which may be placed at any desired position throughout the process. As to the hot-stretching bath, hot water is

ordinarily used, but the water may be substituted by unsaturated superheated steam or saturated atmospheric or superatmospheric pressure steam. In spite of a hot-stretching operation, the coagulated filament does not suffer from such reduction of its degree of swelling which would prevent the salt-impregnating operation of the instant method.

In case the unsaturated superheated steam or saturated atmospheric or superatmospheric pressure steam is employed as the hot-stretching bath in place of hot water, it is possible to place the salt-impregnating bath before the stretching process, since the coagulated filament is not desalted during the stretching operation. One example thereof is shown in FIG. 3, wherein 17 is the salt-impregnating bath, 15 is a tubular hot-stretching tube and 18, 19 and 20 are guide rollers.

These steps can suitably be modified within the general concept of the present invention. For example, in case the hot-stretching bath is conducted in hot water, the stretching bath may be used as a salt-impregnating bath. FIG. 2 shows one example thereof wherein a water-washed coagulated filament is hot-stretched in a salt-containing hot-stretching bath 16.

Furthermore, even though hot water is employed as the stretching bath, if a small amount of salt is employed in the bath it is possible to control the amount to be desalted, and the salt-impregnating bath may be provided before the stretching process. Also, in case a relatively large amount of salt has previously been added to the salt-impregnating bath, it is readily possible to hot-stretch the coagulated filament in hot water after treating it in the salt impregnating bath. Further, an additional salt-impregnating bath may be placed after said hot-stretching bath to control the salt content of coagulated filament. However, in case hot dried air is used as a heating medium of the stretching bath, the lowering in swelling degree during stretching is relatively large so that it is preferable to provide the salt-impregnating bath before the heat-stretching process. Although it is of course possible in theory to carry out a process for incorporating salt in the coagulated filament by washing said filament with water containing salt in the water bath, such process is not desirable from the economical point of view.

The method of the present application is not restricted to the process just described. For instance, the water-washing and hot-stretching steps are not limited to merely one stage but can be carried out in a multi-stage process. Also, when a multi-stage stretching is conducted, there are some cases where a drying step is inserted among said stages. Moreover, in case the hot-stretching is carried out by a multi-stage process, there is oftentimes adopted such a condition that the temperature of each stage is elevated successively. Further in the aforesaid drawings, the squeezing rollers may be replaced by Nelson type rollers or multi-stage rollers. As mentioned above, all the well known processes may ordinarily be employed in connection with the instant method. All the variations would not depart from the basic idea of the present invention as set out in the appended claims.

The following examples illustrate the present invention without limiting its scope.

EXAMPLE 1

14.5 parts of a copolymer consisting of 92% of acrylonitrile and 8% of methyl acrylate (polymerized by using the initiator system of $K_2S_2O_8$ and thioglycolic acid; molecular weight: 50,000) were dissolved in 85.5 parts of 72% HNO_3 at $-3^\circ C$. This solution was extruded into a coagulating bath of 33% HNO_3 maintained at $-3^\circ C$. through a spinneret having 2,000 holes of 0.1 mm. diameter each. After being thoroughly washed with water, the filament was stretched to 10 times its length in a boiling water bath maintained at a pH of 3.5 by sulfuric acid. The amount of NH_4^+ in a stretching bath was varied using NH_3 while maintaining the pH constant.

The stretched fibers thus obtained were dried at $90^\circ C$. in air for 30 minutes. In order to examine the dyeability of these fibers with the basic dyestuffs, they were dyed in a 0.0625% solution of malachite green having a pH of 3.5 with fiber to liquor ratio of 1:40, at $100^\circ C$. for one hour. The dyeability of the fiber thus obtained is shown in Table 1. The dyeability is defined as the percent ratio of the amount of dyestuffs absorbed in the fiber to that of dyestuffs originally present in the dyeing bath.

Concentration of NH_4^+ in fibers (mol/100 g. fiber)	Dyeability (percent)	Whiteness of fibers
0	13	bright.
0.0011	15	Do.
0.0024	18	Do.
0.0030	24	Do.
0.0045	33	Do.
0.0067	40	Do.
0.0106	53	slightly bright.
0.015	68	slightly dark.
0.018	69	Do.
0.021	70	dark.

When these dry fibers were steamed at $120^\circ C$. for 10 minutes, the dyeability became as follows:

Fibers not containing NH_4^+ ion: ca. 0%
Fibers containing 0.0067 mol/100 g. fibers of NH_4^+ ion: 63%

EXAMPLE 2

A copolymer consisting of 97% of acrylonitrile and 3% of sodium acrylate (polymerized by the initiator system of $K_2S_2O_8$ and $NaHSO_3$; molecular weight: 47,000) was dissolved in 65% nitric acid at $-5^\circ C$. This solution was extruded into 38% nitric acid containing 1% of ammonium nitrate at $0^\circ C$. After being washed thoroughly with water, this was stretched in the stretching bath maintained at a pH of 3.5 by sulfuric acid and squeezed by means of rollers until the water content thereof becomes 50%. This was immersed in a bath having various concentrations at Na_2HPO_4 and then dried in air at $90^\circ C$. for 30 minutes. The dyability and the whiteness of the fibers dyed by the same process as described in Example 1 are set forth in Table 2A.

Table 2A

Na^+ concentration in fibers (mol/100 g. fibers)	Dyeability (percent)	Whiteness of fibers
0	30	slightly bright.
0.0013	32	do.
0.0025	35	do.
0.003	40	do.
0.008	75	do.
0.015	98	slightly dark.
0.024	98	dark.
0.050	99	Do.

To the fibers, was added 40 times by weight of a 0.125% by weight Sevron Red L solution (pH=5) and the mass then subjected to heating at $100^\circ C$. for 1 hour. Dyeability is set forth in Table 2B.

Table 2B

Na^+ concentration in fibers (mol./100 g. fibers):	Dyeability (Percent)
0	36
0.0013	40
0.0025	43
0.008	50
0.015	92
0.024	99
0.050	99

EXAMPLE 3

A copolymer consisting of 97.3% of acrylonitrile, 2% of acrylamide and 0.7% of sodium salt of 3-sulfopropyl methacrylate (polymerized by the initiator system of sodium hydroxynitrosulfonate and $NaHSO_3$; molecular

5

weight: 48,000) was dissolved in 72% nitric acid containing 1% of magnesium nitrate, maintained at -5°C . This solution was extruded into 30% nitric acid maintained at -3°C . After washing thoroughly with water, the fiber was stretched to 6 times its length in a stretching bath kept at a pH of 4 by phosphoric acid and then was squeezed until the water content becomes about 65% by means of rollers. Then the fibers were immersed in an aqueous potassium sulfate solution having various concentrations of K^{+} ion and in aqueous potassium lauryl sulfate solution, respectively. The fibers thus stretched were dried at 80°C . These fibers were dyed by placing them in a dye solution containing 0.0875% of Sevron Red L, at a pH of 5 (fiber to liquor ratio; 1/40), and treating at 100°C . for 2 hours. After thoroughly washing with water, the fibers were dried at 80°C . The fibers were put in a 0.5% aqueous solution of "Marcel soap" of 50 times the weight of the fibers. Then a cotton cloth was immersed therein and the solution was treated at 70°C . for 10 minutes. The extent of contamination is shown in Table 3.

Table 3

K^{+} ion concentration in fibers (mol./100 g. fibers)	Extent of contamination of cotton cloth
0	contaminated.
0.005	slightly contaminated.
0.011	Do.
0.017	Do.
0.012 (introduced in as potassium lauryl sulfate)	much contaminated.

EXAMPLE 4

A copolymer consisting of 94% of acrylonitrile and 6% of methyl methacrylate (polymerized by the initiator system of potassium persulfate and β -mercaptoethanol; molecular weight: 43,000) was dissolved in 70% nitric acid at -3°C . and was extruded into 34% nitric acid maintained at -3°C . After washing thoroughly with water, the material was stretched to 6 times in a bath at 100°C . of pH 3 by means of sulfuric acid and was dried in a dryer at 70°C . to vary the water content ratio (based on the weight of swelled gel). Then, the fibers were immersed in an aqueous potassium nitrate solution and were treated to contain K^{+} ion in the fibers. After drying until the water content became about 4%, the fibers were dyed according to the same method as described in Example 1. The results are shown in Table 4.

Table 4

Water content ratio of fibers before treatment to contain K^{+} ion (percent)	K^{+} ion concentration in dry fibers (mol./100 g. fibers)	Dyeability (percent)
4.3	0	10
8.1	0.011	12
13.5	0.012	14
15.9	0.013	22
18.8	0.012	24
25.3	0.009	28
43.9	0.011	37
45.3	0.012	38
51.3	0.011	40
61.1	0.009	40
73.1	0.008	39

EXAMPLE 5

A copolymer consisting of 93% of acrylonitrile and 7% of vinyl acetate (polymerized by the initiator system of sodium hydroxynitrosulfonate and NaHSO_3 ; molecular weight: 51,000) was dissolved in 77% nitric acid at -5°C . and was extruded in 37% nitric acid maintained at -5°C . After being coagulated, the fibers were washed with water and stretched to 5 times in boiling water. The fibers then were immersed in an aqueous solution containing about 0.01 mol/100 g. H_2O of various cations. Then, the material was dehydrated by means of a centrifugal

6

separator until the water content ratio became about 50% and was dried at 70°C . In this instance, cations were contained in an amount of about 0.01 mol per 100 g. of dry fibers. The results obtained by dyeing said fibers according to the same method as set forth in Example 1 are shown in Table 5A.

Table 5A

Kinds of ion treated:	Dyeability percent
None	25
NH_4Cl	79
LiNO_3	83
NaCl	79
NaNO_2	80
KHCO_3	85
$(\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4$	81
MgCl_2	23
$\text{Al}_2(\text{SO}_4)_3$	22

Non-treated, NaCl -treated or MgCl_2 -treated fibers mentioned in Table 5A, were dyed with solutions of various dyes (pH=3.8) at a fiber to liquor ratio of 1/40, at 100°C . for 1 hour. The results are set forth in Table 5B.

Table 5B

Kinds of dyes	Conc. of dye, percent	Kinds of ion treated		
		none	NaCl	MgCl_2
Sevron Blue B	0.20	30	99	28
Sevron Green B	0.30	23	77	20
Sevron Brilliant Red 4G	0.25	20	64	21
Basacryl Red GL	0.25	20	67	18

As appears from the above table, bivalent and trivalent metals are not effective in improving dyeability but rather bring about undesirable influences.

EXAMPLE 6

A copolymer consisting of 98.5% of acrylonitrile and 1.5% of methallyl sulfonate (polymerized by the initiator system of azobisisobutyronitrile and lauryl mercaptan; molecular weight: 53,000) was dissolved in 70% nitric acid at -5°C . and was extruded into 33% nitric acid maintained at -5°C . The material was washed thoroughly with water after being coagulated and was squeezed by means of rollers so that the water content ratio became 80%. These squeezed fibers were immersed in an aqueous solution prepared by dissolving 0.7 g. of Na_2HPO_4 per 100 g. of water and maintained at a pH of 2.8 by sulfuric acid at room temperature. Then, the fibers were stretched to 6 times in steam heated to 120°C . and were dried at 100°C . after squeezing until the water content ratio became 50%. 0.009 mol of Na was contained per 100 g. of this fiber. The dyeability of this fiber obtained by dyeing according to the same method set forth in Example 1, was 32%. When similar fibers were prepared according to the same method without employing any Na_2HPO_4 , the dyeability was 8%.

What we claim is:

1. In a wet spinning method for producing fibers of acrylonitrile polymers selected from the group consisting of polyacrylonitrile and copolymers of at least 85% by weight of polyacrylonitrile and up to 15% by weight of monoethylenically unsaturated monomers copolymerizable therewith the said method involving dissolving the polymers in a nitric acid solvent, extruding and spinning the solution thus obtained in a coagulating bath and drying the spun article, the improvement comprising treating the fibers with a water soluble, univalent cation-containing inorganic acid salt until the univalent cation is incorporated in the fiber to the extent of between 0.003 and 0.02 mol per 100 gram fibers, the said treatment being effected after carrying out the coagulation and before reducing the water contents of the fibers in the drying to below 15% and the said univalent cation being

7

selected from the group consisting of ammonium and alkali metal ions.

2. The method of claim 1 wherein the alkali metal ions are selected from the group consisting of sodium and potassium ions.

3. The method of claim 1 wherein the water soluble inorganic salts are selected from the group consisting of salts of sulfuric acid, phosphoric acid and nitric acid.

4. In a wet spinning method for producing fibers of acrylonitrile polymers selected from the group consisting of polyacrylonitrile and copolymers of at least 85% by weight of acrylonitrile and up to 15% by weight of mono-ethylenically unsaturated monomers copolymerizable therewith the said method involving dissolving the polymers in a nitric acid solvent, extruding and spinning the solution thus obtained in a coagulating bath and drying the spun article, the improvement comprising treating the fibers with a water soluble, univalent cation-containing inorganic acid salt until the univalent cation is incorporated in the fiber to the extent of between 0.003

8

and 0.02 mol per 100 gram fibers, the said treatment being effected after carrying out the coagulation and before reducing the water contents of the fibers in the drying to below 45% and the said univalent cation being selected from the group consisting of ammonium and alkali metal ions.

5. The method of claim 4 wherein the alkali metal ions are selected from the group consisting of sodium and potassium ions.

6. The method of claim 4 wherein the water soluble inorganic salts are selected from the group consisting of salts of sulfuric acid, phosphoric acid and nitric acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,558,730	Cresswell	July 3, 1951
2,904,391	Bennett et al.	Sept. 15, 1959
2,916,348	Cresswell	Dec. 8, 1959