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2,967,085

PROCESS OF WET-SPINNING FIBERS CONTAINING POLYACRYLONITRILE

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This invention relates to the manufacture of fibers and the like of polyacrylonitrile and copolymers thereof by extruding a solution thereof in a solvent therefor into a coagulant. More particularly the invention relates to a continuous wet spinning method in which the polymer solvent and the coagulant are so chosen as to give a product of high quality, by a technically advantageous spinning procedure in which the polymer solvent and the coagulant readily may be recovered in a cyclical process for reuse. Different aspects of the invention such as (a) the method of spinning (b) the method of solvent and coagulant recovery (c) the cyclical process including the methods of spinning and solvent and coagulant recovery (d) the composition of the coagulating bath from which coagulant and solvent are recovered and (e) the intermediate fiber product are defined in the appended claims.

This application is a continuation-in-part of our application Serial No. 327,429, filed December 22, 1952, and now abandoned.

We have found that by a proper choice of the polymer solvent and the coagulant the results outlined above may be accomplished.

Our invention resides basically in the use of dimethylformamide or dimethylacetamide as the polymer solvent in conjunction with the use of normally liquid paraffinic, including cycloparaffinic hydrocarbon mixtures as the coagulant. These two solvents are substantially equivalent in our invention although dimethylformamide is the more powerful solvent for the polymer.

The polyacrylonitrile and copolymers used in the method of our invention are well known materials having molecular weights within the range from about 40,000 to about 200,000 as calculated from viscosity measurements by the Staudinger equation (see U.S. Patent No. 2,404,714, column 11, and Encyclopedia of Chemical Technology, by Kirk-Othmer, vol. 10, page 967). The invention is applicable generally to polyacrylonitriles containing up to about 15% of other monoolefinic monomer units and which are soluble in dimethylformamide and dimethylacetamide at the spinning temperature. The following are examples of suitable comonomers, methacrylonitrile, acrylic acid, acrylamide, methylacrylate, methylmethacrylate and vinyl acetate including partially hydrolyzed vinyl acetate. These and other known comonomers may be used within the range from 0 to 15% and preferably from 1% to 8% by weight based upon the weight of the acrylonitrile.

Various solvents for polyacrylonitrile are known but we have found that dimethylformamide and dimethylacetamide are specially suited in our process.

The preferred liquid paraffinic hydrocarbon for use in our process is kerosene containing not more than about 35% and preferably from 0 to 25% by weight of aromatic hydrocarbons, the remainder of the composition consisting of paraffine hydrocarbons and cycloparaffinic hydrocarbons. Kerosene is defined in Hack's Chemical Dictionary, third edition, as being "A mixture of hydrocarbons b.150–280° C.; the fifth fraction in the distillation

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of petroleum (after the gasoline and before the oils)." Commercial kerosenes which are preferred for use in our process always contain small amounts of impurities such as olefinic hydrocarbons, oxygen and sulfur compounds which give rise to gummy and colored products when the kerosene is heated in contact with air. Such gummy and colored products must be removed from the kerosene if it is to be continuously reused in the spinning process.

Kerosene suitable for use in our process may be further defined as containing from 0% to about 35% of aromatic hydrocarbons and from 65% to 100% of paraffinic hydrocarbons including hydroaromatic or cycloparaffinic hydrocarbons. In a typical instance a kerosene suitable for use in our process contains about 55% to 60% of paraffinic hydrocarbons, about 25% of cycloparaffinic hydrocarbons and 15% to 20% of aromatic hydrocarbons. Another example of a kerosene suitable for use in our process is a trade kerosene known as Shell's Odorless, which contains 0% to 2% of aromatic hydrocarbons, about 30% of cycloparaffinic hydrocarbons and 68% to 70% of paraffinic hydrocarbons.

As stated above the liquid paraffinic hydrocarbon coagulant may contain up to about 35% of aromatic hydrocarbons. This is not a critical upper limit of the aromatic hydrocarbon content of the coagulant but has been determined to be the practical upper limit due to the fact that the aromatic hydrocarbon content of the coagulant tends to modify the spinning process i.e. to coagulate the polyacrylonitrile too rapidly and to produce spongy fibers and also tends to interfere with or complicate the separation and recovery of the solvent and the coagulant for reuse.

As indicated the kerosene may be free of aromatic hydrocarbons. Other hydrocarbons and hydrocarbon mixtures which are not petroleum distillates but which otherwise fall within the definition of kerosene and do not contain more than about 35% of aromatic hydrocarbons may be used. Generally however from the standpoints of both utility and economy we prefer to use commercially available kerosenes as the coagulant.

In carrying out the process of our invention we prepare a solution of the polyacrylonitrile in dimethylformamide or dimethylacetamide, said solution containing from about 10% to about 30% and preferably from about 15% to about 25% by weight of the polyacrylonitrile or copolymer and spin the solution into a bath of the selected coagulant maintained at an elevated temperature i.e. above room temperature, which is below the boiling point of the coagulating bath. The coagulating bath temperature may be as low as about 60° C. but preferably higher e.g. above 100° C. such as 30° C. and may go as high as 160° C. or to the initial boiling point of the kerosene used. In the spinning process the spun fiber is suitably stretched during precipitation and again after the precipitation but before washing i.e. while it still contains solvent and kerosene. Depending upon operating conditions the fiber may contain from 2% to 5% of solvent and from 2% to 15% of hydrocarbons dissolved in the polymer after coagulation. It may then be washed and dried with or without crimping and cutting into staple fiber lengths as is well known in the art.

When the coagulating bath has accumulated an amount of polymer solvent, i.e. dimethylformamide or dimethylacetamide which exceeds the saturation point thereof at a lower temperature, the coagulating bath can be withdrawn and cooled whereby it separates into two liquid phases. The bath can be used until it has a solvent content of from 2% to 30%, preferably 10% to 20%. The cooling range should be at least about 40° C. but preferably as high as 100° C. or higher. The lower phase consists principally of the dimethylformamide or dimethylacetamide with an amount of the coagulant dissolved

therein which depends upon the character of the coagulant, particularly its aromatic hydrocarbon content, and the temperature. The upper phase consists principally of the coagulant with an amount of dimethylformamide or dimethylacetamide dissolved therein which depends upon the character of the coagulant and the temperature. For instance at about 20° C. using kerosene which is practically free of aromatic hydrocarbons, as the coagulant, the kerosene phase will contain only about 2-8% of the dimethylformamide or dimethylacetamide and the dimethylformamide or dimethylacetamide phase will contain only about 2% to 6% of kerosene.

After the phase separation of the used coagulating bath described above the kerosene phase is suitable to be reheated to the spinning temperature and returned to the coagulating bath. Moreover the kerosene phase is pure and well adapted for reuse in the process directly due to the fact that harmful impurities such as polymeric residuals, gums, colored material and oxidation products have been separated into the dimethylformamide or dimethylacetamide phase.

This separation of impurities in the dimethylformamide or dimethylacetamide phase is an important feature of our invention and is an essential feature in the cyclical operation of the process.

It is a fact that in the operation of the process, possibly due to breakdown of polymer or solvent or to oxidation of the coagulant or one or more constituents thereof at the elevated spinning temperature, gummy and colored materials form and tend to accumulate in the coagulating bath in amounts varying from 0 to 1% by weight. In the phase separation of the used or spent coagulating bath these gummy and colored products pass into the dimethylformamide or dimethylacetamide phase, leaving the kerosene phase purified for reuse directly. In order to eliminate the gummy and colored impurities and recover the dimethylformamide or dimethylacetamide for reuse, the dimethylformamide or dimethylacetamide phase may be distilled directly. The first or lightest distillate is an azeotropic mixture of the dimethylformamide or dimethylacetamide and kerosene, generally amounting to about 2% to 10%, which separates upon cooling into a second kerosene phase and a second dimethylformamide or dimethylacetamide phase both of which may be returned directly to the corresponding first separated phases for reuse in the cyclical process. The next distillate fraction is practically pure dimethylformamide or dimethylacetamide which may of course be returned directly to the cyclical process. Finally the distillation gives a residue containing some heavy kerosene fractions and the gummy and colored impurities which, so far as the present invention is concerned, may be discarded or used as fuel.

The recycling of the kerosene has the advantage over the use of fresh kerosene that it largely avoids the introduction of new impurities, which always accompany kerosene, into the process. New kerosene is added only to the extent required to replace losses. In the process the kerosene extracts the dimethylformamide or dimethylacetamide from the fiber at the elevated spinning temperature and then in the recovery step the dimethylformamide or dimethylacetamide phase extracts the impurities from the kerosene phase, the impurities being finally removed from the cycle in the treatment of the dimethylformamide or dimethylacetamide phase before it is returned to the cycle.

In actual practice a preferred procedure is as follows. The coagulating bath is first cooled and separated into two liquid phases. The kerosene phase containing 2-8% of solvent may be returned directly to the coagulating bath but preferably it is washed with a small amount of water, generally about 2% to 6% calculated upon the weight of the kerosene phase, thereby giving a kerosene product containing less dimethylformamide or dimethylacetamide than the original kerosene phase and an aqueous solution or dimethylformamide or dimethylacetamide.

The washed kerosene is then returned to the coagulating bath and the water solution of dimethylformamide or dimethylacetamide is added to the dimethylformamide or dimethylacetamide phase. This mixture of the dimethylformamide or dimethylacetamide phase and the water solution of dimethylformamide or dimethylacetamide is agitated and allowed to stand and separate into two liquid phases (1) a kerosene phase which is returned to the coagulating bath and (2) a dimethylformamide or dimethylacetamide water phase containing the colored and gummy impurities. This last phase (2) is then distilled as described above to yield dimethylformamide or dimethylacetamide which is returned to the process and a residue which is discarded.

The relatively slow coagulation of the polyacrylonitrile due to the high paraffinic hydrocarbon content and low aromatic hydrocarbon content of the coagulating bath facilitates the production of a high quality of fibers having a lower sponginess and brittleness than when a coagulant of higher aromatic content is used.

The technically possible spinning rate may be varied within a wider range by variation of the temperature and composition of the coagulating bath, higher temperatures or higher contents of aromatic hydrocarbons being used to increase the spinning rate. By using kerosene with the limited amount of aromatic hydrocarbons stated the coagulated fiber develops its strength very slowly and it must be handled with great care. This disadvantage is overcome by using a cross-linked polymer according to application Ser. No. 539,558, filed October 10, 1955 in the names of Olof Sundén, Sten Erik Arne Lennart Tunefors and Sven Hugo Sonnerskog and assigned to Stockholms Superfosfat Fabriks Aktiebolag.

It is, as noted above, advisable to subject the spun filaments to stretching during the precipitation thereof i.e. during their passage through the coagulating bath because such stretching promotes complete precipitation and improves the strength and decreases the porosity of the resulting fibers. This stretching preferably is at least twice the jet rate of the filaments. The fibers are further stretched to from 2 to 15 preferably 4-10 times their initial length after leaving the coagulating bath but before washing and while still containing kerosene to the amount of 2-15% and about the same amount of polymer solvent. This stretching may be effected at any suitable temperature above 100° C. preferably within the range from 120° C. to 150° C. The fibers may be washed before, during or after stretching preferably by passage through another bath of kerosene or another organic solvent.

Aside from the technological improvements in the process of making synthetic polyacrylonitrile fibers effected by the use of the specific solvent and coagulant as described above the fiber product possesses certain advantages as compared with the dry-spun polyacrylonitrile fibers heretofore available. They have a softer feel, possess greater dyeability, are less liable to absorb dirt and dust and have a remarkably high strength and toughness. The bending and torsion fatigue lives are much improved as compared with dry-spun fibers.

The consumption and/or loss of dimethylformamide or dimethylacetamide and kerosene per unit weight of fiber produced is very low.

Fiber produced in accordance with the above described process is suitable for use either as monofilaments or in the form of staple fiber. It has a tenacity of 2 to 6 grams per denier at a corresponding elongation at break of 50 to 20% depending upon the degree of stretch applied. The corresponding figures for dry spun fibers is about 2 grams per denier at 25% elongation at break.

The invention is further described in and illustrated by the following specific examples.

Example 1

An 18% solution of carefully dried homopolyacrylonitrile containing 0.05% by weight of divinyl acetylene

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(molecular weight 90,000 measured according to Staudinger) in dimethylformamide is, after being filtered, extruded through a spinneret with 48 holes of 0.15 mm. diameter. The spinneret is situated at the bottom of a 3.5 m. high tube through which "Odorless" kerosene from Shell Chemical Co. stated by the manufacturer to have a content of aromatic hydrocarbons of less than 1% and a boiling range from 180° C. to 280° C., passes downward from the top to the bottom of the tube, i.e. in counter current to the fiber. The spinning temperature is 135° C. The spinning solution is extruded at a rate of 10 cc./min. and the filament is collected in the upper part of the tube at a rate of 30 m./min., which means that while coagulating, the fiber is subjected to a stretch of 2-3 times its jet-rate. The godet which collects the yarn at the top of the tube dips into the kerosene which is kept at the constant temperature of 135° C. by a steam jacket. From this godet the yarn passes directly on to another godet having a peripheral speed of 210 m./min., and is then collected by a bobbin. The yarn is consequently subject to 7-fold stretch directly on leaving the precipitating bath which has a temperature of 135° C. The kerosene is fed into the top of the tube at a rate of 40 cc./min. and contains about 18% dimethylformamide on leaving the tube at the bottom. After being cooled to 15° C. the precipitating bath is separated into a dimethylformamide phase and a kerosene phase which latter is colorless and contains 2.5% dimethylformamide. It can be directly fed into the tube at the top after being reheated. If the kerosene is washed in a counter current washer with only 2% of water calculated on the weight of the kerosene, the content of dimethylformamide decreases to 0.1%. The dimethylformamide phase, on the other hand, is distilled, its content of hydrocarbons thereby decreasing from 5 to 1.0%. To separate the remaining 1% of hydrocarbons by distillation seems hardly practicable because of azeotropic conditions arising during the distillation and the fact that this hydrocarbon content is harmless to its use as solvent. If, however, the dimethylformamide phase is mixed with the water used earlier to wash the kerosene and amounting to about 10% of the weight of the dimethylformamide, further hydrocarbons can be separated, and the content of hydrocarbons in the dimethylformamide can then, by distillation, be lowered to less than 0.1%. Whether containing 0.1% or 1.0% hydrocarbons, the dimethylformamide can directly be reused to prepare fresh spinning solution. The distillation residue containing the impurities is discarded. About 250-300 g. kerosene adhere to 1 kg. fibers leaving the precipitating bath and about 50 g. of hydrocarbons seem to be dissolved in the polymer. The dimethylformamide content of the fiber is about 4%. Besides that no substantial loss of dimethylformamide occurs. After being collected on the bobbin the yarn is twisted and allowed to relax at 130° C. before being rewound. After being washed with water and soap the yarn possesses a titer of about 100 denier, a strength of 3.0 g./denier with an elongation on rupture of 24%. The knot strength is as high as 2.5 g./denier. The single fiber, tested in the Instron tester, shows a strength of 4.2 g./denier at 30% elongation.

Example 2

A solution of polyacrylonitrile in dimethylformamide similar to that of Example 1 is extruded into a precipitating liquid at 130° C. comprising $\frac{2}{3}$ "Odorless" kerosene from Shell Co. and $\frac{1}{3}$ cymene. Said coagulating bath comprises about 33% of aromatics. (Another coagulating bath with the same aromatic content is for example the composition $\frac{1}{3}$ "Odorless" kerosene and $\frac{2}{3}$ "Sangajol" kerosene.) When the dimethylformamide content of the coagulant exceeds 6%, a dimethylformamide phase begins gradually to separate upon cooling of the bath to 25° C. Aside from the difference in the aromatics content of the coagulant the process of this ex-

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ample is identical with that of Example 1. However, this aromatic content of the coagulant results in a higher content of the dimethylformamide in the kerosene phase than in Example 1, i.e. about 6% compared to about 2.5%. The content of kerosene in the solvent phase will also decrease up to 10% or more. This circumstance increases the difficulty and cost of the dimethylformamide and kerosene recovery. The strength of the fiber made according to this example is very little less than that of Example 1 but the elongation at break of the single fiber is lower to the extent of about 24%. Also the fiber of this example is much stiffer, more brittle and more spongy than the fiber of Example 1. It is however a useful textile fiber.

Example 3

The process of Example 1 is repeated with a "White Spirit" kerosene stated by the manufacturer to contain about 15% of aromatics as the coagulant. The strength and elongation properties of the fiber is intermediate between those of Examples 1 and 2.

The specific gravity of the fibers of Examples 1, 2 and 3 which measure the sponginess thereof are as follows:

Example 1=1.13

Example 2=1.06

Example 3=1.09

The specific gravity of non-spongy polyacrylonitrile is about 1.17.

The torsional fatigue strength of the fibers of Examples 1 and 3 measured at the Textile Research Institute of Delft, Netherlands, is as follows:

Example 1=3400 cycles

Example 3=450 cycles

Dry spun acrylic fiber has a torsional fatigue strength of only 4 cycles.

Example 4

The process of Example 1 is repeated with a polyacrylonitrile containing 4% of methyl acrylate and 0.05% of triacryloperhydrotriazine. Due to the slower development of gel strength the spinning rate must be lowered to about 15 m./min. at the top of the tube. The fiber properties are very similar to those of Example 1 but the dyeability is better.

Dimethylacetamide may be substituted for the dimethylformamide in the foregoing Examples 1 to 4 in wet spinning an 18% solution of a polyacrylonitrile containing 0.05% by weight of divinyl acetylene (molecular weight 70,000 measured according to Staudinger) with substantially identical result.

Other comonomers may be substituted for the methyl acrylate of Example 4. The following amounts of comonomers have been used with results similar to those of Examples 4; 3% and 5% of methacrylonitrile, 1%, 2%, 3% and 4% of acrylic acid, 3% and 5% of acrylamide, 2% to 8% of methylacrylate, 2-6% of methylmethacrylate and 3-15% of vinyl acetate including partially hydrolyzed vinyl acetate.

The process of the present invention has, in addition to the advantages described above, the further advantage that the cost of an installation for a given output of fiber is considerably reduced as compared with the cost of an equivalent dry-spinning installation and the cost of the fiber product is substantially less than when the solvent and coagulant are not recovered or are recovered by more complicated or expensive procedures.

We claim:

1. Process of producing synthetic fiber which comprises spinning a solution of from about 10% to about 30% of a polymer selected from the group consisting of polyacrylonitrile and copolymers thereof with from 0 to 15% of comonomers, said polymers having a molecular weight within the range from 40,000 to 200,000 as calculated from viscosity measurements by the Staudinger

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equation, in a solvent selected from the group consisting of dimethylformamide and dimethylacetamide into a coagulating bath consisting of kerosene at a temperature within the range from 60° C. to 180° C., said kerosene containing not more than about 35% of aromatic hydrocarbons.

2. Process as defined in claim 1 in which the coagulating bath is cooled down at least 40° C., the resulting two liquid phases are separated, the phase containing the bulk of the kerosene is heated and returned directly to the coagulating bath, and the phase containing the bulk of the solvent is purified by distillation and returned to the process.

3. As a new product a filament made by the process defined in claim 1, said filament consisting essentially of a polymer selected from the group consisting of polyacrylonitrile and copolymers thereof with from 0 to 15% of comonomers, said polymer having a molecular weight within the range from 40,000 to 200,000 as calculated from viscosity measurements by the Staudinger equation, said filament containing in the fiber structure about 2-15% by weight of a solvent selected from the group consisting of dimethylformamide and dimethylacetamide calculated on the weight of the polymer and about 2-15% by weight of kerosene hydrocarbons calculated on the weight of the polymer.

4. In wet spinning a polymer selected from the group consisting of polyacrylonitrile and copolymers thereof with from 0 to 15% of comonomers, the cycle comprising the steps, dissolving said polymer in a solvent selected from the group consisting of dimethylformamide and dimethylacetamide, extruding the resulting solution into a coagulating bath consisting essentially of kerosene containing not more than about 35% by weight of aromatic hydrocarbons based upon the weight of the kerosene at a temperature within the range from 60° C. to 180° C. thereby extracting said solvent out of the extruded solution into said coagulating bath, cooling said coagulating bath containing the extracted solvent at least 40° C., separating the resulting two liquid phases, distilling the lower of said two phases to separate its solvent content from kerosene and gummy and colored impurities and dissolving more polyacrylonitrile in said recovered solvent in a repetition of the cycle.

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5. Process as defined in claim 4, comprising mixing the separated lower phase with water, separating the resulting mixture into two phases, and delivering the lower of said two phases to said distillation step.

6. In wet spinning a polymer selected from the group consisting of polyacrylonitrile and copolymers thereof with from 0 to 15% of comonomer, the cycle comprising the steps, extracting a solvent selected from the group consisting of dimethylformamide and dimethylacetamide out of a solution of said polymer therein by means of kerosene containing not more than 35% by weight of aromatic hydrocarbons based upon the weight of the kerosene at a temperature within the range from 60° C. to 180° C., cooling the resulting kerosene solution of said solvent at least 40° C., separating the resulting two liquid phases, and using the separated kerosene phase for extracting more said solvent from said solution of polyacrylonitrile.

7. Process as defined in claim 6 in which said kerosene phase is washed with water before extracting more of said solvent.

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