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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 the cyclical process including the methods of spinning and solvent and coagulant recovery are defined in the appended claims.

This application is a continuation-in-part of our application Serial No. 327,429, filed December 22, 1952, 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 dimethylsulfoxide, cyclic ethylene carbonate or cyclic propylene carbonate as the polymer solvent in conjunction with the use of normally liquid hydrocarbon mixtures as the coagulant. These three solvents are substantially equivalent in our invention although dimethylsulfoxide 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). Or 1.3 to 4.0 referred to the relative viscosity of a solution containing 0.5% of the polymer in dimethylformamide measured at +25° C. The invention is applicable generally to polyacrylonitriles containing up to about 15% of other monoolefinic monomer units and which are soluble in the dimethylsulfoxide, ethylene carbonate or propylene carbonate 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 dimethylsulfoxide, ethylene carbonate and propylene carbonate are specially suited in our process.

The preferred liquid hydrocarbon for use in our process is kerosene containing more than about 30% and preferably from 50% to 75% by weight of aromatic hydrocarbons, the remainder of the composition consisting of paraffine hydrocarbons and cycloparaffinic hydrocarbons. Kerosene is defined in Hackh's Chemical Dictionary, third edition, as being "A mixture of hydrocarbons b. 150–280°

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C.; the fifth fraction in the distillation 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 50% to about 75% of aromatic hydrocarbons and from 50% to 25% of aliphatic hydrocarbons including hydroaromatic or cycloparaffinic hydrocarbons. In a typical instance a kerosene suitable for use in our process contains about 30% of paraffinic hydrocarbons, about 20% of cycloparaffinic hydrocarbons and 50% of aromatic hydrocarbons. Another example of a kerosene suitable for use in our process is a trade kerosene known as Shell's Sangajol, which contains about 60% of aromatics as stated by the Shell Company.

As stated above the liquid hydrocarbon coagulant may contain up to about 75% 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.

Lower contents of aromatic than 50% on the other hand give too slow coagulation and such kerosenes therefore cannot serve as coagulants. Other hydrocarbons and hydrocarbon mixtures which are not petroleum distillates but which otherwise fall within the definition of kerosene and contain 50 to 75% of aromatic hydrocarbons may be used. Generally however from the standpoints of both utility and economy we prefer to use commercially available kerosenes and kerosene mixtures as the coagulant.

In carrying out the process of our invention we prepare a solution of the polyacrylonitrile in dimethylsulfoxide, ethylene carbonate or propylene carbonate, said solution containing from about 10% to about 30%, preferably 15–25% 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 130° C. and may go as high as 160° C. or to the boiling point of the kerosene. 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 2–15% of solvent and 2–15% of coagulant 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. dimethylsulfoxide, ethylene carbonate or propylene carbonate 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 from 2% up to 30%, preferably 10–20%. 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 dimethylsulfoxide, ethylene carbonate or propylene carbonate 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 dimethylsulfoxide, ethylene carbonate or propylene carbonate dissolved therein which depends upon the character of the coagulant and the temperature. For instance at about 20° C. using kerosene which contains 50–60% of aromatic hydrocarbons, as the coagulant, the kerosene phase will contain only about 1–3% of the dimethylsulfoxide, ethylene carbonate or propylene carbonate and the dimethylsulfoxide, ethylene carbonate or propylene carbonate phase will contain only about 1–3% 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 dimethylsulfoxide, ethylene carbonate or propylene carbonate phase.

This separation of impurities in the dimethylsulfoxide, ethylene carbonate or propylene carbonate 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 dimethylsulfoxide, ethylene carbonate or propylene carbonate phase, leaving the kerosene phase purified for reuse directly. In order to eliminate the gummy and colored impurities and recover the dimethylsulfoxide, ethylene carbonate or propylene carbonate for reuse, the dimethylsulfoxide, ethylene carbonate or propylene carbonate phase may be distilled directly. The first or lightest distillate is an azeotropic mixture of the dimethylsulfoxide, ethylene carbonate or propylene carbonate and kerosene, generally amounting to about 2–10% which separates upon cooling into a second kerosene phase and a second dimethylsulfoxide, ethylene carbonate or propylene carbonate 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 dimethylsulfoxide, ethylene carbonate or propylene carbonate 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 dimethylsulfoxide, ethylene carbonate or propylene carbonate from the fiber at the elevated spinning temperature and then in the recovery step the dimethylsulfoxide, ethylene carbonate or propylene carbonate phase extracts the impurities from the kerosene phase, the impurities being finally removed from the cycle in the treatment of the dimethylsulfoxide, ethylene carbonate or propylene carbonate 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 may be returned directly to the coagulating bath but preferably it is washed with a small amount of water thereby giving a kerosene

product containing less dimethylsulfoxide, ethylene carbonate or propylene carbonate than the original kerosene phase and an aqueous solution of dimethylsulfoxide, ethylene carbonate or propylene carbonate. The washed kerosene is then returned to the coagulating bath and the water solution of dimethylsulfoxide, ethylene carbonate or propylene carbonate is added to the dimethylsulfoxide, ethylene carbonate or propylene carbonate phase. This mixture of the dimethylsulfoxide, ethylene carbonate or propylene carbonate phase and the water solution of dimethylsulfoxide, ethylene carbonate or propylene carbonate 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 dimethylsulfoxide, ethylene carbonate or propylene carbonate water phase containing the colored and gummy impurities. This last phase (2) is then distilled as described above to yield dimethylsulfoxide, ethylene carbonate or propylene carbonate which is returned to the process and a residue which is discarded.

The relatively slow coagulation of the polyacrylonitrile due to the aliphatic 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 economically 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 described above the coagulated fiber develops its strength very slowly. This explains why it must be handled with great care. This disadvantage is overcome by using a cross-linked polymer as disclosed in application Serial No. 539,558, filed October 10, 1955, in the names of Olof Sundén, Sten Erik Arne Lennart Tunefors and Sven Hugo Sönnerskog 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 properties 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 times, preferably 4 to 10 times, their initial length after leaving the coagulating bath but before washing and while still containing kerosene to an amount of 2–15% and about the same amount of 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. After washing and stretching the fibers are relaxed at a temperature above 100° C. preferably in steam or hot water and are finally washed with water and dried. Crimping and cutting into staple fiber lengths may be interposed between the stretching and the water-washing steps.

Aside from the technicological improvements in the process of making synthetic polyacrylonitrile fibers effected by the use of the specific solvent and coagulant as described above the fiber products 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 dimethylsulfoxide, ethylene carbonate or propylene carbonate and kerosene per unit weight of fiber produced is very low.

Fiber produced in accordance with the above described

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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 a copolymer of acrylonitrile with 5% methylacrylate and 0.1% methylene-bis-acrylamide with a relative viscosity of 2.4 (molecular weight 80,000 measured according to Staudinger) in dimethylsulfoxide is, after being filtered, extruded through a spinneret with 36 holes of 0.18 mm. diameter. The spinneret is situated at the bottom of a 1.0 m. high tube through which "Sangajol" kerosene from Shell Chemical Co. stated by the manufacturer to have a content of 60% aromatic hydrocarbons 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 130° C. The spinning solution is extruded at a rate of 7 cc./min. and the filament is collected in the upper part of the tube at a rate of 15 m./min., which means that while coagulating, the fiber is subjected to a stretch of twice its jet-rate. The godet which collects the yarn at the top of the tube dips into a kerosene bath 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 105 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 13% dimethylsulfoxide on leaving the tube at the bottom.

After being cooled to 15° C. the precipitating bath is separated into a dimethylsulfoxide phase and a kerosene phase which latter is colorless and contains 2% dimethylsulfoxide. 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 dimethylsulfoxide decreases to 0.1%. The dimethylsulfoxide phase, on the other hand, is distilled, its content of hydrocarbons thereby decreasing from 2 to 0.5%. To separate the remaining 0.5% 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 dimethylsulfoxide phase is mixed with the water used earlier to wash the kerosene and amounting to about 10% of the weight of the dimethylsulfoxide, further hydrocarbons can be separated, and the content of hydrocarbons in the dimethylsulfoxide can then, by distillation, be lowered to less than 0.1%. Whether containing 0.1% or 0.5% hydrocarbons, the dimethylsulfoxide 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 dimethylsulfoxide content of the fiber is about 2%. Besides that no substantial loss of dimethylsulfoxide 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 120 denier, a strength of 4.0 g./denier with an elongation on rupture of 24%. The knot strength is as high as 2.0 g./denier. The single fiber, tested in the Instron tester, shows a strength of 4.0 g./denier at 30% elongation. The module was 0.60 g./denier for 1% elongation.

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Example 2

A solution of 12 parts of acrylonitrile polymer possessing an average molecular weight of approximately 60,000 as determined from viscosity measurements by the Staudinger formula, in 88 parts of propylene carbonate is extruded at a temperature of 130° C. through a 36 hole-spinneret (hole diameter of 0.18 mm.) into a spinning bath consisting of kerosene containing 70% of xylene heated to a temperature of 130° C., the solution being extruded at a jet velocity of 4.5 cc. per minute. The yarn is led through the vertical bath for a total distance of 1 m., the yarn being subjected during its travel to a stretch of twice its jet velocity. On leaving the bath, the yarn is passed over a positively driven feed roll heated to 135° C., possessing a peripheral speed of 10 m. per minute, the yarn being subsequently collected on a rotating bobbin possessing a peripheral speed of 70 m. per minute. The wound bobbin package is then washed free of kerosene with water and dried.

After being cooled to 30° C. the precipitating bath is separated into a propylene carbonate phase containing 2% of kerosene and a kerosene phase which latter contains 1-2% of propylene carbonate. The kerosene phase can be directly fed into the tube at the top after being reheated. The propylene carbonate phase on the other hand is distilled, its content of hydrocarbon thereby decreasing from 2% to about 0.5%.

The spinning according to this example is repeated, using ethylene carbonate as polymer solvent into the same coagulating bath containing 70% of xylene. The separation of the polymer solvent and the coagulant is performed in the same way. The results are substantially identical as when propylene carbonate is used as polymer solvent.

We claim:

1. 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 dimethylsulfoxide, ethylene carbonate and propylene carbonate, extruding the resulting solution into a coagulating bath consisting essentially of kerosene containing 50-75% by weight of aromatic hydrocarbons based upon the weight of the kerosene at a temperature within the range from 60° C. to 160° 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.

2. Process as defined in claim 1, 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.

3. 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, extracting a solvent selected from the group consisting of dimethylsulfoxide, ethylene carbonate and propylene carbonate out of a solution of said polymer therein by means of kerosene containing 50-75% by weight of aromatic hydrocarbons based upon the weight of the kerosene at a temperature within the range from 60° C. to 160° 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.

4. Process as defined in claim 3 in which said kerosene

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phase is washed with water before extracting more solvent.

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