

UNITED STATES PATENT OFFICE

2,273,638

SPINNERETTE LUBRICANT

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No Drawing. Application March 24, 1939,
Serial No. 264,038

5 Claims. (Cl. 18—54)

This invention relates to improvements in the preparation of artificial fibers, and particularly to the use of spinnerette lubricants in spinning.

Artificial fibers are in general prepared by two methods: (1) by wet spinning which consists in extruding a solution of the fiber-forming material through small orifices, i. e., through a spinnerette, into a liquid which precipitates the fiber-forming material, and (2) by dry spinning which consists in passing a solution of the fiber-forming material through a spinnerette into a heated chamber whereupon filaments are formed due to evaporation of the solvent. A third method, which has thus far found little application but which may be successfully practiced by means of the invention disclosed herein, consists in extruding the molten fiber-forming material through a spinnerette.

In dry spinning difficulty is sometimes encountered in starting and in maintaining smooth spinning performance because the solution tends to flow along the surface of the spinnerette and fall off in drops instead of in a uniform steady flow. Various methods for overcoming this difficulty have been used, including the application of a film of liquid (solvent or non-solvent) to the spinnerette surface prior to spinning. The liquids which have been suggested for this purpose are low molecular weight substances, such as benzene and toluene. Substances applied to the spinnerette to facilitate spinning are herein referred to as spinnerette lubricants. In wet spinning fouling of the spinnerette is seldom encountered unless the spinnerette is placed outside the coagulating bath. In melt spinning, however, this difficulty is particularly acute since no solvent is used and the spinning is conducted at an elevated temperature. In melt spinning the fiber-forming material has a pronounced tendency to adhere to or "cake on" the surface of the spinnerette and thus prevent smooth spinning. Application of the solvents or non-solvents recommended for overcoming this difficulty in the case of dry spinning is of limited utility in melt spinning due to the fact that these agents decompose or volatilize readily and therefore are removed from the spinnerette surface at the temperatures used in this process. No satisfactory agents or lubricants have been suggested for use in this connection.

This invention has as an object improvements in the spinning of artificial fibers. A further object is to prevent the fouling of spinnerette orifices during the spinning of artificial fibers. A further object is to coat spinnerettes with a sub-

stance which will prevent the fiber-forming composition from adhering to the surface thereof. A still further object is to coat the spinnerette with a non-volatile, stable, inert composition which will adhere to the spinnerette surface even at elevated temperatures such as those used in melt spinning. Other objects will appear hereinafter.

These objects are accomplished by coating the spinnerette surface or face with a thin film of a polymerized hydrocarbon.

The disadvantages referred to above are overcome in whole or in part by the use of polymerized hydrocarbons which we have found to be particularly effective as spinnerette lubricants. These products are in general non-solvents for the fiber-forming material and appear to increase the surface tension of the fiber-forming material to a greater extent than do previously described non-solvents. They are non-volatile, heat stable and, when applied to the spinneret surface, prevent the fiber-forming material from adhering thereto. These lubricants are especially useful when the spinning operation is conducted at elevated temperatures as in melt spinning.

The term "polymerized hydrocarbon" is used to designate polymers derived from the polymerization (with or without subsequent hydrogenation) of unsaturated hydrocarbons, such as ethylene, propylene, isobutylene, butadiene, isoprene, styrene, cyclopentadiene, indene, cumaron, unsaturated petroleum products, etc., as well as polymeric hydrocarbons derived from the condensation polymerization of monomeric hydrocarbon derivatives, such as benzyl chloride. These products range in properties from viscous oils to resins or rubber-like materials. They are non-volatile and stable even at temperatures as high as 300° C. Especially useful spinnerette lubricants of this class are polymerized olefins, polymerized cracked gasolines, meta-styrene (polymerized styrene), polyphenyls, plasticized rubber, and hydrogenated rubber. Of this group polymerized isobutylene of molecular weight ranging from 2,000 to 100,000 is especially useful. This product may be prepared among other methods by polymerizing isobutylene in the presence of a halide of a polyvalent metal, such as aluminum chloride, stannic chloride, or boron trifluoride. The product is a soft, semi-rubber-like material, soluble in aliphatic and aromatic hydrocarbons. Polymeric hydrocarbon products sold as "Vistanex" (trade-mark Serial No. 369,113, November 26, 1935) and "Viskanol"

(trade-mark Serial No. 368,764, November 12, 1935) are also very useful.

The spinnerette lubricants of this invention are applied to the spinnerette surface either as such, or in the form of a solution in a suitable solvent therefor, such as benzene or toluene. The lubricant is preferably applied to both the inside and outside of the spinnerette. Common procedure consists in wiping the face and inside of the spinneret with a cloth or sponge soaked with the lubricant or solution of lubricant. This is preferably done immediately prior to spinning.

As already indicated, application of the polymerized hydrocarbon to the surface of the spinnerette greatly facilitates the spinning of the fiber-forming material, particularly when the spinning operation is carried out at elevated temperatures. The properties of the spinnerette lubricants described herein make them particularly valuable in the melt spinning of fiber-forming linear polymers and especially the so-called fiber-forming linear "condensation" polymers. By the term fiber-forming linear "condensation" polymers is meant fiber-forming linear polymers which are obtainable by the process of condensation described in the U. S. Patent No. 2,071,250 of W. H. Carothers and in Carothers & Hill, J. Am. Chem. Soc. 54, 1559 (1932). Fiber-forming linear polymers, although obtainable by a condensation process, may be in some instances obtainable by other processes and therefore the term "condensation" is meant to include compounds of the type disclosed hereinafter whether or not such compounds are produced by chemical combination, condensation, or by some other process. Fiber-forming linear condensation polymers are tough, opaque solids which exhibit sharp X-ray powder diffraction patterns (indicating crystallinity) and have definite melting points. These fiber-forming polymers will be referred to as "superpolymers." Thus, the term "superpolyamide" will signify a polyamide capable of yielding useful and pliable fibers. Linear superpolymers in general melt without decomposition which means that they can be spun from melt without the addition of a solvent. The temperature at which the polymer is spun will of course depend upon its melting point. The most useful superpolymers from the standpoint of fiber qualities are the superpolyamides, i. e., products obtainable by the polymerization of amino acids or their amide-forming derivatives including caprolactam or from the reaction of suitable diamines with dicarboxylic acids or amide-forming derivatives of dibasic carboxylic acids. This latter class of compounds is more fully described in Carothers U. S. Patent No. 2,130,948. These products are characterized by high melting points, insolubility in most organic solvents and excellent fiber-forming qualities. The most useful for the preparation of textile fibers are those having a melting point above 220° C. In order to melt spin these high melting products, it is necessary to use a spinnerette lubricant which is non-volatile even at high temperatures, is stable, adheres well to the spinnerette surface, and prevents the fiber-forming material from wetting the surface of the spinnerette.

The following examples are illustrative of the methods used in carrying out our invention:

Example I

A metal spinnerette having ten orifices, each having a diameter of 0.0078 inch, placed at the bottom of 0.0125 inch cone-shaped protrusions

extending downward from the face of the spinnerette, was coated inside and outside with a kerosene solution of polymerized isobutylene having a molecular weight of approximately 14,000. Through this spinnerette was then spun at a temperature of 280 to 290° C. under a pressure of 50 lb./sq. in. applied with oxygen-free nitrogen, 75 parts by weight of polyhexamethylene adipamide, a linear superpolyamide derived from the reaction of hexamethylene diamine with adipic acid. The filaments which came from the spinnerette were wrapped around one or more times on a motor driven drum having a peripheral speed of 304 ft./min. and then collected on a second drum having a peripheral speed of 600 ft./min. The extent of stretching or cold-drawing thus produced was 100%. Spinning proceeded smoothly from start to finish without any interruptions until the entire charge had been spun. This required 45 minutes. The resultant oriented fibers were unusually strong (tenacity 5.2 grams per denier based on the denier at break) and had excellent elastic properties.

Coating of the spinnerette with a liquid such as toluene, benzene, or the like had little beneficial effect, since these liquids volatilized almost immediately at the high temperature used in this spinning operation.

Example II

A melt of cellulose acetate composition consisting of 66.7% cellulose acetate and 33.3% dimethoxyethyl phthalate was spun at a temperature of 200 to 205° C. at 100 lb./sq. in. through a two-orifice (0.0091 inch diameter) staple spinnerette, the face of which had been coated with a thin film of polymerized isobutylene. No difficulty was encountered in drawing the filaments from the spinnerette. The acetate came out of the orifices uniformly in a plastic condition without any fouling; the face of the spinnerette remained clean throughout the spinning operation. The spinning and wind-up rates were 150 ft./min.

As already indicated, this invention is particularly useful in the melt spinning of superpolyamides. The most useful polymers of this type are those obtainable from the reaction of suitable diamines of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and dicarboxylic acids of formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$ or their amide-forming derivatives (i. e., the ester anhydride, amide, or acid chloride) in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms. Of this class the most useful are those in which R is $(\text{CH}_2)_x$ and R' is $(\text{CH}_2)_y$ wherein x and y are integers and x is at least two. As examples falling within one or both of these classes might be mentioned polytetramethylene sebacamide, polypentamethylene adipamide, polypentamethylene sebacamide, polyhexamethylene adipamide, polyhexamethylene sebacamide, polydecamethylene adipamide, polyp-xylylene sebacamide and polydecamethylene p-phenylene diacetamide. Superpolyamides derived from polymerizable monoaminomonocarboxylic acids and amide-forming derivatives thereof, e. g. the superpolyamides derived from 6-aminocaproic acid, epsilon caprolactam, 9-aminononanoic acid, and 11-aminoundecanoic acid, are also readily spun from melt with the use of the spinnerette lubricants herein described.

Although the use of polymerized hydrocarbons

as a spinnerette lubricant in the melt spinning of linear superpolymers of the kind mentioned in Example I and described in the application previously referred to has been emphasized, these lubricants are broadly applicable in the spinning art. They can, for example, be used in the spinning of various cellulosic materials, particularly cellulose esters and ethers, vinyl resins, etc. The polymerized hydrocarbons can be used alone, in admixture, or in conjunction with other materials, such as low boiling solvents therefor. If the spinning operation is being carried out at ordinary temperatures, it is generally desirable to dilute the polymerized hydrocarbon with a solvent which will reduce its viscosity. In most cases it is not necessary to coat both the inside and outside of the spinnerette; coating of the outside or face of the spinnerette is usually sufficient. The spinnerette lubricants of this invention are applicable regardless of the material from which the spinnerette is made. For example, the lubricants can be used to advantage in the spinning of superpolyamides from spinnerettes constructed of or lined with silver, gold, tantalum, platinum and various alloys.

It will be seen from the foregoing description that we have disclosed new spinnerette lubricants which possess to a high degree the properties most desired in materials of this kind. The heat stability and non-volatility of these lubricants make them particularly valuable in the manufacture of artificial fibers by processes which require that the spinning operation be carried out at elevated temperatures.

As many apparently widely different embodiments of this invention may be made without

departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. The process of improving the spinning property of a filament-forming spinnerette which comprises coating the same with a lubricant to prevent fouling of the spinnerette orifices, said lubricant composed of a polymer of an unsaturated hydrocarbon material.
2. The process of improving the spinning property of a filament-forming spinnerette which comprises coating the same with a lubricant to prevent fouling of the spinnerette orifices, said lubricant composed of a polymer of isobutylene.
3. The process of improving the spinning property of a filament-forming spinnerette which comprises coating the same with a lubricant to prevent fouling of the spinnerette orifices, said lubricant composed of metastyrene.
4. The process of improving the spinning property of a filament-forming spinnerette which comprises coating the same with a solution of a lubricant to prevent fouling of the spinnerette orifices, said lubricant composed of a polymer of an unsaturated hydrocarbon material.
5. The process of improving the spinning property of a filament-forming spinnerette which comprises coating the inner and outer surfaces of said spinnerette with a lubricant to prevent fouling of the spinnerette orifices, said lubricant composed of a polymer of an unsaturated hydrocarbon material.

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