United States Patent Office 3,655,853 Patented Apr. 11, 1972

3,655,853

PROCESS FOR PRODUCING POLYTETRAFLUOROETHYLENE FILAMENTS

Arthur R. Gallup, Bon Air, Va., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del.

No Drawing. Filed Aug. 10, 1970, Ser. No. 62,627
Int. Cl. B27j 5/00
U.S. Cl. 264—127 4 Claims

ABSTRACT OF THE DISCLOSURE

Polytetrafluoroethylene filaments of improved strength are produced by extruding a mixture of viscose and PTFE aqueous dispersion having an average particle size of from 0.1 to 0.17 micron into an acidic coagulating and regenerating bath.

This invention relates to polytetrafluoroethylene filaments of improved tenacity and to dispersions of polytetrafluoroethylene in viscose, which are used for making the filaments.

BACKGROUND OF THE INVENTION

The outstanding stability of polytetrafluoroethylene to light, heat, solvents, electrical stresses and chemical attack makes it highly desirable for a variety of uses including those in which an inert woven or fibrous material is required. Consequently, polytetrafluoroethylene fibers and filaments have been used in laundry press pads, liquid and gas filters, non-lubricated bearing surfaces, spacesuits, biologically inert sutures, bandages and prosthetic devices. A difficulty with such articles and the production thereof often arises due to the low yarn strength attainable by prior art methods of producing the filaments, however. Accordingly, it is an object of this invention to provide a method for making polytetrafluoroethylene filaments of improved tenacity.

Due to the chemical inertness and heat stability of polytetrafluoroethylene, it cannot be processed into filaments by conventional solution or melt spinning techniques. One process for making polytetrafluoroethylene filaments, described in U.S. Pat. 2,772,444, is to disperse finely divided tetrafluoroethylene polymer in viscose of the type used for production of viscose rayon fibers; extrude the dispersion into a coagulating, non-regenerating bath or a coagulating and regenerating bath to form filaments consisting of a cellulose matrix containing the polytetrafluoroethylene particles; heating the filaments to a relatively high temperature to decompose the cellulose and coalesce the polytetrafluoroethylene particles; and finally drawing the heated polytetrafluoroethylene filaments. It has been found that the use of polytetrafluoroethylene particles having a size of from about 0.1 to about 0.17 micron in conjunction with an acidic coagulating and regenerating bath unexpectedly improves the tenacity of filaments produced by the process.

SUMMARY OF THE INVENTION

The improved process for the production of polytetrafluoroethylene filaments comprises forming an aqueous mixture of viscose with an aqueous dispersion of tetrafluoroethylene polymer particles having an average particle size of from about 0.1 to about 0.17 micron, extruding the mixture into an acidic coagulating and regenerating bath to form filaments consisting of a cellulosic matrix containing said polymer particles, heating the filaments at a temperature sufficiently high to decompose said cellulosic material and coalesce said polymer particles, and drawing said filaments.

The mixture to be extruded comprises an aqueous dispersion of tetrafluoroethylene polymer particles admixed with viscose, said polymer particles constituting from about 75% to about 96% of the combined weight of said polymer particles and the cellulose in said viscose, and having an average particle size of from about 0.1 to about 0.17 micron.

DETAILED DESCRIPTION OF THE INVENTION

The preparation of the viscose, the aqueous dispersion of polytetrafluoroethylene, and the mixture thereof are described in U.S. Pats. 2,478,229; 2,772,444; and 3,391,099, the disclosures of which are incorporated herein by reference.

A viscose solution containing 4 to 8% cellulose (in the form of cellulose xanthate), 4 to 7% alkali (calculated as sodium hydroxide), and having a total sulfur content of 1.8 to 2.2% may be prepared by methods well known in the art. The viscose solution is then filtered, deaerated and permitted to ripen to increase its coagulability, the salt index at spinning being preferably in the range of 2.5 to 6.0.

A preferred method of preparing the dispersion of tetrafluoroethylene polymer particles is to carry out the polymerization of the tetrafluoroethylene in the presence of a surface-active agent which is added in a programmed manner as described by Punderson in U.S. Pat. 3,391,099. The average particle size is controlled primarily by adjustment of the concentration of surface-active agent during the nucleation phase as taught by Punderson. Increasing the concentration in this phase leads to an increase in the number of nuclei and a lower particle size. Polymer particle dispersions of the critical average particle size of from 0.10 to 0.17 micron may be prepared by this method.

The average particle sizes referred to herein are those determined by a relationship based on light-scattering theory, from the percentage of incident light transmitted at 5.16 millimicron wavelength through a unit measure of a dilute dispersion (ca. 0.02 wt. percent solids), using a nominal value of 0.020 cc./g. for the refractive index increment, $\Delta n/\Delta a$, of said dispersion at 25° C. These values are in theory nearly equal to the weight-average particle diameter, as confirmed by ultracentrifuge analysis, and are further in reasonable agreement with those determined directly by examination of electron micrographs of the particles at 20,000 diameters magnification.

The viscose solution and the dispersion of tetrafluoroethylene polymer particles are admixed to form a composition having the unique property of being capable of being spun into filaments of improved strength. This composition is an aqueous mixture and contains about 10% to about 60%, by weight, of said tetrafluoroethylene polymer particles and about 1% to about 8%, by weight, of cellulose. The weight of the tetrafluoroethylene polymer particles is from about 75% to about 96% of the combined weights of the tetrafluoroethylene polymer particles and cellulose in the aqueous mixture.

This aqueous mixture is extruded into a combination coagulating and regenerating bath to set the filaments and convert the cellulose xanthate into cellulose. For this purpose, a bath containing sulfuric acid, sodium sulfate and a small amount of zinc sulfate is preferred. Preferably, the bath contains 5 to 10% sulfuric acid, 10 to 20% sodium sulfate, and 0.5 to 5% zinc sulfate, and the temperature is in the range of 45 to 65% C.

After passing through the coagulating and regenerating bath, the yarn is washed to remove residual acid, salt and other impurities. The yarn is then dried and thereafter passed in contact with a heated surface, at a temperature of 350 to 500° C. and, preferably, between 370 and 390° C. to decompose the cellulose and coalesce the polyetera-

fluoroethylene particles. The resulting polytetrafluoroethylene filaments are then drawn while maintained at a high temperature as described in U.S. Pats. 2,776,465 and 2,772,444. Preferably, a draw ratio of from 4 to 35 times is employed. To develop optimum properties, a drawing of at least 7 times is generally applied.

Example I

A viscose solution containing 5.5% by weight of cellulose in the form of cellulose xanthate and 5.0% alkali, calculated as sodium hydroxide, is prepared from wood pulp using sufficient carbondisulfide based on the weight of air-dried pulp to provide 2% by weight total sulfur content in the viscose. The viscose is filtered, deaerated and permitted to ripen to a salt index of 3.25. The viscose is then mixed with an aqueous dispersion containing 60% of finely divided polytetrafluoroethylene having an average particle diameter of 0.16 micron and containing 5% of "Triton" X-100, a nonionic octylphenoxyethanol surfactant as a stabilizer. The resulting spinning mixture contains 28.0% polytetrafluoroethylene and 2.8% cellulose. This mixture is filtered and extruded at a temperature of 10° C. through a spinneret having 60 orifices into an aqueous coagulating and regenerating bath maintained at a temperature of 55° C. and containing 7.0% sulfuric acid, 17% sodium sulfate and 1.0% zinc sulfate. The filaments are converged into a yarn and passed for a distance of 72 inches through the bath. The yarn is then passed to an advancing reel where it is washed with water at a temperature of 95° C. to remove the residual acid and salt. The yarn is then dried by passage over heater rolls followed by passage over a series of sintering rolls ranging in temperature from 370° C. at the inlet to 388° C. at the outlet for 16.5 seconds to decompose the cellulose and coalesce the polytetrafluoroethylene particles. The resulting polytetrafluoroethylene filaments are then drawn at a temperature of 388° C. to a ratio of 8.6 by means of draw rolls. The polytetrafluoroethylene yarn is then wound into a package in the conventional manner. The denier of the drawn yarn is about 400.

Table 1 below shows the average tenacity, number of yarn breaks per pound of yarn and percent waste yarn for a spinning machine operated for a period of five months under conditions described above. These results show that there is not only a marked increase in tenacity using the smaller particle size dispersion, but that the number of yarn breaks and the amount of waste yarn are reduced. The results of spinning with the 0.20 micron dispersion on another machine were improved but still inferior to the 0.16 dispersion.

TABLE 1

Particle diameter, microns	Tenacity, g.p.d.	Breaks/pound	Waste, percent
0.16	1.62	0.06	1.8
0.20	1.32	0.40	14.9

In addition to the improved strength attained with 400 denier yarns, it has been found possible to draw 1200 denier yarn at a higher ratio than heretofore practicable, e.g., increasing the ratio from 5.0 to 6.5, thus obtaining a yarn tenacity of about 1.6 g./den. as compared to 0.8 g./den. usually obtained with 1200 denier yarn using the larger particle dispersions. This results in a tenacity of 1.0 g./den. in bleached yarn, i.e., yarn treated with strong oxidizing agents or hot air to remove residual cellulose decomposition products, as compared to 0.5 g./den. preciously obtained.

I claim:

1. A process for producing polytetrafluoroethylene filaments of improved strength comprising
   forming an aqueous mixture of viscose with an aqueous dispersion of tetrafluoroethylene polymer particles having an average particle size of from about 0.1 to about 0.17 micron,
   extruding said mixture into an acidic coagulating and regenerating bath to form filaments consisting of a cellulosic matrix containing said polymer particles,
   heating the filaments at a temperature sufficiently high to decompose said cellulosic material and coalesce said polymer particles, and
   drawing said filaments.

2. The process of claim 1 wherein said tetrafluoroethylene polymer particles comprise from about 75% to about 96% of the combined weights of the tetrafluoroethylene polymer particles and cellulose in said aqueous mixture.

3. The process of claim 2 wherein said aqueous mixture contains about 10% to about 60%, by weight, of said tetrafluoroethylene polymer particles and about 1% to about 8%, by weight, of cellulose.

4. The process of claim 1 wherein said heating is conducted at a temperature between 370° C. and 390° C.

References Cited

UNITED STATES PATENTS

2,478,229	8/1949	Berry	161—Teflon
2,559,750	7/1951	Berry	260—29.6 T
2,559,752	7/1951	Berry	260—29.6 T
2,772,444	12/1956	Burrows	260—17.4 CL
2,776,465	1/1957	Smith	264—191
3,051,545	8/1962	Steuber	264—182
3,301,807	1/1967	Hoashi	260—29.6 T
3,303,154	2/1967	Hirose et al.	260—29.6 T
3,372,082	3/1968	Komethani et al.	161—178
3,391,099	7/1968	Punderson	260—29.6 T
3,513,144	5/1970	Kometani et al.	161—169

JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

260—29.6 F; 264—44, 184, 210 F