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PRODUCTION OF POLYCHLOROTRIFLUOROETHYLENE TEXTILES

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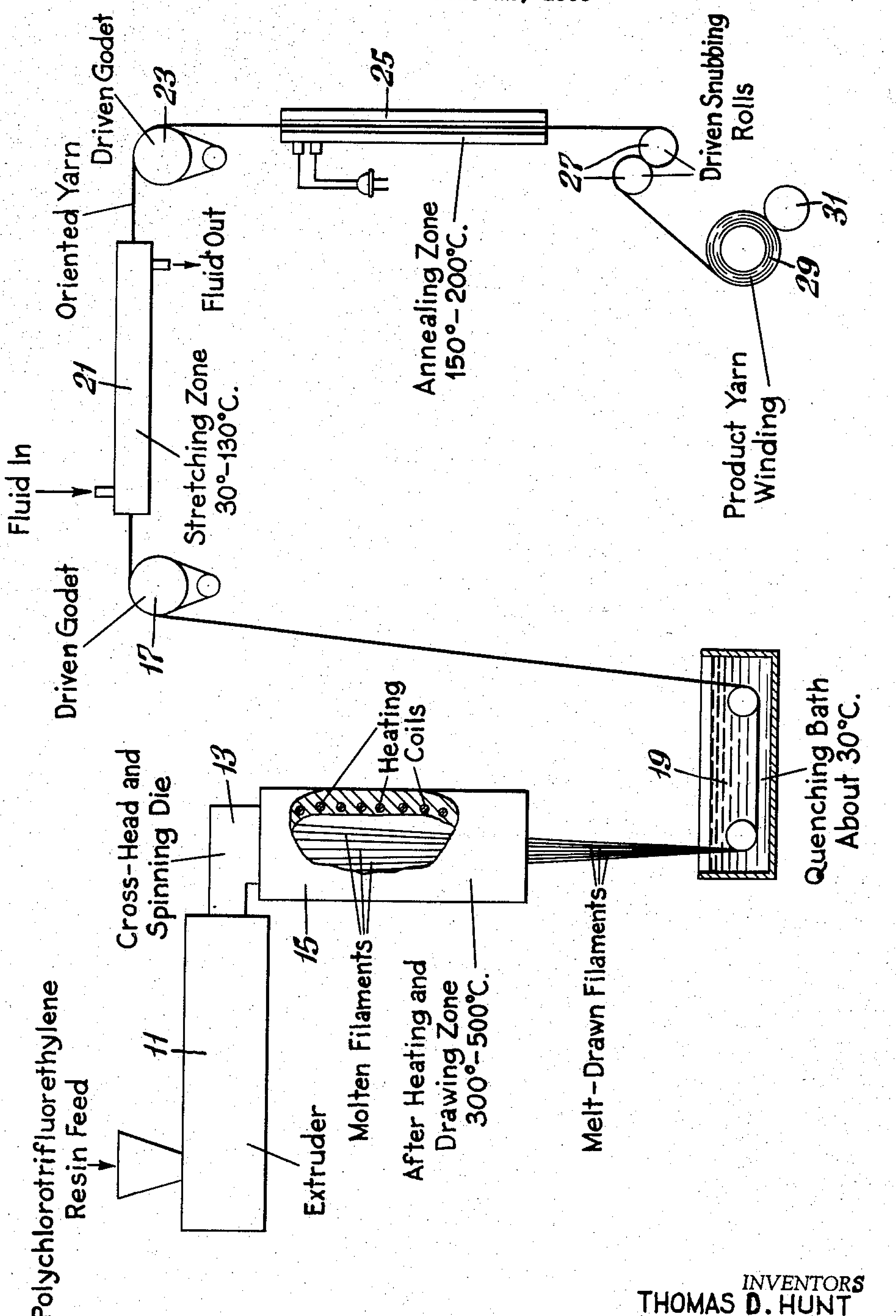

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PRODUCTION OF POLYCHLOROTRIFLUORO-ETHYLENE TEXTILES

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This invention relates to the production of high-strength polychlorotrifluoroethylene multifilament yarns and particularly those having a low denier per filament. It also concerns a novel process for preparing such low denier filaments and yarns by means of a melt spinning technique in association with the use of a very high draw-ratio of the molten filaments leaving the spinneret, while maintaining the filaments at high temperatures during the stretching step, after which the individual filaments are quenched and subjected to a novel annealing treatment. By this process it is now possible to obtain fine yarns suitable for textile applications from this important new polymer.

Heretofore, no method has been described in the literature whereby continuous filaments and multifilament yarns having a low denier per filament and high strength can be obtained from polychlorotrifluoroethylene due to certain characteristics of the polymer distinguishing the same widely from other well known polymeric materials useful in the making of synthetic textiles.

The textile articles of this invention have valuable properties adapting them for special services, such as excellent resistance to chemicals and heat and excellent abrasion resistance and toughness. To illustrate, yarns made from this polymer by the invention have been exposed to air at 165° C. for 5 months, and have been submerged in concentrated sulfuric acid, nitric acid and sodium hydroxide solutions at room temperature for 3 months, without discoloration or significant loss in mechanical properties. These yarns, and fabrics made therefrom are useful for industrial filtration of corrosive liquids at either high or low temperatures, for protective work clothing, for pump packing material, and for numerous applications where good resistance to sunlight, mildew and fire are required. The polychlorotrifluoroethylene resins particularly adapted for use in the production of these textile materials are those polymers having estimated molecular weights of from around 25,000 to around 75,000 and having melt viscosities at 230° C. of not less than 0.1 megapoise, and preferably 0.5 megapoise or greater, the melt viscosity being measured according to the procedure described by G. J. Dienes and H. F. Klemm, "Journal of Applied Physics," vol. 17, No. 6, pp. 458–471. Such polymers are quite crystalline in their natural state and show a sharp melting point at about 205° to 210° C., depending somewhat upon the molecular weight. However, unlike other crystalline polymers, such as Nylon 66, Nylon 6 and polyester resins that are commonly used for melt spinning synthetic fibers, these high molecular weight polychlorotrifluoroethylenes do not show a low viscosity at temperatures above their melting point. Whereas Nylon 66, for example, has a viscosity of only about 400 to 500 poises at a temperature 13° C. above its melting point (265° C.), the polychlorotrifluoroethylenes show melt viscosities of from one million to one hundred million poises at a temperature 25° C. above their melting point. Furthermore the

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decrease in viscosity with increasing temperature is not great, and it is therefore necessary to extrude filaments at temperatures ranging from 300° C. to 360° C., which are 100° C. to 150° C. above the melting point. At these temperatures, however, depolymerization of the resin occurs quite rapidly and, if allowed to proceed too far, yields an extruded product that is too weak for many services.

Prior attempts to extrude high molecular weight polychlorotrifluoroethylene resins having melt viscosities of 1 megapoise or higher through the usual fine spinneret to form fine filaments suitable for ordinary textile applications have been uniformly unsuccessful for the foregoing reasons.

This invention is based in important part upon the discovery that fine filaments which may have filament deniers as low as 25 or less can be made by extruding the polychlorotrifluoroethylene resin through a spinneret, the holes of which are relatively large, e.g., 20 to 50 mils, immediately followed by the stretching of the relatively coarse filaments thus obtained to a very fine filament denier while they are still in the molten state at around 300° C.–500° C. This drawing operation must be carried out under carefully controlled conditions as hereinafter described.

In order to secure filaments of the desired size (circa one mil) it is necessary to employ draw-ratios of the order of 75 to 1 and 200 to 1 on the molten fiber leaving the spinneret. This cannot be accomplished by practicing the known art of melt spinning synthetic fibers wherein it has been found desirable to cool the extruded fibers even while the drawing is occurring. In the case of polychlorotrifluoroethylene fibers, on the contrary, the viscosity is so much greater than that of other melt spinning polymers that sufficient drawing cannot be accomplished unless, contrary to the known practice in the melt extrusion of synthetic fibers, considerable additional heat is supplied to the extruded filaments to insure retention of their fluidity during the drastic reduction in size. Indeed, the use of a high temperature heating tube or chimney, heated electrically or in other suitable manner, has been found necessary to achieve a degree of hot drawing required to produce satisfactory small-diameter or low-denier fibers.

After drawing of the filaments in the molten state is completed the filaments, or the collected multifilament yarn, can be quenched in a cool air stream or in a water bath, and then is wound on a suitable wind-up spool or bobbin. In this state the yarn shows very little or no molecular orientation, and it must later be cold drawn at temperatures from about 30° C. to about 130° C. to the extent of about 300% to 700% in order to attain the maximum strength. By this general procedure multifilament yarns having an overall denier of 200, formed from filaments each having a denier of only 10, have been obtained from polychlorotrifluoroethylene resins; and filaments having even smaller deniers are readily possible by lengthening the path of the extruded molten filament during which it is hot stretched at temperatures around 300° C. to 500° C., to insure that the filaments are maintained in the low viscosity state for a period sufficiently long to effect the desired reduction in size by the drawing operation.

The fibers produced by the process of the invention generally have tenacities ranging from 1.0 to 2.2 grams per denier, and elongations ranging from about 10% to around 25%. The yarns following the cold drawing step, tend ot shrink as much as 15% in boiling water and as much as 20% in air at 175° C. Such yarns however can be stabilized against shrinkage by an annealing step at high temperatures around 150° C. to 200° C., and preferably around 175° C. This conveniently can be accomplished by passing the cold drawn yarn through a passage or groove in a metal bar heated to about 150° C. to 200° C., thereby heating the yarn by radiation for about 2 seconds as it moves to a driven take-up mechanism. The latter preferably is so driven as to allow yarn shrinkages of around 15%, although shrinkage can be prevented, or controlled shrinkages up to 20% can be obtained in this step. After this treatment, the filament or yarn wil withstand elevated temperatures as high as 180° C. without shrinking more than a few percent.

The principal reason why it has been impossible heretofore successfully to melt spin fluorothene resins into practical and useful fibers having low filament deniers is due to the fact that it has not been possible to force such resins, of sufficiently high molecular weight to produce a high strength fiber, through orifices of less than 0.025 inch in diameter with reasonable speed (10 to 100 feet per minute) at spinneret temperatures low enough to prevent excessive degradation (below about 375° C.). Nor has it been possible to extrude through larger diameter orifices and obtain fine filaments by hot drawing to a high degree as it is generally practiced in the melt spinning of polyamide and polyester fibers. Filaments extruded through smaller orifices, or at greater speeds, or at lower spinneret temperatures, have rough instead of smooth surfaces, and are brittle and cannot be further processed into satisfactory fibers. If the filaments are extruded into air at room temperature, the filaments can only be drawn about 30 to 50 times their initial length, i.e., they can only be wound up at a speed of about 30 to 50 times the rate at which they are extruded. This produces a final yarn of coarse filaments unsatisfactory for most textile applications.

Applicants' invention has effectively solved this problem. In one modification thereof a vertically-disposed electrically-heated chimney or heat jacketed tube surrounds the molten fibers as they are extruded through the spinneret. By maintaining the temperature of the zone within the chimney or tube at about 300° C. to 500° C., surprisingly the filaments and collected yarn can be hot drawn, quenched, and wound up at a rate as high as 200 times the rate of extrusion without seriously injuring the resin or causing decomposition thereof.

The accompanying drawing illustrates somewhat schematically apparatus for conducting the critical after-heating and drawing step, and the means for conducting the subsequent improving and finishing steps.

In the drawing, granular polychlorotrifluoroethylene resin is fed to a conventional extruder **11** where it is melted and fluxed, and forced through a cross-head and spinning die **13**. The plurality of molten filaments issuing from the die are passed down through a hot after-heating and drawing tube **15** where they are further heated while being drawn at least 75-fold and as much as 200-fold their extruded length under action of the driven godet **17**. The hot drawn filaments are promptly cooled by submerging them in a suitable quenching bath **19**, from which they are withdrawn by the first godet roll assembly **17**. The filament bundle or yarn leaving the godet **17** is drawn through a heated stretching tube or zone **21**, and thence to and around a driven godet **23** under action of the latter. The resultant stretched yarn leaving godet **23** then passes through a slotted annealing bar or zone **25** where it is heat-set and relaxed, and is conducted to a pair of snubbing rolls **27** and thence to a winding spool or bobbin **29** driven by surface contact of the yarn thereon with a driven roll **31**. The drawing tube **15**, the stretching tube **21**, and the annealing bar **25**, respectively, are provided with suitable means for heating the same to the desired operating temperatures, as herein described.

The following examples serve to illustrate the invention.

Example 1

Granulated polychlorotrifluoroethylene resin having a melt viscosity at 230 C. of 5 megapoises was charged to the hopper of a conventional single-screw extrusion machine. The temperature of the barrel around the screw was maintained at 275° C. to 300° C. causing melting of the resin which then was forced through the cross-head and to the die or spinneret. Temperature of the cross-head was maintained at 360° C. and that of the die was maintained at 360° C. to 375° C. A spinneret die having 20 holes each 0.047 inch (47 mils) in diameter was used; and a flow of 54 grams of polymer per minute through the die was secured. The twenty-filament yarn was extruded downward in and through a glass heating tube 2.5 inches in diameter and 18 inches long, located immediately at the spinneret outlet, and the yarn was spun down through the center of the tube which was heat insulated with asbestos tape and maintained electrically at a temperature of 425° C. inside the tube. The yarn was drawn while still in the molten state as it passed through the tube and then was immediately quenched by passing horizontally through a water bath at 30° C. for a distance of 40 inches, and then was withdrawn and wound up on a driven rotating bobbin at a rate of 540 feet per minute. This represented a hot draw ratio of 137 to 1; and the quenched spun yarn had a denier of 3070, each filament having a denier of 153. This yarn then was passed continuously through a steam stretching tube 30 inches in length and maintained at 120° C., at a feed rate of 20 feet per minute to achieve molecular orientation and further reduce the size of the yarn, during which stage the yarn was stretched 500% in the presence of steam and collected on a bobbin at a rate of 120 feet per minute. The resultant stretched yarn had the following properties: denier 498 (filament denier of 25); tenacity 1.5 grams per denier; elongation 9%; knot strength 1.1 grams per denier; shrinkage in boiling water 8.5%, and in 175° C. air, 16%. This stretched yarn was then passed continuously through a slotted bar heated to 180° C. for a 2 seconds contact time, the yarn take-up device being so operated that the yarn was permitted to shrink 10%. The thus annealed yarn had a tenacity of 1.8 grams per denier; an elongation of 23%; a knot strength of 1.4 grams per denier; and shrinkages in boiling water and in 175° C. air, respectively, of 1% and 4%. The yarn was sufficiently fine to easily be twisted and knitted on conventional textile equipment. Fabrics made from this yarn were soft and pliable. Because of the high specific gravity of polychlorotrifluoroethylene these fibers were comparable in size (in diameter) to 10 to 15 denier filaments of commercially available synthetic fibers. The melt viscosity of the resin of the fiber at 230° C. was 0.99 megapoise, demonstrating that a high molecular weight resin had been maintained throughout the spinning process.

Example 2

Following the procedure described in Example 1, with the exception that the extruded filaments of molten resin were hot drawn at a rate of 500 feet per minute, corresponding to a hot-draw ratio of 125 to 1, the resultant yarn, after quenching and being subsequently stretched 630% in the steam stretching tube at 120° C. and a time of contact of one second, had the following properties: denier 506; tenacity 1.8 grams per denier (47,500 p.s.i.); elongation 10%; knot strength 1.2 grams per denier; shrinkage in boiling water 8%; and in 175° C. air, 17%. It is significant that, using the same starting resin and the same extrusion conditions set forth in Example 1, with the exception that the filaments leaving the spinneret were extruded downwardly for 30 inches in unheated air, and were incapable of being drawn at a rate faster than 180 feet per minute, which is equivalent to a draw ratio of 45 to 1, each resultant filament had a denier of 462.

After stretching that yarn in a steam stretching tube at 120° C., in the manner described in Example 1, the maximum stretch possible without breakage was approximately 400%, and the filament denier of the resultant product was 99. Thus, it was surprising to find that the yarn of Example 1, which was hot drawn at the spinneret, could be oriented to a much higher degree, and yielded filaments of much lower denier than those produced by the usual melt spinning process, while at the same time maintaining the tenacity, and even improving the knot strength and shrinkage resistance of the textile article.

The invention is susceptible of modification within the scope of the appended claims.

We claim:

1. Process for making fine filaments and multi-filament yarns from polychlorotrifluoroethylene resins, which comprises hot-drawing a molten, freely extruded filament of polychlorotrifluoroethylene leaving an extrusion die from 75 to 200 times its original length while subjecting said articles to a temperature within the range from around 300° C. to 500° C.

2. Process for making fine filaments and multi-filament yarns from polychlorotrifluoroethylene resins, which comprises extruding a filament of molten polychlorotrifluoroethylene at temperatures within the range from about 325° C. to about 375° C. and, while applying further heat to the filaments and yarns thereby subjecting freshly extruded filament leaving the extrusion zone to a temperature within the range from about 300° C. to about 500° C., hot drawing the filament from 75 to 200 times its original length, and thereafter cooling the drawn filament to a temperature below its softening point.

3. Process for making fine filaments and multi-filament yarns from polychlorotrifluoroethylene resins, which comprises extruding a filament of molten polychlorotrifluoroethylene at temperatures within the range from about 325° C. to about 375° C. and, while applying further heat to the extruded filament, thereby subjecting the freshly extruded filament leaving the extrusion die to a temperature within the range from about 300° C. to about 500° C., hot drawing the filament at between 75 and 200 times its original length, quickly cooling the hot drawn filament to below the softening point of the resin, and thereafter stretching the drawn filament from about 200% to about 700% of its length while at a temperature within the range from about 50° C. to about 150° C.

4. Process for making fine filaments and multi-filament yarns from polychlorotrifluoroethylene resins which comprises hot drawing a molten freely extruded filament of polychlorotrifluoroethylene leaving an extrusion die from 75 to 200 times its original length while subjecting said articles to a temperature within the range from about 300° C. to about 500° C., cooling the hot drawn filament to below the softening point of the resin, thereafter stretching the drawn filament from about 200% to about 700% of its length while at a temperature within the range from about 50° C. to about 150° C., and annealing the stretched article by briefly exposing the same to temperatures of about 150° C. to 200° C. under conditions preventing shrinkage in excess of 20% of said stretched article, said polychlorotrifluoroethylene having estimated molecular weights in the range from around 25,000 to around 75,000 and having melt viscosities at 230° C. of at least 0.5 megapoise.

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