

April 30, 1946.

R. J. TAYLOR

2,399,259

METHOD OF MAKING HOLLOW FILAMENTS AND PRODUCT THEREOF

Filed May 29, 1943

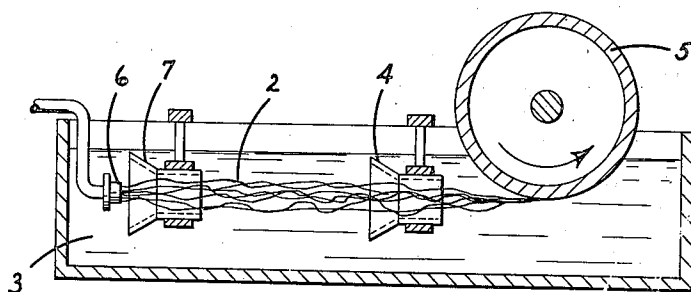


Fig. 1

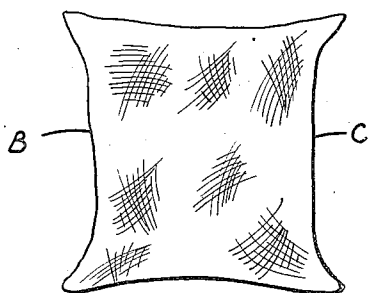


Fig. 2



Fig. 3

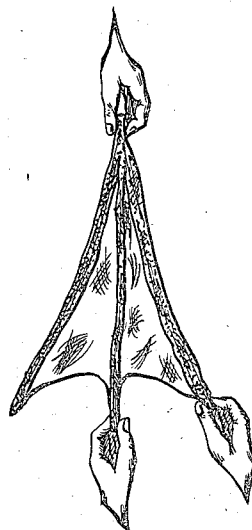


Fig. 4

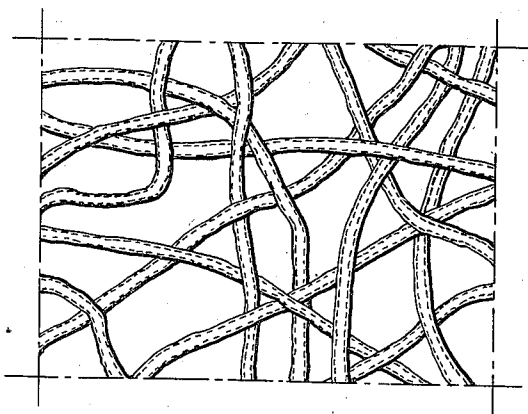


Fig. 5

INVENTOR.
Robert J. Taylor
BY
Carl A. Castellon
Atty.

UNITED STATES PATENT OFFICE

2,399,259

METHOD OF MAKING HOLLOW FILAMENTS
AND PRODUCT THEREOF

Robert J. Taylor, Claymont, Del., assignor to
American Viscose Corporation, Wilmington,
Del., a corporation of Delaware

Application May 29, 1943, Serial No. 489,071

9 Claims. (Cl. 28—76)

This invention relates to the production of hollow filaments and products thereof from synthetic linear polymers of a hydrophobic character such as the vinyl resins.

It has heretofore been suggested to make hollow filaments from hydrophilic materials, such as regenerated cellulose from viscose and cuprammonium cellulose, and cellulose esters, such as cellulose acetate, by wet spinning processes in which bubbles of gas are caused to develop within the filaments after extrusion from the spinneret. The coagulating medium used in such cases has generally been an aqueous acid solution and a common method of developing the gas within the filament was to incorporate within the solution to be spun an alkali carbonate soluble therein which after extrusion would react with the acid in the spinning bath to develop the gas. The products obtained by these procedures, however, are not entirely satisfactory because of the fact that the hydrophilic materials of which the filaments are formed remain in a strongly swelled or solvated condition throughout their travel through the spinning bath and nearly entirely throughout the drying period. Because of this swollen or solvated condition of the filamentary mass, the filaments undergo considerable collapse during passage over guides, about the godets, and under their own pressure as they are being collected on bobbins or within spinning buckets. Even after drying, should there be an appreciable inflation or hollow characteristic remaining in the filaments, further deflation generally occurs whenever products containing such hollow filaments are either accidentally or intentionally brought into contact with moisture, particularly when they are under any compression. Frequently, special precautions must even be taken against the possibility of coming into contact with air of high humidity, especially when products made of such filaments are under any compression, such as in cushions or as a stuffing in mattresses, bed clothing or wearing apparel.

It is an object of this invention to provide hollow filaments which are of a hydrophobic character and which are not subject to such disadvantages as the materials of the prior art when brought into contact with moisture. A further object of this invention is to provide an improved process for the production of hollow filaments in which there is substantially no loss in inflation accompanying the manipulations associated with the production of the filaments. A further object of the invention is to provide novel products

made of such hollow filaments. Further objects and advantages of the invention will be apparent from the description thereof hereinafter.

In accordance with the invention, these disadvantages are overcome by spinning a solution of a hydrophobic synthetic linear polymer in an organic solvent containing dissolved therein or suspended therein in a finely divided state a gas-generating agent which can be incorporated into the spinning mass to produce a solution whose stability against gelation is sufficient to avoid clogging of the orifices of the spinneret during spinning. The spinning is effected into an aqueous medium whose hydrogen ion concentration is adjusted to effect liberation of the gas from the gas-generating substance within the extruded filaments upon contact therewith. For the gas-developing substances, there may be used any salt or acid salt which is capable of generating gas upon being subjected to the appropriate conditions of pH. The aqueous spinning bath may be adjusted to the appropriate pH by the addition of either acid or alkali depending upon the particular salt incorporated in the solution. Salts such as sodium bicarbonate or calcium carbonate which generate an acidic gas upon being introduced into an acid medium may be suspended in the spinning solution and the coagulating medium may be adjusted to a pH of less than 7. On the other hand, salts such as ammonium chloride or ammonium sulfate which develop ammonia upon being introduced into an alkaline solution may be incorporated into the spinning solution and the resulting solution may be spun into an alkaline medium, that is one having a pH greater than 7.

The organic solvent employed for making the spinning solution must be miscible with water so that upon extrusion of the filament-forming solution through the spinneret orifices into the coagulating medium, the water will withdraw the organic solvent from the filaments structure and at the same time will be drawn into the extruded form by the solvent. This assures that the water having the proper pH will penetrate the filament-forming mass and generate gas therein. The rapid migration of the solvent from within the filament-forming mass to the surrounding bath and the rapid entry of the aqueous bath having the proper pH into the filament-forming mass causes the rapid desolvation of the external layers of the mass concurrently with the generation of gas therein. Thus, the expansion or inflation occurring within the more or less porous skin first formed on the filamentary mass

is allowed free play because of the fact that the filament-forming mass is in a more or less plastic, swollen or solvated condition at the time of generation of the gas. Desolvation, while not complete, is sufficient on the external surface of the filaments to prevent cementing of the filaments together as they pass over the guides or godets used for directing them to the take-up device. Surprisingly, it has been found that the passages of the filaments over the godets or guides does not cause their collapse, or if any momentary collapse occurs, the original fully inflated condition is immediately restored after departure from the godet by a certain amount of elasticity in the filament body or skin, in spite of the fact that the filaments at the time of their passing over the guides are still, at least in parts of their cross-sections, far from a condition of complete desolvation. It is thought that this may possibly be attributable to the fact that the external skin is sufficiently desolvated at this stage to maintain the shape of the structure or possibly to the fact that the partially solvated or plasticized resin filament has a rubbery elasticity which is sufficiently pronounced to cause recovery after deformation, and/or possibly to the additional circumstance that the internal portion of the filaments being in a liquid condition seal the gas bubbles within tending to assist the elastic recovery. Also any shrinkage that takes place after the initial formation of the skin merely draws and spreads the internal layer within the skin without further shrinking the skin. This is in contrast to the desolvation of hydrophilic hollow filaments which does not begin until drying is started and is accompanied by shrinkage and collapse throughout the entire mass as a unit.

The precise upper limit of concentration in which the organic solvent for the spinning mass is permissible within the coagulating bath depends upon the particular polymer and the particular solvent. Generally, if the concentration of the organic solvent within the coagulating medium is kept below from 8 to 10%, the swelling tendencies of the medium upon the filaments are insufficient to cause cementing and collapse at the guides or godets. Where the equipment is at hand, reduction of the concentration of the solvent to less than 5% is preferred. However, certain solvents may be allowed to collect in the coagulating bath in concentrations considerably above 10% without encountering harmful solvation or swelling on the filaments produced.

Hollow filaments may be spun in the manner just described from solutions of any synthetic linear polymer or copolymer of hydrophobic character. For practical purposes, a polymer is hydrophobic if in filament form it shows a water pick-up of less than 2% at 75° F. and a relative humidity of 58%. Preferred examples of the numerous vinyl and acrylic derivative polymers and copolymers are straight polyvinyl chloride which may be dissolved in tetrahydrofurane, chlorinated polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate containing at least 80% by weight of the chloride monomer, chlorinated copolymers of vinyl chloride and vinyl acetate, and copolymers of vinyl chloride and acrylic acid esters, such as the copolymer of vinyl chloride and acrylonitrile. Various solvents, such as acetone, dioxane and the like, which are miscible with water may be used depending upon the particular resin and its solubility characteristic.

In general, a solution in the organic solvent having a concentration of the order of 10% of the polymer and containing from 1 to 5% or more of the gas-generating agent suspended therein is spun into a coagulating medium having the appropriate pH at temperatures of at least 40° C. At temperatures below 40° C., the generation of the gas is ordinarily too sluggish for satisfactory operation. However, the temperature of the coagulating bath should not be at the boiling point or too close to the boiling point of the organic solvent used for making the polymer spinning solution. For acetone and ordinary spinning speeds, a temperature of as high as 50° to 55° C. is satisfactory while it is possible to go above these temperatures if higher speeds are used, the higher speeds preventing the solution within the jet from reaching the boiling point of the acetone, which condition would cause the formation of undesirable bubbles in the spinning solution within the jet and foul it. As stated before, the pH of the bath depends upon the particular gas-generating agent used. For sodium bicarbonate and calcium carbonate, a coagulating bath having a concentration of at least 10% sulfuric or hydrochloric acid and preferably as high as 20% sulfuric or hydrochloric acid is satisfactory. The gas-developing agent is ground to small size, a size as small as 1/2 to 1 micron in effective diameter being preferable.

Filaments having diameters ranging from about 10 to 300 microns or greater may be produced in accordance with the processes just described. The spinning of the filaments may be accomplished with just sufficient stretching to withdraw them from the orifices or this so called "jet stretch" may be supplemented by a greater amount of jet stretch or with a step of subsequent stretching between godets or rollers operating at different speeds or any other equivalent after-stretching procedure. The strength of the filaments can be increased by this after-stretching. That is, filaments of a given weight and cross-section which have been produced by an after-stretching procedure are stronger than those made without such after-stretching and having the same weight and cross-section area.

The filaments produced in general are characterized by centrally disposed voids which may be separated from one another by transverse partitions through the filaments occurring at regular or irregular intervals therealong. Those filaments that are made without much stretching are generally substantially cylindrical in cross-section and substantially uniform along their lengths. Those produced with considerable after-stretching or with considerably more than the necessary minimum amount of stretch exhibit numerous points of necking down along their length, generally coincident with the transverse partitions between the voids and the voids or lumens themselves become bulbous in character as compared to the voids of substantially uniform diameter in those filaments produced with little stretch. The filaments exhibit a delustered appearance and while they exhibit porosity to hydrophobic liquids, such as the paraffins, which are non-solvent and non-swelling to the polymer, they are so repellent to water that it cannot enter the filament structure as the hydrophobic non-solvent liquids do.

The filaments may be converted into staple fiber, carded and spun to produce textile yarns and knitted or woven fabrics which are especially

useful in the manufacture of wearing apparel or bed clothing where protection from cold is an important factor. Carded mats of the material may be used as fillers for the production of comforts, wearing apparel, cushions, life preservers, vibration damping, sound insulation or generally as a heat insulation material for filling spaces between the walls of buildings or other structures to be insulated, such as ice boxes, cold rooms, ships, railway cars, automobiles, airplanes and the like.

Another important application of the hollow filaments of the present invention is in the production of mats of the character and in the manner described in my copending application Serial No. 479,889, filed on March 20, 1943.

In the drawing, which is illustrative of the invention, Figure 1 shows one arrangement by which the method of the invention may be performed; Figure 2 is a face view of an expanded product of the present invention; Figure 3 is an edge view of the expanded product of Figure 2; Figure 4 illustrates the cleavage between the strata of the product of Figure 2; and Figure 5 is a greatly enlarged face view of a portion of the product of Figure 2, roughly illustrating the network of the filaments.

In the same manner as described in that application, and as shown in Figure 1 hereof a multiple filament bundle 2 extruded from a spinneret 6 having on the order of 500 to 3000 holes may be allowed to pass through funnel guides 7 and 4 in the spinning bath 3 in a manner such that free intercrossing between the filaments occurs and instead of condensing the bundle to a yarn-like structure at the take-up device 5 which is submerged partially in the bath, the multiple filament bundle of hollow filaments is allowed to proceed while remaining in the bath as a wide sheet-like web of the intercrossed filaments to the point of take-up on the winding drum which may or may not be traversed with respect to the filamentary web. After collection under the coagulating medium in the form of an annular band comprising the superimposed convolutions of the wound web, the band is slit transverse of the periphery of the winding drum, opened up into a flat sheet and allowed to dry, after which it is gripped at its opposite sides and stretched in the direction of its width. As in my prior application, the mat thus stretched is reduced in length, increased in width and surprisingly increased in thickness. Preferably, for producing mats of this character, filaments of the smaller sizes are employed though satisfactory results may be obtained with filaments of any size.

The expanded product obtained in this manner is composed of a number of separable strata or layers, as shown in Figures 2 to 4, each of which is composed of an intricate network of the hollow filaments. By separating the strata of a mat having a given specific gravity and then recombining them merely by laying the strata on top of one another a mat of lower bulk specific gravity is obtained. The network of an individual stratum is of three-dimensional rather than two-dimensional character as a result of the fact that the filaments constituting it are disposed in a generally wavy configuration and because of the fact that the plane of this waviness may be inclined at different angles along the length of each filament. The term "stratum" as used herein refers to a filamentous layer bounded by any two adjacent internal surfaces along which cleavage takes place with comparative

ease. It ordinarily comprises a plurality of convolutions or sheets of the original winding as most of them tend to cohere to their neighbors. This tendency to cohere may be attributed partly to the fact that in winding the irregularly arranged sheet of filaments, grooves of various depths and lengths may occur between the outermost filaments of the winding at any time during its formation. These grooves follow an irregular path about the periphery of the winding and do not necessarily continue completely therearound. Their presence permits some of the filaments of one or more succeeding convolutions to enter them. This causes an intermingling of irregular character between the filaments of a plurality of successive convolutions. When the wound band is subsequently stretched, the expansion in thickness is apparently caused by this intermingling. The motion of the intercrossed and intermingled filaments during expansion may be likened to a certain extent to the action of the mechanical device referred to as lazytongs. However, the filaments apparently acquire a wavy configuration because of their tendency to cohere at numerous points of tangency, though considerable slipping probably also occurs at many of these points. The fact that occasionally during the winding the occurrence of relatively shallow grooves may offer but little opportunity for intermingling gives rise to the surfaces of ready cleavage. The strata thus defined can frequently be subdivided with the exercise of special care into thinner laminations comprising a smaller number of individual convolutions of the original winding. With considerable difficulty and the exercise of extreme care laminations consisting of a single convolution can sometimes be obtained and such may be designated as a web. This web may have an overall area as large as that of the strata, but ordinarily, it is smaller in area, especially when the winding is produced under conditions permitting a certain amount of traverse. This web is usually not flat but generally is an irregularly undulated plane. The filaments within the individual strata form an intricate network as a result either of their intercrossing or of the tendency of the tangent waves of adjacent filaments to cohere. The interstitial character of the network may in numerous places depend on both of these factors. Each filament in the product usually lies within a definite stratum and usually extends substantially the entire distance from one side B to the opposite side C of the product as viewed in Figure 2.

The mat product made by substituting the hollow filaments of this invention for the filaments described in my prior application are characterized by extremely light weight and somewhat lower heat conductivities. For example, mat products of this type have been produced having one-half the density of similar products made from kapok and its resiliency as indicated by creep test is superior to kapok. The creep test indicates the tendency of the material to pack down under successive loading and is carried out by subjecting the mat to a load of 0.6 pound per square inch (which is equivalent to 86.4 pounds per square foot) for a period of sixteen hours after which the load is removed, the immediate recovery measured at a pressure of 0.01 pound per square inch and thereafter the recovery is measured at various intervals up to 7 hours. Finally, the material is fluffed by hand shaking

and final recovery is measured. This is repeated three or more times to determine the extent of packing. The hollow filament material made in accordance with this invention shows only 5% packing whereas kapok exhibits 11% packing under similar conditions. The mats of the present invention are also free of the fiber disintegration and "dusting" which kapok shows under repeated subjection to compression. The buoyancy of this material is far superior to a similar mat of kapok in that it sustains 62 times its own weight in water while a similar kapok material sustains only from 35 to 40 times its weight in water but is subject to wetting out which reduces this buoyancy.

The filaments either per se or in the form of a yarn-like bundle or in the form of a mat, carded or otherwise may be crimped by effecting shrinkage in hot fluids, such as in air or water at 80° C. or in swelling agents. This increases the bulk of products thereof by from 150 to 200%. The filaments may be coated with a wax or other water-repellent material dissolved in a paraffinic solvent which has no tendency to swell or dissolve the filaments themselves in order to improve their water-resistance. This treatment is of importance only where mats or yarn-like structures of such filaments which have large capillaries between the filaments are concerned. Where large capillaries are not involved, as is the case in products of the finer sized filaments, such additional wax treatment is not needed because of the hydrophobic character of the filaments themselves.

Mats and other structures, such as yarn-like structures, fabric structures and so forth which comprise hollow filaments of thermoplastic nature with or without non-thermoplastic filaments which may or may not be hollow may be activated in any manner heretofore suggested in order to obtain products of improved lightness in weight and compressional resilience, which properties in so far as the hollow filaments of the present invention are concerned are unaltered by subsequent humidity conditions or accidental or intentional contacts with moisture.

In the claims hereinafter, the word "polymer" is to be understood in a generic sense to include copolymers as well as simple polymers unless the context indicates the latter sense is intended.

While preferred embodiments of the invention have been disclosed, it is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined by the appended claims.

I claim:

1. A method of making a light-weight fila-

mentous product comprising the steps of passing a multiple-filament bundle of hollow filaments through a fluid medium under turbulent conditions, condensing the bundle into a sheet of a width comparatively large with respect to its thickness, collecting the sheet in the form of a multiple-layered winding and expanding the winding substantially as a unit by pulling two of its opposite edges apart in a direction generally transverse of the lay of the filaments therein to produce a filamentous mass of greater volume and thickness.

2. In a method of making a light-weight filamentous product, the steps of passing a multiple-filament bundle of hollow filaments through a liquid medium under turbulent conditions, condensing the bundle into a sheet of a width comparatively large with respect to its thickness, collecting the sheet in the form of a multiple-layered winding, severing the winding along its width and subsequently stretching it out while in substantially dry condition in a direction generally transverse to the lay of the filaments therein to produce a filamentous mass of greater volume and thickness.

3. In a method of making a light-weight filamentous product, the steps of passing a multiple-filament bundle of hollow filaments through a liquid medium under turbulent conditions, condensing the bundle into a sheet of a width comparatively large with respect to its thickness, collecting the sheet in the form of a multiple-layered winding, severing the winding along its width and subsequently stretching it out while in substantially dry condition in a direction generally transverse to the lay of the filaments therein to produce a filamentous mass of greater volume and thickness.

4. A low-density, expanded, filamentous product made by the process of claim 1.

5. A low-density, expanded, filamentous product made by the process of claim 2.

6. A low-density, expanded, filamentous product made by the process of claim 3.

7. A low-density, expanded, filamentous product made by the process of claim 3, said product comprising filaments made of a hydrophobic synthetic linear polymer.

8. A low-density, expanded, filamentous product made by the process of claim 3, said product comprising filaments of a copolymer of vinyl chloride and vinyl acetate.

9. A low-density, expanded, filamentous product made by the process of claim 3, said product comprising filaments of a copolymer of vinyl chloride and acrylonitrile.

ROBERT J. TAYLOR.