ABSTRACT

Water and a linear polymer in the molten state are kneaded in a high-pressure region to disperse the water minutely and uniformly throughout the polymer, which is then extruded together with supplementary water into a low-pressure region through an orifice, whereby a mass of fine fibers of excellent molecular orientation and rigidity and of hydrophilic character is produced.

10 Claims, 5 Drawing Figures
PRODUCTION OF FINE FIBER MASS

BACKGROUND OF THE INVENTION

This invention relates generally to fine fibrous structures and to synthetic paper-like structures. More particularly, the invention relates to a process for producing fine fiber masses for providing fine fibers suitable for making synthetic papers.

One kind of synthetic paper has a structure comprising fibers in intertwined state, that is, is formed by the ordinary paper-making process through the use of fibers of one or more synthetic polymers as a part of or in place of a paper-making material of natural cellulose fibers.

A synthetic paper of this character is desirable in that its structure is substantially the same as that of conventional paper. However, fibers for synthetic papers are required to have a high degree of molecular orientation, to be thin, and to have a highly fibrillated structure, and difficulties are encountered in adapting synthetic polymeric fibers of the type which have been generally used for fabrics and clothing to fulfill these requirements. Furthermore, synthetic polymeric fibers of this character are deficient in hydrophilic properties. For these reasons, satisfactory synthetic papers of this class have not been available.

On one hand, there is a known method for producing fine fibers suitable for use in making synthetic papers of this class which comprises jetting or ejecting a solution of a linear polymer in a solvent of low boiling point from a high-pressure region into a low-pressure region and thereby producing fine fibers by the blowing action due to the vaporization of the solvent. By this method, fine fibers of a high degree of fibrillation and a high degree of molecular orientation can be produced. However, the fibers thus produced are soft and have low rigidity. Moreover, these fibers are not hydrophilic. Furthermore, the necessary use of a large quantity of a solvent of low boiling point gives rise to difficulties.

SUMMARY OF THE INVENTION

It is an object of this invention to provide, on the basis of a new concept, masses of fine fibers of high rigidity and normally hydrophilic nature which are suitable for use in making synthetic papers possessing highly desirable properties.

According to this invention, briefly summarized, there is provided a process for producing fine fiber masses which is characterized by the steps of dispersing water into a molten linear polymer within a high-pressure region and extruding the water-dispersed, molten linear polymer thus obtained together with supplementary water into a low-pressure region.

The nature, utility, and further features of this invention will be apparent from the following detailed description beginning with a consideration of the general aspects of the invention and concluding with specific examples of practice illustrating preferred embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a flowsheet showing the essential organization of apparatus for carrying out one example of the process according to this invention; and

FIG. 2 is a flowsheet showing apparatus for carrying out another example of the process according to this invention; and

FIGS. 3, 4, and 5 are longitudinal sections respectively showing examples of extrusion suitable for the practice of this invention.

DETAILED DESCRIPTION

In the practice of this invention, in general, a starting material polymer is first melted under high-temperature and high-pressure conditions and kneaded in the presence of water, and water is dispersed uniformly and finely in the molten polymer, it being the ordinary method to effect this dispersion by kneading a molten-polymer and water system. The water which has been thus dispensed beforehand within the polymer abruptly expands in volume and exhibits foaming and cooling effects, when the molten polymer is extruded into a low-pressure region.

We have found further that when water is supplementarily added to the polymer immediately prior to the extrusion into the low-pressure region, this water also exhibits the same effects and, at the same time, also exhibits an elongation or stretching effect due to jetting action of the water in the extrusion direction. The stretching and orientation thus obtained result from rapid cooling due to the abrupt expansion and evaporation of the water and are automatically set. As a result, a mass of fine fibers of high rigidity are produced.

Furthermore, in order to promote the dispersion of water into the molten polymer and the wettability of the molten polymer with the supplementary water, a surface-active agent (surfactant) and a water-sorption agent are ordinarily used in the practice of this invention. We have found that the use of such additives renders the resulting fine fiber mass hydrophilic.

We have found that by macerating, disintegrating, or beating the fine fiber mass thus obtained by means of a machine such as an ordinary beater or refiner, fine fibers having excellent properties as a fiber material for synthetic papers can be readily obtained. A synthetic paper made from these fine fibers, moreover, has high rigidity and, correspondingly, a stiffness comparable to that of cellulosic papers.

Specific details of this invention will now be described.

1. Materials

1.1. Linear polymer

In general, for the polymer to be used in accordance with this invention, almost any linear polymer capable of forming fibers can be used. For imparting ample molecular orientation effect, a crystalline polymer is desirable. Furthermore, in view of the kneading of this polymer with water under high-temperature and high-pressure conditions, the possibility of the occurrence of hydrolysis must be considered. Accordingly, it can be said that a polymer prepared by a polyaddition process is preferable to a polymer prepared by a polycondensation (condensation polymerization) process.

Examples of such linear polymers are polyolefin resins, polychloroethylene resins, polyvinyl aromatic resins, polyamide resins, polyester resins, polynimide resins, and polycarbonate resins, used singly or as copolymers. Of these polymers, the most representative are polyolefin resins, among which isotactic polypropyl-
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3. High-density polyethylene resins ethylene-
propane copolymers are the most representative. These linear polymers can be used singly or as mixtures thereof. We have found that, in this latter case, by blending a polymer whose adhesiveness, polarity, or hydrophilic property is more conspicuous than its capability to form fibers with a crystalline polymer, it is possible to improve the physical properties of the fine fibers of the crystalline polymer.

The linear polymer may contain a pigment, a filler, a blowing agent, a bridging agent, a stabilizer, and other additions ordinarily used in polymers.

1.2. Water-sorption agent

In order to promote the dispersion of water into the molten polymer, the use of a substance which is water-soluble or has a property ranging from water-absorptivity to water-adsorption (herein called a water-sorption agent) is desirable. This water-sorption agent may be mixed beforehand within the polymer, or it can be mixed by introducing it under pressure together with water.

The water-sorption agent may be a substance which contains water of crystallization and is capable, itself, of introducing water into the molten polymer, or it may be a substance which, although having water-sorbitivity, does not contain water of crystallization and is capable of functioning as a so-called filler.

Examples of water-sorption agents having water of crystallization which can be used in this invention are organic and inorganic salts such as Na₂SO₄·7H₂O, Na₂B₄O₇·10H₂O, CaC₂O₄·H₂O, and CaC₂H₄O₄·4H₂O. In the practice of this invention, a hydrated salt of a decomposition temperature above the melting temperature of the polymer, such as Na₂B₄O₇·10H₂O, is particularly suitable.

Examples of substances which are simply water sorptive are: ordinary hygroscopic, porous fillers such as titanium oxide, barium sulfate, clays, calcium carbonate, silica, and diatomaceous earth; water-soluble and water-absorbing inorganic salts such as Na₂CO₃, NaHCO₃, (NH₄)₂CO₃, NH₄HCO₃, BaCO₃, CaSO₄, Na₂SO₄, MgSO₄, Mg(OH)₂, Al(OH)₃, and Ca(OH)₂; and water-soluble high-polymer substance such as polyvinyl alcohol, polyacrylic acid and salts thereof, polyacrylamide, polyethylene glycol, and polyethyleneimine.

These water-sorption agents can be used in combinations. While these agents may be blended with the polymer in a concentration up to approximately 60 percent, we have found that a preferred concentration is ordinarily in the range of from 10 to 30 percent. It desirable that the water-sorption agent exist within the polymer in a uniformly and finely dispersed state. In general, the effectiveness of the water-sorption agent increases with decreasing particle diameter thereof.

1.3. Surfactant

In accordance with a preferred embodiment of this invention, a surface-active agent (surfactant) is added to the polymer and/or water in order to promote the introduction and dispersion of water into the molten polymer and to promote the wettability of the molten polymer with the supplementary water, which is introduced under pressure immediately prior to extrusion into a low-pressure region, thereby to derive maximum stretching effect due to the supplementary water introduced under pressure.

For the surfactant, any non-ionic, anionic, cationic, amphoteric (ampho-ionic), or zwitter ionic surfactant can be used singly or as a mixture provided that it is stable under the high-temperature, high-pressure conditions of this invention. The surfactant is added to the polymer in a quantity of more that 0.1 percent by weight of the polymer, a quantity less than 0.1 percent being ordinarily sufficient for deriving satisfactory effect of the surfactant.

1.4. Other materials

Depending on the necessity, various auxiliary materials may be used in the process of this invention provided that they have no detrimental effect on the results and do not constitute a departure from the spirit and support of the invention. Examples of such auxiliary materials are the auxiliary material mentioned previously with respect to the polymer and materials for adjusting values such as the pH value of the water, specific gravity, and viscosity when necessary.

2. Dispersion of water into the molten polymer

2.1. Dispersion water

It is desirable that the water dispersed in the polymer exist as a liquid within the polymer. One reason for this is that, in the case where the water is in liquid form, it occupies a relatively small volumetric proportion within the polymer, and kneading and dispersing can be carried out with greater facility than in the case where the water is in vaporous form. Another important reason for this is that, when the water is in liquid form, the expansion force during extrusion into a low-pressure region is incomparably greater.

The water which has been uniformly and finely dispersed in the form of independent cells within the polymer undergoes instantaneous expansion and evaporation upon being abruptly released from high pressure at the time of extrusion and, rupturing the water cell walls, is jetted further in the extrusion direction thereby to stretch the polymer with great force and cause it to split into fine fibers.

2.2. Kneading

In order to cause the water to disperse uniformly within the molten polymer, the polymer and water are kneaded together under temperature and pressure conditions conducive to uniform dispersion and preferably in the presence of a surfactant and/or water-sorption agent as described hereinabove.

The kneading process step can be carried out by any appropriate method, examples of which are: (1) the method which comprises mixing at one time the polymer, water, surfactant and/or water-sorption agent and kneading the resulting mixture for a specific time under specific conditions of temperature and pressure; (2) the method wherein the polymer (and water-sorption agent and/or surfactant) are caused to assume a molten state, and then water (and surfactant) are introduced under pressure into the molten mixture to form a mixture which is then kneaded; and (3) the method wherein water (and surfactant and/or a water-sorption agent which dissolves with difficulty) are introduced under pressure into the polymer (and surfactant) in molten state, and the resulting mixture is kneaded.

A desirable method includes the step of introducing water under pressure into the polymer in the molten state. While an apparatus such as an extruder used for
admixing an auxiliary material for polymers such as an antistatic agent or a stabilizer into a molten polymer, a continuous Banbury mixer, or a kneader can be used in this case, we believe that the simplest and most practical procedure is to carry out kneading by means of an extruder as water at a high temperature and high pressure is introduced directly into the extruder, and amply high pressure therewithin is maintained.

2.3. Temperature and pressure

The dispersion of the water in the molten polymer is influenced greatly by the degree of kneading and the temperature and pressure conditions at the time of kneading.

While the kneading temperature should be at least as high as the melting temperature of the polymer since the water is to be dispersed in the molten polymer, an amply higher temperature is preferable. Furthermore, the temperature and pressure of the water influences the blowing action of the water at the time of extrusion (spinning) into a low-pressure region, and this blowing action increases with increasing water temperature and pressure. The reason for this is that if the temperature is low, the kneading effectiveness will decrease because of the rise in the viscosity of the molten polymer, and the dispersion of the water is relatively impeded.

Accordingly, when the water is to be introduced under pressure into the molten polymer, it is desirable that the water temperature be above the temperature of the polymer in a molten state. Of course, if the kneading time is prolonged after the water has been introduced into the kneading system, this problem will not arise.

Furthermore, as was mentioned hereinafore, it is desirable that the water exist as a liquid within the polymer. Accordingly, the pressure at the time of kneading should be higher than the saturated steam pressure of water at that temperature. In addition, the higher the pressure under which the water is introduced is, the deeper will the water infiltrate into the interior of the molten polymer, and the easier will the dispersion due to kneading become. Accordingly, a high water introduction pressure is preferable.

More specifically, we have found that in the case where water is introduced into a molten polyolefin, good results can be obtained when the pressures of the molten olefin and the pressure of the water are both above 40 kg./cm², preferably over 100 kg./cm².

In any case, it is necessary that the water be dispersed in the form of minute cells with ample fineness and uniformity within the molten polymer.

2.4. Quantity of water within the molten polymer

Since the quantity of the water dispersed in the molten polymer, together with the temperature and pressure, influences the blowing action, a large quantity of the water which will not impair the kneading and dispersion operation is desirable.

A system wherein dispersed water particles are spherical particles of equal diameter and have been introduced with maximum density in a polymer will now be considered. Ideally, in the case where a limiting concentration of the dispersed water of 74 percent is sought, and the dispersed water particles have amply small diameter and thin cell walls, it may be presumed that uniform and fine fibrillation is accomplished by the blowing and stretching force of the dispersed water itself.

In an ordinary extruder as mentioned before or like kneading apparatus, however, differences in viscosity cause the individual water particles to mutually and secondarily aggregate, whereby, it is difficult in practice to knead and disperse more than 50 percent of water uniformly and finely in the molten polymer.

With dispersed water of only this quantity, the stretching and orientation effects are insufficient, and it is difficult to obtain a mass of fibers which have been highly oriented and uniformly and finely fibrillated at the time of extrusion and pressure release. In accordance with this invention, therefore, supplementary water is forcibly introduced into the polymer immediately prior to its extrusion into a low-pressure region, and the stretching effect of the supplementary water is utilized to further facilitate splitting of the polymer into fine fibers and thereby to produce highly oriented fine fibers.

In the case where 50 percent is exceeded, and a further great quantity of water is introduced into the polymer, the water can no longer maintain its dispersed state in the form of independent fine cells, and, in addition to the dispersed state of fine cells, mutually communicative continuous phases are formed in one part. At the same time, the cell diameter or distance between the continuous phases decreases. Accordingly, similarly as in the case of dispersion of water in the form of independent cells as described before, by introducing the supplementary water and utilizing the stretching effect of this supplementary water, the objective highly oriented fine fibers can be obtained.

The quantity of water dispersed in the polymer prior to the forcible introduction of the supplementary water according to this invention, on the basis of the polymer with finely dispersed water, is over 2 percent, preferably from 25 to 50 percent. When this quantity is less than 2 percent, the resulting foaming power is deficient. While it is possible in this case to achieve fine fibrillation of the polymer by adding a large quantity of the supplementary water and utilizing its jetting power, the resulting fine fibers will be hard and non-uniform, whereby they will require additional after-treatment for application to making of synthetic paper.

3. Preparation of composition for extrusion into a low-pressure region

3.1. Supplementary water

In order to produce a mass of fine fibers of high rigidity by extruding into a low-pressure region a molten polymer obtained in this manner wherein water is finely dispersed, supplementary water should be caused to exist in addition to this dispersed water, as mentioned hereinafore. This supplementary water assists and facilitates the discharge of the water-dispersed polymer into the low-pressure region and, moreover, as described hereinafore, is jetted vigorously in the extrusion direction by the abrupt release of pressure occurring when the polymer is extruded into the low-pressure region. This action of the supplementary water imparts a high degree of stretching and orientation to the polymer containing finely dispersed water and traveling in the same extrusion direction, whereby the polymer is split into fine fibers by the combined foaming and stretching force of the dispersed water.
Thus, in the practice of this invention, the blowing action of the water dispersed in the molten polymer and the stretching and orientation actions due to the supplementary water occur almost simultaneously to render the polymer into fine fibers. Accordingly, the quantity of the supplementary water is determined by the balance of its effect with the blowing action of the water (dispersed water) dispersed in the molten polymer. More specifically, in the case where the quantity of the dispersed water is small, and the blowing action is weak, a relatively large quantity of the supplementary water is required. On the other hand, when the blowing action is sufficiently powerful, a relatively small quantity suffices.

Furthermore, the blowing action of the dispersed water is influenced also by the conditions of temperature and pressure in the high-pressure region relative to those of the low-pressure region. That is, the higher the temperature and pressure are, the better are the results.

In general, the supplementary water does not exhibit a splitting effect due to the rupturing of the cell walls from the interior as in the case of the dispersed water, and the polymer splitting effect due to stretching and orientating from the inside is predominant. For this reason, the contribution of the supplementary water to splitting of the polymer is somewhat less than that of the dispersed water. Accordingly, in an effective mode of practice of this invention, it is desirable that as large a quantity as possible of water be dispersed uniformly and finely in the polymer and that the supplementary water be used in a secondary manner.

More specifically, in the case where, for example, a polyolefin such as polypropylene is used for the polymer, the quantity of the dispersed water on the basis of the water-dispersed polymer is from 40 to 50 percent, and extrusion is carried out into a low-pressure region at room temperature and atmospheric pressure from a high-pressure region under the conditions of a temperature of from 230⁰ to 280⁰C and a pressure of from 100 to 150 kg./cm², the quantity of the supplementary water is from 1 to 5 or more times the quantity of the water-dispersed polymer. We have found that it is possible with this quantity of the supplementary water and under these conditions to produce a fine fiber mass which is amply suitable for paper making.

On the other hand, when the quantity of the dispersed water is from 2 to 5 percent, it is necessary to add the supplementary water in a tremendous quantity of the order of from 40 to 50 times that of the water-dispersed polymer.

It will be obvious that the supplementary water is added at a high temperature and under a high pressure similar to those of the dispersed water.

3.2. Introduction of the Supplementary Water

While the supplementary water can be introduced by adding water after the required quantity of the dispersed water has been introduced in the aforesaid kneading step, the most desirable method is to forcibly introduce the supplementary water under pressure into the interior of the orifice of the device for extrusion in the low-pressure region or into the polymer flowpath immediately upstream from the orifice. The reason for this is that, when the supplementary water is introduced too early, the uniformly and finely dispersed state of the dispersed water within the molten polymer, which state should be maintained at the time of extrusion, tends to be destroyed.

Furthermore, in order to utilize the effect of the supplementary water at its maximum limit, the area of contact between the supplementary water and the water-dispersed polymer should be made as large as possible, and this can be accomplished by appropriately designing the extrusion orifices of the extruder part where the supplementary water is to be introduced.

It is desirable that this supplementary water also contain a surfactant. Furthermore, as mentioned before, the supplementary water should be introduced at an amply high temperature.

Representative examples of construction of the above-mentioned part for introducing the supplementary water are illustrated in FIGS. 3, 4, and 5, each of which is a longitudinal section taken along a plane passing through the axis of extrusion and showing an extrusion orifice. FIG. 3 shows an example of a nozzle for an inner feed method wherein, within an extrusion orifice 113, supplementary water is introduced through an inner member or torpedo 213 into the inner part of a water-dispersed polymer, and the aforementioned stretching is imparted to the polymer from its inner part.

FIG. 4 shows an example of a nozzle for an outer feed method wherein the supplementary water is introduced along the inner surface of the extrusion die wall, and the polymer is stretched from the outside. The outer structure or die wall of the orifice 113A is substantially the same as that of the orifice 113 in FIG. 3, the orifices 113 and 113A differing only in their inter structure 213 and 213A, respectively.

The area of contact between the supplementary water and the water-dispersed polymer is greater in the orifice 113A shown in FIG. 4 than that in the orifice 113 shown in FIG. 3, and, consequently, the stretching effect is greater. Furthermore, by the outer feed method, the supplementary water flows along the inner surface of the extrusion die wall, whereby the frictional drag or resistance to flow becomes extremely low, and this method is thereby inferior in maintaining internal pressure of the die. However, the low die resistance makes possible high-velocity, high-flowrate extrusion.

Because of this feature, together with the above mentioned increase in the contact area, the effect of forming fine fibers by the outer feed method indicated in FIG. 4 is superior in spite of the lowering of the blowing action due lowering of the internal pressure of the die.

The area of contact between the supplementary water and the water-dispersed polymer can be further increased thereby to further promote the effect of rendering the polymer into fine fibers by the use of extrusion orifices of various constructions, a representative example of which is illustrated in FIG. 5.

3.3. Pressure Maintenance

As mentioned hereinabove, the dispersion water must be dispersed in liquid form in the molten polymer under high-temperature and high-pressure conditions in order to achieve maximum utilization of the blowing action of water.

Accordingly, the flowpath interval from the aforesaid kneading means to the outlet opening of the orifice should be maintained at a pressure above the saturated steam pressure of water at the temperature of the flowpath. If the pressure maintenance is unsuitable and
When a pressure decrease to a value below the saturated steam pressure occurs, the water will immediately expand and evaporate, thereby cooling the polymer. Consequently, the viscosity of the molten polymer rises, and the resistance at the time of foaming and rendering of the polymer into fine fibers in the low-pressure region increases.

Furthermore, the lowering of the blowing action in the low-pressure region due to a lowering of the water temperature and pressure and a secondary aggregation of the dispersed water due to the water expansion give rise to a separation of the water and the molten polymer. As a result, the polymer is not sufficiently disintegrated, whereby not only is the objective fine fiber mass unobtainable, but in extreme cases, the molten polymer is cooled to solidification and thereby gives rise to trouble such as clogging of the orifice.

Accordingly, it is necessary to provide means for coordinative regulation of the pressure rise conditions (for example, supply of the starting material polymer and water into the kneading region) in the system from the kneading region through the orifice outlet and the pressure decreasing conditions (for example, transfer of the molten polymer in the transfer region from the kneading region to the orifice and the discharge into the low-pressure region from the orifice) thereby to maintain the pressure of the entire system above a specific standard value which is higher than the saturation steam pressure of the system.

4. Extrusion Into the Low-Pressure Region

The molten polymer prepared in this manner is extruded from the high-pressure region where it initially exists, through the orifice, and into the low-pressure region thereby to render the molten polymer into a mass of fine fibers.

In general, while the low-pressure region is ordinarily at room temperature and atmospheric pressure, it is also possible use increased temperature and reduced pressure conditions in the low-pressure region in order to promote the expansion and jetting of the water.

For this extrusion of the molten polymer, an orifice having one or a plurality of ejection outer openings of any suitable shape such as round or slit-shaped may be used. While the extrusion velocity from the ejection opening is preferably above the velocity of sound (330 meters/second), a velocity equal one half the velocity of sound or a lower velocity may be used.

5. Product Formed

The polymer produced by the process step of extruding a molten polymer in which water is minutely and uniformly dispersed into a low-pressure region in the above described manner thereby to cause the polymer to shatter into fine fragments is obtained as a fine fiber mass in which a large number of very thin fine fibers are randomly joined.

Provided that the dispersion of the dispersed water in the molten polymer is fine and uniform, the resulting fine fiber mass is obtained as an aggregate of separate short fibers and can be readily fed, as it is, directly into a macerator or disintegrator. Furthermore, this fine fiber mass resulting from the above stated condition can be used, in its state as produced, as fine fiber starting material for paper making.

Even in the case where the fiber mass cannot be obtained as separate short fibers, since the individual constituent fibers are highly oriented, they can be readily macerated by a machine such as a refiner or beater generally used in the papermaking industry, whereby the fine fibers of high orientation and rigidity are obtained.

The maceration conditions become even more advantageous in the case where a blend of two or more polymers is used as the process polymer. Particularly fine fibers produced by the use of blends of polymers having adhesive power (for example, polyvinyl alcohol, polyacrylic acid and salts thereof, polyamide acrylate, polyethylene oxide, and polyethylene amine) exhibit high effectiveness in forming the paper film during paper making.

Since at least some fraction of the surfactant and water-sorption agent used in the above described process remain in the product, the fine fibers of the product are highly hydrophilic. These fine fibers have a shape similar to that of wood pulps and can be supplied as they are to a papermaking machine. Moreover, the wet-paper strength after forming of the paper film with these fibers is of the same order as that of "natural paper."

The fine fibers produced in accordance with this invention can also be used in mixed state with wood pulp fibers to make paper and, in addition to their use as starting material for synthetic papers, can be used for a wide range of products from unwoven fabrics to disposable sheets and sheet products.

6. Flowsheet

One example of embodiment of this invention is indicated by the flowsheet shown in FIG. 1. In the method indicated therein, the polymer melting section and the water-injection and kneading section are separately provided.

In another example of embodiment of this invention as indicated in FIG. 2, the melting of the polymer, injection of water, and kneading and dispersion of water are carried out in a single extruder. The parts in FIGS. 1 and 2 designated by the same reference numerals are the same or are equivalent except that the reference numerals in FIG. 2 have the letter "A" appended thereto.

In a process wherein an extruder is used to accomplish kneading and water dispersion therewithin as in this example, it is necessary in order to obtain the optimum state of dispersion of the water to determine, in addition to the aforesaid polymer composition and water injection conditions, certain factors such as the shape and rotational speed of the screw, the distribution of pressure within the extruder, and the point of water injection in accordance with the objects of the production process.

While the effect on dispersion of the point of water injection differs with the shape and rotational speed of the screw, it is desirable that the water be injected at an upstream part of the screw to afford ample kneading time. Furthermore, in order to carry out the kneading and water dispersion step with even higher effectiveness, the use of a screw of a high shearing and kneading action type is preferable.

Referring again to FIG. 1, the process indicated by the flow sheet illustrated therein will be described. The starting material polymer is continuously melted by an extruder 1 and continuously supplied into a kneading and water-dispersion region. Water stored in a water
reservoir 2 is amply heated by a heat exchanger 4 and supplied continuously by a pump 3 for constant-rate injection at high pressure into the kneading and water-dispersion region. The pressure of the polymer is indicated by a pressure gauge mounted on the extruder. The water pressure is maintained at a constant value as a constant flowrate is maintained by a pressure-control valve 5.

The polymer in molten state and water at high temperature and high pressure are supplied into a kneading region (i.e., the extruder in this example), where the polymer is continuously and thoroughly kneaded under a high pressure and high shearing action by means of a continuous kneader 6, whereby the water is dispersed in the molten polymer to form a polymer — finely dispersed water body.

This polymer — dispersed water body is transferred by way of a transfer zone 14 to a high-pressure metering pump 8, by which it is further transferred to an extrusion orifice 13. The pressure in the kneading region is measured and indicated by a pressure gauge 15. This pressure is maintained above a predetermined value by controlling the feed rates of the extruder 1 and the high-pressure injection pump 3 and controlling the transfer rate in the high-pressure metering pump 8 of the transfer zone.

In the vicinity of the orifice, which has been comply heated by a heat exchanger 11 is injected by means of a high-pressure metering pump 10 into the transfer zone. The pressure at which this water is injected is adjusted by a pressure-control valve 12 at a constant pressure value as the flowrate is maintained constant.

The polymer-finely dispersed water body and the water injected at the transfer zone are both continuously sent to the orifice 13 and, through this orifice of specific dimension, are continuously ejected at very high speed and high pressure into a region at atmospheric pressure. Consequently, the molten polymer is finely splintered and cooled by the abrupt expansion and evaporation of the water and is thereby rendered into a mass of uniform fine fibers of high rigidity.

The pressures in the flowpath upstream from the orifice 13 and in the transfer zone are sensed by pressure gauges 17 and 18 and are maintained above respective standard values by controlling the rate of transfer of the high-pressure metering pump.

Temperature control of the entire system is accomplished automatically by automatic temperature regulators installed at suitable positions therein. Furthermore, the temperature of the water is maintained constant by heat exchangers of specific capacities. By thus maintaining pressures at standard values above predetermined pressures and, at the same time, maintaining the temperatures at respective constant values as the molten polymer is extruded through the orifice, uniform fine fibers can be continuously produced.

In order to indicate still more fully the nature and utility of this invention, the following examples of practice illustrating preferred embodiments of this invention are set forth, it being understood that these examples are presented as illustrative only, and that they are not intended to limit the scope of the invention.

**EXAMPLE 1**

To an isotactic polypropylene powder of a melt index (MI) of 20, an 80-percent aqueous solution of sodium oleate in a quantity of 2 percent with respect to the polymer and 10 percent of calcium carbonate were added, and the resulting batch was mixed by means of a mixer into a uniform mixture.

This mixture was continuously melted at 210°C in a 50-mm. diameter bent type extruder of an L/D ratio of 29 and extruded under 80 kg/cm² at a rate of 20 kg/hour.

Furthermore, water with 2 percent of sodium oleate prepared separately and added thereto was sent by a high-pressure metering pump through a heat exchanger, and a pressure of 50 kg/cm² was maintained by a pressure regulating valve whereby to prepare pressurized water heated to 210°C. This pressurized and heated water was introduced through the bent hole of the extruder and kneaded with the polymer under high shearing force with an inner pressure of the extruder of 80 kg/cm². The resulting polymer containing dispersed water was then transferred by a gear pump to an orifice.

Water containing 2 percent of an anionic surfactant prepared in a separate reservoir was sent by another high-pressure metering pump at a heat exchanger. The pressure of this water was adjusted to 80 kg/cm² by means of a pressure-regulating valve, and the temperature thereof was raised to 210°C. The resulting water was injected through an intermediate part of the orifice, and, together with the above described polymer extruded by the gear pump, was extruded into the atmosphere through an orifice of 2-mm. diameter and an L/D ratio of 30.

The temperature of the system was maintained constant at 210°C by temperature regulators installed at all regions. Furthermore, by varying the quantity of water injected into extruder and varying the extrusion flowrate of the gear pump and the quantity of the water injected into the orifice, the pressure at which extrusion was carried out through the orifice was adjusted. Thus, by injecting water at a rate of 10 liters/hour into the extruder and at a rate of 100 liters/hour into the orifice part, extrusion was carried out at a pressure of 100 kg/cm².

The fine fibers thus produced was recovered as a mass of highly fibrillated fine fibers. This fine fiber mass was disintegrated by means of a 12-inch single-disk refiner and under the conditions of a concentration of 10 percent and a clearance of 5/1,000 inch. As a result, stiff fine fibers having a flat shape similar to that of pulp of an average diameter of 20 microns and a length of from 3 to 4 mm. were obtained.

**EXAMPLE 2**

A mixture of 44 parts of an isotatic polypropylene of a MI of 20, 24 parts of a high-density polyethylene of a MI of 20, 10 parts of calcium carbonate, 20 parts of aluminum hydroxide, and 2 parts of polyvinyl alcohol was mixed in a mixer to form a uniform mixture. This mixture was continuously melted at 250°C in a 90-mm. diameter extruder (L/D = 29) having an end damage and extruded with an tip pressure of 400 kg/cm² at a rate of 100 kg/hour.

Pressurized water at high temperature and high pressure prepared separately to be at 250°C and 200 kg/cm² and maintained at a flowrate of 120 liters/hour by a high-pressure metering pump, a heat exchanger, and a pressure-regulating valve was introduced into an
upstream stage of the extruder, and the resulting process materials were kneaded with high shear force. The tip pressure of the extruder dropped to from 150 to 200 kg/cm², because of the kneading and dispersion of water. The polymer in which water had been finely dispersed by the kneading was sent to an orifice connected directly to the downstream end of the extruder and was thus extruded through the orifice. Pressurized water at 250°C and 200 kg/cm², prepared separately was introduced as supplementary water at a flow rate of 130 liters/hour into a point upstream from the orifice and, together with the above described polymer with finely dispersed water, was extruded through a 2-mm. diameter, L/D = 50 orifice into a region at atmospheric pressure.

As a result, a continuous mass of fine fibers fibrillated to a high degree were produced. This mass of fine fibers was beaten by means of a 24-inch, single-disk refiner with a clearance of 3/1,000 inch, whereupon fine pulp-like fibers of flat shape with an average diameter of 15 microns and lengths of from 2 to 3 mm. were obtained. These fine fibers were found to be extremely hydrophilic and to be readily dispersible uniformly in water without the addition of any dispersant.

EXAMPLE 3

To 60 parts of an isotactic polypropylene of a MI of 9, 30 parts of a high-density polyethylene of a MI 8, 2 parts of an anionic surfactant, 8 parts of calcium carbonate, and 5 parts of gypsum were added, and the resulting batch was mixed in a mixer to prepare a uniform mixture, which was then melted at 230°C in a 50-mm. diameter bent extruder and continuously extruded under a pressure of 100 kg/cm² and at a rate of 40 kg./hour.

Furthermore, water at 80 kg./cm², and 210°C containing 2 percent of an anionic surfactant and prepared separately was injected through the bent hole at 30 liters/hour and kneaded with the above described polymer. The resulting preparation was injected by means of a gear pump at a pressure of 130 kg./cm², through an orifice of 2-mm. diameter and an L/D ratio of 40 into a region at atmospheric pressure, whereupon a mixture of a mass of fine fibers of a highly advanced degree of fibrillation and foamed structures contained at scattered positions therein was obtained.

In this case, water at 210°C containing 2 percent of a monionic surfactant prepared separately was injected into an upstream part of the orifice under a pressure of 130 kg./cm², and at a supply rate of 80 liters/hour. This water and the polymer were injected together into a region at atmospheric pressure, whereupon it was possible to produce continuously fine fibers similar to those produced in Example 1.

EXAMPLE 4

To a polypropylene powder of a MI of 5, 40 percent of a fine powder of Na₂B₄O₇·10H₂O and 5 percent of calcium carbonate were added, and the resulting mixture was rendered in a mixer into a uniform mixture.

The mixture thus prepared was melted and kneaded in a two-stage extruder having a kneading section of end dama Georgia, type, at 200°C in the first stage and at 230°C in the second stage. The mixture thus kneaded was sent under 80 kg./cm², and at 20 kg./hour to a gear pump, by which the mixture was pressurized further to 150 kg./cm², and injected through an orifice into a region at atmospheric pressure.

In this case, water at 230°C separately prepared and containing 2 percent of an anionic surfactant was introduced under a pressure of 160 kg./cm², and at a rate of 100 liters/hour and was then injected, together with the above described polymer into the atmosphere. As a result, it was possible to produce continuously a mass of fine fibers similar to those of Example 1.

EXAMPLE 5 (reference example)

The fine fibers produced in accordance with Example 1 were dispersed in water to a concentration of 0.3 percent. These fine fibers were found to be extremely hydrophilic and to exhibit good dispersion even in their as-prepared state, but 0.01 percent of a surfactant was further added to prepare a fine fiber dispersion liquid, which was used to make paper in a small continuous papermaking machine of a film forming speed of 3 meters/minute. As a result, a synthetic paper of a weight per area of 40 grams/square meter, a thickness of 90 microns, and a bulk density of 0.45 and of good texture was obtained.

It was found that these fine fibers could be used directly in their as prepared state in a papermaking machine presently in use in making paper thereby to produce good synthetic paper.

EXAMPLE 6

60 parts of a polypropylene of a MI of 9, 30 parts of a high-density polyethylene of a MI of 8, 5 parts of a clay, 5 parts of calcium carbonate, and 10 parts of a 30 percent aqueous solution of sodium stearate were mixed thoroughly in a mixer to form a uniform mixture.

This mixture was passed through the two-stage extruder used in Example 4 and was melted and kneaded at 230°C. The molten mixture thus kneaded was extruded under a pressure of 100 kg./cm², and at a rate of 20 kg./hour through a circular orifice of 2-mm. diameter. In this case, pressurized water prepared separately to contain a small quantity of an active agent and be under a pressure of 100 kg./cm², and at a temperature of 250°C was introduced into the polymer at an upstream part of the orifice at a rate of 200 liters/hour similarly as in Example 1. This water and the polymer were injected into a region at atmospheric pressure.

As a result, a mass of fine fibers containing at scattered positions foamed structures stretched into ribbon state. By disintegrating these fine fibers by means of a single-disk refiner similarly as in Example 1, fine fibers of an average diameter of from 20 to 30 microns and lengths of from 1 to 3 mm. were produced.

These fibers and kraft pulp were mixed in a proportion of 4:1, and the resulting mixture was dispersed in water to a concentration of 0.3 percent. The aqueous dispersion thus prepared was used in a small continuous papermaking machine to make paper at a film forming speed of 3 meters/minute, whereupon a mixture paper of a weight per area of 45 grams/square meter and a thickness of 100 microns and of uniform texture was obtained.

EXAMPLE 7 (reference example)

The fine fibers obtained in Example 6 was dispersed uniformly in water to a fiber concentration of 0.3 percent together with a binder of acrylic emulsion type in a quantity by weight of 5 percent with respect to these
fine fibers. The resulting dispersion was then used to make paper in a small papermaking machine operating with a film-forming speed of 3 meters/minute, whereupon a synthetic paper of a weight per area of 45 grams/square meter and a thickness of 100 microns and of a uniform texture was obtained.

This synthetic paper had a breaking length of from 2 to 2.5 km., having a strength comparable to that of natural pulp paper, and had ample value as a paper. It was found, moreover, that even after being made into a paper, these fibers could be readily disintegrated into their original form as fine fibers by means of a machine such as a pulper or mixer and, in fact, could be treated in exactly the same manner as wood pulp.

When polyolefin fibers prepared by an ordinary method such as melt spinning are used in papermaking with a similar binder for effecting adhesion, a binder quantity of at least 30 percent is ordinarily considered to be necessary to obtain ample strength. In contrast, when the fine fibers of the present invention are used, substances such as the active agent and the water-sorption agent remaining within the fibers have an effect such that the binder is selectively adsorbed. For this reason, ample strength is afforded with a small quantity of binder as in the instant example.

We claim:

1. A process of producing a mass of fine fibers which comprises:

1. introducing water into a mass of molten linear water-insoluble polyolefin polymer under an elevated temperature and pressure in a quantity of from 2 to 50 percent by weight of the resulting mixture;
2. kneading the resulting mixture while maintaining the mixture at an elevated pressure thereby to produce a molten polymer mass which contains water finely and uniformly dispersed therein;
3. transferring the resultant molten polymer mass under an elevated temperature and pressure to an orifice with an introduction of supplementary water under an elevated temperature and pressure in a quantity of at least 100 percent by weight of said molten polymer mass produced from step (2) at a part immediately before or just at the orifice; and then
4. extruding the mixture of water and molten polymer mass obtained from the step (3) into a region of lower pressure so as to evaporate the water dispersed in the molten polymer mass and the supplementary water introduced into the step (3) whereby the molten polymer mass is cooled and subdivided into a mass of fibers.

2. A process for producing a mass of fine fibers as claimed in claim 1 in which the linear polyolefin polymer is selected from the group consisting of homopolymers and mutual copolymers of ethylene, propylene, and butene-1, copolymers of ethylene, propylene and butene-1 as predominant constituents with monomers copolymerizable therewith, and mixtures of said polymers.

3. A process for producing a mass of fibers as claimed in claim 1 in which a water-sorption agent is added to said molten linear polyolefin polymer which water-sorption agent is a fine solid selected from the group consisting of nitrates, oxalates, acetates, sulfates, sulfites, carbonates, phosphates, hydroxides, and halides of alkali metals, alkaline earth metals including magnesium and ammonium.

4. A process for producing a mass of fine fibers as claimed in claim 1 in which a fine water-insoluble solid water-sorption agent is added to the molten linear polyolefin polymer, said water-insoluble solid comprising a silicate.

5. A process for producing a mass of fine fibers as claimed in claim 1 in which the pressure used during the kneading process is above 40 kg/cm².

6. A process according to claim 3 in which the water-sorption agent is used in an amount of between 10 and 30 percent by weight of the molten polymer mass.

7. A process according to claim 1 wherein the kneading temperature is above the melting temperature of the molten polymer.

8. A process according to claim 7 wherein the pressure used during the kneading process is above the saturated steam pressure of the water introduced into the molten polymer.

9. A process according to claim 1 wherein the pressure used during the kneading process is above 100 kg/cm².

10. A process according to claim 1 wherein the pressure used during the kneading process is above 40 kg/cm².