An aqueous disperse system, preferably an aqueous emulsion, comprising a molten linear polymer droplets dispersed in the aqueous phase and containing a fine water-sorption agent and a positive solvent with respect to the polymer is ejected from a high-pressure region at a temperature above the polymer melting point and below the critical temperature of the disperse system and at a pressure above the saturated vapor pressure of the disperse system into a low-pressure region at a temperature and pressure permitting evaporation of a liquid phase within the disperse system thereby to produce a fine fibrous structure of the polymer.
PROCESS FOR PRODUCING FINE FIBROUS STRUCTURES

This is a continuation of application Ser. No. 182,524, filed Sept. 21, 1971, and now abandoned.

BACKGROUND

This invention relates generally to techniques in the production of fine fibrous structures and more particularly to a new process for producing fibrous structures for providing fine fibers suitable for use in making synthetic papers. Papers of a structure wherein fibers are in intertwined state are known as one class of synthetic paper. A paper of this class is made through the use of fibers of a synthetic polymer as one constituent of a natural cellulosic paper-making material or as the predominant paper-making material.

One advantageous feature of a synthetic paper of this class is that its structure is substantially the same as that of conventional or cellulosic papers. 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 general character are deficient in hydrophilic property. 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 usable in making synthetic papers of this class which comprises abruptly jetting or ejecting a solution of a crystalline polymer under pressure and at a temperature above room temperature through orifices into a low-pressure region and thereby reproducing the polymer as a fine fibrous structure simultaneously with the resulting evaporation of the solvent used.

By macerating or beating the fine fibrous structure thus obtained by this spinning method, fine fibers of fibrillated structure having ample fineness and ample strength due to molecular orientation can be produced. When these fine fibers are used in paper making, synthetic papers even more closely resembling conventional paper can be produced.

Fine fibers of this character and the method for producing the same, however, cannot be said to be entirely free of problems. More specifically, for example, the choice of a usable solvent is limited since this solvent must have a low boiling point and, moreover, must be used in a large quantity. Furthermore, fine fibers produced in this manner lack hydrophilic property and, consequently, cannot be easily used in paper making.

SUMMARY

It is an object of this invention to provide a relatively simple process for producing fine fibrous structures wherein the above described difficulties and problems are overcome. We have found that this object can be achieved by ejecting an aqueous dispersion or disperse system of a molten linear polymer droplets dispersed in the aqueous phase under pressure into a low-pressure region.

In the production of fine fibers by diminution of mass of polymer, the fine fibers can be produced by dispersing blowing agent in the polymer mass and subjecting the blowing agent-containing polymer mass to a lower pressure to allow the expansion of the blowing agent thereby to split the polymer mass into fine fibers. For this, it is the most important to employ a blowing agent having a large expansion capacity and to disperse the blowing agent in a polymer mass finely enough to split the polymer mass to desired fine fibers.

Further, in order to obtain a molecularly oriented polymer, it is desirable to finely-disperse a large amount of blowing agent which has a large expansion capacity in the polymer mass and improved wettability at the interface between the blowing agent and the polymer, and to quench the blown polymer by means of latent heat of vaporization of the blowing agent and Joule-Thomson effect by the gas generated by the blowing agent thereby to fix the molecular orientation.

The most important features of this invention thus reside in the use as the blowing agent of water which has a large expansion capacity and has a large latent heat of vaporization; the improvement in dispersion of the water finely in the polymer mass by the use of a water-sorption agent; and the improvement is wettability at the surface of the water and the polymer by the use of a surface active agent.

According to this invention, briefly summarized, there is provided a process for producing fine fibrous structures wherein an aqueous disperse system comprising a molten linear polymer containing a fine water-sorption agent and a positive solvent with respect to the polymer is ejected from a high-pressure region at a temperature above the melting point of the polymer and below the critical temperature of the disperse system and at a pressure above the saturated vapor pressure of the disperse system into a low-pressure region at a temperature and pressure conducive to evaporation of a liquid phase within the disperse system thereby to produce a fine fibrous structure of the polymer.

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

DETAILED DESCRIPTION

In accordance with this invention, as mentioned hereinabove, an aqueous disperse system is used as a "spinning solution" of the linear polymer to be spun by ejection into a low-pressure region. The droplets or particles of the polymer within the aqueous disperse system contain a fine water-soluble or water-adsorbent water-absorptive material, that is, a water-sorption agent. Since the droplets of molten polymer contain a hydrophilic substance of this nature within an aqueous disperse system, these droplets contain therewithin a substantial quantity of water.

Accordingly, by the practice of this invention, the following desirable effects and results are afforded.

1. Blowing effect

The blowing effect of the water contained within the polymer droplets is utilized. More specifically, when the aqueous disperse system is ejected into the "low-pressure region," the pressure on this water within the droplets is abruptly released, whereby this water vaporizes instantaneously and exhibits a blowing effect. This abrupt pressure release is accompanied by a rapid cooling effect (Joule-Thomson effect and latent heat of va-
3,914,354

porization), whereby the molten polymer is cooled simultaneously with its blowing action.

The water within the molten polymer fluid droplets may be broadly classified into two kinds as distinguished by their states of existence. That is, the first kind is water with a water-sorption agent as its center which exists as a dispersed phase within a continuous phase of the molten polymer, while the second kind is the water corresponding to the case where this dispersed phase has consolidated considerably and become communicative with the outer side of the polymer droplets. The blowing effect is particularly pronounced with the former kind of water, that is, the water which is enveloped by the walls of the molten polymer.

In the case where a positive solvent with respect to the polymer is used in the preparation of the aqueous disperse system of the polymer, a further blowing effect can be expected also from the evaporation in the “low-pressure region” of the positive solvent which has infiltrated into the interior of the polymer fluid droplets.

2. Molecular orientation effect

Two kinds of water exist in this polymer disperse system, namely, water which has infiltrated into the interior of the above mentioned polymer droplets and water which has not so infiltrated and is present outside of the droplets.

The latter water evaporates at the instant when the disperse system is extruded or ejected into the low-pressure region and becomes a stream of water vapor, which advances with extremely high energy in the ejection direction. This stream of water vapor exerts a great stretching action on the polymer in the ejection or spinning direction.

Since the quantity of the former water becomes considerable in accordance with this invention, the contribution of the evaporation of this water to the stretching action also amounts to a considerable degree.

The abrupt evaporation of the water (and positive solvent) inside and outside of the polymer droplets as described above also gives rise to a rapid cooling of the interior and exterior of the polymer, which thereupon solidifies. These blowing, stretching, and cooling actions take place substantially simultaneously, whereby a structure comprising fine fibers which has a highly oriented structure and, moreover, is highly fibrillated is produced.

The degree of orientation and stiffness of these fine fibers differ with whether or not the water enclosed within the molten polymer droplets is existing as a dispersed phase within the continuous phase of the molten polymer. More specifically, in the former case, the contribution toward polymer stretching due to the evaporation and expansion of the enclosed water is great, whereby fine fibers of high orientation and high stiffness are produced. Accordingly, beating is facilitated, and, moreover, the stiffness of a synthetic paper made from these fibers is comparable to that of a natural pulp paper.

On the other hand, in the latter case wherein the water enclosed within the polymer droplets is not existing as a dispersed phase, the enclosed water is communicative with the water (dispersion medium of the aqueous disperse system) outside of the droplets. For this reason, the evaporation and expansion action of the enclosed water at the time of the ejection into the low-pressure region is less than that in the former case, and the orientation of the polymer due to the stretching action of the water outside of the polymer droplets becomes predominant.

Consequently, the degree of orientation of the resulting fine fibers is somewhat lower than that in the former case, but synthetic papers made with these fibers are highly useful depending on the use, such as, for example, uses where pliability and softness are required and uses as disposables.

3. Reduction of quantity of solvent used

For the “spinning solution” in the practice of this invention, a solution of the polymer in an organic solvent is not used, and the polymer droplets within the intended aqueous disperse system of emulsive liquid moreover, are not in the form of a solution of the polymer but are in molten state. Accordingly, in such a mode of utilization of the polymer, a solvent is not absolutely necessary.

According to this invention, however, a positive solvent with respect to the polymer used is used for the purposes of facilitating the preparation of the aqueous disperse system and facilitating the infiltration of water into the fine water-sorption agent within the polymer droplets in the disperse system.

In view of these purposes of use of a solvent, the quantity used thereof is remarkably small, being less than 100 percent, preferably less than 50 percent and ordinarily less than 30 percent, of the weight of the polymer used.

As mentioned hereinafter, this invention contemplates the use of a molten substance in the form of fluid droplets of the polymer instead of a solution of the polymer. However, the coexistence, albeit in a small quantity, of a positive solvent in the “high-pressure region" under high-temperature and high-pressure conditions gives rise to the possibility of the existence of the polymer within the liquid droplets in a swollen state or the form of a solution to some extent. Accordingly, according to this invention the term "polymer droplets" is intended to include the case of a solution of the polymer.

4. Extensibility of the range of usable solvents

By the conventional spinning process wherein a spinning solution is ejected into a low-pressure region, it has not been feasible to use a solvent of high boiling point because of difficulties relating to the blowing force and the removal of residual solvent.

By the practice of this invention, however, high-boiling-point solvents can also be used. Even if a high-boiling-point solvent remains within the product polymer, it can removed with relative ease by washing the product with water containing an emulsifier. The emulsified liquid containing a small quantity of the solvent and formed during this washing can be effectively utilized as a starting material for the preparation of a polymer emulsive liquid.

5. Hydrophilic property

In accordance with a preferred embodiment of this invention, an emulsifier is used for preparing a stable polymer disperse system.

This emulsifier and the water-sorption material used remains within the polymer even when water evaporates in the low-pressure region. Accordingly, the fine fibrous structure obtained in this case has excellent hydrophilic property and has ample water-dispersibility even without the addition of a dispersing agent. Furthermore, this fibrous structure is not accompanied by problems such as foaming and can be readily sent to the
succeeding process steps of macerating or beating and paper making. Furthermore, the fibers of this fibrous structure can be used to make synthetic papers having excellent “water wettability” which was unattainable in the prior art.

1. Materials: Linear Polymer
   For the polymer to be used in accordance with this invention, any linear polymer capable of forming fibers can be used. For full utilization of the molecular orientation effect, a crystalline polymer is desirable. Furthermore, in view of the fact that this polymer is mostly placed in the state of an aqueous disperse system under pressurized and heated conditions, and in consideration of hydrolysis which may occur, it may be said, if a choice is to be made, that a polymer produced by polyaddition is preferable to a polymer produced by polycondensation.

Examples of such linear polymers are polyolefin resins, polychloroethylene resins, polyvinyl aromatic resins, polyamide resins, polyester resins, polyimide resins, and polycarbonate resins, as homopolymers and copolymers. Of these, polyolefin resins such as homopolymers of ethylene, propylene, and butene-1; copolymers of at least two of the monomers of ethylene, propylene and butene-1 such as ethylene-propylene copolymers; copolymers, wherein said monomer or monomers are predominant constituents, of said monomers with other monomers copolymerized therewith such as ethylenevinylacetate copolymers, ethylene-acrylate copolymers; and mixtures of said polymers, are representative, and among these, isotactic polypolypropylenes and high-density polyethylene are most typical. These polymers can be used singly or as mixtures thereof.

Water-sorption agent

Another important feature of this invention is the fine watersorption agent caused to exist within the droplets of the molten polymer in the aqueous disperse system.

The water-sorption agents usable according to this invention may be broadly classified into water-soluble materials a) and materials b) which are difficult to dissolve or are insoluble in water and which sorb, namely adsorb or absorb water. These agents may be materials which decompose when they contact water which has infiltrated into the droplets of the molten polymer in the “high-pressure region”.

a. Water-soluble materials

Inorganic compounds and organic compounds which dissolve in water or which dissolve water in the “high-pressure region” are usable.

Specific examples of usable water-soluble materials are inorganic materials such as nitrates, acetates, sulfates, sulfites, carbonates, phosphates, hydroxides, and halides of alkali metals, alkali earth metals, and ammonium and complex salts or double salts thereof, as, for example, NaNO₃, CH₃COONa, MgSO₄, Na₂CO₃, NaH₂PO₄, NaOH, NaCl, and (NH₄)₂Al(SO₄)₂, and organic water-soluble materials such as CMC, starch, gum arabic, agar, polycrylamide, polyacrylic acid or Na salt thereof, polyethylene imine, polyethylene oxide, polyvinyl pyrrolidone, and polyvinyl alcohols. While liquid materials such as ethylene glycol and glycerine are also effective, it is difficult to blend these substances to a high concentration.

Of these compounds, particularly salts having water of crystallization as, for example, MgSO₄·7H₂O, Na₄SO₄·10H₂O, and Na₂SO₄·7H₂O, exhibit pronounced effectiveness in forming fine fibers. The transformation of the polymer into fine fibers is accomplished by the expansion of the water enclosed within the polymer droplets and by the stretching effect of the water outside of the droplets, as mentioned hereinbefore. The splitting force of the polymer droplets when a salt having water of crystallization is used is equal to the splitting force of an expanding organic solvent in the case where a solution of the polymer in the organic solvent is spun by ejection into a low-pressure region.

That is, one percent by volume of the water within the polymer droplets in the process of this invention corresponds to one percent by volume of the solvent in the process wherein an organic solvent solution of polymer is used. Thus, by the practice of this invention, the same effectiveness in forming fine fibers as in the conventional method of flash spinning a polymer solution through the use of an organic solvent of lower boiling point than water is attained. This is an important feature of this invention.

b. Water-insoluble material

Inorganic materials and organic materials which, although incapable of being dissolved in water or of dissolving water in the “high-pressure region,” adsorb or absorb water.

In this case, since the quantity of the water enclosed within the polymer droplets is small, the splitting effect decreases somewhat, but the fibration in the beating process step is facilitated by the material remaining in the fine fibers. Accordingly, the fine fibers finally obtained are identical to five fibers obtained by blending a water-soluble material.

Specific examples of usable water-insoluble materials are inorganic and organic “fillers” such as calcium carbonate, water-insoluble solids comprising silicates such as clays (Kaoline, Pyrophyllite), white carbon (or silica amorphous), talc Mica, Fuller earth, and diatomaceous earth (or siliceous marl), basic magnesium carbonate, cellulose powder and pulp, and hydrates which are difficult to dissolve in water such as magnesium oxalate and magnesium phosphate. For sorption of water in large quantity, porous substances are particularly effective.

Positive solvent

In order to disperse the linear polymer in a stable manner as fluid droplets in molten state in a water phase and, moreover, to facilitate the infiltration of water into the fine water-sorption agent within the polymer droplets in the aqueous disperse system, a solvent, more specifically, a positive solvent, is preferably used.

The term “positive solvent” is herein used to designate a solvent in which the given molten polymer is at least partially soluble under the temperature and pressure conditions of the “high-pressure region”. Accordingly, this solvent may or may not have a positive characteristic of this nature in the “low-pressure region” or under the conditions of room temperature and atmospheric pressure. In general, however, this solvent is probably capable of causing the given solid polymer to at least swell at least under heating.

Solvants capable of promoting the infiltration of water (and an emulsifier) into the droplets of molten polymer are all usable. For example, with polyolefin polymers, aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, and the like, such as, for example, n-pentane, n-
hexane, n-heptane, cyclopentane, cyclohexane, dichloromethane, benzene, toluene, xylenes, decalin, tetralin, napthalene, are used singly or as mixtures.

Emulsifier

In accordance with a preferred mode of practice of this invention, the aqueous disperse system is an aqueous emulsive liquid or aqueous emulsion of molten polymer prepared by the use of an emulsifier. Any emulsifier is usable provided that it is capable of forming a stable emulsive liquid in the "high-pressure region." Accordingly, a suitable emulsifier may be selected from those generally sold on the market.

Specific examples of suitable emulsifiers are non-ionic, anionic, cationic, amphoteric, and surfactants used singly or as mixtures.

In the resulting aqueous emulsive liquid or aqueous emulsion of polymer, the polymer may be present in the form of fine particles or of larger or agglomerated particles.

2. Polymer aqueous disperse system

In the practice of this invention, use is made of a special polymer aqueous disperse system. More specifically, the droplets of the molten polymer contain a fine water-sorption agent, which makes possible the enclosure of water therewithin.

As mentioned hereinbefore, this enclosed water exists as a dispersed phase within the continuous phase of molten polymer or exists in a state wherein it is communicating with the outside of the polymer droplets because of the consolidation of this dispersed phase. Whichever state this enclosed water assumes is determined by the quantity of the enclosed water. On one hand, this quantity of the enclosed water is determined by the quantity of the water-sorption agent within the polymer droplets.

More specifically, when the (water + water-sorption agent) content within the droplets is up to the order of approximately 60 percent, the former state is assumed, and the enclosed water exists as independent cells. When this content exceeds approximately 60 percent and is of a value up to approximately 80 percent, the enclosed water exists in the latter state.

The lower limit of the content of the water-sorption agent is approximately 20 percent, preferably approximately 30 percent. The above stated percentages are by weight. While this enclosed water is composed principally of water, it ordinarily contains the water-sorption agent and the emulsifier.

The aqueous dispersion of molten polymer of this character can be prepared, in general, by any method by which the desired disperse system can be prepared. That is, it is desirable to make a stable disperse system and, moreover, to prepare it in the form of an aqueous emulsive liquid by using an emulsifier and a positive solvent relative to the polymer thereby to facilitate the infiltration of water into the droplets of molten polymer.

Examples of suitable methods for preparing the aqueous disperse system of the molten polymer are set forth below.

1. Preparatory forming method

1.1 Preparatory mixing

First, the polymer and the water-sorption agent are uniformly blended beforehand by an ordinary method wherein additives such as a pigment, a filler, a stabilizer against oxidation, an antistatic agent, and a reinforcing agent are blended with a thermoplastic polymer. For this blending, a mixing machine such as an extruder, kneader, rolls, a Banbury mixer, and a co-kneader is used.

While the polymer blend after mixing may be in the state of lumps, granules, fine powder, and other forms, it is preferably in a fine powder form of an average particle diameter of from 50 to 300 microns. If the particles are made excessively fine, however, the dropping-out phenomenon of the mixed materials will tend to become remarkable, whereby care must be exercised with respect to this tendency.

Blending with the solvent is also effective particularly for elevating the degree of mixing. Furthermore, as a special mixing method the water-sorption agent and the fine polymer powder to be mixed may be formed in a semi-molten state under a high pressure into a lumpy substance.

1.2 Forming the aqueous disperse system

The polymer blend after mixing is caused to be suspended in an emulsive liquid prepared by emulsifying a small quantity of a positive solvent in water. The suspension thus formed is heated to a temperature above the melting point of the polymer and subjected to a pressure above the critical pressure of this emulsive liquid system.

The action of the solvent and the emulsifier causes water to infiltrate into the interior of the polymer droplets to dissolve the admixed water-sorption agent or be adsorbed on the water-sorption agent to be captured within the polymer. In addition, with this water as a nucleus, a portion of the water is caused by the positive solvent and the emulsifier to penetrate into the interior of the polymer droplets.

In this manner, water is a quantity corresponding to the volume or sorbed quantity of the admixed water-sorption agent and the quantity of infiltration due to the action of the positive solvent and emulsifier is held within the polymer droplets.

Particularly in the case of a blend of the polymer in the state of a fine powder, the molten polymer undergoes recombination enclosing excess water existing on the outer peripheral surface, whereby polymer droplets are formed. Furthermore, the capillaries produced at the time of water infiltration are closed by variations in the system conditions such as pressure and temperature, whereby independent cells can be formed.

2. Direct forming method

In this method, the enclosure of water and water-sorption agent existing at the outer periphery due to mutual refusion of polymers is utilized.

A water-sorption agent which is difficult to dissolve in water and a polymer powder are suspended in an emulsive liquid comprising water, a positive solvent, and an emulsifier, and the resulting suspension is heated and pressurized to a high temperature above the melting point of the polymer and above the saturated vapor pressure of the emulsive liquid.

A small quantity of the water is caused by the action of the positive solvent and emulsifier in the emulsive liquid to infiltrate into the interior of the polymer droplets. At a temperature above its melting point, the polymer undergoes coupling in a state wherein it is enclosing water and the water-sorption agent existing at the outer peripheries of the fine polymer particles, whereby an aqueous disperse system of molten polymer in a state similar to that in the case (1.1) where preparatory mixing is carried out. In the instant case, the finer
and more porous the polymer powder is, the better is the resulting droplet structure, i.e., the formation of the enclosed water cells.

In all of the above described methods, pigments, reinforcing agents, stabilizers, and other additives for polymers may be added to the polymer. Furthermore, this polymer aqueous disperse system may contain other auxiliary ingredients depending on the necessity. For example, in addition to the above mentioned emulsifier, water-soluble salts, water-soluble polymers, and other additives can be added for the purpose of adjusting characteristics such as the viscosity and the stability of the emulsive liquid and for other purposes. The water-soluble polymers can be removed by washing from the resulting fine fibrous structures or rendered insoluble in water.

Furthermore, other materials such as fine fillers and blowing agents can be added. In the case where this disperse system is an aqueous suspension, a suspension stabilizer can be used.

The composition of this aqueous disperse system of a polymer is preferably as follows. The polymer concentration within the disperse system is from 5 to 70 percent, preferably from 20 to 30 percent. The quantity of the water-sorption agent relative to that of the polymer is from 20 to 80 percent, preferably from 30 to 50 percent. The quantity of the positive solvent relative to that of the polymer is greater than zero percent and of a value less than 100 percent, preferably less than 50 percent and ordinarily less than 30 percent. The above stated percentages are all by weight. When an emulsifier is used, its content in the aqueous disperse system (emulsive liquid) of the polymer is of the order of less than a number of percent.

3. Spinning

The “high-pressure region” in which the above described aqueous disperse system of the molten polymer initially exists should be at a temperature sufficient for the existence therein of the polymer as droplets in molten state. Furthermore, since this aqueous disperse system should exist as a disperse system, this temperature should be below the critical temperature of the disperse system, and, at the same time, the pressure of the region should be at a value above the saturated vapor pressure of the water (and solvent) at that temperature.

Since the blowing action of water is principally utilized in the practice of this invention, the temperature and pressure conditions of the “high-pressure region” are selected with consideration of their relationships with the pressure and temperature conditions of the “low-pressure region”. Accordingly, in the case where the “low-pressure region” is at atmospheric pressure, for example, the blowing action of the water does not become sufficient at a temperature of the “high-pressure region” of less than 130°C.

In order to apply or sustain this pressure condition in the “high-pressure region,” any pressure-applying means can be used. However, the ordinary measure is to introduce a pressurized gas, which is preferably inert with respect to the disperse system. One example of the conditions of the “high-pressure region” is that wherein, in the case where an aqueous emulsive liquid of high-density polyethylene or polypropylene is to be ejected into a “low-pressure region” at room temperature and atmospheric pressure, fine fibers which can be used to make paper can be produced at a temperature of the order of from 180°C to 200°C and at a pressure of the order of from 50 to 60 kg/cm².

The extrusion or ejection of the aqueous emulsive liquid of the polymer from the “high-pressure region” to the “low-pressure region” may be carried out through an ejection orifice device which has a single orifice, a plurality of orifices, or orifices of slit shape or some other shape. We have found that, while an ejection velocity from the ejection orifice device is preferably above the velocity of sound (330 meters/second), a velocity of approximately one half of the velocity of sound or lower velocity may be used.

While the “low-pressure region” is ordinarily at atmospheric pressure and room temperature, it is also possible to maintain this region under reduced pressure and heated conditions in order to promote the evaporation of the liquid phase, particularly water, within the emulsive liquid.

4. Product

The fine fibrous structure thus obtained is dried directly as it is or is washed with an aqueous solution of an emulsifier and then dried, whereupon the objective product is obtained.

This fine fibrous structure can be utilized as an open-mesh or network structure, or by macerating or beating this fine fibrous structure by a dry or wet process, it can be also utilized as a staple fiber or as a starting material for paper making. According to a preferred embodiment of this invention, as mentioned hereinbefore, there are provided fine fibers of good hydrophilic characteristic which are particularly suitable for use as a starting material for paper making and, moreover, has excellent compatibility with natural cellulose pulp.

In order to indicate still more fully the nature and utility of this invention, the following specific examples of practice constituting preferred embodiments of the invention and results 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

Fifty parts of linear polyethylene of a melt index, MI, of 5 and a density of 0.956 gram/cc. in powder form and 50 parts of magnesium sulfate dried for 4 hours at a temperature of from 160 to 170°C and passing through a 40-mesh sieve were blended in a roll blender operated with a roll surface temperature of 175°C. The mixture thus blended was pelletized, and then the pellets were pulverized into a powder in a mill.

Separately, one part of a non-ionic emulsifier of a HLB 18 was dissolved in 83 parts of water, and then one part of n-pentane was added to the resulting solution to prepare a homogeneous emulsive liquid. To this liquid, 15 parts of the above described powder of the blend was added and uniformly dispersed, whereupon an aqueous mixture was obtained.

This aqueous mixture was placed in a sealed vessel, the interior pressure of which was increased to 40 kg/cm² with pressurized nitrogen. Then, as the mixture was agitated, it was heated to and at 180°C. After 50 minutes, the pressure within the vessel rose to 53 kg/cm² because of the heating. The interior of the sealed vessel was communicative through a gate valve to a slit nozzle of a width of 0.5 mm. and a length of 10 mm.
After 50 minutes, the system pressure was further increased with pressurized nitrogen to 70 kg/cm², and the gate valve was abruptly opened to eject the system mixture into the atmosphere. As a result, a mass of a fine fiber having a highly orientated structure was obtained.

EXAMPLE 2

Fifteen parts of a linear polyethylene of MI of 5 and a density of 0.965 gram/cc. was dissolved at a temperature of from 120° to 140°C in 70 parts of xylene. To the resulting solution, 15 parts of sodium chloride dried for 4 hours at a temperature of from 160° to 170°C and passing through a 40-mesh sieve was added while the solution was vigorously agitated.

After thorough agitation, the resulting mixture was poured gradually into methyl alcohol to cause a blend of the polyethylene and sodium chloride to precipitate. This precipitate was lightly pulverized in a mixer to obtain a blend in powder form, which was then washed from 2 to 3 times with methyl alcohol to remove the xylene. The resulting mass was then dried at 60°C for 24 hours for complete removal of the solvents.

15 parts of the blend thus obtained was added to an emulsive liquid comprising 81 parts of water, 3 parts of n-pentane, and 1 part of a non-ionic emulsifier of a HLB 14 thereby to form an aqueous mixture, which was then processed in accordance with the procedure set forth in Example 1. As a result a three-dimensional network structure of fibers each having a high degree of orientation was produced.

EXAMPLE 3

Fifty parts of a linear polyethylene of a MI of 5 and a density of 0.965 gram/cc. and 50 parts of a clay dried for 4 hours at a temperature of from 160° to 170°C and consisting of particles of an average diameter of 5 microns were blended in a roll blender and then pulverized.

15 parts of the resulting blend was added to an emulsive liquid comprising 81 parts of water, 3 parts of n-pentane, and one part of a non-ionic emulsifier of a HLB 14 to form an aqueous mixture, which was processed according to the procedure specified in Example 1. As a result, a fine fibrous structure was produced.

EXAMPLE 4

Fifty parts of an isotactic polypropylene of a MI of 9 in powder form and 50 parts of magnesium sulfate dried for 4 hours at a temperature of from 160° to 170°C and passing through a 40-mesh sieve were blended by means of a roll blender operated with a roll surface temperature of 210°C. The mixture thus blended was pelletized and then pulverized into a powder in a mill.

Separately, a homogeneous emulsive liquid was prepared by dissolving one part of a non-ionic emulsifier of a HLB 18 in 83 parts of water and then adding one part of heptane to the resulting solution.

To this emulsive liquid, 15 parts of the above described blended powder was added to form an aqueous mixture, which was then processed for 50 minutes in an autoclave at 180°C and 50 kg/cm² pressure and then ejected into the atmosphere. As a result, a fine fibrous structure having stiffness was produced.

EXAMPLE 5

Seventy parts of Nylon-6 and 30 parts of sodium sulfite dried for 4 hours at a temperature of from 160° to 170°C were granulated at a maximum temperature of 270°C by means of a 45 mm φ extruder, and then the resulting granules were pulverized.

Separately, a homogeneous emulsive liquid was prepared by dissolving one part of an anionic surfactant of a HLB 18 in 83.5 parts of water and then adding 0.5 part of cresol to the resulting solution.

In this emulsive liquid, 15 parts of the above described powder was uniformly dispersed to form an aqueous mixture. This mixture was placed in a sealed vessel, the interior pressure of which was increased with pressurized nitrogen to 40 kg/cm², and the aqueous mixture was heated to and at 240°C as it was agitated.

After 60 minutes, the pressure within the vessel had increased to 65 kg/cm², at which point a discharge valve of the vessel was abruptly opened to eject the aqueous emulsive liquid of the polymer into the atmosphere. As a result, fine fibers having a highly orientated and fibrillated structure of substantial stiffness were produced.

EXAMPLE 6

Fifteen parts of the blended mixture of a polyethylene and magnesium sulfate prepared according to Example 1 was added to a solution prepared by dissolving one part of an anionic surface-active emulsifier of a HLB 12 in 84 parts of water thereby to form an aqueous mixture in which the blended mixture was uniformly dispersed.

This aqueous mixture was placed in a sealed vessel, and the pressure within the vessel was increased with pressurized nitrogen to 45 kg/cm². The aqueous mixture was then heated to and at 180°C as it was agitated.

After 120 minutes, the vessel interior pressure had risen to 55 kg/cm², at which point a discharge valve of the vessel was opened to discharge the polymer aqueous emulsive liquid into the atmosphere. As a result, a foamed structure having as a major part, uniform cells foamed from 5 to 10 times and, as one part, fine fibers having a fibrillated structure.

EXAMPLE 7

A homogeneous aqueous suspension was prepared by dissolving 2 parts of an anionic surface-active emulsifier of a HLB 18 in 35 parts water and adding to the resulting solution 25 parts of calcium carbonate and 40 parts of an isotactic polypropylene of a MI of 5 in pelletized form.

This suspension was placed in a sealed vessel and, after the pressure within the vessel was raised to 45 kg/cm² with pressurized nitrogen, was heated to and at 180°C under agitation. After 120 minutes, the pressure within the vessel had increase to 55 kg/cm², at which point, a discharge valve of the vessel was opened to discharge the suspension into the atmosphere. As a result, fine fibers having a fibrillated structure and stiffness were produced.

We claim:

1. A process for producing fine fibrous structures which comprises the steps of:
   1. preparing a heterogeneous aqueous dispersion system comprising a molten polyolefin dispersed therein in a quantity of from 5 to 70 percent by weight of the aqueous dispersion system, water, and a substantially water-immiscible positive sol-
vent for the polymer, said molten polyolefin containing water and a fine water-sorption agent which is inherently solid in a quantity of from 20 to 80 percent by weight of the polyolefin; said positive solvent being in a quantity of less than 50% by weight of the polymer, at least a part of which is present within the molten polyolefin, and

2. passing said aqueous dispersion system from a high-pressure region at a temperature above the melting point of the polymer and below the critical temperature of said aqueous dispersion system and at a pressure above the saturated vapor pressure of said system into a low-pressure region at a temperature and pressure at which the liquid phase within the dispersion system can evaporate thereby to produce a fine fibrous structure of the polymer.

2. A process according to claim 1, wherein the positive solvent is selected from the group consisting of n-pentane, n-hexane, n-heptane, cyclopentane, cyclohexane, dichloromethane, benzene, toluene, xylene, deca-lin, tetralin, naphthalene, and mixtures thereof.

3. A process according to claim 1 wherein the positive solvent is present in a quantity of less than 30% by weight of the polymer.

4. A process according to claim 1 wherein the molten polyolefin is selected from the group consisting of high density polyethylene and high density polypropylene and the heterogeneous aqueous dispersion system is passed from a high pressure region in which the pressure range is between 50 to 60 kg/cm² and the temperature is between 180° to 200°C to a low pressure region in which the pressure is atmospheric pressure and the temperature is room temperature.

5. A process for producing fine fibrous structures as claimed in claim 1 in which the aqueous dispersion system is prepared by blending the fine water-sorption agent with the polymer in a molten or solution state, suspending the resulting blend in an aqueous emulsion, and heating and pressurizing the resulting suspension to and at a temperature above the melting point of the polymer and a pressure above the critical pressure (Saturated Vapour Pressure) of the suspension.

6. A process for producing fine fibrous structures as claimed in claim 1 in which the aqueous dispersion system is prepared by suspending a fine water-sorption agent which substantially does not dissolve in water and the polymer in powder form in an aqueous emulsion of the positive solvent and heating and pressurizing the resulting suspension to and at a temperature above the melting point of the polymer and a pressure above the critical pressure of the suspension.

10. A process for producing fine fibrous structures as claimed in claim 1 in which the aqueous dispersion system is prepared by blending the fine water-sorption agent with the polymer in a molten or solution state, suspending the resulting blend in an aqueous emulsion, and heating and pressurizing the resulting suspension to and at a temperature above the melting point of the polymer and a pressure above the critical pressure of the suspension.

11. A process for producing fine fibrous structures as claimed in claim 1 in which the concentration of the polyolefin in the dispersion system is from 5 to 70 percent by weight relative to the quantity of the dispersion system.

12. A process for producing fine fibrous structures as claimed in claim 1 in which the polyolefin is a member selected from the group consisting of homopolymers of ethylene, propylene, and butene-1; copolymers of at least two of the monomers ethylene, propylene, and butene-1; copolymers, wherein said monomers are predominant constituents, of said monomers with other monomers co-polymerizable therewith; and mixtures of said polymers.

13. A process for producing fine fibrous structures as claimed in claim 12 in which the aqueous dispersion system is prepared through the use of a surfactant selected from the group consisting of nonionic surfactants and anionic surfactants, said surfactants being water-soluble and capable of forming an emulsive liquid in the high pressure region.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,914,354 Dated October 21, 1975

Inventor(s) Shiro Ueki et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

First (title) page, Col. 1, in the line designated "[73]", relating to the assignee's name, change "Oki" to -- Oji --.

Signed and Sealed this

ninth Day of March 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks