United States Patent [19]

Kato et al.

[11] **3,891,499**

[45] **June 24, 1975**

[54] **SYNTHETIC PAPERMAKING PULP AND PROCESS OF MANUFACTURE**

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[21] Appl. No.: **257,609**

[30] **Foreign Application Priority Data**

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Dec. 28, 1971 Japan 46-105654

[52] **U.S. Cl.** ..... **162/157 R**; 264/13; 264/205
[51] **Int. Cl.**[2] **D21F 11/00**
[58] **Field of Search** ..... 162/157 C, 157 R, 146; 264/5, 13, 14, 121, 205

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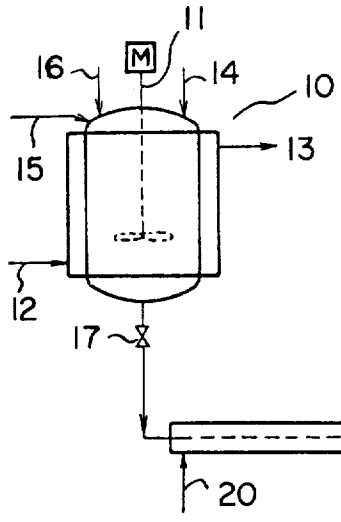
Assistant Examiner—Peter Chin
Attorney, Agent, or Firm—Corwin R. Horton; Stanley M. Teigland; Robert E. Howard

[57] **ABSTRACT**

A pulp of synthetic polymer fibers useful for papermaking. The fibers have the appearance of rolled or folded sheets at a magnification of about 500X and are distinct from one another, being only mechanically intertwined. The fibers are of papermaking size, no more than about 10 percent by weight of the fibers being retained on a 20 mesh screen but at least about 25 percent by weight are retained on a 65 mesh screen. The pulp has a drainage factor greater than about 0.2 seconds/gram and a compressibility constant N greater than about 0.2. The pulp is preferably formed of high molecular weight polyethylene or polypropylene. Also, a process for forming polymer fibers comprising forming a solution of a crystalline polymer in a solvent at a temperature above the melt dissolution temperature of the polymer, passing the polymer solution through a precipitation zone into a region of reduced pressure whereby a portion only of the solvent is adiabatically vaporized and the polymer is precipitated as a highly swollen fibrous mass or gel, separating the solvent vapor from the gel, and subjecting the fibrous gel to attritional forces to liberate the individual, discrete polyolefin fibers therefrom.

1 Claim, 7 Drawing Figures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M
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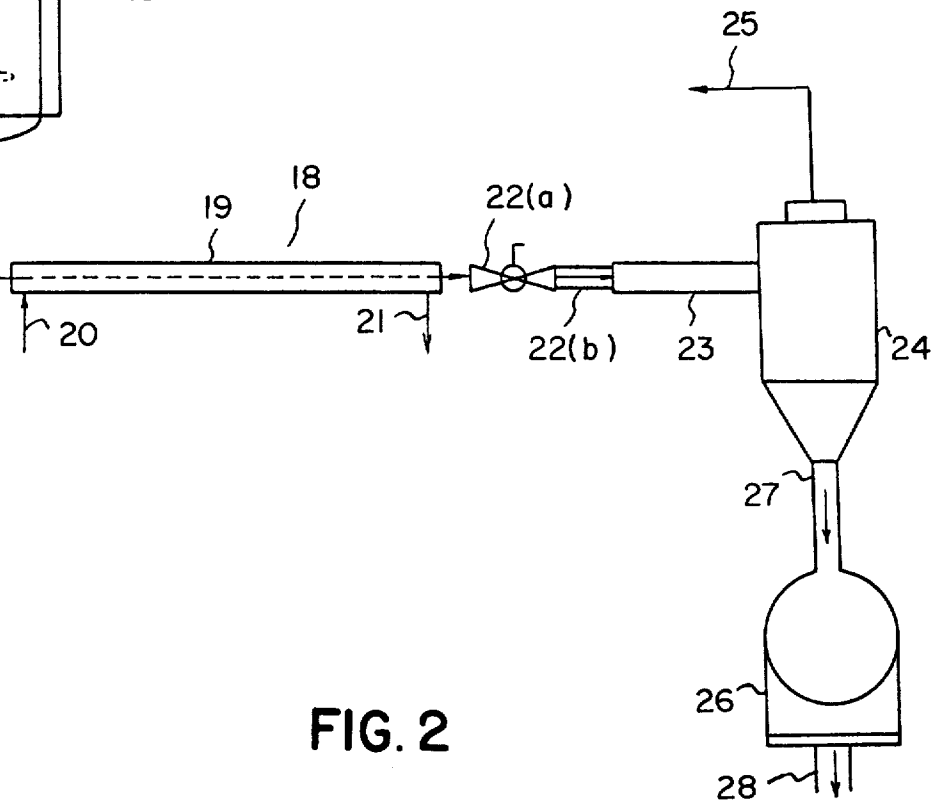
FIG. 1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18
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22(a)
20
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22(b)
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26
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FIG. 2

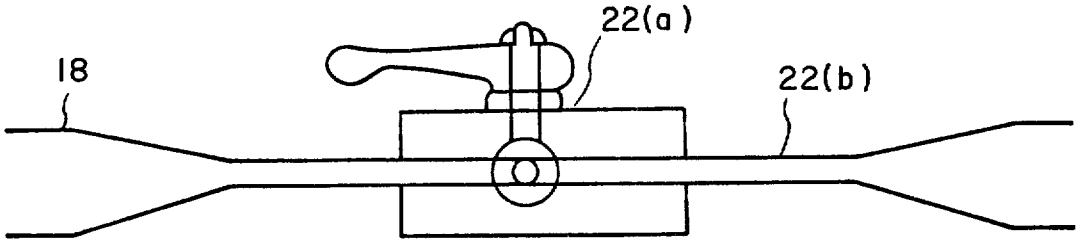
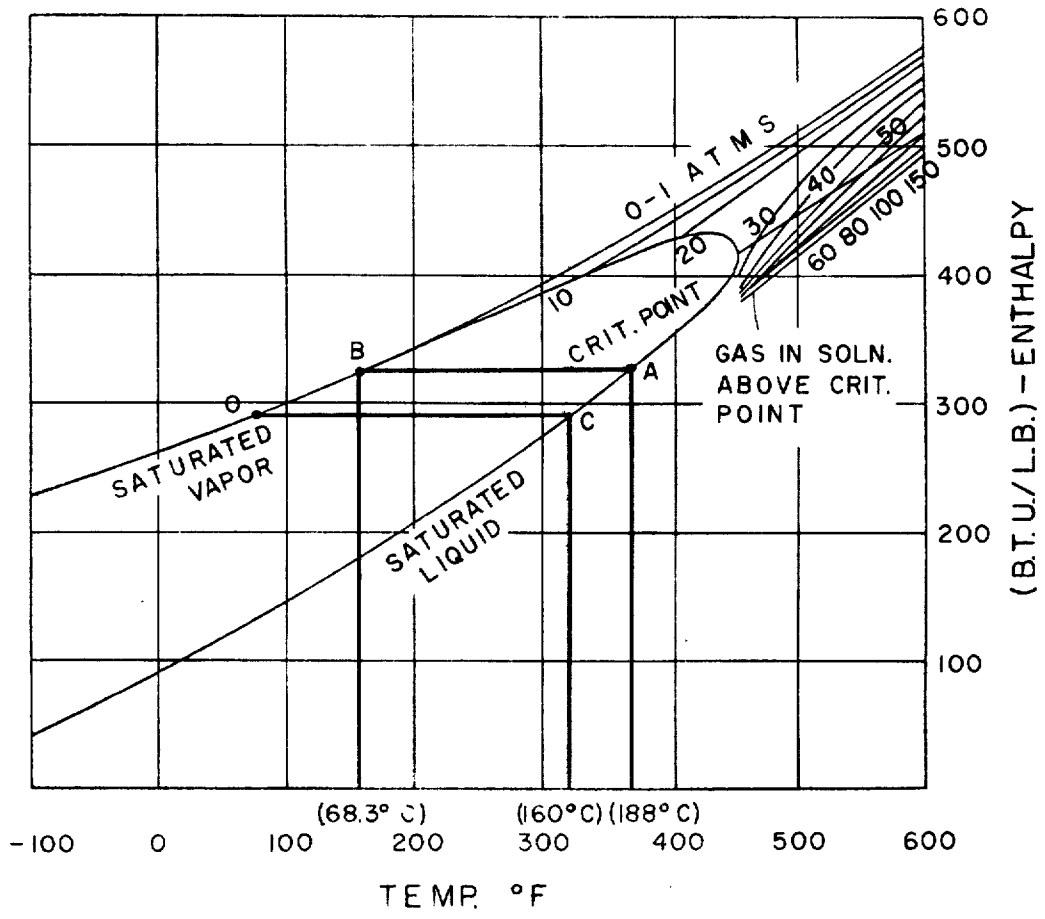

22(a)
18
22(b)

FIG. 3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500
400
300
200
100
(B.T.U./L.B.) - ENTHALPY
0-1 ATMS
10
20
30
40
50
60 80 100 150
CRIT. POINT
GAS IN SOLN. ABOVE CRIT. POINT
A
B
C
D
SATURATED VAPOR
SATURATED LIQUID
(68.3° C)
(160° C)
(188° C)
-100
0
100
200
300
400
500
600
TEMP. °F

FIG. 4

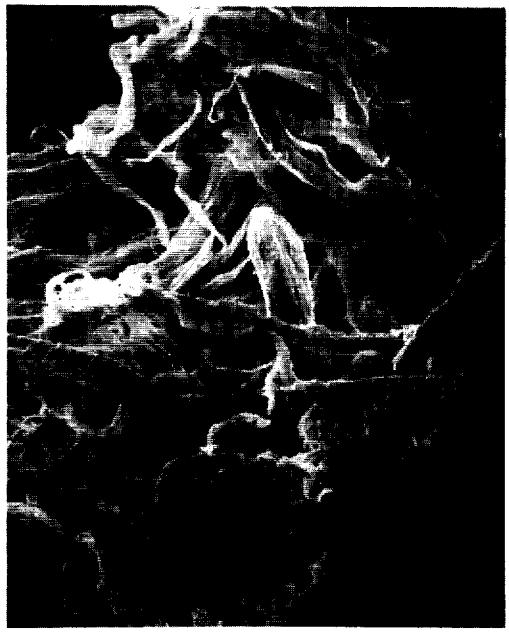


FIG. 5

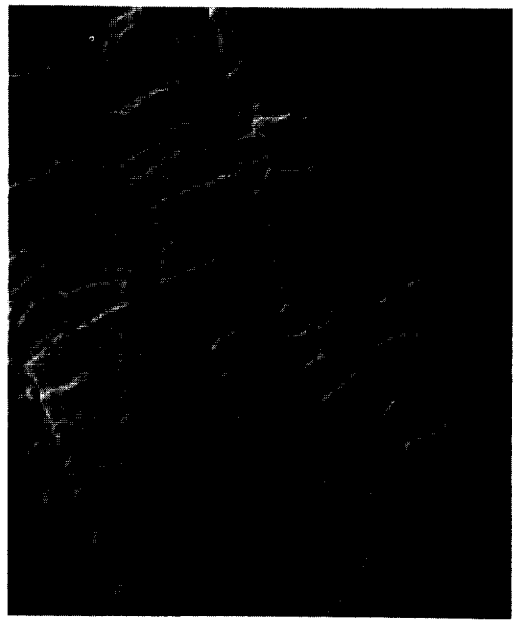


FIG. 6

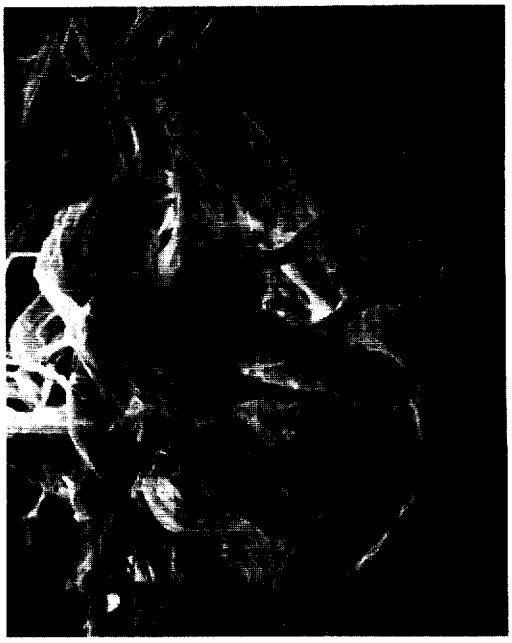
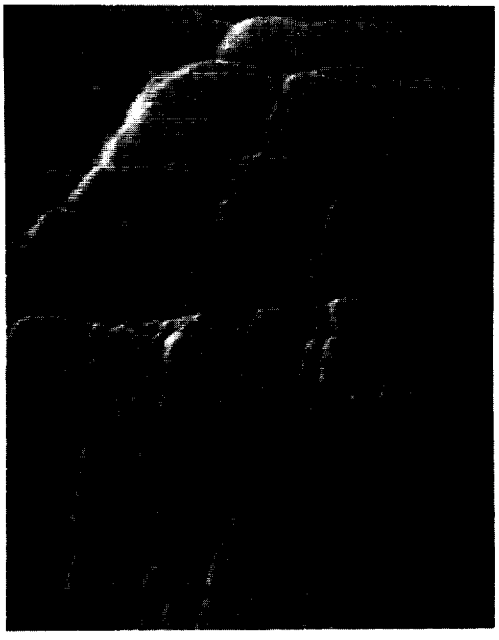


FIG. 7



SYNTHETIC PAPERMAKING PULP AND PROCESS OF MANUFACTURE

BACKGROUND OF THE INVENTION

This invention relates to a synthetic pulp for making paper and similar products. The invention provides a novel pulp of olefin polymers, and provides also a method of making a synthetic paper-making pulp from an olefin polymer.

Paper is traditionally made from a pulp of cellulose fibers (primarily wood fibers); in idealised form a cellulose fibre in papermaking pulp comprises a longitudinally extending body of roughly circular cross-section, having a length typically in the range 0.1 mm. to 4.0 mm. and an average diameter typically in the range 0.01–0.05 mm. from which body project fine hair-like "fibrils"; the body of the fibre is thought to be made of tightly wound fibrils, some of which are caused to project in the course of pulp preparation.

There have been many prior attempts to use synthetic polymers as a substitute for wood in papermaking. Among the earliest is the use of conventional staple fibres. Polymer staple is the product obtained by making a filament of the polymer (either by extruding a melt of the polymer through an orifice so that it cools as a continuous solid filament or by extruding a solution of the polymer into an atmosphere hot enough to evaporate the solvent and leave a continuous filament) and chopping the filament into pieces of the desired length. Staple fibres are produced for use mainly as textile fibres, and do not make good paper; staple fibres are essentially smooth-surfaced cylinders.

There have been proposals to make synthetic fibres having a structure more elaborate than the structure of staple, and some of these structures appear to give a better paper than staple.

For example, the so-called "plexifilaments" described in British Patent Specification No. 891,943 and German Patent Specification No. 1,292,301 are made up of very thin (less than 2 μ) film or ribbon-like structural units which are interconnected to form a unitary three-dimensional network; this filamentary structure comprises a plexus composed of film-like or ribbon-like elements which unite and separate at random intervals.

Another structure of fibres for paper-making is disclosed in German laid-open Specification No. 21 21 512. This is described as consisting of interior fibrils which converge, while the number of outside fibrils is small; this is alternatively described as a bundle of fibrils, bands or threads.

Both plexifilaments and the fibres of German Specification No. 21 21 512 are made by flash evaporation of a heated, pressurised liquid containing dissolved polymer; in the case of plexifilaments a hot solution under pressure is expanded through a nozzle into a lower pressure zone so that all the solvent flashes off to cause bubble nucleation, while according to German Specification No. 21 21 512 a hot aqueous emulsion containing a polymer solution as disperse phase is similarly flashed to evaporate the solvent.

The polymer precipitated from its solution on flash evaporation of the solvent appears to be basically in thin sheet form in both the foregoing procedures.

Other processes of flash evaporation of solvent from a solution of polymer have been described in German Patent Specifications Nos. 1,958,609 and 1,951,609;

though the products of those processes have been less clearly described, they also appear to have a sheet as their basic unit. The product of German Specification No. 1,958,609 appears to consist of micro-flakes which are loosely aggregated, so that the micro-flakes can be de-aggregated in an organic solvent, whereby there is obtained a suspension of flakes in solvent which suspension is made into paper. The product of German Specification No. 1,958,609 contains fibre-like elements which are fused at their ends, like plexifilaments.

None of the foregoing products is commercially satisfactory as a paper-making material in substitution for wood-pulp. The object of this invention is to provide a polymeric substitute for wood-pulp, and we have achieved this by directing attention to not only the individual fibre structure, but the collection of fibres as a whole.

DETAILED DESCRIPTION OF THE INVENTION

We have invented a pulp useful for papermaking based on sheets of the polymersuch as are formed by flash evaporation of a solution of the polymer, which makes very good paper. In our pulp, the fibers are rolled or folded thin films or sheets which are in the form of rolls or tubes, and these rolls or tubes are distinct from each other so that instead of extending in bunches in the same general longitudinal direction, they extend in random directions relative to each other and are mechanically intertwined rather than bonded together at crossover points and can be separated from one another by pulling apart. This random orientation of longitudinally extending rolls of polymer sheet or fibers is seen best at a magnification of 500X or 1000X, and to facilitate appreciation of this structure which we find to give uniquely satisfactory properties we refer to FIGS. 4 to 7 of the accompanying drawings which are electron micrographs at 500X and 10,000X of the products obtained respectively in Example 1 and in Example 3 run 5 of the following description.

In FIG. 4 there can be seen in the foreground a number of rolls extending from side to side of the picture, not joined to each other, and behind them other distinct rolls which extend from top to bottom. The ends of some of these rolls are clearly visible. Similarly in FIG. 6 there can be seen rolls of polyolefin film, the ends of some of the rolls being visible, and as in FIG. 4 the significant feature of these rolls is that, while each has its own longitudinal direction, the longitudinal directions of the rolls are criss-cross.

The fibers, or rolls of polymer sheet, may be convoluted or intertwined in the pulp of our invention, but the fact of being convoluted indicates that they are distinct fibers or rolls. (By "convoluted", we mean that one fiber or roll and another are wound longitudinally as loose helices around each other).

Thus the present invention provides a synthetic pulp for paper-making comprising a polymer in the form of thin films produced by flash evaporation of solvent from a solution of the polymer, characterised in that the thin film is in the form of longitudinally extending rolls which are distinct from one another, the longitudinal directions of adjacent rolls being different from each other.

In our pulp, it is preferred that the surfaces of a large number of the separate rolls in any given sample of pulp exhibit a "shark-skin" texture. A shark-skin texture is a succession of wrinkles or corrugations parallel

to each other and transverse to the longitudinal direction of the roll. A pulp containing few fibers or rolls with little or no shark-skin texture can be a good pulp for paper-making, but we find that a pulp wherein there are many shark-skin-surfaced fibrous elements is particularly good. We prefer a special form of shark-skin surface in which there are grooves or valleys which extend in the direction of the roll and wrinkles which extend, transversely of the roll, between the grooves. The shark-skin texture may however degenerate to a pebbled texture; both shark-skin surface and pebbled surface appear to contribute to the valuable properties of the fibres and are a preferred secondary characteristic of our pulp. The preferred shark-skin surface is shown in FIGS. **5** and **7**, which shows the central area of the micrographs of FIGS. **4** and **6** respectively at twenty times greater magnification, i.e, at 10,000X.

The thin sheet or film of the fiber or roll can be at least partially unrolled by an ultrasonic probe, and has an uneven thickness that is generally between about 1 and 10 microns.

Thus the pulp of this invention can be recognised by its "course" morphology of separate, randomly oriented rolls of thin film which is visible at a magnification of 500X, and its "fine" morphology of a shark-skin surface visible at a magnification of 10,000X.

A majority (by weight) of the fibers that may be produced in accordance with this invention for use in papermaking have average lengths (as measured by TAPPI Test T232 SU68) between about 0.3 mm. and 10 mm. and preferably between about 1.0 mm. and 5.0 mm. If the fibers are longer than about 5.0 mm., the danger of flocculation during papermaking increases. Stated another way, less than about 10 percent by weight of the fibers are retained on a 20 mesh Tyler Standard screen, but at least about 25 percent by weight are retained on a 65 mesh screen and, preferably, at least about 25 percent are retained on a 35 mesh screen.

A majority (by weight) of the fibers that may be produced in accordance with this invention have a diameter between about 0.01 mm., 0.10 mm. and preferably between about 0.01 mm. and 0.03 mm.

Since the diameter of individual fibers varies along the length thereof, it is sometimes more convenient to characterize the slenderness of the fibers by reference to their coarseness.

A majority (by weight) of the fibers of the present invention have an average coarseness (as measured by TAPPI Test T234 SU67) between about 1 and 5 decigrex (mg/100m) and typically between about 3.5 and 5 decigrex. Fibers having a coarseness larger than about 5 decigrex have increasingly poor drainage characteristics which makes them less suitable for papermaking.

The gas adsorption surface area of the fibers of the present invention is greater than 1.0 m^2/gram. Typically, the gas adsorption surface area will range as high as about 30 m^2/gram for steam stripped or solvent exchanged (through isopropanol to water from the solution solvent) fibers and as high as 200 m^2/gram for fibers freeze dried from the solution solvent.

The hydrodynamic surface area of the fibers of the present invention is greater than about 0.6 m^2/gram and typically will range between about 0.6 and 1.0 m^2/gram. This latter characteristic is more closely related to the drainage characteristics of fibers to be used in papermaking from an aqueous slurry than is the gas adsorption surface area.

Determination of hydrodynamic specific surface area is made in accordance with the procedures described in the article "The Filtration Resistance of Pulp Slurries" W. L. Ingmanson et al., TAPPI 37, No. 11: pp. 523–534 (1954). Equations 9 and 10 on pages 515 and 526 of this article were employed in determining the "hydrodynamic" surface area (S) discussed herein.

Since it is difficult and time consuming to measure the hydrodynamic surface area of fibers, their drainage characteristics can be more easily characterized by drainage time. The drainage time of the fibers produced by the present process is greater than about 5 seconds and typically between about 5 and 6 seconds. Drainage time is measured by introducing 400 ml. of a 0.5 percent consistency slurry of fibers into the standard sheet mold described in TAPPI Test T205 M-58 having a 150 mesh stainless steel wire screen in the bottom thereof and having water covering the screen prior to introduction of the fiber slurry. Water is added up to the mark in the sheet mold. The slurry is agitated by four up and down strokes of the standard stirrer. The valve on the sheet mole is opened and the water drained from the mold. The time between opening the valve and the first sound of air suction through the handsheet mat deposited on the forming screen is recorded on a stop watch and is reported as the drainage time in seconds.

A more accurate characterization of drainage characteristics, and one that is highly correlated to the hydrodynamic surface area, is the drainage factor. The drainage factor for the present fibers is greater than about 0.2 preferably greater than 0.5 and typically ranges up to 1.0 seconds/gram. This characteristic is determined substantially in accordance with TAPPI Test T221 OS-63 with a slight modification in the method of calculation. Briefly, approximately ten grams of a fiber sample is weighed and dispersed in water. The slurry is then added to the standard sheet mold and water added to the mark. The slurry is stirred by four up and down strokes of the standard stirrer, which is then removed. The water temperature in the mold is measured and the drainage valve opened. The time between the opening of the valve and the first sound of suction noted. The procedure is repeated with water only (no fiber) in the sheet mold and the temperature and drainage time noted. The drainage factor in seconds per gram is then calculated as follows:

$$DF = \frac{[D + 0.3\ (\frac{1}{V_T} - 1)\ (D-4)] - [d + 0.3\ (\frac{1}{V_T} - 1)\ (d-4)]}{W}$$

where

DF = drainage factor, seconds/gram.
D = drainage time with pulp in mold, seconds.
d = drainage time without pulp in mold, seconds.
V_T = viscosity of water at temperature T.
W = weight of fibers employed in test, grams.

The quantity $(1/V_T - 1)$ is tabulated in the aforementioned TAPPI Test T221 OS-63. This quantity is multiplied by 0.3 which has been empirically determined for the present fibers.

A further measure of the drainage characteristics of fibers is the compressibility constant (N) as determined from the slope of the curve obtained in making a logarithmic plot of c versus p in the relationship.

$$c = Mp^N$$

wherein c is the apparent pad density in grams/cubic centimeters, p is the compacting pressure in grams per square centimeter, and M and N are compressibility constants. Reference is made to equation (8) on page 525 of the above cited TAPPI article by Ingmanson etal.

The compressibility constant N of cellulosic fibers is typically between 0.3 and 0.4. The compressibility constant (N) of the present fibers is greater than about 0.2 and typically between about 0.2 and 0.3.

The values given above for the various drainage characteristics, i.e., hydrodynamic surface area, drainage time, drainage factor and compressibility constant were all determined on fibers treated with 2 percent by weight polyvinyl alcohol but similar values would be expected with other water dispersing agents.

According to the present invention, there is provided a process of making polymer pulp suitable for making paper. The process of this invention, like the prior art processes discussed above, depends on flash-evaporation of solvent from a solution of the polymer. But our process calls for particular evaporation conditions followed by a further attritional treatment (refining) step which produces a pulp containing discrete fibrous elements of optimum properties.

In our process, a solution of polymer, at temperature sufficient to cause the polymer to dissolve in the solvent and at a pressure at least sufficient to keep the solvent in liquid phase at said temperature, is subjected to reduction in pressure such that part but not all of the solvent evaporates so that the polymer precipitates from solution as a highly swollen fibrous mass or fibrous gel. Thus there is formed a fibrous structure containing interconnecting capilary spaces filled with solvent. The gel should be of low enough polymer concentration to permit liberation or separation of discrete fibers by attritional forces preferably imparted by mechanical refining. After refining the fibers have the structure described above. By refining, we mean that mechanical treatment of pulp which in the paper-making industry is termed refining. The favoured instrument for refining is a disc-refiner, so in its preferred form the refining step in the process of this invention comprises passing the gel of polymer in solvent continuously through a refining space defined by mutually opposed, relatively rotating, surfaces.

Disc refiners are of two main types, "single-disc" refiners which have two coaxial discs of which one is stationary while the other rotates on the axis at a short axial spacing from the stationary disc, and "double-disc" refiners which have two coaxial discs which both rotate, in opposite senses of rotation, on the axis at a short axial spacing from each other.

Disc refiners are constructed so that the clearance between the discs can be varied, and for the refining step of our process which follows the production of a refinable gel, we prefer a clearance of between about 100 to 125 microns for the initial fiber liberation. Additional, or secondary refining of the fibers is preferably accomplished at a clearance of between about 25 and 75 microns.

A disc refiner is the preferred refining or beating apparatus for imparting attritional forces to the fibrous gel to liberate or separate discrete fibers; however, an alternative but less preferred refining apparatus is a "beater", generally known in the paper industry, as a Jordan.

Thus, in general, refining the fibrous gel consists of subjecting the gel to attritional forces in a space defined by surfaces moving relative to each other in close proximity.

In the flash evaporation of a solution, there are many operating parameters which can affect the nature of the product, and in the first, flash evaporation, step of our process these are controlled primarily to give only partial evaporation, so that at most 60 percent or perhaps 70 percent of the solvent evaporates (preferably at least 20 percent of the solvent evaporates) and a refinable gel is formed.

These parameters are:

Concentration of the solution.

A relatively dilute solution. is preferred, especially a solution containing less than 5 percent by weight of polymer. Such dilution is especially important in the case of high molecular weight polyolefins (as discussed below) in order to permit ease of handling, since a concentrated solution of high molecular weight polyolefin can have a viscosity at the solution temperature in excess of 500 cp. Even with low molecular weight polymers, however, it is also advantageous to keep the polymer concentration below 5 percent by weight, to ensure formation of a fibrous gel having the preferred polymer concentration. A polymer concentration in the range 10–20 percent may be used for lower molecular weight polymers; however this presents difficulties which will be discussed further below.

Temperature of the solution.

The solvent must of course be hot enough to cause the polymer to dissolve, i.e. above the melt dissolution temperature which depends on the solvent. Types of solvent and determination of melt dissolution temperature are discussed below. Moreover, the temperature of the solution must not be so high that the sensible heat of the solution is sufficient to evaporate more than about 70 percent of the solvent when the pressure on the solution is relieved; determination of the sensible heat is also discussed below.

Pressure on the solution.

The pressure of the solution immediately before flash evaporation is in general at least the autogeneous pressure of the solution at the given temperature, in order to have the solvent in liquid phase up to the time of evaporation. A pressure higher than the autogeneous pressure can be established by use of an inert gas in the vapor space of the solution vessel or by pumps as described below with reference to the drawings. Furthermore a small proportion of solvent may be present as vapour even before the adiabatic expansion, as this seems to cause "vapor cutting". By vapor cutting, we mean that the bubbles of vapor cut the fibrous gel noodles to more suitable lengths.

Pressure and viscosity determine speed of flow, which in turn affects shear as discussed below.

Pressure drop on evaporation.

Normally the flash evaporation is effected by discharging the pressurised solution into a zone at substantially atmospheric pressure, although slightly super-atmospheric or sub-atmospheric pressures may be employed. Simple thermodynamic calculations will determine the appropriate temperature of the solution to cause a predetermined evaporation of solvent boiling at a given pressure.

The expansion of the solution into the lower pressure zone is an adiabatic expansion wherein the heat for evaporation of the solvent is taken from the body of solution, as opposed to evaporation for which the heat is supplied from outside. It is not necessary to ensure strictly adiabatic conditions, by insulating the apparatus to prevent all heat-exchange with the environment.

Flow-rate.

The simplest and most practical way to cause sudden evaporation of part of the solvent — with consequent reduction in temperature of the solution and precipitation of polymer — is to pass the solution continuously through an adiabatic expansion nozzle. The size of the nozzle, together with the viscosity of the solution (which in turn is concentration and temperature dependent) determines the speed of flow which generally should exceed 10 meters per second and preferably is in the range 50–150 meters per second. The speed of flow should be sufficient to cause turbulence on exiting from the nozzle. Flow which is unstable but below the velocity needed for melt fracture (elastic turbulence) can produce the desirable shark-skin effect.

Desirably the flow rate is in the range 60–127 m./sec., and a flow rate of 70–90 m./sec. is found commercially useful.

The operating parameters will be selected on the principles outlined above to give fibres of the described characteristics, having regard to the polymer and to the solvent used.

Any crystallizable polymer may be used in accordance with the present invention to form a synthetic pulp provided that a suitable solvent may be found to dissolve the polymer. In particular crystallizable addition polymers, especially crystallizable polyolefins are useful. Particularly preferred are crystalline polyethylene, crystalline or predominantly crystalline (isotactic) polypropylene and crystalline ethylenepropylene copolymers. Additionally, polybutenes, polymethyl pentenes and polystyrene may be desirable polymers in the practice of this invention. Crystalline poly-amides and polyesters may be used.

The preferred crystalline polyolefin homopolymers or copolymers for papermaking purposes that may be employed are those of high molecular weight. By "high" molecular weight is meant a polyolefin having a melt index (as determined by ASTM Standard Test No. D- 1238) of less than 0.5 and preferably essentially zero. A zero melt index for high density polyethylene corresponds to a viscosity average molecular weight greater than about 100,000 ($n = 3.0$), and a zero melt index (or melt flow) for substantially isotactic polypropylene corresponds to a viscosity average molecular weight greater than about 300,000 ($n = 2.0$). Alternatively, high molecular weight is any crystalline polyolefin having an intrinsic viscosity (n) greater than about 2.0 dl/g. However, for uses other than papermaking and even for some papermaking applications, the viscosity average molecular weight employed may be as low as 30,000 to 40,000 i.e., the intrinsic viscosity (n) may be as low as about 1.0 dl/g.

The viscosity average molecular weights referred to herein are determined by first measuring the specific viscosity of the polymer in decalin at 135°C., using Ubbelohde No. 50 or 75 viscometers. The viscosity average molecular weight is then determined by the relationship

$$(n) = K M_v^a$$

where

(n) = intrinsic viscosity, and is determined from specific viscosity by the Schulz and the Blaschke equation.

K = constant, from literature ($2.74 \times K^4$ for polyethylene and 5.43×10^{-4} for polypropylene.)

a = constant, from literature (0.81 for polyethylene and 0.65 for polypropylene.)

The polymer employed in practicing the present process may have been preformed, i.e., previously prepared in the form of dried powders or pellets, or, preferably, is prepared as an integral part of the present process. It is preferred to prepare the polymer solution by a solution polymerization process. Alternatively, a slurry process may be employed and the slurry heated above the melt dissolution temperature to effect solution.

Generally, any substituted or unsubstituted aliphatic, aromatic or cyclic hydrocarbon which is a solvent for the polymer employed at elevated temperatures and pressures, which is relatively inert under the conditions of operation and which preferably has a boiling point at the pressure conditions existing after the precipitation zone (preferably atmospheric pressure) less than the softening point of the polyolefin. The solvent may be liquid or gaseous at room temperature and atmospheric pressure although it is preferred that it be liquid at such conditions as otherwise the system after the precipitation zone will have to be pressurized. Among the solvents which may be utilized are aromatic hydrocarbons, e.g., benzene, toluene; aliphatic hydrocarbons, e.g., butane, pentane, hexane, heptane, octane and their isomers and homologues; alicyclic hydrocarbons, e.g., cyclohexane, chlorinated hydrocarbons, e.g., methylene chloride, carbon tetrachloride, chloroform, ethyl chloride, methyl chloride; alcohols; esters; ethers; ketones; nitriles; amides; fluorinated compounds, e.g., fluorohydrocarbons; sulphur dioxide; nitromethane; and mixtures of the above solvents.

As mentioned previously, the temperature of the solution which is flashed to evaporate a portion only of the solvent is maintained above the melt dissolution temperature of the polymer. The melt dissolution temperature of any particular polymer in a solvent is easily determined. Low concentrations of the polymer (e.g., 0.1 and 1.0 percent by weight) are placed into the solvent in a vial, which is sealed and placed in an oil bath. The temperature of the oil bath is raised slowly (10°C/hr) until the last trace of polymer disappears. This temperature is the melt dissolution temperature. For ultra-high molecular weight (about 10 million) polyethylene at low concentration (0.1 percent by weight) in cyclohexane, the melt dissolution tempera-

ture is 118.5 + 1.9°C. For a dilute solution of high molecular weight polypropylene in cyclohexane, the melt dissolution temperature is 130°C. At higher concentrations, the melt dissolution temperature approaches the melting point of the polyolefin. Lowering of molecular weight lowers the melt dissolution temperature at a given concentration.

It is preferred to operate between the melt dissolution temperature and that temperature at which, for the solvent employed, does not cause vaporization of more than 60–70 percent of the solvent when the solution is adiabatically fed through a precipitation zone into a region of reduced pressure. Such maximum temperature for partial vaporization may be determined for any particular solvent by use of enthalpy charts. It is preferred to operate at a temperature sufficiently above the melt dissolution temperature to cause at least about 20 percent of the solvent to vaporize upon adiabatic precipitation. For n-hexane, the maximum desirable temperature for dissolving polyethylene is about 160°C., and the minimum about 120°C.

Since it is very desirable to have a polymer concentration less than about 7 percent by weight and preferably less than about 5 percent by weight in the fibrous gel as it enters the mechanical refining step, it is preferable to operate at a solution temperature which, for the solvent type and polymer concentration employed in the solution, does not cause such excessive vaporization that the polymer concentration in the gel is substantially greater than about 7.0 percent by weight and preferably less than about 5 percent by weight. some solvent may be added to the gel prior to introduction into the refiner if the consistency is greater than 5 percent by weight to obtain a polymer slurry having a consistency less than 5 percent, particularly where use of lower molecular weight polymers permits solutions containing more than 5 percent polymer concentrations to be employed. However since it is desirable for the fibers to be in an uncollapsed state and separated from each other by solvent during refining of the gel and since added solvent may not function as well in this regard as that solvent already present in the gel, it is preferable to have the polymer concentration in the gel less than about 7 percent by weight so that little additional solvent need be added and, as stated previously, it is much preferred to operate so that the gel as precipitated contains less than about 5 percent by weight polymer. It is most preferred in practice to employ a polymer consistency of less than about 2.0 percent during refining of the gel.

In summary, then, the process of the present invention for making a synthetic pulp for papermaking by discharge of a hot solution of the polymer from a zone of higher pressure into a zone of lower pressure, whereby flash evaporation of solvent is effected and polymer is precipitated, is characterized in that the discharge at constant rate is effected under parameters of solution concentration, solution temperature, and pressure of the lower pressure zone such that only part of the solvent is evaporated and so much solvent remains in the liquid phase that there is formed a gel of precipitated polymer in solvent, and further characterized by mechanical refining of the gel.

The concentration of the hot solution should be within the range 0.5 to 5 percent polymer by weight. The flow rate of the polymer solution into the reduced pressure zone is 60–120 m/sec. The proportion of solvent evaporated from the total solvent is desirably from 20 to about 70 percent; otherwise expressed, the proportion is desirably such that the ratio of evaporated solvent to residual liquid solvent is in the range 0.3:1 by weight to 1.5:1 by weight (strictly, evaporation of 23 percent to 66 percent).

The conditions of evaporation are such as to form a gel (suspension of fibres in solvent) which is capable of being refined to provide a pulp of the invention as defined above. Thus a further characteristic of the process of the invention is that the gel formed by partial evaporation of the solvent contains at most about 7 percent by weight polymer and desirably contains only up to 5 percent by weight polymer and preferably less than 2 percent by weight. Such a gel is then, according to the invention, refined by attritional action between proximate surfaces which are in motion relative to each other.

Before giving specific examples of the pulp and process of this invention, we describe next a preferred general procedure, together with some optional process steps which may be adopted with advantage.

FIG. **1** is a diagrammatic view of an apparatus that may be suitably employed in the process of the present invention.

FIG. **2** is a cross-sectional view of precipitation zone **22** illustrated diagrammatically in FIG. **1.**

FIG. **3** is the enthalpy chart for hexane.

FIGS. **4** to **7** are microphotographs of the fibers produced by the process of the present invention.

In the pressure-vessel **10** shown in FIG. **1,** a solution of the polymer is heated to desired temperature; if a suspension of polymer chip, or a slurry of polymer crumb produced by a low-temperature polymerization process, is used, this suspension or slurry can be dissolved in vesel **10.** Vessel **10** is equipped with a stirrer **11** and is jacketed whereby heating fluid may be introduced via conduit **12** and exited via conduit **13.** Solvent may be introduced into the vessel via conduit **14** and a high molecular weight polyolefin introduced via conduit **15.** An inert gas may be introduced via conduit **16** to maintain the desired pressure in the vessel. Alternatively, the vessel **10** may be a polymerization reactor vessel in which an olefin or mixture of olefin, which will form a crystalline polyolefin, may be polymerized. As a further alternative, the polymerization may be carried out in another vessel and the polyolefin solution or slurry fed into vessel **10.** While a solution process would be the preferred method of carrying out such a polymerization in view of the fact that the polymer already would be in solution, slurry polymerization procedure could be employed and the resulting polyolefin suspension or slurry heated above the melt dissolution temperature of the polyolefin in vessel **10** to form the solution. The actual polymerization procedure employed forms no part of the present invention since any such polymerization procedure conventional in the art can be employed; it should be noted however that the procedure preferred is a procedure capable of forming a relatively high molecular weight polyolefin, as was discussed above.

Once the polyolefin solution is formed in vessel **10,** it is fed through shutoff valve **17** into transfer conduit **18.** Transfer conduit **18** is surrounded by jacket **19** into which heating fluid such as steam is introduced via conduit **20** and exited via conduit **21.** The heating fluid en-

sures that the polyolefin solution is maintained at a temperature above the melt dissolution temperature.

The polyolefin solution is then passed through nozzle **22** into precipitation zone (low pressure zone) **23.** During passage of the polyolefin solution through nozzle **22** the pressure and temperature of the solution is adiabatically reduced and a portion of the solvent is vaporized therefrom. The loss of heat effected by this vaporization cools the residual solution so that the polyolefin precipitates as a highly swollen fibrous mass or fibrous gel. By fibrous gel is meant a fibrillar structure of discrete crystalline polyolefin fibres containing interconnecting capillary spaces filled with the solvent. The polyolefin content in such gel should not exceed about 7 percent by weight of the gel; otherwise one is compelled to dilute the gel with solvent before refining the gel.

The fibrous gel and the free solvent vapor is then passed through tubular shear conduit **24.** It is believed that some molecular orientation is imparted during traverse of the gel through the precipitation zone and conduit **24.**

From the tubular shear conduit **24** the fibrous gel passes via post-precipitation transfer conduit **25** into separation vessel **26** which is maintained at preferably atmospheric or subatmospheric pressure. Free solvent vapor vaporized during passage of the polyolefin solution through precipitation zone **33** is separated from the fibrous gel via conduit **27.** The solvent vapor thus removed may then be condensed and recycled back to vessel **10.**

The fibrous polyolefin gel which is in the form of relatively short "noodles" (preferably less than about 10 cm) caused by solvent vapor pockets formed during precipitation and which still contains a substantial amount of solvent drops to the bottom of vapor separation vessel **26** and from there into disc refiner **28** via conduit **27.** While the process is illustrated as preferably employing a disc refiner at this stage, alternative apparatus for imparting attritional forces to the fibrous gel could be employed, such as are known in the papermaking industry and discussed above.

The polymer gel is fed into disc refiner **28,** and discrete polymer fibers separated or liberated therefrom during passage therethrough. The fibres and the small amount of separated solvent drop from the bottom of disc refiner **26** into a receiving vessel (not shown) via conduit **28.** Any separated solvent and some further non-separated solvent may be filtered, decanted or centrifuged from the fibers and the solvent remaining on or within the fibers, which is still a substantial amount, may be removed therefrom by conventional steam stripping or solvent extraction techniques.

Transfer conduit **18** is not essential to the practice of the present process; it is merely employed to convey the polyolefin solution from solution vessel **10** to precipitation zone **22.** It could be removed completely and precipitation zone **22** located on vessel **10.** Transfer conduit **18** is heated in order to maintain the polyolefin in solution. The dimensions of the transfer conduit **18** are not critical; however, it is very desirable to employ a diameter such that there is little or no pressure drop along the tube.

It has been found to be useful to effect some solvent vaporization before the polymer solution passes through precipitation nozzle **22,** to cause the vapor cutting mentioned above. Such vaporization aids in the development of the proper length of the fibrous gel noodles entering vaporization vessel **24.** The greater the vaporization, the shorter the noodle. Such partial vaporization may be effected by slight heating of transfer conduit **18**; the temperature of the solution is not raised by such heating due to maintenance of constant pressure conditions. Alternatively, a valve (not illustrated) may be inserted in transfer conduit **18** somewhere prior to nozzle **22.** However, such partial vaporization should not be sufficient to effect precipitation of the polymer.

The size of precipitation nozzle **22** should be such as to create sufficient pressure-drop to cause rapid precipitation of the polymer and partial vaporization of the solvent. The pressure drop should be such as to cause violent vaporization of that portion of the solvent which does vaporize. Such violent vaporization imparts turbulence and causes the precipitated fibrous gel to break up into relatively short noodles which is a highly desirable form for subsequent operations. Such a turbulent flow condition is important in developing fiber properties. The amount of turbulence necessary to develop good fiber properties depends at least partially upon the molecular weight of the polyolefin employed. The lower the molecular weight, the greater the turbulence must be in order to subsequently produce fibers of good quality. If low turbulence is employed with low molecular weight polyolefin (e.g. polyethylene with $\overline{M}_v = 40{,}000$) the polymer will be precipitated as a powder rather than as a fiber. It is difficult to quantitize the minimum degree of turbulence required to produce fibers since it depends on several variables; in practice the minimum or optimum turbulence is imparted to the precipitating polymer by adjusting the size of nozzle **22** which is, in a preferred embodiment, an adjustable throttling ball valve, to increase the degree of turbulence by restricting the nozzle to a more narrow opening. This adjustment can be continued until the gel product becomes fibrous in nature, and can be optimized to produce fibers having the best characteristics for the particular end use desired.

A portion of the pressure drop, and thus of the precipitation and vaporization, occurs in the precipitation conduit **23** located immediately after precipitation nozzle. While not essential to the process, precipitation conduit **23** has been found to be desirable to continue to impart shear stress to the precipitating polymer and to aid in preventing the formation of continuous strands which are difficult to process. The length of precipitation conduit **23** is adjusted to form noodles having a length between about 5 and 15 cm, preferably less than about 10 cm. If the precipitation conduit is too long, undesirably long noodles may be obtained. If the noodle is continuous, there is a tendency for it to become entrained in the exhaust line of vapor separation vessel **24,** and for twisting or roping to occur in the disc refiner **28.** The diameter of precipitation conduit **23** is preferably not substantially larger than the full open size of nozzle **22.**

After precipitation conduit **23,** the fibrous gel is transferred into vapor separation vessel **24** via post-precipitation transfer conduit **23.** The size of the conduit **23** is not critical except its diameter should be sufficiently large that little pressure drop occurs during traverse of fibrous gel therethrough. Therefore, very little additional solvent is vaporized, and the solvent that is removed in vapor separation vessel **24** is that solvent which was vaporized in the precipitation zone **23.**

From vapor separation vessel **24** the fibrous gel drops into disc refiner **28** via conduit **27.** In order to be able to feed the fibrous gel through disc refiner **28,** the concentration of polymer (consistency) should be less than about 7 percent by weight, desirably less than 5 percent and preferably is less than about 2.0 percent by weight. While it is preferred to operate the precipitation zone under conditions that provide a fibrous gel having a proper consistency, if the consistency is too high due to excessive vaporization, additional solvent may be introduced to the fibrous gel prior to passage through the disc refiner to lower the consistency to an appropriate level.

Disc refiner **26** may be any conventional disc refiner employed in the paper industry. However, it has been found desirable to employ coarse-patterned plates in the refiner to prevent plugging which seems to occur more frequently with fine-patterned plates. The gap between the discs should be low, preferably of the order of about 100 to 125 microns. However, this may be adjusted to develop various fibre properties.

The fibers obtained after refining still contain a substantial amount of solvent typically 80–98 percent by weight, which may be removed by conventional techniques such as centrifuging followed by solvent exchange to water or steam stripping if the fibers are to be used for making paper by the water laying technique. Steam stripping may lead to some loss of the very fine structure of the pulp described above, but not sufficiently to significantly impair its properties for papermaking. During solvent removal, care should be taken not to press the fibers together too tightly as solvent bonding may take place between fibers which is very undesirable.

If a nonwoven web, such as paper, is to be made by solvent-laying techniques, then the residual solvent need not necessarily be removed. Also, it is very desirable that any additional (secondary) refining of the fibers to further develop their strength properties to be carried out while the fibers are still present in solvent rather than in water.

After steam stripping or solvent exchanging the fibers into an aqueous slurry, the fibers may be processed for papermaking in the normal manner. The fibers may be screened and/or centricleaned to remove undesirable polymer chunks. If the fibers are not made into paper immediately, the aqueous slurry can be thickened to a consistency of 50–60 percent and stored in wet cake form. If the fibers are to be shipped, the wet cake can be compacted and baled.

The fibers are treated with a water dispersing agent, preferably prior to or during steam stripping to prevent fiber agglomeration and preferably with polyvinyl alcohol since this material is not subsequently washed off the fibers to any great extent. The polyvinyl alcohols employed have a degree of hydrolysis greater than 77 percent and preferably 88 to 100 percent hydrolysis. The molecular weight of the polyvinyl alcohol is not critical although lower molecular weights, i.e., weight average molecular weights of 10,000 to 20,000 are generally preferred. Generally, the polyvinyl alcohol is employed in amounts of up to about 2 percent by weight of the fibers.

EXAMPLE 1

Twenty kilograms of high density polyethylene having a viscosity average molecular weight of 200,000 was dissolved in 2000 liters of n-hexane at a temperature of 138°C. in a 7000 liter glass lined vessel to form a solution wherein the polyethylene concentration was 10.0 grams/liter. The solution was agitated at about 100 rpm. The pressure in the solution vessel was maintained at 5.0 kg/cm^2. The polyethylene solution was fed through a transfer conduit which was slightly heated to maintain the temperature at 138°C. and the pressure at 5.0 kg/cm^2. The transfer conduit was 30 meters in length and had an outside diameter of 25 cm. The solution was then adiabatically passed at a rate of 800 liters per hour through a ½ inch nozzle throttling ball valve (which was maintained 60–80 percent open throughout the run) to atmospheric pressure. The material then passed through a precipitation conduit having a diameter of 0.5 inch and a length of about 270 mm. From the precipitation conduit the fibrous gel, having a temperature of about 70°C. and at atmospheric pressure passed into a post-precipitation transfer conduit which was 2 inches in diameter. The fibrous gel then passed into a vapor separation vessel (cyclone) which removed vaporized hexane from the top thereof. About 50 percent by weight of the hexane was vaporized. The fibrous gel noodles (which were less than about **10** cm. in length) containing about 3 percent by weight polyethylene were collected in the bottom, from which they were passed along with enough added hexane to give a consistency of about 1 percent by weight polyethylene through a single disc refiner having 12 inch discs with medium coarse plates. The refiner was operated at 2000 rpm. The refined fibrous slurry was then collected in a glass lined vessel and recirculated through the refiner for a total of four passes. The fiber slurry at 1.0 percent consistency was then pumped through a filter and the resulting wet cake having a consistency of 13 percent was fed into a 2000 liter glass lined steam stripping vessel along with 1500 liters of water and 150 grams of polyvinyl alcohol having a molecular weight of 10,000 and 94 percent hydrolyzed (to aid dispersion) and the remaining hexane steam stripped from the fibers at a temperature of 60°C. The resulting aqueous slurry of polyethylene fibers at a consistency of 1 percent was then centrifuged to remove water and provide a wet fiber cake at about 50 percent oven dry consistency.

The fibers thus produced had a gas adsorption surface area of 4.8 m^2/g.

The fibers were fractionated on Tyler standard screens in accordance with TAPPI Test T 233 SU 64 and the following fiber fractions obtained:

TABLE 1A

Mesh	Weight %	Length (mm)	Coarseness (decigrex)
On +20 mesh	6.9	1.88	31.3
On +35	32.7	1.54	15.9
On +65	25.2	1.18	13.1
On +150	18.1		
On +270	7.3		
Thru 270	9.8		

Two sets of standard handsheets were prepared, one set from 100 percent of the fibers and one set from a 50 percent by weight blend of the fibers and 400 Canadian Standard freeness bleached alder kraft cellulose fibers. The handsheets, having a basis weight of about 37 pounds/3,000 sq. ft. were formed on a British sheet

machine using the 150-mesh stainless steel screen in accordance with TAPPI Test T205 M-58. The sheets were couched from the screen or wire in the standard manner and subjected to a 15-second cold (70°F.) press at 100 psi against a polished caul. The sheets were given a second identical press after turning them over on the caul so that both sides of the handsheet were given a smooth finish. The final drying was done on a rotary dryer at 220°F. The sheets were then tested for strength and optical properties in accordance with standard TAPPI testing methods:

TABLE 1B

Property	100% PE Fiber	50% Blend*
Basis weight (lbs./3000 ft.²)	39.79	38.3
Caliper (mils)	10.3	7.0
Density (g/cc)	0.248	0.350
Tear (g/sheet)	4.8	27.0
Breaking Length (meters)	13.6	2856
Tensile (lbs./inch)	0.29	5.9
Stretch (%)	1.5	2.5
TEA (ft.-lb./ft.²)	0.027	1.2
Scott Internal Bond	11.0	42.0
TAPPI opacity (%)	93.6	87.2
Brightness (Elrepho 8)	84.8	87.9

*Wet pressed at 60 psi.

The fibers were further blended with 400 Canadian Standard freeness bleached alder kraft as 40 percent and 80 percent by weight blends and the blends formed into paper on a small papermachine, and the resulting paper webs tested for strength and optical properties as above. These tests, which more nearly correspond to actual commercial papermaking indicate that strength properties are higher than for handsheets:

TABLE 1C

Property	40% Blend	80% Blend
Basis weight (lbs./3000 ft.²)	33.8	33.6
Caliper (mils.)	3.4	5.3
Density (g/cc)	0.636	0.405
Tear (g/sheet) WMD	32	26
CMD	34	28
Tensile (lbs./inch) WMD	16.0	5.6
CMD	8.5	4.0
Stretch (%) WMD	1.5	2.9
CMD	3.2	0.6
TEA (ft.-lb./ft.²) WMD	1.8	1.3
CMD	2.5	2.5
Scott Internal Bond	121	187
TAPPI opacity (%)	75	68
Brightness (Elrepho 8)	80	85

NOTE: WMD is with machine direction; CMD is cross machine direction.

EXAMPLE 2

This example illustrates the preparation of fibers in accordance with the present invention from high density polyethylenes of various viscosity average molecular weights. The procedure of Example 1 was substantially repeated for the various polyethylenes. Process details are set forth in Table 2A below, the fiber fractionation results are set forth in Table 2B below and handsheet properties are set forth in Table 2C below. In all cases, hexane was added to the gel prior to refining to lower the consistency to about 1 percent by weight polyethylene.

TABLE 2A

Process Conditions	RUN NUMBER 1	2	3	4	5	6	7
$\bar{M}v$ (X 10^{-3})	40	65	100	200	300	400	600
PE, kg	120	22.5	20	20	15	15	20
Hexane, l	2000	1500	2000	2000	2000	2000	2000
PE g/l	60	15	10	10	7.5	7.5	10.0
Temp. (°C)	140	141	140	141	140	138	139
Press (kg/cm²)	5.0	5.5	5.0	5.1	5.1	5.3	5.8
Refining (passes or hours recycle)	—	2 hrs.	2 hrs.	4 passes	1.75 hrs.	2 passes	3 passes
% PVA	2.0	1.0	1.0	—	1.0	2.0	2.0
Steam strip Temp. (°C)	—	63	63	63	63	80	80
Gel consistency (wt %)	15.4	4.4	3.0	3.0	2.2	2.2	3.0

TABLE 2B

Screen Mesh	RUN NUMBER 1	2	3	4	5	6	7
On 20	0.6	0.1	0.9	1.6	0.1	8.3	7.9
On 35	0.1	3.4	5.4	13.0	5.7	21.6	24.9
On 65	14.0	14.5	22.0	25.5	28.0	27.9	28.0
On 150	35.3	36.2	37.3	32.9	36.1	21.8	18.1
On 270	24.4	21.2	15.8	15.8	10.4	8.1	2.7
Thru 270	25.6	24.6	18.6	11.2	19.7	12.3	18.4

TABLE 2C

Property	RUN NUMBER 1*	2	3	4	5	6	7
Basis Weight	35.7	37.6	38.6	39.6	37.6	38.7	41.6
Caliper	4.4	6.9	7.2	10.4	6.7	11.5	12.3
Density	0.52	0.35	0.34	0.245	0.36	0.216	0.216
Tear	20	3.0	3.0	3.2	5.0	3.0	3.2
Breaking Length	2249	86	111	155	223	—	—
Tensile	7.3	0.29	0.39	0.33	0.77	0.249	—
Stretch	2.4	0.82	1.5	2.0	1.8	2.8	2.6
TEA	1.2	0.02	0.04	0.049	0.11	0.055	0.065
Scott Internal Bond	70.0	11.0	15.0	12.0	16.0	15.0	6.0
Opacity	85.4	90.0	91.3	93.6	94.9	91.7	93.0
Brightness (Elrepho 8)	82.3	90.3	88.7	87.6	86.9	89.1	90.4

*50/50 Blend - 100% sheets stuck to wire.

It is seen from the foregoing example 2 that an increase in molecular weight generally provides improved handsheet properties.

EXAMPLE 3

This example illustrates operation of the present pregress under different temperature conditions. The solvent employed was n-hexane. The procedure of example 1 was generally followed. Table 3A sets forth specific process conditions, Table 3B sets forth fiber fractionation results and Table 3C provides handsheet properties.

TABLE 3A

Process Conditions	RUN NUMBER 1	2	3	4	5
Temp. (°C)	132	136	138	140	142
Press (kg/cm²)	4.8	5.4	5.7	5.7	5.1
$\overline{M}_v$ (X 10^{-3})	600	600	600	600	200
PE, kg	22.5	22.5	22.5	30.0	20.0
Hexane, l	3000	3000	3000	3000	2000
PE g/l	7.5	7.5	7.5	10.0	10.0
Refining, passes	3	3	3	4	4
% PVA	2.0	2.0	1.0	2.0	1.0
Steam strip Temp. (°C)	—	80	80	80	63
Gel consistency, wt. %	2.2	2.2	2.2	3.0	3.0

TABLE 3B

Mesh	RUN NUMBER 1	2	3	4	5
On 20	3.9	1.1	4.4	2.2	2.2
On 35	16.9	7.3	14.1	3.8	8.7
On 65	27.4	24.9	28.9	30.9	24.9
On 150	22.1	34.5	27.7	29.2	38.6
On 270	9.7	18.1	7.8	13.0	16.1
Thru 270	20.0	14.1	17.1	20.9	9.5

TABLE 3C

Handsheet Property	RUN NUMBER 1	2	3	4	5
Basis Weight	38.0	38.1	37.1	36.0	35.0
Caliper	10.29	10.33	10.0	9.91	6.0
Density	0.236	0.236	0.237	0.232	0.376
Tear	5.0	3.0	3.0	3.0	3.8
Breaking Length	—	—	—	—	233
Tensile	0.380	0.424	0.271	0.406	0.74
Stretch	2.4	2.3	2.5	3.1	1.1
TEA	0.067	0.098	0.050	0.099	0.056
Scott Internal Bond	15.0	13.0	12.0	13.0	24.0
Tappi Opacity	94.1	95.1	94.2	93.3	93.6
Brightness (Elrepho 8)	87.8	88.4	92.7	92.6	89.1

The importance of the maximum temperature limitation previously discussed can perhaps be best illustrated by reference to FIG. 3 which is a graph of the enthalpy of hexane, the solvent employed in foregoing example 3. As can be seen by reference to this graph, if the solution temperature exceeds about 188°C. (point A on the saturated liquid curve), upon precipitation of the polymer all of the solvent is in the vapor phase and none in the liquid phase since the temperature of the precipitated polymer would be substantially the boiling temperature of hexane (68. 3°C) at atmospheric pressure, corresponding to point B on the saturated vapor curve of the graph. Therefore, the solution temperature employed should be less than the temperature on the saturated liquid curve (point A) corresponding (at constant enthalpy) to the point on the saturated vapor curve (point B) representing the boiling point of the solvent. The temperature chosen therefore should be less than that of Point A so a portion of the solvent will be in the liquid phase, and depends upon the polymer concentration in the starting solution, keeping in mind that the polymer concentration in the fibrous gel should not exceed about 5 percent by weight.

For example, since it is desirable that the polymer concentration in the gel not exceed about 5 percent by weight, and since the maximum concentration of polymer in the solution employable with the high molecular weight polymers described herein is about 2 percent, the solvent should not vaporize in excess of about 60–70 percent at that concentration level. By reference to FIG. 3, and for hexane as the solvent, it is seen that this maximum vaporization corresponds to a temperature of about 160°C. (see line C-D), since the portion of line C-D to the left of the boiling point of hexane ordinate represents to the liquid phase portion (about one-third of line C-D) and the portion of line C-D to the right of the boiling point ordinate represents the vapor phase (about two-thirds of line C-D).

A similar analysis will provide maximum solution temperatures usable in the present process for other solvent and/or other pressure conditions.

EXAMPLE 4

This example sets forth typical valves of hydrodynamic surface area, compressibility constant and drainage time of the fibers of the present invention. Some of the fibers are those produced by earlier examples. All fibers were treated with 2 percent PVA added during steam stripping as in Example 1.

TABLE 4A

Drainage Resistance Characteristics

Example No.	Run No.	S	V	M	N	DT	DF
1	—	0.65	2.21	0.0045	0.291	—	0.22
2	1	0.81	2.24	0.0124	0.218	5.3	0.65
2	2	0.70	1.83	0.0101	0.245	5.1	—
2	3	0.79	1.88	0.00595	0.283	—	0.41
2	5	—	—	—	—	—	0.69
2	7	0.72	2.66	0.0045	0.291	—	0.31
4	1	0.88	1.95	0.0072	0.266	5.5	—
4	2	0.83	1.88	0.00695	0.270	—	—
4	3	0.93	2.03	0.00635	0.274	5.7	—
4	4	0.98	2.24	0.00521	0.287	—	—

Note:
S = hydrodynamic surface area, m^2/g.
V = hydrodynamic volume, cc/g.
M & N = compressibility constants
DT = drainage time, seconds
DF = drainage factor, seconds/gram

The polyethylene fibers designated Example 4, runs 1–4 in Table 4 above were made by the procedure set forth in Example 1, with the following specific condition differences:

TABLE 4B

Run No.	Mv	n	Solution Temperature	Polyethylene Concentration in Solution
1	220,000	2.6	140°C	10 kg/m³
2	220,000	2.6	140°C	10 kg/m³
3	820,000	6.2	137°C	7.5 g/l
4	65,000	2.2	141°C	15 g/l

Note: Runs 1, 2 and 4 were refined for 2 hours, recycling.
Run 3 was refined by 4 passes through the refiner.

EXAMPLE 5

This example illustrates the preparation of a fibrous gel suitable for subsequent refining into discrete fibers. A 3 percent by weight polymer solution was prepared by dissolving polyethylene having a viscosity average molecular weight of 400,000 ($n = 9.4$) produced by Ziegler method into hexane at 135°C. The dissolution vessel containing this polymer solution was connected with a reduced pressure vessel (receiving vessel) which was at atmospheric pressure, through a pipe of 5 cm. diameter. A valve was attached to this pipe a short distance from the dissolution vessel.

The polymer solution was then transferred to the reduced pressure vessel by opening the valve. The flow rate of the solution between the valve and the reduced pressure vessel was 80 m./sec. at steady state and the vapor-liquid ratio of hexane was 1/1.

The fibrous gel material produced had a noodle length of 5 cm., a diameter or thickness of 50 μ, and the fibers therefrom had a gas adsorption surface area of 80 m²/g and a strength of 2 g./d.

EXAMPLE 6

This example illustrates the preparation of a polypropylene gel suitable for subsequent refining into discrete fibers. A 3 percent by weight solution was prepared by dissolving polypropylene having an intrinsic viscosity of 5.2 into benzene at 135°C. The resulting polymer solution was discharged into an atmospheric pressure according to the same method as in Example 5. The flow rate of the mixture was 85 m./sec. and the vapor-liquid ratio of benzene was 1.5/1.

The fibrous gel noodle material obtained had an average shape measuring 7 cm. in length, 35 μ in diameter or thickness, and the fibers therefrom had a gas adsorption surface area of 30 m²/g and a strength of 1.5 g./d.

EXAMPLE 7

A fibrous polypropylene gel as prepared in Example 6 diluted to a consistency of 2 percent by weight was refined by passing it once through a disc refiner with the plates 0.003 inch apart. The refined fibers were then placed into a waring blender and exchanged to water through isopropanol, accomplished by first adding 100 percent isopropanol, filtering, adding 50/50 isopropanol/water, filtering and finally dispersing in 100 percent water. Potato starch (5 percent by weight of the fibers) was added to the water to render the fibers water dispersible. The fibers thus produced had a gas adsorption surface area of 1.5 m²/gram.

Standard handsheets were prepared from 100 percent of the polypropylene fibers thus prepared in accordance with TAPPI Test T 205 m-58 and as disclosed in Example 1. The sheets were then tested in accordance with standard TAPPI testing methods and the following properties noted:

TABLE 5

Basis weight (lbs/3000 ft²)	35
Tensile (lbs/inch)	1.4
Tear (grams/sheet)	16.4
Breaking length (meters)	440
Stretch (%)	3.0
TEA (ft-lbs/ft²)	37.0
Scott Internal Bond	286
Brightness (%)	84.5
TAPPI opacity (%)	92.9
Scattering coefficient	76.4

We claim:

1. A process for forming a synthetic pulp of discrete polyolefin fibers comprising forming a solution of a crystalline polyolefin selected from the group consisting of polyethylene, polypropylene and copolymers of ethylene and propylene in a solvent the polyolefin being present in an amount between about 0.5 and 5 percent by weight of the solution, the solution being formed at autogeneous or higher pressure at a temperature above the melt dissolution temperature and at a temperature which will cause between about 20 percent and about 70 percent by weight of the solvent to vaporize upon adiabatic flashing into a zone of reduced pressure, rapidly passing the solution into said zone of reduced pressure to vaporize a portion only of said solvent and precipitate a fibrous polyolefin gel containing less than about 7 percent by weight of the polyolefin, and passing the fibrous polyolefin gel through a disc refiner to liberate discrete polyolefin fibers.

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