

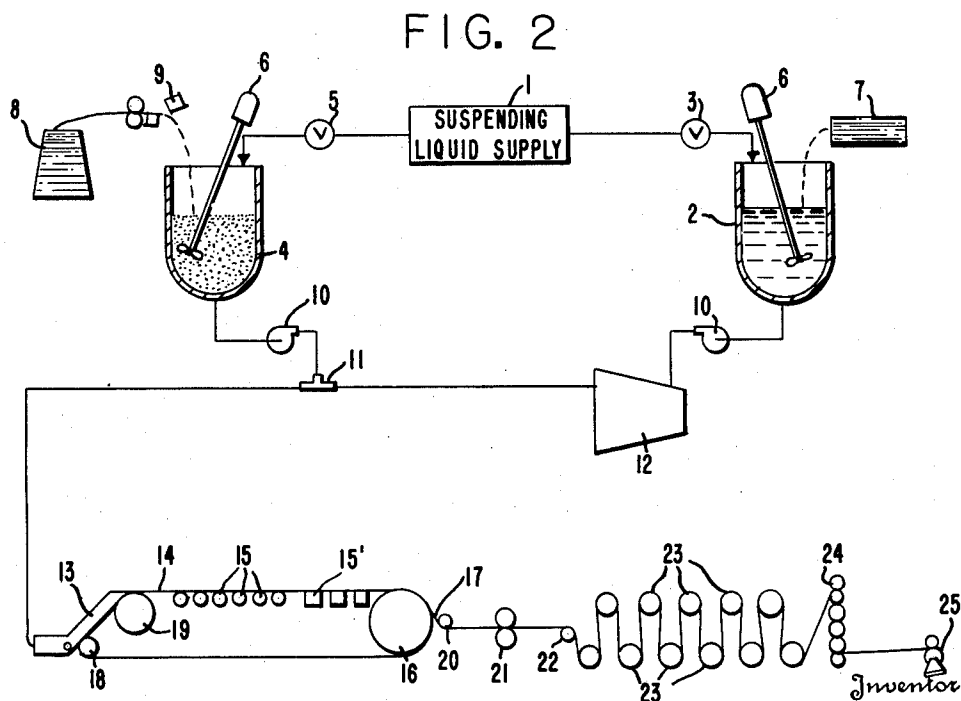
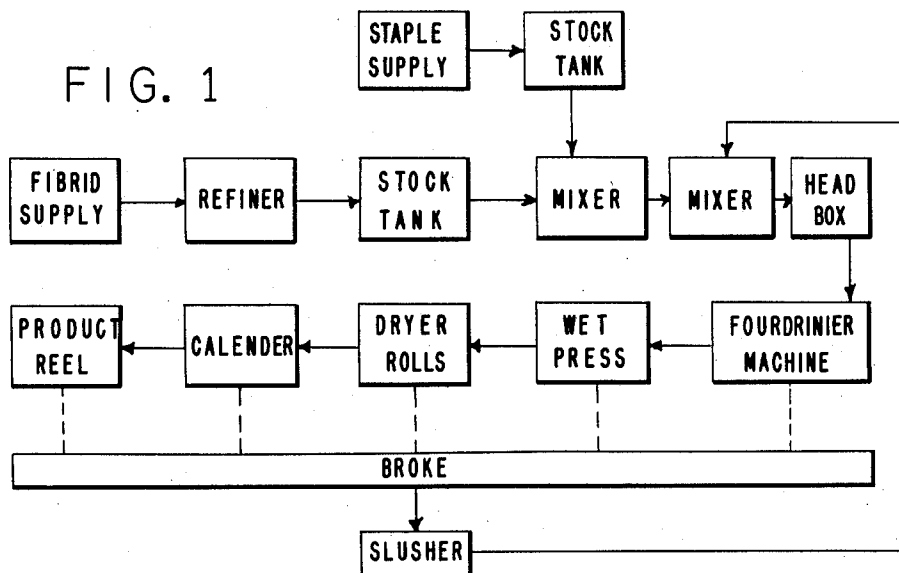
March 3, 1964

R. W. BUNDY
PROCESS FOR FORMING A NON-WOVEN SHEET
OF FIBERS AND FIBRIDS

3,123,518

Filed Dec. 5, 1960

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

FIG. 3

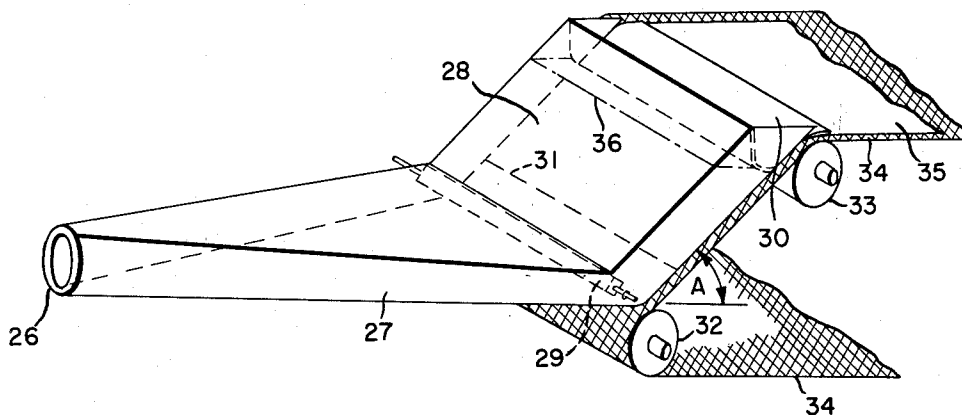


FIG. 4

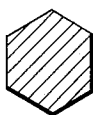
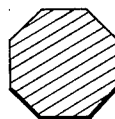


FIG. 5



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3,123,518 PROCESS FOR FORMING A NON-WOVEN SHEET OF FIBERS AND FIBRIDS

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1 Claim. (Cl. 162-216)

The present invention relates to a novel and useful process for the formation of a sheet-like structure. More specifically, it relates to a process for the formation of a continuous, non-woven sheet-like structure.

It is an object of the present invention, therefore, to provide a novel process for the formation of a sheet-like structure. Another object is to provide a process for the continuous formation of a non-woven sheet-like structure on a papermaking machine. Other objects will become apparent from the descriptions, the drawings and the claim.

In accordance with the present invention, a process for forming a continuous sheet-like structure on a papermaking machine is provided which comprises forming a slurry of staple fibers and fibrids in a liquid, the said slurry containing not less than about 0.03 and not more than about 0.35% solids by weight at least about 5% of which is fibrids, maintaining the slurry in continuous turbulent flow, substantially eliminating said turbulence at the area of deposition, continuously depositing the fiber-fibrid mixture from the slurry onto a moving screen traveling at an angle of from about 20° to about 45° with the horizontal and thereafter removing the resulting sheet-like structure formed on the screen.

The term "papermaking machine" is used to designate a Fourdrinier machine or other such conventional papermaking apparatus wherein a slurry is continuously laid down on a moving screen so as to form a continuous sheet.

The term "staple fiber" is used to signify fibers or filaments of textile denier which are short in length as opposed to continuous filaments. In general, the lengths of the fibers may vary from a fraction of an inch to several inches. For the present invention, however, it is preferred that the fibers be of from 1/8 to about 1 inch in length although minor amounts of longer fibers may be substituted in part for the staple fibers herein employed.

The concentration of solids in the slurry should be kept at a value of less than about 0.35% in order to prevent "clumping" and a corresponding unevenness in the final sheet-like structure. The preferred range of concentration is from about 0.03 to about 0.10%, with the lower concentrations being used for the longer length fibers. Slurry concentrations which are substantially less than 0.03% are unsuitable since they require such a large volume of water flow that the necessary phase of greatly reduced agitation just prior to deposition, critical in that it leads to the formation of a uniform even layered, smooth sheet, renders inoperable such a process involving said low concentrations which require continued agitation up to the moment of deposition.

The term "turbulent flow" is given its conventional meaning, as in hydraulics, to signify that the flow is non-viscous or non-laminar.

The "liquid" which may be used in the practice of the present invention is any liquid which is inert to both the fibers and the fibrids. Water from an economic standpoint is, of course, preferred, although other inert liquids may also be used.

To be designated a "fibrid," a particle must possess (a) an ability to form a waterleaf having a couched wet tenacity of at least about 0.002 gram per denier when a plurality of the said particles is deposited from a liquid suspension upon a screen, which waterleaf, when dried at a temperature below about 50° C., has a dry tenacity at

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least equal to its couched wet tenacity and (b) an ability, when a plurality of the said particles is deposited concomitantly with staple fibers from a liquid suspension upon a screen, to bond a substantial weight of the said fibers by physical entwinement of the said particles with the said fibers to give a composite waterleaf with a wet tenacity of at least about 0.002 gram per denier. In addition, fibrid particles have a Canadian freeness number between 90 and 790 and a high absorptive capacity for water, retaining at least 2.0 grams of water per gram of particle under a compression load of about 39 grams per square centimeter. By "wholly synthetic polymeric" is meant that the fibrid is formed of a polymeric material synthesized by man as distinguished from a polymeric product of nature or derivative thereof.

Any normally solid wholly synthetic polymeric material may be employed in the production of fibrids. By "normally solid" is meant that the material is non-fluid under normal room conditions. By "... an ability to ... bond a substantial weight of ... (staple) fibers ..." is meant that at least 50% by weight of staple based on total staple and fibrids can be bonded from a concomitantly deposited mixture of staple and fibrids.

It is believed that the fibrid characteristics recited above are a result of the combination of the morphology and non-rigid properties of the particle. The morphology is such that the particle is non-granular and has at least one dimension of minor magnitude relative to its largest dimension, i.e., the fibrid particle is fiber-like or film-like. Usually, in any mass of fibrids, the individual fibrid particles are not identical in shape and may include both fiber-like and film-like structures. The non-rigid characteristic of the fibrid, which renders it extremely "supple" in liquid suspension and which permits the physical entwinement described above, is presumably due to the presence of the "minor" dimension. Expressing this dimension in terms of denier, as determined in accordance with the fiber coarseness test described in Tappi, 41, 175A-7A, No. 6 (June) 1958, fibrids have a denier no greater than about 15.

Complete dimensions and ranges of dimensions of such heterogeneous and odd-shaped structures are difficult to express. Even screening classifications are not always completely satisfactory to define limitations upon size since at times the individual particles become entangled with one another or wrap around the wire meshes of the screen and thereby fail to pass through the screen. Such behavior is encountered particularly in the case of fibrids made from soft (i.e., initial modulus below 0.9) polymers. Hard polymers (i.e., initial modulus above 0.9 g./denier) are more readily tested. As a general rule, however, fibrid particles, when classified according to the Clark Classification Test (Tappi, 33, 294-8, No. 6 [June] 1950) are retained to the extent of not over 10% on a 10-mesh screen, and retained to the extent of at least 90% on a 200-mesh screen.

Fibrid particles are usually frazzled, have a high specific surface area, and as indicated, a high absorptive capacity for water.

Preferred fibrids are those the waterleaves of which when dried for a period of twelve hours at a temperature below the stick temperature of the polymer from which they are made (i.e., the minimum temperature at which a sample of the polymer leaves a wet molten trail as it is stroked with a moderate pressure across the smooth surface of a heated block) have a tenacity of at least about 0.005 gram per denier.

Fibrid particles are described in detail and claimed in United States patent application Serial No. 788,371, now Patent No. 2,999,788.

The term "synthetic polymer" is intended to designate a polymeric material synthesized by man as distinguished

from a polymeric product of nature or a derivative thereof. The term "hard" polymer is applied to those wholly synthetic polymers which have an initial modulus of about 0.9 gram per denier and above. Those polymers whose initial modulus falls below this limit are referred to as "soft" polymers.

One method for forming fibrils involves beating a liquid suspension of the shaped structure produced by the interfacial spinning process described in United States Patent 2,708,617, dated May 17, 1955. This structure may be in the form of a collapsed tube, the walls of which are no greater than about 0.020 inch in thickness, described and claimed in United States Patent 2,798,283. The tearing or shredding operation may be accomplished by leading the tubular filament, while still wet, into a liquid such as water, which is being violently agitated. A Waring Blendor is well adapted to perform this operation.

A second process for preparing fibrils comprises introducing a solution of a synthetic polymer into a non-solvent for the said polymer (referred to hereinafter as a "precipitant") under fibril forming conditions of turbulence and precipitation such that when the precipitation is fast, a high degree of turbulence accompanies the dispersing, whereas when the precipitation is slow, a low or moderate degree of agitation accompanies the dispersing and the precipitate formed is thereafter shredded in a liquid medium. A typical fast precipitation is one which is complete in a time period in the order of about 50×10^{-6} seconds. A "slow precipitation" is one where in the precipitation period is more in the order of about 0.1 second. In the case of fast precipitations, the variables of the system are controlled such that the precipitation number (the "P" value) of the system, as defined hereinafter, is within the limits of about 10 and 80,000 with the proviso that where the polymer is "soft" the value does not exceed about 10,000 and where the polymer is "hard" the value is at least 15. Systems having P values within the limits of from about 40 to about 7,000 are preferred for the production of fibrils of "soft" polymers, while limits of from about 25,000 to about 75,000 are preferred for "hard" polymers.

The precipitation number (or "P" value) is defined by the expression:

$$P = \frac{V_p}{V_s} Q$$

wherein V_p is the viscosity in poises of the precipitant and V_s is the viscosity in poises of the polymer solution both measured at the temperature at which the precipitation is carried out and Q is an agitation factor which may be expressed in terms of the rate, in revolutions per minute, at which the agitating device is rotated in the precipitant.

As an example of the physical significance of these "P" values a P number of 300,000 corresponds to rapid stirring in a Waring Blendor of a low viscosity polymer solution in a very viscous precipitant. The high shear encountered by the precipitating polymer under these conditions results in the formation of a dispersion of fine particles, e.g., they are not retained by a 200-mesh screen. At the other extreme, a P value as low as 0.14 corresponds to conditions where a viscous polymer solution is added to a very low viscosity precipitant. Under these conditions, not enough force is applied to disperse the polymer solution before a skin forms, resulting in the formation of lumps. Thus where the objective in separating polymers from solution is to precipitate them in a readily filterable, easily washable form, a relatively slow stirring speed and rather low viscosity precipitant is usually employed, generally corresponding to P values below about 1. As is apparent from the formula, P is directly proportional to both the viscosity of the precipitant and the amount of agitation and inversely proportional to the viscosity of the polymer solution. Thus,

the degree of agitation can be reduced, provided the viscosity of the precipitant is adequately increased and/or the viscosity of the polymer solution reduced. When the precipitation occurs under conditions of relatively low agitation, the product tends to be a loosely associated web-like structure from which fibrils may be separated by extended or turbulent agitation, such as in a Jordan.

There is provided a headbox for a papermaking machine which comprises a flowably connected supply means, a substantially horizontal entrance chamber and an upwardly inclined exit chamber having the forward and upper sides open, with the said entrance chamber having a downstream cross-sectional area of less than about three times the upstream cross-sectional area and being connected to the bottom portion of the exit chamber and with the said forward open side of the exit chamber forming an angle from about 20° to about 45° with the horizontal.

The headbox is provided with a turbulence inducing rotatable prismatic bar to promote and induce turbulence in the slurry. The turbulence inducing bar must be positioned within the path of flow of the slurry from the flowably connected supply means to the exit chamber to maintain a constant turbulence in the slurry, yet in a position below the point of deposition on the screen so that turbulence is not present when deposition on the moving screen takes place. The exact position of the bar will vary depending on the size of the headbox and the volume of slurry. Turbulence at the point of deposition would result in a non-uniform sheet due to uneven deposition. Preferably the turbulence inducing bar is positioned at the juncture of the horizontal entrance chamber with the upwardly inclined exit chamber and would be of rectangular, hexagonal or octagonal cross section.

The position of the turbulence bar with relation to the point of deposition on the moving screen is very important since unless the bar is positioned a sufficient distance from the point of deposition to allow a substantial reduction of turbulence, the sheet deposited on the screen will not be characterized by uniformity of thickness but will exhibit thick and thin areas resulting from the clumping or the bunching of the fibers or filaments just prior to deposition. When the turbulence is substantially reduced just prior to deposition, the filaments in suspension remain in their thoroughly intermixed state and are, therefore, evenly deposited on the screen since there are then no channels or eddy currents present which would cause the bunching or clumping of filaments or fibers.

The turbulence bar is necessary to thoroughly mix the filaments and fibers in the slurry so that they will be deposited in an intertwined and interlaced relationship to form a strong sheet. The position of this turbulence bar is then very important and it must be positioned such a distance from the point of deposition on the screen to allow substantial reduction in turbulence just prior to deposition since this would allow the fibrils and fibers to float to the surface or settle to the bottom and in either case, greatly reduce the degree of interlacing or intertwining of filaments deposited on the moving screen. This, of course, would result in a weak sheet unsuited for most of the uses contemplated by this invention.

The term "flowably connected" designates that the supply means, the entrance chamber and the exit chamber are so connected that a liquid may flow therethrough. By the term "substantially horizontal" is meant that the direction of flow of a liquid passing through the entrance chamber is principally in the horizontal direction. The entrance chamber, therefore, may be tilted upward or downward providing that the direction of flow of the liquid remains principally in a horizontal direction.

The terminology "having a downstream cross-sectional area of less than about three times the upstream cross-sectional area" is used to signify that the entrance chamber is not appreciably greater in area than the supply con-

duit. The entrance chamber may thus have a lower cross-sectional area than the supply conduit, the same cross-sectional area, or a larger cross-sectional area providing it is not more than about three times as large. It is preferred, however, that the supply conduit area be larger than that of the entrance chamber in order to increase the velocity of the liquid flowing through it. By so regulating the cross-sectional area, the liquid remains in turbulent flow and the slurry does not tend to "clump" or settle out.

The invention will be more readily understood by reference to the drawings.

FIGURE 1 is a flow sheet diagramming a continuous process for producing a sheet in which a suspension containing a mixture of staple and fibril is deposited on a Fourdrinier machine.

FIGURE 2 illustrates diagrammatically the process of FIGURE 1, identifying the equipment and the principal parts of the Fourdrinier machine as discussed more in detail hereinafter.

FIGURE 3 is a diagrammatic representation of the headbox 13 of the present invention which is shown on the Fourdrinier machine in FIGURE 2.

Typical processes wherein papermaking machinery may be used in producing sheet products from fibrils are illustrated in FIGURES 1 and 2. As mentioned previously, FIGURE 1 is a flow sheet showing a suitable commercial system wherein a slurry of fibrils is fed from "Fibril Supply" through a "Refiner" into a "Stock Tank." The staple is slurried with water in another stock tank or in a slurrying device such as a "Hydrapulper." At the first "Mixer" the two slurries are brought together in a region of high velocity, intense turbulence, and low hold-up volume such as in a pipe T. Following the first "Mixer," the mixture may be diluted further and broke added in a second "Mixer." The second "Mixer" then feeds the "Fourdrinier Machine" wherein the waterleaf is laid down, progressing thereafter through the "Wet Press," the "Dryer Rolls," the "Calender" and finally to the "Product Reel." The "Broke," i.e., collection of scraps in various stages of dryness, is fed through a "Slusher" for recycling to the second "Mixer."

FIGURE 2 is a diagrammatic representation of the flow sheet showing a supply of suspending liquid 1, feeding fibril mixing vessel 2 through valve 3 and the staple suspending vessel 4 through valve 5. Each vessel is supplied with an agitator 6. A supply of fibril is fed to vessel 2 from a "fibril cake" 7. A supply of yarn 8 is fed through cutter 9 into staple suspending vessel 4 or alternatively pre-cut staple fibers are metered from a bale. The slurries in each of the suspending vessels are pumped by pumps 10 into mixing T 11, the fibril slurry optionally passing through a Refiner 12. The pumps used for the fiber slurry should be of a type which does not generate foam and does not tend to clog. A suitable pump is, for example, the Vanton "Flex-i-liner" (made by the Vanton Pump Company of Hillside, New Jersey), which is an eccentric rotor pump with no rotating or oscillating parts in contact with the liquid. Also suitable is the Ingersoll Rand centrifugal pump having an Egger closed impeller, or other centrifugal pumps of similar design. The fibril pump may be of any conventional design. The mixed slurry then flows through a headbox 13 and onto moving screen 14, the water passing through the said screen and being removed in part by table rolls 15 and suction boxes 15'. As the screen reaches couch roll 16, a waterleaf 17 of the suspended solids is formed. The screen 14 being continuous passes back over stretch roll 18 and breast roll 19. Waterleaf 17 passes under fly roll 20, between wet press rolls 21, over guide roll 22 to a series of dryer rolls 23, to a calender stack 24 and finally to a windup reel 25. A sheet containing only a low proportion of fibrils may tend to delaminate as it passes under the wet press roll 21 in such a way that fibers are

pulled up from the surface of the sheet and, in some cases, even adhere to the surface of the wet press roll 21. This difficulty can be minimized by using a press roll with a low friction surface, for instance a roll coated with polytetrafluoroethylene.

FIGURE 3 is a diagrammatic representation of the headbox 13 of the present invention which is shown on the Fourdrinier machine in FIGURE 2. The supply orifice 26 supplies the slurry to the entrance chamber 27 which in turn supplies it to the exit chamber 28. A rotating non-round turbulence inducing bar 29 in the exit chamber 28 maintains the slurry in turbulent flow until the sheet-like structure 35 is deposited on moving screen 34 as it passes between the stretch roll 32 and breast roll 33. The screen may be supported along its inclined portion by the use of open-faced rolls such as conventional dandy rolls. The upper face of the exit chamber 28 is enclosed. The lower face of the exit chamber is open down to the forward lip 31 which rests against the moving screen 34. The liquid level 36 is maintained above the forward lip 31 so as to deposit the solids from the slurry onto the moving screen 34. A flexible film 30 is draped from the top portion of the headbox onto the liquid level 36 so as to eliminate the free surface of the slurry. The flexible film 30 may be held below the liquid level 36 by means of a rod (not shown) passing through the headbox. The flexible film 30 causes a uniform sheet-like structure 35 to be formed on moving screen 34. The angle A is maintained between about 20° and about 45° for optimum quality sheet formation. For very small angle A, the force of the incoming slurry passing over the top of the newly-deposited, half-formed sheet causes masses of fiber to be picked up from one spot on the sheet and deposited elsewhere. The result is an inhomogeneous sheet having unacceptable thick and thin spots. In addition for small angle A the properties of the sheet are highly directional which may be undesirable. In order to avoid these difficulties, in the process of this invention the angle A should be at least about 20°. It is preferable that angle A be less than about 45° in order to avoid irregularities in the sheet structure due to sliding back of the newly-deposited, slushy material. Slide-back is especially noticeable at the point where the sheet structure breaks the surface of the slurry. It can be minimized by applying suction at the point at which the sheet emerges from the slurry. It can also be reduced by bringing the level of the slurry up onto the nearly-horizontal portion of the wire. (This portion of the wire will not actually be horizontal, but will be tilted rearwardly at a slight angle, which is usually less than about 3°.)

FIGURES 4 and 5 show the non-round turbulence bar with hexagonal and octagonal cross sections, respectively.

The headbox is provided with a turbulence inducing rotatable non-round bar to promote a controlled turbulence in the slurry. The said bar must be positioned within the headbox across the flow of the slurry, yet in a position before the point where deposition on the moving screen takes place so that turbulence is not present when deposition occurs. The exact position of the bar will vary depending on the size of the headbox and the volume of the slurry. Uncontrolled turbulence at the point of deposition would result in a non-uniform sheet due to uneven deposition. Preferably the turbulence inducing bar is positioned at the juncture of the horizontal entrance chamber with the upwardly inclined exit chamber and would be of rectangular, hexagonal or octagonal cross section.

The position of the turbulence bar, with relation to the point of deposition on the moving screen, is very important since unless the bar is positioned a sufficient distance from the point of deposition to allow a substantial reduction of turbulence, the sheet deposited on the screen will not be characterized by uniformity of thickness but will exhibit thick and thin areas resulting from the clumping or bunching of fibers just prior to deposition. When

the turbulence is substantially reduced, just prior to deposition, the fibers in suspension remain in their thoroughly intermixed state and are, therefore, evenly deposited on the screen since there are no channels or eddy currents present which would cause the bunching or clumping of fibers.

The following examples are cited to illustrate the invention. They are not intended to limit it in any manner.

PREPARATION OF FIBRIDS

Example I

HARD POLYMER FIBRIDS

A copolymer of caprolactam, hexamethylene diamine, and adipic acid is prepared, containing 80% by weight of caproamide units and 20% by weight of hexamethylene adipamide units. The polymer flake is cut to pass through a $\frac{3}{8}$ -inch screen. A 15% solution with a viscosity of 150 centipoises is prepared by adding this polymer (50 pounds) to a mixture of 255 pounds of ethylene glycol and 28.3 pounds of water in a 50-gallon tank and stirring at 115° C. for $3\frac{1}{2}$ hours. The precipitant is prepared by mixing 108 gallons of ethylene glycol with 100 gallons of water and cooling to -16° C. This precipitant, which has a viscosity of approximately 10 centipoises at this temperature, is fed into a tank with a 15 gallon holdup at the rate of 3.54 gallons per minute. After 8-10 gallons have been added to the tank, addition of the polymer solution at a temperature of approximately 110° C. is started at a rate of 4.24 pounds per minute while addition of the precipitant is continued at the same rate. The stirrer in the tank is operating at 4100 r.p.m. The "precipitation value" for P, is calculated in accordance with the equation previously discussed.

The fibrid slurry is removed from the bottom of the tank to maintain a constant volume. Blending is continued until 235 pounds of polymer solution have been used. The temperature of the product slurry rises to -7° C. during the process. A total of 237 gallons of slurry containing 1.7% solids is obtained. The slurry of fibrids is filtered on an Eimco rotary drum filter and washed with water until substantially free of solvent. The final filter cake obtained contains 17-18% of fibrids having the properties hereinbefore set forth. Classification of these fibrids in a Clark pulp classifier shows the following results:

Screen mesh—	Cumulative percent retained
30	50.5
50	79.3
100	93.3
150	98.8

Example II

SOFT POLYMER FIBRIDS

A segmented elastomer is prepared by condensing 124.5 grams (0.12 mol) poly(tetramethylene oxide) glycol having a molecular weight of about 1000 and 10.50 grams (0.06 mol) of 4-methyl-m-phenylene diisocyanate with stirring in an anhydrous atmosphere for 3 hours at steam bath temperatures. 30.0 grams (0.12 mol) of methylene bis(4-phenyl isocyanate) dissolved in dry methylene dichloride is added to the hydroxyl-terminated intermediate and the mixture is stirred for 1 hour on a steam bath to produce an isocyanate-terminated derivative which, after cooling, is dissolved in 400 grams of N,N-dimethylformamide. A polymer solution containing about 28% solids is formed on addition of 3.0 grams (0.06 mol) of hydrazine hydrate dissolved in 26 grams of N,N-dimethylformamide.

The polymer solution produced as described above is diluted to an approximately 15% solids content. A red pigment (Watchung Red RT-428-D) is then mixed with this solution at a concentration of 2.1 parts of pigment per 100 parts of elastomer. The pigmented solution is

then diluted with N,N-dimethylformamide to an elastomer concentration of 11%. This solution, which has a viscosity of 1700 centipoises, is fed into a bank of 6 one-quart Waring Blenders at a total rate of 625 milliliters per minute simultaneously with 4400 milliliters per minute of a precipitant comprising a mixture of 14 parts of N,N-dimethylformamide and 86 parts of glycerine. The solution and precipitant streams are divided on entering each Blender by means of a manifold, so that each liquid enters as 20 individual streams. The Blenders are operating at top speed, so that the converging streams are thoroughly beaten to continuously form a fibrid slurry, which is withdrawn continuously from an outlet in the wall of each Blender. The effluent slurry contains approximately 1.37% solids. The equipment is run continuously for 5 hours to produce approximately 45 pounds of fibrids slurried in a mixture of glycerine and N,N-dimethylformamide.

The solvent/precipitant mixture is removed from the slurry by repeated decantation followed by redispersion of the floating fibrid cake in water. When substantially all of the organic liquids are removed, the fibrids having the properties hereinbefore set forth are diluted with water to a consistency of 0.4%. An alkylphenoxy poly(ethylene oxide) non-ionic wetting agent (0.1% by weight) ("Triton X-100," made by Rohm and Haas Company, Philadelphia, Pennsylvania) is added to maintain the dispersion.

(The Waring Blender is modified in this experiment by removing the nut which holds the blade of the shaft, welding a small nut to the under side of the blade, and remounting the blade on the shaft so that the end of the shaft does not protrude above the top surface of the blade.)

HEADBOX CONSTRUCTION

A headbox is constructed according to FIGURE 3 having the following approximate dimensions (with the upper side of the entrance chamber being horizontal).

Entrance chamber 27:	
Supply means area (pipe)-----	3 square inches.
Length-----	36 inches.
Opening at exit chamber-----	12 inches x $\frac{1}{2}$ inch.
Exit chamber 28:	
Vertical Height (above horizontal)----	12 inches.
Width (across the sheet)-----	12 inches.
Depth (perpendicular to moving screen)-	2 inches.
Forward lip length-----	2 $\frac{1}{2}$ inches.
Angle A-----	45 degrees.
Roller 29:	
Shape-----	Hexagonal.
Outer diameter-----	1 $\frac{1}{2}$ inches.
Flexible film 30:	
Polyethylene film.	

The headbox of the Fourdrinier is replaced by the modified headbox above-described. The moving screen of the machine is adjusted to move at an angle of 45° with the horizontal so that it corresponds to the open face of the headbox. The breast roll 33, which is normally a solid roll, is replaced with a 6-inch open roll of dandy roll construction. Inflatable flexible tubing (rubber) is used around the open face of the headbox to form a seal with the moving screen and prevent leakage. In each of the following examples the roller 29 was rotated at 100 r.p.m.

PREPARATION OF SHEET-LIKE STRUCTURES

Example III

HARD FIBER/FIBRID PAPER

The 20/80 6-6/6 fibrids prepared as in Example I are slurried to a concentration of 0.25%. This slurry is refined by passage at a throughput rate of 14 gallons per minute through an 8-inch disc mill set at .0005-inch clearance with disc pattern No. 6946. The disc mill is made by the Bauer Brothers Company, Springfield, Ohio. The

slurry is then diluted to 0.03%. A fiber slurry is prepared at a concentration of 0.07% from ¼-inch, 3-denier per filament, 6–6 nylon fibers which have been soaked and then dried in a solution of a non-ionic wetting agent (the condensation product of 20 moles of ethylene oxide with 1 mole of a mixture of long-chain fatty alcohols having an iodine number of 50 and a hydroxyl number of 220 and containing principally C₁₆ and C₁₈ alcohols, approximately 50% of which are unsaturated).

The fiber and fibril slurries are mixed at a mixing T and are pumped (while in turbulent flow) into the headbox described above of the modified Fourdrinier machine at a volume rate of flow of 32 gallons per minute. The lifetime of the fiber/fibril slurry is about 9 seconds. The ratio of fibers to fibrils in the slurry is 70 to 30, and the consistency of the slurry is 0.05%. The slurry is deposited on the wire, traveling at a rate of 7½ feet per minute, as a one-foot wide sheet. The sheet is dried and wound up. It has a basis weight of 2½ ounces per square yard. When it is bonded by calendaring twice at 190° C. at 20 feet per minute and a pressure of 1000 pounds per inch, the tensile strength in the machine direction is 18.3 pounds per inch per ounce per square yard and in the transverse direction 15.1 pounds per inch per ounce per square yard. When bonded by calendaring at 190° C. 6 times at 20 feet per minute and 2000 pounds per inch, the properties are 14.1 pounds per inch per ounce per square yard in both the machine direction and the transverse direction.

Example IV

GLASS FIBER REINFORCED PLASTIC SHEET

A 15% solution of polymethyl methacrylate compression molding resin, "Lucite" 140 (inherent viscosity 0.45, molecular weight 115,000), is prepared by dissolving the polymer chip in methyl ethyl ketone at 65° C. Fibrils are prepared from this solution using the apparatus of Example I. The polymer solution is introduced into the mixing tank through a spinneret having 50 ¼-inch holes at a rate of ½ gallon per minute. The precipitant, water, is introduced at a rate of 6 gallons per minute. The stirring rate is 3500 r.p.m. The effluent slurry has a fibril concentration of 1.15%. It is pumped to a stock tank and diluted to 0.20%.

Owens-Corning 707 ¼-inch, 9 micron diameter glass fibers are soaked in a 1% solution of non-ionic wetting agent (the condensation product of 20 moles of ethylene oxide with 1 mole of a mixture of long-chain fatty alcohols having an iodine number of 50 and a hydroxyl number of 220 and containing principally C₁₆ and C₁₈ alcohols, approximately 50% of which are unsaturated) for 2 hours. This slurry is diluted to 0.24% and stirred for an additional hour. The fiber slurry is pumped at 10 gallons per minute into the mixing T, where it meets the fibril slurry flowing at 27 gallons per minute. The fiber/fibril slurry formed at the T has a consistency of 0.21%. The slurry is maintained in turbulent flow until it reaches the area of deposition where it is deposited on the screen by the headbox described above. The lifetime of the fiber/fibril slurry is about 6 seconds. A one-foot wide sheet is formed on the wire moving at a rate of 7.5 feet per minute. The sheet is dried on the machine and is cut into 2-foot lengths at the dry end. These cardboard-like sheets are ½-inch thick after drying and have a basis weight of 12.9 ounces per square yard. They are composed of 70% polymethyl methacrylate fibrils and 30% glass fibers. The sheets are laminated and pressed at 175° C. and 1500 p.s.i. The properties of the product are: tensile strength—8,580 p.s.i.; tensile modulus—891,000 p.s.i.; elongation—1.8% yield strength—6,520 p.s.i.; flexural strength—15,200 p.s.i.; flexural modulus—856,000 p.s.i.

Example V

The soft polymer fibrils of Example II are prepared as a 0.24% aqueous slurry and pumped into the mixing T. A 0.06% aqueous slurry of ½-inch, 2-denier polyhexa-

methylene adipamide fibers, previously coated with the non-ionic wetting agent of Example III, meets the fibril slurry at the T. The mixed slurry has a consistency of 0.15%. It is deposited on the screen traveling at 5 feet per minute as a one-foot wide sheet. Most of the water is removed on the drier rolls; final drying and curing is completed by passing between infrared heaters. The sheet has the appearance and hand of felt and the following properties: basis weight—10 ounces per square yard; tensile strength—1.9 pounds per inch per ounce per square yard; elongation—30%; tongue tear 0.655 pound per ounce per square yard. An 8 inch x 8 inch portion of the sheet is pressed between polytetrafluoroethylene-coated plates at 170° C. and 650 p.s.i. for four minutes to give a fiber-reinforced elastic structure with the following properties: tensile strength—6.64 pounds per inch per ounce per square yard; elongation—35%; tongue tear—0.281 pound per ounce per square yard.

The fibrils used in this invention can be formed from any soluble, synthetic, preferably fiber-forming polymer as well as any condensation polymer which can be formed by interfacial spinning. As previously mentioned, it is convenient in considering such polymers to classify them as "hard" and "soft" polymers.

"HARD" POLYMERS

Suitable hard polymers include acrylonitrile polymers and copolymers, such as those formed by acrylonitrile with methyl acrylate or vinyl chloride; polyacrylic and polymethacrylic esters, such as poly(methyl methacrylate); poly(vinyl chloride) and copolymers of vinyl chloride with vinyl esters, acrylonitrile, vinylidene chloride, and the like; vinylidene chloride polymers; polyhydrocarbons, such as polystyrene and polyethylene; chlorosulfonated polyethylene; polychlorotrifluoroethylene; poly(vinyl alcohol); partially hydrolyzed poly(vinyl esters); polyamides, such as poly(hexamethylene adipamide), poly(ethylene sebacamide), poly(methylene bis[p-cyclohexylene] adipamide), polycaprolactam, and copolyamides, such as those formed from a mixture of hexamethylenediamine, adipic acid, and sebacic acid, or by a mixture of caprolactam, hexamethylenediamine, and adipic acid; polyurethanes; polyureas; polyesters, such as poly(ethylene terephthalate); polythioesters; polysulfonamides; polysulfones, such as the one prepared from propylene and SO₂; polyoxymethylene; and many others. Copolymers of all types may be used. Derivatives of the polymers, such as the halogenated polyhydrocarbons, are also suitable. Fibrils can be prepared from polymers which are tacky at room temperature, such as poly(vinyl acetate), by chilling the solution and precipitant below the temperature at which the polymer becomes tacky.

"SOFT" POLYMERS

Representatives of "soft" polymers are the plasticized vinyl polymers and the condensation elastomers. The plasticized vinyl polymers are prepared by mixing any suitable plasticizer with a compatible vinyl polymer. The ester type of plasticizer has been found to be quite satisfactory. Plasticized vinyl chloride polymers, including copolymers with vinyl acetate and vinylidene chloride, have been found to be particularly suitable. Fibrils may be made from certain uncured elastomers by the methods applicable to the tacky hard polymers. The properties may then be modified by suitable curing procedures.

A wide variety of low modulus condensation elastomers are available for preparing fibrils. A condensation elastomer will usually form shaped articles having a tensile recovery above about 75% and a stress decay below about 35%.

Segmented condensation elastomers are prepared by starting with a low molecular weight polymer (i.e., one having a molecular weight in the range from about 700 to about 3500), preferably a difunctional polymer with terminal groups containing active hydrogen, and reacting it with a small coreactive molecule under conditions such

that a new difunctional intermediate is obtained with terminal groups capable of reacting with active hydrogen. These intermediates are then coupled or chain-extended by reacting with compounds containing active hydrogen. Numerous patents have been issued in which the low molecular weight starting polymer is a polyester or polyesteramide and the co-reactive small molecule is a diisocyanate. A large variety of co-reactive active hydrogen compound is suggested in these patents for preparing the segmented condensation elastomers. Among the most practical chain-extending agents are water, hydrazine, diamines, and dibasic acids.

United States Patent 2,692,873 describes similar products in which the starting polyesters have been replaced by polyethers of a corresponding molecular weight range. More recent developments have shown that a number of suitable macromolecular compounds, such as polyhydrocarbons, polyamides, polyurethanes, etc., with suitable molecular weights, melting point characteristics, and terminal groups, can serve as the starting point for preparing segmented elastomers of this type. It has also been found possible to replace the diisocyanate with other difunctional compounds, such as diacid halides, which are capable of reacting with active hydrogen. In addition, elastic copolyetheresters are obtained by condensation of a polyether glycol, an aliphatic glycol, and an aromatic dibasic acid or suitable derivative.

Other types of condensation elastomers are also suitable. United States Patent 2,670,267 describes N-alkyl-substituted copolyamides which are highly elastic and have a suitable low modulus. A copolyamide of this type, obtained by reacting adipic acid with a mixture of hexamethylenediamine, N-isobutylhexamethylenediamine, and N,N'-isobutylhexamethylenediamine produces an elastomer which is particularly satisfactory for the purposes of this invention. United States Patent 2,623,033 describes linear elastic copolyesters prepared by reacting glycols with a mixture of aromatic and acyclic dicarboxylic acids. Copolymers prepared from ethylene glycol, terephthalic acid, and sebacic acid have been found to be particularly useful. Another class of condensation elastomers is described in United States Patent 2,430,860. The elastic polyamides of this patent are produced by reacting polycarbonamides with formaldehyde.

POLYMER SOLUTIONS

Useful solvents or solvent mixtures for preparing solutions to be used in the preparation of fibrils by the "shear precipitation" process should dissolve at least about 5% by weight of the polymer, copolymer, or polymer mixture. When solutions containing concentrations below this level are used, the fibrils obtained on precipitating the polymer tend to be too fine and too small to be useful in such applications as the preparation of sheet products. A practical upper limit to solution concentration is approximately 30%. Above this level the solution viscosity becomes so high that it is difficult to disperse the solution into the precipitant and obtain a satisfactory fibril. The preferred concentration range is about 15% for soft polymers and between about 8 and about 15% for hard polymers. The concentration of polymers is usually adjusted to provide a solution with a viscosity between about 100 and about 10,000 centipoises for soft polymers, or between about 350 and about 1500 centipoises for hard polymers, since solutions in this viscosity range have been found to operate more satisfactorily.

POLYMER SOLVENTS

A large variety of organic liquids is suitable for preparing these solutions. The particular solvent chosen will depend upon toxicity, cost, the polymer being used, type of fibril desired, and the like. As is usual, the best balance between cost and optimum product will be selected. The solvents which have been found most widely useful are polar solvents, such as N,N-dimethylformamide and N,N-dimethylacetamide, m-cresol, formic acid, and

sulfuric acid. Plasticized vinyl polymers are frequently soluble in common organic solvents, such as acetone, chloroform, and mixtures of chloroform with alcohols, such as methanol. Another useful group of liquids includes those which dissolve the polymer at high temperatures but which are non-solvents at temperatures in the neighborhood of room temperature. Thus, it is possible to use these liquids as both solvents and precipitants by controlling the temperature, as, for instance, ethylene glycol used with polyamides, tetramethylene sulfone used with poly(ethylene terephthalate), and xylene used with polyethylene.

POLYMER PRECIPITANTS

A liquid is suitable as a precipitant if it dissolves no more than about 3% by weight of the polymer. It is preferable, but not absolutely essential, that the precipitant be miscible with the polymer solvent in the proportions used. Some degree of miscibility is, of course, essential. Suitable precipitants are water, glycerin, ethylene glycol, ether, carbon tetrachloride, acetone/hexane and dioxan/hexane mixtures, triethanolamine, etc. Water-miscible precipitants are preferred and aqueous organic liquid mixtures, particularly water-glycerol mixtures, are an important group of precipitants. Glycerol alone or aqueous solutions containing small amounts (i.e., up to about 20%) of water have been found to be the best precipitants for the condensation elastomers. Mixtures of solvents and precipitants, such as diluent aqueous solutions of the solvent, have also been found to be useful. Water alone is particularly desirable for economic reasons and can be used as a precipitant, particularly when a thickener, such as sodium carboxymethylcellulose has been added.

The viscosity of the precipitating medium may be controlled over a wide range by changing the temperature or by the use of additives, including thickeners such as poly(vinyl alcohol). Precipitants are operable over a wide range of viscosities, e.g., from about one to about 1500 centipoises. The effectiveness of the shearing action provided by the stirrer is enhanced by decreasing the viscosity of the solution and/or increasing the viscosity of the precipitant. Relatively viscous precipitating media are preferred.

The staple fibers which may be employed are not limited to synthetic fibers although fibers of any of the hereinbefore mentioned "soft" or "hard" polymers as well as others may be so used. Thus other materials such as wool, cotton, spun glass, asbestos, or the like, or combinations thereof, may be employed as the staple fibers for this process.

In a preferred embodiment of the invention each element of fiber/fibril slurry is deposited on the moving screen within about 15 seconds after its formation. This is preferably done by mixing the fibers and fibrils continuously in a mixing T and, as soon as possible thereafter, depositing the slurry on the moving screen. By holding each element or portion of the fiber/fibril slurry to a lifetime of less than about 15 seconds, flocculation problems are substantially avoided.

In another preferred embodiment, the staple fibers are dispersed using a wetting agent which results in a uniform dispersion being formed and consequently uniform sheet-like structures. The wetting agent may be added directly to the dispersion of fibers, or the fibers may be coated with the wetting agent prior to the formation of the dispersion. When using synthetic fibers this is conveniently accomplished by leading the tow through a solution of the wetting agent prior to the tow being cut into staple. In general, the conditions should be so regulated that the final slurry contains only a few percent of the wetting agent (based on the weight of the staple fibers). When a non-ionic wetting agent is employed about 0.5 to about 1.0% of the wetting agent is sufficient to obtain good results. A cationic wetting agent, however, requires from

about 3 to about 5% to accomplish the same results and the non-ionic wetting agent is preferred.

When such coated fibers are dispersed no prohibitive additional expense is incurred because of the very small amounts of hydrophilic agents applied. These agents also tend to minimize the formation of objectionable foam. The proper selection of agitators, pumps, dilution water entrances, etc., are all designed or chosen with this in mind. In some instances deaeration of the slurries, particularly the fiber slurry, is also desired to prevent foaming. If the fibers are properly cut, with no fused or long ends, gentle agitation will be sufficient to produce a uniform suspension of the fibers in water, particularly if they are dropped gradually onto the surface of the gently agitated water. The coatings are retained on the surface of the fibers sufficiently well to permit redispersion of the fibers, even after they have been processed into papers or sheets. This is particularly advantageous in the reprocessing of broke.

Another advantage derived from the use of properly cut, hydrophilically-coated fibers is the ease and simplicity of continuous processing. Water and fibers may be continuously metered (by the cutter or other suitable staple metering devices) in the desired proportion to the dispersing tank. Dwell time in the tank need only be long enough to assure uniform dispersion (not more than 3 to 5 minutes). A minimum of mechanical work is thus required to produce a smooth and uniform dispersion and an economical advantage of low stock chest capacity is realized.

The sheet-like products produced according to this invention vary from a paper-like sheet to sheets having leather-like qualities. In general, the "soft" polymer fibrils produce sheets having a fabric-like drape and a pleasing soft hand similar to that of suede, leather, or chamois whereas the "hard" polymer fibrils tend to produce a harder finish and hand. As the amount of staple fibers in the fibril sheet increases it tends to produce stiffer and stronger sheets. The sheet properties may also be modified by mixing both "soft" and "hard" polymer fibrils or by blending cellulosic pulps into the fibril slurry.

The properties of the sheet-like structures may also be modified by increasing the speed of the moving screen and by increasing the amount of vacuum used to deposit the slurry. As the speed of the moving screen is increased less of the solids from the slurry are deposited and a thin paper-like product results. With a slower moving screen the solids tend to build up and a thicker sheet is produced. By controlling the vacuum on the paper-making machine the compactness as well as the thickness may be varied. Thus, when a higher vacuum is used the sheet-like structure tends to be more compact and less porous.

Another method of controlling the type of product produced is by calendering the sheet prior to or after its removal from the machine. By using heat and pressure the fibrils may be fused partially or completely into a solid mass. This may also be accomplished in the absence of pressure by using infrared panels or the like. While the structure of the fibril is generally lost in such an operation the resulting product is of quite high strength which is probably due to the uniform distribution of the fibers in the polymer.

The sheet-like products of the present invention may be used in a variety of ways depending on the various modifications used to produce these products. The thin paper-like sheets may be used as paper for such applications such as maps, blueprints, and packaging ma-

terials for use in humid climates. The thicker products are useful as non-woven fabrics, felts, synthetic leather, tarpaulins, tentage materials, cardboards and other sheet structures having a great range in basis weights and a great variety of composition.

Many equivalent modifications will be apparent to those skilled in the art from a reading of the above without departure from the inventive concept.

This application is a continuation-in-part of the United States patent application Serial No. 676,013, filed August 2, 1957, now abandoned.

What is claimed is:

In a continuous process for forming a continuous non-woven sheet-like structure, said sheet-like structure having uniform thickness and uniformity of physical properties throughout its length and width, said process comprising, in combination, the following steps; forming a first slurry of fibers having a length of from about $\frac{1}{8}$ to about 1 inch, and a wetting agent in water, forming a second slurry of fibril elements in water, continuously blending the first and second slurries in a first zone to form a resulting slurry containing between about 0.03% and about 0.10% solids by weight, the solids comprising at least about 5% by weight of fibrils, moving the resulting slurry rapidly and continuously to a second zone adjacent to a screen conveyor moving in a path inclined at an angle of from about 20° to about 45° to the horizontal plane, maintaining the resulting slurry in continuous condition of high turbulence during its movement from said first zone to said second zone to evenly distribute the solids in the slurry and cause entwinement and interlacing of the fibers and fibril elements, applying a pressure differential tending to move the resulting slurry through the moving screen conveyor at a given position in said second zone to cause said solids to collect on one side of the screen conveyor to form a continuous sheet-like non-woven structure, while simultaneously in a limited portion of said second zone which portion includes said given position in said zone, significantly reducing the turbulence of said resulting slurry, the location of said given position in the limited portion of said second zone, the speed of movement of the screen conveyor, the magnitude of the pressure differential all selected so that the resulting slurry is evenly smoothly applied to said one side of said screen conveyor with said fibril elements and fibers evenly distributed and entwined and interlaced, before said elements and fibers can settle out or form clumps due to the reduced turbulence in the said limited portion of said second zone, the movement of the resulting slurry after blending being such that the resulting slurry is collected on said screen in a time period of no more than about 15 seconds after the resulting slurry is formed, the improvement comprising controlling the upper surface of the resulting slurry to prevent free surface action during formation of the sheet-like structure on the moving screen conveyor.

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