May 6, 1969 J. C. DAVID 3,442,740

PROCESS FOR PRODUCING A BONDED NONWOVEN SHEET

Filed April 12, 1965 Sheet 1 of 3

FIG. 1

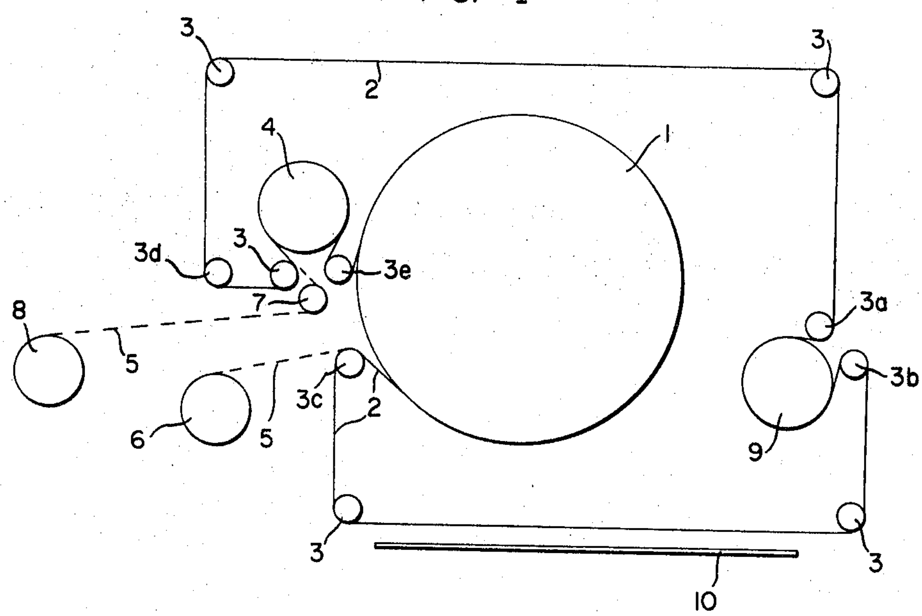

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FIG. 2

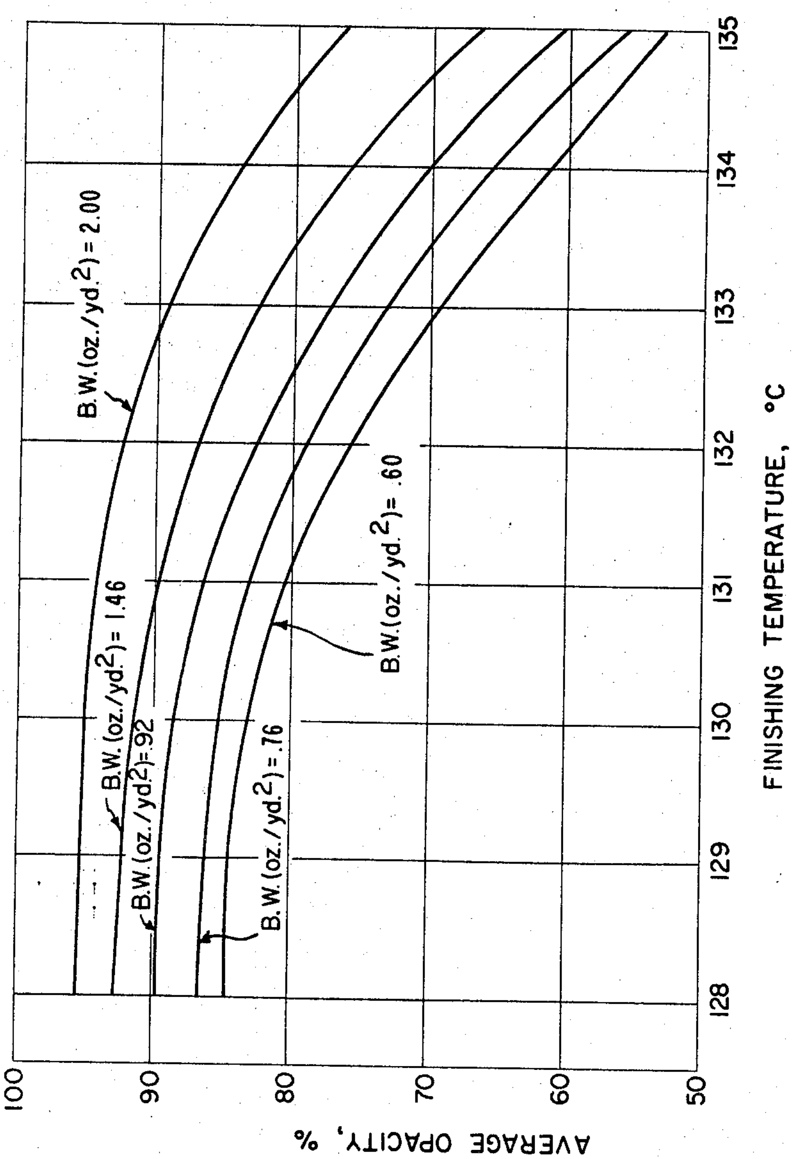

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FIG. 4

SURFACE AREA OF SHEETS HOT PRESSED AT VARIED TEMPERATURES
(NITROGEN ADSORPTION METHOD)

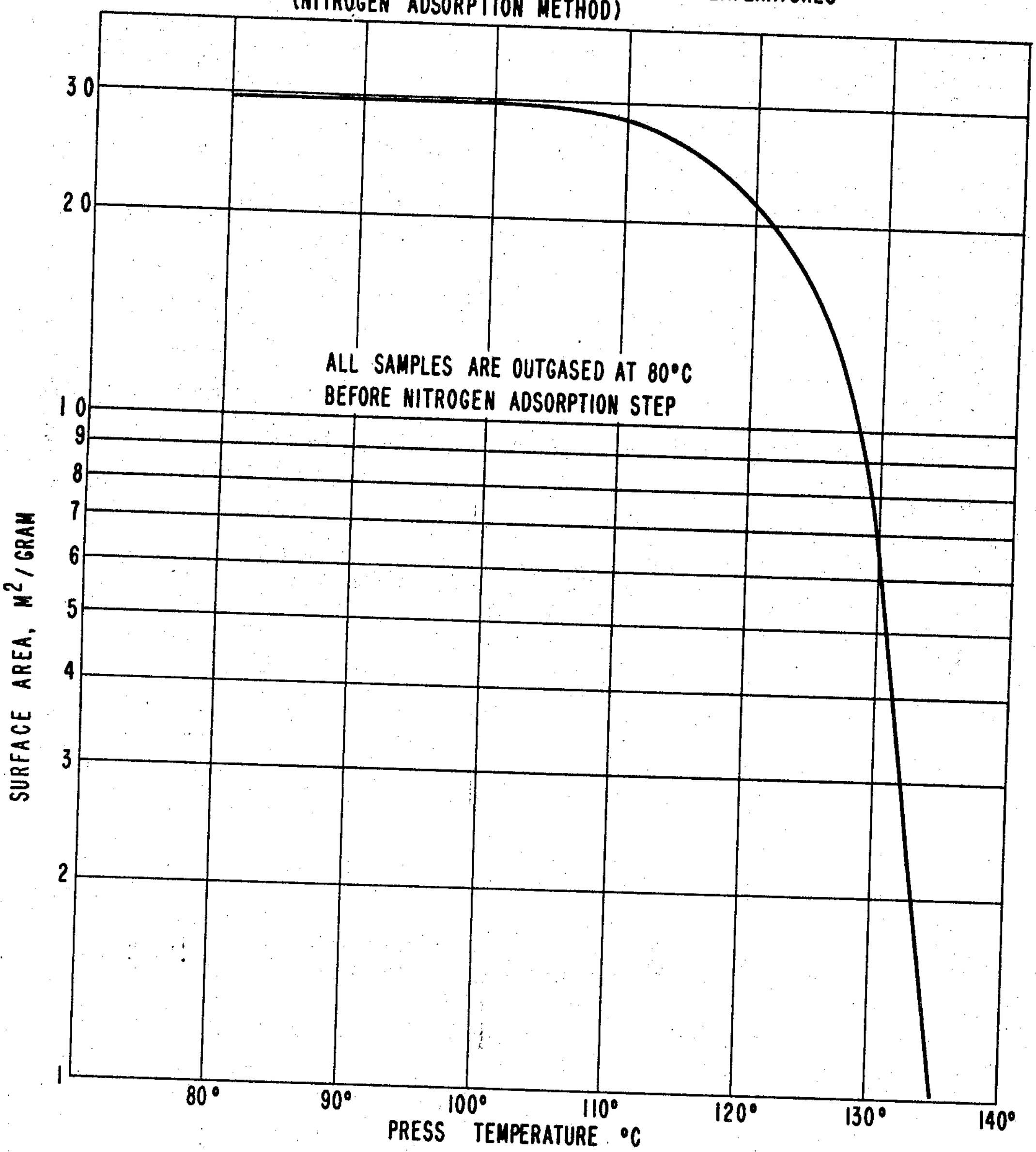
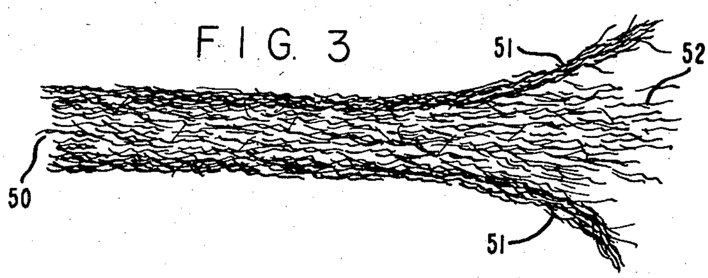


FIG. 3



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3,442,740

Patented May 6, 1969

3,442,740

PROCESS FOR PRODUCING A BONDED NON-WOVEN SHEET

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Continuation-in-part of application Ser. No. 358,694, Apr. 10, 1964. This application Apr. 12, 1965, Ser. No. 448,582

Int. Cl. B32b 27/12, 31/20

U.S. Cl. 156—181 5 Claims

This application is a continuation-in-part of United States patent application Ser. No. 358,694 filed Apr. 10, 1964, now abandoned.

This invention relates to a finishing procedure for nonwoven sheets of film-fibril strand material. More particularly it relates to such a finishing procedure whereby the surface of the sheet achieves a flat stable condition without the over-all sheet undergoing excessive losses in opacity, uniformity of opacity, or thickness. The invention also relates to the products formed by these procedures having high delamination resistance.

U.S. Patent No. 3,169,899, to Steuber describes the formation of "film-fibril" sheets by the random overlapping deposition of continuous fibrillated strands. These strands, described in Blades et al. U.S. Patent No. 3,081,519, are each characterized as a three-dimensional network of film-fibrils which are interconnected at random intervals along and across the strand. The individual film-fibrils are composed of molecularly oriented crystalline organic polymer, the average polymer thickness in the film-fibrils being less than 4 microns. The initially deposited film-fibril sheets may be compressed and/or fused, e.g. by calendering or by hot air treatments, to further develop certain desired qualities. However, a sheet treated in such a manner tends to be translucent, stiff, low in bulk, or tends to have translucent areas and a nonplanar wavy surface. For certain applications such as book binding a film-fibril sheet should exhibit constant opacity throughout its area, good flatness, and, on one surface at least, high abrasion resistance or surface stability. In this particular use it is advantageous for the other surface to be sufficiently porous so as to readily accept adhesives for gluing the sheet to an adjacent backing layer during the book assembly operation. Similar properties are needed in a sheet used for wall covering, but in this case the hard surface is used against the wall to promote easy removal, and the porous surface is used to collect a coating material. In uses such as these it is decidedly advantageous to have a distinct "one-sidedness," i.e. a surface-to-surface gradient with respect to properties such as density and surface area per gram. Such materials should also have high resistance to delamination so that the wall covering may later be removed from the wall without leaving fibers behind.

In other cases it is advantageous to maintain a less bonded center in the sheet but at the same time to develop hard surfaces on both sides of the sheet.

It is accordingly an object of this invention to provide a thermally bonded film-fibril sheet having uniform high opacity, a high degree of flatness, and high surface stability, and high delamination resistance. A further object of the invention is to provide a film-fibril sheet wherein the density and degree of fusion varies markedly between one surface and the center of thickness. Still another object of the invention relates to thermal bonding procedures for obtaining film-fibril sheets whose opposite surfaces are characteristically dissimilar. Other objects will be apparent from the disclosure hereinafter.

The nonwoven sheet of this invention comprises a differentially bonded film-fibril sheet of randomly-laid yarn-like strand material, the strand material comprising a

three-dimensional integral plexus of crystalline, oriented polymeric film-fibril elements, said elements being coextensively aligned with the strand axis and having an average film thickness of less than 4 microns and an average electron diffraction orientation angle of less than 90°, the strand material being partially fused such that the surface area provided by the film-fibril elements is 0.5 to 5 m.^{2}/g. in any layer throughout the thickness of the nonwoven sheet and is at least 0.3 m.^{2}/g. higher at the center of thickness than at one outside layer of the nonwoven sheet. In one embodiment, this paper-like nonwoven sheet has a surface area provided by the film-fibril elements which is at least 0.3 m.^{2}/g. higher at the center of thickness than at either outside layer of the nonwoven sheet.

The process of the invention comprises thermally bonding a film-fibril sheet by subjecting it in a heating zone to light compression between two surfaces thereby preventing shrinkage, the first surface being a hard heat-conducting material and being maintained at a temperature substantially equal to or greater than the upper limit of the melting range of the film-fibril elements throughout the treatment, the second surface being a flexible, poor heat conductor, the film-fibril sheet being exposed long enough to allow the face of the sheet exposed to the hard heat conducting material to reach a temperature within 7° C. of the upper limit of the melting range of the film-fibril elements, but not substantially above said upper limit, and to allow the second face of the sheet to reach a temperature 0.8 to 10° C. lower than the first face of the sheet, finally directly passing the sheet while under light restraining compression through a cooling zone wherein the temperature of the film-fibril sheet throughout its thickness is reduced to a temperature less than that at which the sheet will distort or shrink when restrained. Normally the sheet should be cooled to at least 30° C. below the upper limit of the melting range of the film-fibril elements.

FIGURE 1 illustrates schematically an end view of an apparatus suitable for treating film-fibril sheet according to this invention.

FIGURE 2 is a graph showing a plot of temperature versus opacity of linear polyethylene film-fibril sheets of various weights for purposes of an indirect determination of certain processing conditions.

FIGURE 3 is a schematic cross-section of a partially dissected sheet of the invention showing a surface layer with relatively high density and a layer at the center thickness with relatively low density.

FIGURE 4 is a second chart showing surface area/g. of sheets after equilibrium treatment in a press at various temperatures.

THE PROCESS AND APPARATUS

An apparatus suitable for performing the process of this invention is shown in FIGURE 1. Essentially it is a modification of the palmer apparatus commonly used in textile finishing. In textile dictionaries it is sometimes referred to as a palmer finisher or a palmer dryer. The apparatus is ordinarily used for drying or for heat-setting of woven fabrics at relatively mild temperature. The process of the present invention requires certain modifications to be made to the palmer apparatus as customarily used, for instance to enable cooling of the fabric while under compressional restraint. A modification which accomplishes this is shown in FIGURE 1.

The principal source of heat in the system is a rotating heated drum **1**. A heavy endless belt **2** of felt or other material and which is driven by the drum passes around the drum and by means of numerous idler rolls **3**, **3**_a_, **3**_b_, **3**_c_, **3**_d_ and **3**_e_ is continuously fed back to the heated drum. Certain of the idler rolls may be adjusted with means to enable control of the belt tension. The belt after passing around the drum, goes around idler roll *3e* and then passes around cooling roll **4**.

In operation of the process, the film-fibril sheet **5** passes around idler roll *3c* and is carried into the nip between the heated drum and the endless belt. It is carried from the heated drum around idler roll *3e* to cooling roll **4**, and is separated from the moving belt by idler roll **7**. The treated film-fibril sheet is wound up on roll **8**.

For certain operations it may be desirable to preheat the heavy endless belt by means of pre-heat roll **9**. The belt is guided onto the pre-heat roll by idler rolls *3a* and *3b*. Any loss in heat may be compensated by heated plate **10** underneath the belt. However, it has been found that the most critical heat control must be imposed at the main drum **1**. One side of the sheet is heated by the main drum to a temperature substantially equal to or slightly less than the upper limit of the melting range of the film-fibrils of the sheet.

While the face of the sheet is heated to a temperature at or near the upper limit of the melting range of the film-fibrils, the back side of the sheet (facing the belt) must be kept somewhat lower. Preferably the temperature of the back side should be within the melting range of the film-fibrils to give appreciable bonding of the film-fibrils throughout the sheet thickness. It has been established that the desired temperature for the backside is 0.8 to 10° C. less than the temperature of the other face of the sheet. By maintaining a temperature differential during bonding, a sheet is obtained having greater density and greater abrasion resistance on the side nearest the hot roll. But on both sides of the sheet the abrasion resistance is superior to that of unfinished sheet. The side of the sheet facing the belt tends to accept many surface coatings more readily than the other face, because the belt side is less severely bonded. The other side of the sheet has a hard surface which is particularly useful for the open surface of book binding wherein superior abrasion resistance is necessary. The hard surface also is an asset in wall covering material, since, when used next to the wall, it permits easy removal of the covering from the wall.

The temperature differential of 0.8 to 10° C. can be established by varying the drum temperature, the belt temperature, and the speed or exposure time of the sheet between the two surfaces. The minimum heating period need only be sufficient for the sheet side adjacent the heat-conducting surface to attain the upper limit of the melting range of the film-fibrils. Accordingly heating periods of as little as one second may be used. The heating period may be as long as one minute or more although for operating efficiency exposure times of less than 10 seconds are most advantageous. It will be understood that in general shorter time periods can be used with higher temperatures and vice-versa.

The light compression which is obtained by tensioning the belt against the drum roll need only be sufficient to prevent shrinkage of the sheet. It is estimated that this pressure is about 1 lb./in.^{2}. Excessive pressures should be avoided as they will tend to cause losses in opacity and bulk.

The drum roll may have any type of surface finish, it being possible to develop a variety of textures or patterns on the sheet by using these various textures. It is necessary that the roll surface be a good heat conductor such as steel. The belt on the other hand should be a relatively poor heat conductor and should provide firm support for the film-fibril sheet during treatment over its entire surface. It has been found that a felt belt approximately 6 mm. thick composed of wool fibers is quite satisfactory for this purpose. It conducts heat very poorly, which is desirable. The insulating properties of this material are indicated by the fact that the back surface of the belt during operation will normally have a temperature 50 to 70° C. lower than the surface which faces the main drum.

The present process has important advantages over conventional fabric finishing procedures such as hot rolling or hot air tentering methods. The product has more uniform opacity and more uniform weight distribution throughout its area. One problem commonly associated with the heat treatment of nonwoven film-fibril sheets by prior art procedures is the tendency of the sheets to shrink, and particularly to shrink unevenly. This causes redistribution of the fibers and gives rise to thin spots. In a tenter frame the thinnest areas in the sheet will heat up faster than the thicker areas, thereby accentuating the nonuniformity. On the other hand if a hot roll is used, the thicker spots become translucent, giving nonuniform opacity. Another important advantage for sheets of the invention is their improved flatness. It has been found that film-fibril sheets which are heated and which are then cooled without restraint, have a wavy character or curl. Even when the over-all shrinkage is very low the wave-to-trough height may be as much as 10 cm. This makes the ordinary palmered products unsatisfactory for laminating to any planar surface. In the process of the invention the heat-conducting drum surface may attain a temperature well above the upper limit of the melting range of the film-fibrils provided that the exposure time is nevertheless such that the sheet surface in contact therewith attain a temperature between that upper limit and 7° C. therebelow. The sheet should not be permitted to attain a temperature much above that upper limit, at least for any significant period of time, lest excessive fusion and losses in opacity result.

Once the sheet has been heated to the required temperature and a temperature differential established from one surface of the sheet to the other, the necessary bonding has been accomplished and subsequent cooling of the sheet may then be effected. At least the initial portion of the cooling must be conducted while the sheet is under restraint or otherwise distortion and shrinkage will occur. The temperature at which this will happen can readily be ascertained by experimentation, but will normally be at least 30° C. below the upper limit of melting range of the film-fibrils. In this regard, it wll be noted in FIGURE 1 that cooling roll **4** and idler roll *3e* are positioned as close as practicable to the heated drum **1** so that the sheet is essentially under a restraining force at all times. It will be apparent that a variety of various cooling techniques could be devised to accomplish this objective.

Special methods have been developed for measuring the actual surface temperature of the sheet on the face side (next to the roll) and on the back (next to the belt). The necessity for keeping the sheet under compression in the machine wherever hot makes direct temperature measurements difficult. In addition with a dynamic situation, i.e., with high heat flow across the thickness of the sheet, errors in measurement are easily made. Even the mass and geometry of the thermocouple under these circumstances can affect the actual temperature recorded, especially when thin film-fibril sheets are used. For these reasons the properties of layers of the sheet have been adopted as the best indication of temperature experienced in treatment. A reference graph may be constructed as in FIGURE 2. This graph shows the effect of equilibrium heat treatment in a platen press upon the opacity of film-fibril sheets treated at various temperatures. Separate samples approximately 8" x 8" square were treated for 3 min. at each temperature. The samples were heated between layers of aluminum foil which were in turn placed between layers of paper in the platen press. The press temperature was maintained within 1° C. of the set temperature by means of a thermostat and the pressure was maintained at about 30 lbs./in.^{2} on the sheet. Each curve in FIGURE 2 represents data from a sheet of a known basis weight as indicated by the legends.

Data obtained according to the foregoing test method may then be used to determine temperatures experienced by layers of film-fibril sheets. The layers may be dissected by manually starting a tear across a sheet and then splitting the sheet into three layers of approximately equal weight. Circular samples of 2 to 3 inch in diameter are sufficient. The samples are usually inspected and weighed to determine if approximately equal layers are achieved. Opacity values are then obtained and, knowing the basis weight of the layer, are converted into a temperature value from the chart.

SUITABLE STARTING MATERIALS

The initial sheet products to be bonded in accordance with the present invention are made from plexifilamentary strands prepared in accordance with aforementioned U.S. Patent 3,081,519. These strands may be incorporated into the initial sheet structure in substantially the same form as they issue from a spinneret orifice which may be circular, slotted or other irregular shape. The strands appear in fluffy form not unlike that of wool knitting yarns. The strand however, may be spread to a great extent prior to being incorporated into the sheet structure by use of deflection devices. In either case, the polymeric material comprises an integral network of primarily ribbon-like fibrous elements which combine and separate at random longitudinal and cross-sectional intervals in the unitary strand structure. The appearance of the strand material when spread in the course of its preparation by impingement on a deflector differs to an extent from the filamentary strands obtained merely by extrusion through orifices. In the latter case, the polymeric strand is nearly circular in cross section whereas in the former case, the polymeric network is flat in appearance. The fibrous elements comprising the plexifilamentary strands are composed of oriented film-fibrils and have an average film thickness less than 4 microns as measured by the interference microscope and an average electron diffraction orientation angle of less than 90°.

The plexifilamentary strands are prepared from synthetic filament-forming polymers or polymer mixtures which are capable of having appreciable crystallinity and a high rate of crystallization. A preferred class of polymers is the crystalline, non-polar group consisting mainly of crystalline polyhydrocarbons. Examples of these include linear and branched chain polyethylene, polypropylene, copolymers of olefins, etc. Other crystalline polymers such as polyethylene terephthalate and copolymers of ethylene with other monomers can also be employed.

The term "polyethylene" as used herein is intended to embrace not only homopolymers of ethylene but also copolymers wherein at least 85% of the recurring units are ethylene units. Copolymers of ethylene with propylene, 1-butene, and other alpha-olefins can often be used to advantage. Homopolymeric linear polyethylene, a preferred polymer for use in the present invention, will normally have an upper limit of the melting range of about 130–135° C., a density in the range of 0.94 to 0.98 g./cm.^{3}, and a melt index (ASTM method D–1238–57T, condition E) of 0.1 to 6.0.

The plexifilament strands may contain a wide range of additives which will impart special properties to the sheet product. Common additives may be present such as waxes, dyes, pigments, antioxidants, delustrants, antistatic agents, reinforcing particles, adhesion promoters, bactericidal agents, dye promoters, removable particles, ion exchange materials ultraviolet light stabilizers, and other additives customarily employed in the textile, paper and plastics industries. In addition high modulus reinforcing fibers such as glass fibers may be blended with the plexifilamentary yarn in the sheet. Mixed adhesion effects may be obtained by employing a blend of different reinforcing fibers, or by treating a part of the fibers to alter their adhesiveness toward the polymer of the plexifilament.

The random overlapping configuration of the plexifilamentary strands within the initial sheet can be effected directly following extrusion by electrostatic laydown on a moving belt or drum. The initial, bulky, loose unconsolidated batt-like sheet product so obtained is then compacted in a direction normal to the plane of the batt by means of pressure rolls or the like. If the pressure is uniformly applied, the compaction is controlled to produce a bulk density greater than 7 lbs./cu. ft. at which level of densification, consolidation occurs, i.e., a coherent compacted sheet structure having a tensile strength greater than 0.3 lb./in.//oz./sq. yd. is produced. Localized densification, e.g. by embossing or the like, can also be utilized to render an unconsolidated sheet sufficiently coherent. Hence suitable sheets to be bonded in accordance with the invention may have overall bulk density values of as little as 1.9 lb./cu. ft. Sheet weights of 0.3 to 6.0 oz./yd.^{2} are preferred. There can be removed or backwound from such coherent flexible sheets an integral network of fibrous elements having a surface area greater than 2 m.^{2}/gm. Preferably, the integral network has a tenacity greater than 0.5 g.p.d.

An initial consolidation by a treatment consisting of the application of relatively light or moderate pressure gives rise to a substantial increase in strength, apparently because of Van der Waals or analogous weak attractive forces. Within any localized area in the sheet such as one square in., the strand material may be arranged in an overlapping, multidirectional, intersecting pattern with the fibrous material of one layer contacting but being essentially non-entangled, or non-felted with the material of above or underneath layers. The initial sheet may consist of a multitude of discrete plexifilamentary strands or a single continuous plexifilamentary strand arranged in a suitably uniform pattern or, as in the preferred embodiment, a single continuous plexifilamentary strand is spread out or expanded laterally to a width greater than the width of the strand as freshly formed at the orifice. The initially employed sheet products are preferably made from "continuous filamentary strands," e.g., filamentary strands having a length of at least about 5 inches. The use of indefinitely continuous filamentary strands is especially preferred for the production of sheets of improved strength and uniformity.

PRODUCT CHARACTERISTICS

The sheet structures of this invention, which are prepared from the above-mentioned starting materials are characterized by partially fused film-fibrils. The fusion process is delicately balanced to provide high delamination resistance (at least 0.35 lb./inch, preferably at least 0.45 lb./inch) without appreciable loss of opacity. The filmy particles of the starting sheet present special problems in this respect, since sheets of such particles tend to become transparent when pressed. They do this at lower temperatures and pressures than do sheets from ordinary round fibers. The product of the invention is characterized by a distinct degree of fusion throughout its thickness. The degree of fusion may be measured by determining the surface area/gram using nitrogen adsorption techniques, since the surface area/gram is inversely related to degree of fusion. The product of the invention has a surface area between 0.5 and 5.0 square meters per gram (m.^{2}/g.) in any layer throughout its thickness. It is important that the sheet have a reasonably high degree of fusion throughout its thickness to guarantee a high delamination resistance for the sheet. This is assured when the finished surface area is less than 5 m.^{2}/g. On the other hand it is important to avoid excessive heating since the film-fibril sheet tends then to become transparent when overheated. This latter problem is avoided when the surface area/g. is above 0.5. For many paper uses it is important also that the opacity of the sheet be maintained at the highest possible level and that the opacity be uniform throughout the sheet. This objective is achieved in the present invention when the surface area/g. at the center of thickness of the treated sheet is at least 0.3 m.^{2}/g. higher than at one of the outside layers of the sheet. In FIGURE 3 a partially dissected sheet **50** is shown in cross-section, the film-fibril layers at the outside surfaces **51** of the sheet being well fused and of high density while the film-fibril layers at the center of thickness **52** are partially fused and of lower density. In the product of this invention all of the layers **51** and **52** have a surface area of 0.5 to 5.0 $m.^2/g$. but the film-fibril layer at the center of thickness **52** has a surface area at least 0.3 $m.^2/g$. higher than at one of the outside layers **51**.

The importance of differential fusion bonding through the thickness of the sheet may be better understood by a study of the heat transfer characteristics of the sheet. It can be shown that the transfer of heat from a drum to the sheet surface is relatively fast compared to the transfer of heat through the thickness of the sheet from that surface. It is therefore quite difficult to achieve a high degree of bonding at the center of thickness without bonding excessively the outside layers. Fortunately, however, the lower degree of bonding at the center of thickness is an asset when using film-fibril materials since these materials reflect light efficiently when not completely fused. As a result an efficient opaque white layer is provided at the center of thickness of the sheet even when the film-fibrils are sufficiently fused to give good delamination resistance.

It should be noted that the high heat level which is required at the outside surface of the sheet for driving heat into the center of the sheet (for delamination resistance) would be very detrimental to sheet opacity uniformity if the sheet were not restrained by local compressional forces acting across the thickness of the sheet. For example a film-fibril sheet heated in a textile tenter frame tends to melt first in areas of low weight per unit area. Although the sheet is restrained by clips or pins at the sheet edge, a redistribution occurs whereby the partially fused material in the low weight area moves toward a high weight area, intensifying the non-uniformity. This redistribution is avoided in the present invention because of compressional restraint applied throughout the entire heated area of the sheet.

Several analytical procedures have been developed for determining the temperature history or degree of fusion for layers of the treated film-fibril sheet. The sheet must first be dissected by methods described in preceding paragraphs whereby the sheet is split into three layers. Circular samples of 2 to 3 inch in diameter are sufficient. The samples are visually inspected and weighed to determine if approximately equal layers are achieved.

The surface area method for determining the degree of fusion and therefore the temperature history of layers within the sheet is based upon nitrogen adsorption techniques. The surface area/g. is determined by exposure to liquid nitrogen as described by P. A. Faeth and C. B. Willingham in "Technical Bulletin on the Assembly, Calibration, and Operation of a Gas Adsorption Apparatus for the Measurement of Surface Area, Pore Volume Distribution, and Density of Finely Divided Solids," Mellon Institute of Industrial Research, September 1955. In this procedure, the surface area is calculated from the amount of nitrogen adsorbed by the sample at liquid nitrogen temperature by means of the Brunauer-Emmet-Teller equation using a value of 16.2 square Angstroms for the cross-sectional area of the adsorbed nitrogen molecule.

The surface area per gram in the film-fibril layers is inversely related to the temperature obtained during heating. This may be demonstrated by constructing a chart of the type shown in FIGURE 4. The chart shows experimental values of surface area/g. obtained for undissected film-fibril sheets of linear polyethylene treated under equilibrium heating conditions in a thermostatically controlled platen press. Sheet samples approximately 8" x 8" square were treated for 3 minutes at each temperature. The samples were treated between layers of aluminum foil which were in turn placed between layers of paper in a platen press. The press temperature was maintained within 1° C. of the set temperature by means of a thermostat and the pressure was maintained at about 30 $lbs./in.^2$ on the sheet. The heat treated sheets were then analyzed by the nitrogen adsorption method to determine surface area/g. Data were then plotted. It is apparent from the high slope of the curve of FIGURE 4 at temperatures near the melting point that the surface area/g. measurements are a very sensitive indication of temperature. Similar curves may be constructed for other materials. The data of FIGURE 4 may be used as a reference for determining the temperature of layers dissected form sheets as well as for whole sheets. This enables one to determine the degree of fusion or the temperature experienced by each layer of the sheet material.

The opacity of dissected layers of the sheet may also be used as an indication of temperature experienced by that layer. A reference graph may be constructed as in FIGURE 2. This graph shows the effect of equilibrium heat treatment in a platen press upon the opacity of film-fibril sheets of a given basis weight (B.W.) per square yard treated at various temperatures. To determined the temperature experienced by layers of the sheet the sheet is dissected into layers with reasonably uniform weight per square centimeter. The average weight per square area is determined. Opacity values are then obtained and, knowing the basis weight of the layer, are converted into a temperature value from the chart. Using such data it has been established that sheets of the present invention have an opacity difference from one surface to the center of thickness equivalent to temperature differences of 0.5 to 3° C.

Similar curves to FIGURE 2 may be constructed to show the effect of equilibrium heat treatment on tear strength of film-fibril sheets. These data may also be used to determine the actual temperature of layers within the sheet by the dissecting methods described above. The nitrogen adsorption method is preferred over the opacity and tear test methods since the data may be reported very accurately on a weight basis while the other measurements depend on use of dissected layers of very uniform thickness or weight per square area which are difficult to obtain. It should be understood however that the other techniques can be used if adequate care is taken to average the results or to obtain uniform layers.

The products of the invention are further characterized by tongue tear strength greater than about 0.3 $lb.//oz./yd.^2$ and tensile strength above 10 $lb./in.//oz./yd.^2$.

Insofar as the product of the invention is concerned, it is only essential that its properties and characteristics fulfill the requirements described hereinbefore. Thus it is contemplated that processes other than that using the modified palmer apparatus could be devised to make such a product.

The abrasion resistance for examples which follow is determined by means of the Crockmeter tester of Atlas Electric Device Company, Chicago, Ill., S.N. CM-598. A 5" x 5" piece of silicon carbide paper is taped to the base of the crockmeter directly under the full movement of the rubber foot. The carbide paper serves to prevent the sample from moving. A rubber finger stall (finger tip) is fastened to the circular plastic foot on the swing bar. The finger stall is size 12 obtained from Swingline Incorporated, Long Island City, N.Y. The swing bar handle is turned so that the rubber foot traverses back and forth across the surface of the sample. When the first surface fiber is disturbed (i.e., pops up), the number of cycles is determined from the counter on the instrument. The average number of cycles for 5 tests is reported for each sample. In the above test a sheet that withstands 2 full cycles is considered to be very good. If the back or felt side of a sheet fails to withstand at least one stroke (0.5 cycle), the sheet will generally lack adequate delamination resistance for uses in wall coverings, book bindings and the like.

The Elmendorf tear described in the examples is determined by TAPPI test T-414 M-49. Opacity values are measured according to TAPPI test T-425 M-60.

The maximum wave height test of the examples is a measure of the sheet levelness or ability of the sheet to lay flat. A high degree of non-levelness or curl will result if the sheet is improperly cooled following the bonding operation. The wave height test is performed by securing opposite parallel edges of an otherwise unsupported horizontal-lying sheet between two pairs of elongated clamps (one pair stationary, one pair movable) so that the sheet is tight and not sagging in the machine direction. A pair of parallel horizontal bars extending across the width dimension of the sheet is positioned so that one is above the sheet and directly above the other which is positioned below the sheet. The sheet is placed under a tension equal to 0.1 pound tension for each inch width of the sheet plus an added 0.75 pound by adjustment of tension applied to the movable clamp. The bars are moved closer together until they each first touch the sheet and the distance between the two is measured and reported in 32nds of an inch.

The film-fibril strand materials are characterized by a melting range that may extend over several degrees C. The upper limit of the melting range of the film-fibrils, as referred to herein, is the temperature at which the highest peak occurs in a differential thermal analysis. The analysis is performed using a Du Pont 900 differential thermal analyzer and a standard heating block for 2 mm. capillary tubes. A 1–2 mg. sample of polymer is placed in one tube and an equal weight of finely ground glass particles in the other. The block containing the tubes is heated at a rate of 5° C./min. The difference in temperature recorded between the tubes is plotted against the temperature of the polymer sample. The maximum peak of the resultant thermogram is taken as the polymer melting temperature or upper limit of the melting range.

The delamination resistance of the products is outstanding, being above 0.35 lb./in., preferably above 0.45 lb./in. The 0.45 lb./in. limit is particularly important in sheet materials to be used for wall covering since the material can be easily removed from the wall without leaving fragments of the sheet behind.

Delamination resistance is measured using an Instron tester, 1 inch x 3 inch line contact clamps, and an Instron integrator, all manufactured by Instron Engineering Inc., Canton, Mass. Delamination of a 1 inch x 7 inch specimen is manually started across a 1 inch x 1 inch edge area (so that the remaining 1 inch x 6 inch portion remains unseparated) by splitting the sheet with a pin. With a "C" load cell, the following settings are used: gauge length of 4.0 inch, crosshead speed of 5.0 inch/minute chart speed of 2.0 inch/minute and full scale load of 2 lbs. A sample is placed in each of line clamps and the force is measured which is required to pull the sheet apart. Delamination resistance (lbs./in.) equals the integrator reading divided by 2500.

The following examples further illustrate the invention.

Examples 1 to 7

A film-fibril sheet is made from linear polyethylene having a density of 0.953 g./cm.^{3}, a melt index of 0.5 g./10 min. (ASTM method D1238–57T, Condition E), and an upper limit melting range of 130.7±.5°C. Five strands are spun simultaneously from spinnerets positioned above a moving belt at equal distances apart across the width of a belt. Each of the strands impinges against a curved deflector and is thereby spread into a wide three-dimensional web. The five webs are laid in overlapping layers upon the moving belt. The loose material on the belt is then carried by the belt to a pair of rolls which exert a light pressure of 10 lbs./linear inch across the width of the sheet.

An important aspect of the preparation of the raw sheet material is the continuous supply of homogeneous single-phase solution which must be delivered to the spinneret at constant pressure and temperature. The spinning operation is therefore controlled by the continuous dissolving and flash spinning apparatus described in copending patent application, U.S. Ser. No. 239,674, now abandoned, and in particular Example 1 thereof. Solvent for the system is trichlorofluoromethane, 14 parts by weight polymer being employed per 100 parts of solution.

The resulting film-fibril sheet was treated in the device of FIGURE 1 for several experiments with conditions shown in Table 1. In each case the main drum was internally heated by means of steam under pressure to a temperature of 132°–133° C. In some of the experiments a preheating roll and a preheating plate were used as described with reference to FIGURE 1. These devices were heated by steam under pressure to the temperatures indicated. During the process there was essentially no relative movement between the sheet and the drum and belt surfaces.

The sheet passed around the main heated drum and passed immediately to a cooling roll, which was cooled by passing water at a temperature of 10° C. through the interior of the roll. After cooling under compressional restraint provided by the felt belt, the film-fibril sheet passed out of the machine and was wound up on a roll.

The belt used in this operation had the following characteristics:

100% wool felt
12 oz./ft.^{2}
about ¼ inch thick

The data in Table 1 show the actual surface temperatures which were obtained on the front and back sides of the sheet (the drum and belt sides, respectively). It is important to note that one side of the sheet was always heated to a higher temperature than the other side and that the back side of the belt remained at about 68° C. even though the front side of the belt was at a temperature of nearly 130° C. The surface temperature of the sheet was determined by dissecting it and measuring opacity for the layers of the sheet as hereinbefore described.

The properties of the sheets prepared as in Table 1 are shown in Table 2. In Examples 1 to 4, 6 and 7 the lateral shrinkage during processing was less than 3½ percent. But in Example 5, wherein there was no post-cooling, shrinkage was about 7.3 percent. In addition the sheet from Example 5 when unrolled would not lay flat. The maximum wave height was about 7.5 cm. in this sheet. The products made using restraint during cooling were more nearly planar and were completely acceptable for use in book cover or in wall covering.

The optimum products shown in Table 2 are those from Examples 2, 3, 6 and 7. These sheets were characterized by high abrasion resistance on at least one surface (greater than 2.0 cycles) and acceptable abrasion resistance on the back surface. The less dense back surface of the sheet remained sufficiently porous to be suitable for coating. For example, in wall coverings it could be coated with dispersions of various synthetic polymers. On the other hand, the other surface of the sheet which was dense was desirable next to the wall because of the ease with which it could be removed from the wall.

In Table 2, properties are also given for a sheet (Example 7) which has been treated first on one side and then on the other side by two passes through the drum-and-belt apparatus. This product still retained its less bonded center layer but had good abrasion resistance on both sides. The sheets prepared in Examples 1, 2, 3, 4, 5, 6 and 7 were more uniform in opacity and basis weight distribution than hot air tentered products. These products also had a higher level of opacity than tentered products.

TABLE 1.—EFFECT OF SURFACE TEMPERATURES AND COOLING ON SHEET TEMPERATURE *

Example No.	Processing conditions[1] Belt preheat	Cool roll used	Main drum temp., ° C.	Preheat Temp., ° C. Roll	Plate	Residence time on drum[2] (sec.)	Average sheet temp., ° C. at wind-up	Sheet surface temp., ° C., maximum during treatment[3] Drum side	Center layer	Belt side
1	Yes	Yes	132	125	177	9	38-46	133.8	132.7	132.1
2	Yes	Yes	132	125	177	18	38	133.8	133.0	132.3
3	No	Yes	132	None	None	18	33-38	133.9	132.8	132.5
4	No	Yes	132	None	None	9	32-49	133.5	132.0	132.1
5	Yes	No	132	125	177	9	116	133.8	132.7	132.1
6	Yes	Yes	133	125	177	6.5	38-46	133.3	132.0	131.8
7	Yes	Yes[4]	133	125	177	6.5	38-46	134.2	132.9	134.0

*All sheets 2.0 oz./yd.^{2}.
[1] Belt temperature any place on back side was 68° C. regardless of face cooling or heating.
[2] Drum contact surface length=15 ft.
[3] Temperatures derived from opacity values obtained on three dissected portions of sheet.
[4] Example 6 repeated with sheet sides reversed.

TABLE 2.—PROPERTIES OF SHEETS TREATED WITH VARIOUS FACE AND BACK TEMPERATURES

Example No.	Abrasion[1] resistance, cycles	Maximum wave height, inches	Opacity, percent	Tear,[2] lb.//oz./yd.^{2}	Lateral shrinkage in process, percent
1	1.4/<0.5	6/32	92.0	.39/.40	2.7
2	2.8/0.5	7/32	89.6	.33/.37	2.7
3	2.5/0.5	9/32	89.5	.36/.42	3.2
4	2.0/<0.5	13/32	90.5	.39/.41	2.7
5	1.4/<0.5	>3	90.8	.45/.47	7.3
Untreated cold pressed sheet.	<0.5/<0.5	<6/32	96	2-3/2-3	None
6	4.4/0.5	12/32	91.2	.34/.42	<3
7	4.5/2.6	9/32	85.7	.32/.37	<3

[1] Front and back surfaces, respectively.
[2] Machine and cross machine directions, respectively.

Examples 8 to 10

An initial film-fibril sheet of linear polyethylene was made by the process described in Examples 1 to 7. The belt feed was adjusted to give a product weighing 2.15 oz./yd.^{2}. The pressure on the consolidating roll was adjusted to give three sheet samples having densities of 11, 16 and 16 lb./ft.^{3}, respectively.

The sheets were passed through the device shown in FIGURE 1. The conditions of the treatment and properties of the initial sheet are shown in Table 3. Properties of the final product are shown in Table 4. In each case, the sheet was first treated in the apparatus and then the sides were reversed and a second pass made.

TABLE 3

Example No.	Initial sheet density, lb./ft.^{3}	Processing Conditions — First Pass: Temp., ° C. on drum surface	Time exposed, sec.	Second Pass: Temp., ° C. on drum surface	Time exposed, sec.
8	11	137	3	138	3
9	16	133	4	133	4
10	16	136	3	136	3

Dissection of samples of each of the three sheets showed that the products had a satisfactory combination of delamination resistance and opacity, had a surface area/g. throughout their thickness between 0.5 and 5.0 m.^{2}/g. and had a surface area/g. at the center of thickness (center third) which was at least 0.3 m.^{2}/g. higher than at the surface of the sheet exposed to the heat source. The delamination resistance for each of the sheets was greater than 0.35 lb./in. and thus these products were well suited for use as wall coverings. In addition, the products had good abrasion resistance.

TABLE 4

Example No.	Delam. resist. lbs./in.	Opacity, percent	Surface area, m.^{2}/g. Face	Center	Temperature difference by area/g., ° C.	Temperature diff. by opacity, ° C.	Temperature at face by area g., ° C.
8	0.54	94.7	1.3	3.2	2.3	2.6	134.3
9	0.50	92.7	2.6	2.9	0.4	1.1	132.5
10	0.94	88.8	1.0	1.7	1.5	1.1	135.0

What is claimed is:

1. Process for producing a bonded nonwoven sheet from a film-fibril sheet which is a random deposit of yarn-like strand material having a surface area greater than 2 m.^{2}/g. and comprising a three-dimensional integral plexus of crystalline, oriented, polymeric, film-fibril elements, said elements being coextensively aligned with the strand axis and having an average film thickness of less than 4 microns and an average electron diffraction orientation angle of less than 90°, said film-fibril sheet having a density greater than 1.9 lbs./ft.^{3}; said process comprising subjecting said film-fibril sheet in a heating zone to light compression, not substantially in excess of about 1 lb./in.^{2}, between two surfaces thereby preventing shrinkage, the first surface being a hard heat-conducting material and being maintained throughout the treatment at a temperature substantially equal to or greater than the upper limit of the melting range of the film-fibril elements, the second surface being a flexible poor heat conductor, the film-fibril sheet being exposed long enough to allow the face thereof exposed to the hard heat conducting material to reach a temperature within 7° C. of the upper limit of the melting range of the film-fibril elements but not substantially above said upper limit, and to allow the second face of the sheet to reach a temperature 0.8 to 10° C. lower than the first face of the sheet, finally directly passing the sheet while under light restraining compression through a cooling zone wherein the temperature of the film-fibril sheet throughout its thickness is reduced to a temperature less than that at which the sheet distorts or shrinks when unrestrained.

2. Process of claim 1 wherein the film-fibril sheet is cooled to at least 30° C. below the upper limit of melting range of the film-fibril elements before the restraining compression is removed from the sheet.

3. Process of claim 1 wherein said crystalline polymeric film-fibril elements are composed of a polyolefin.

4. Process of claim 1 wherein said crystalline polymeric film-fibril elements are composed of polyethylene.

5. Process of claim 1 wherein the resultant sheet is subsequently treated within the stated conditions but such that said second sheet face is placed adjacent said hard heat-conducting material.

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U.S. Cl. X.R.

156—62.2, 306, 311; 161—150, 170; 264—126