

June 14, 1966

J. T. WELCH ETAL

3,256,138

APPLICATION OF RESIN PARTICLES TO A WET FIBROUS PLY
IN FORMING A MULTI-PLY WATER-LAID WEB

Original Filed June 22, 1962

3 Sheets-Sheet 1

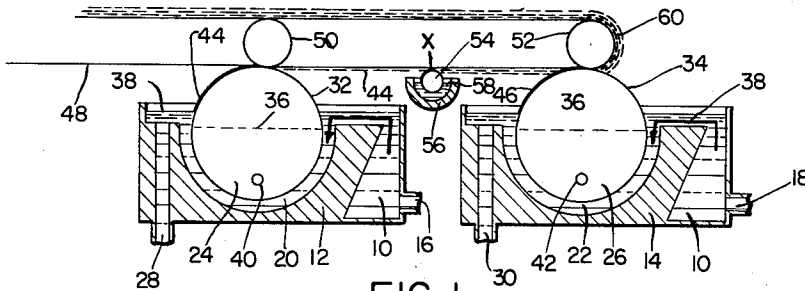


FIG. 1

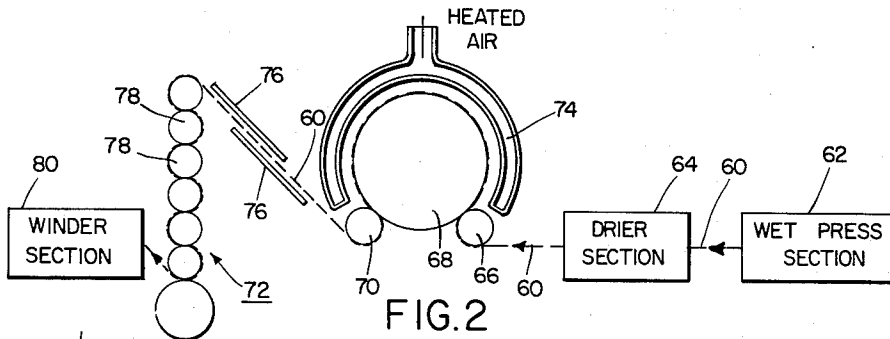


FIG. 2

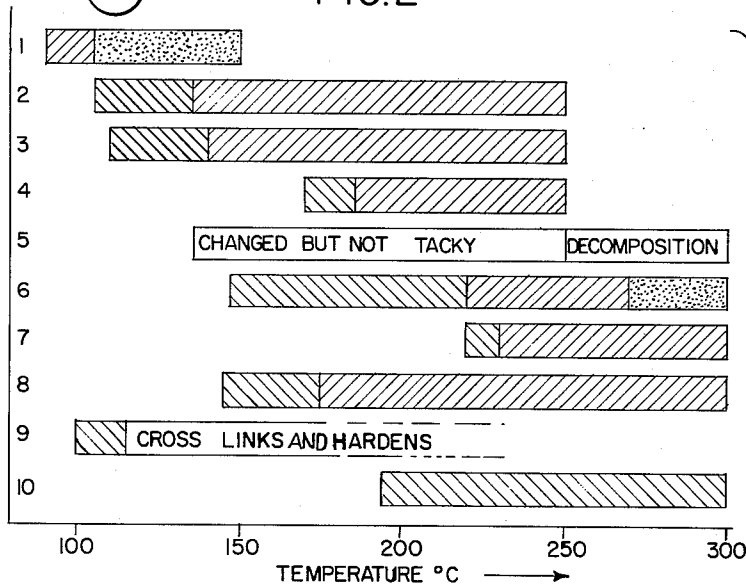


FIG. 3

TACKY MOLTEN FLUID
 VISCOSITY-TEMPERATURE CHARACTERISTICS
 OF VARIOUS RESINS

INVENTORS
 JAMES T. WELCH
 LOUIS R. BUSCHE
 CHARLES E. LANYON

BY

Blair & Buckles

ATTORNEYS

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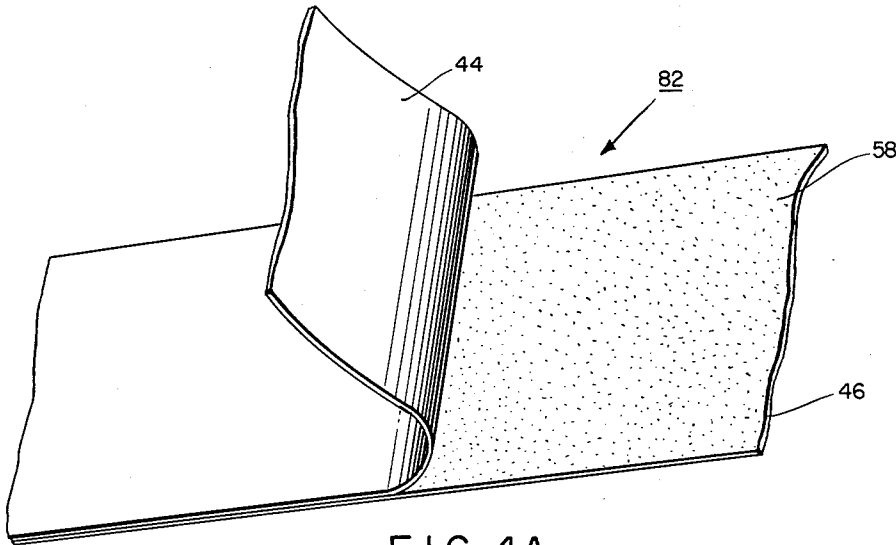


FIG. 4A

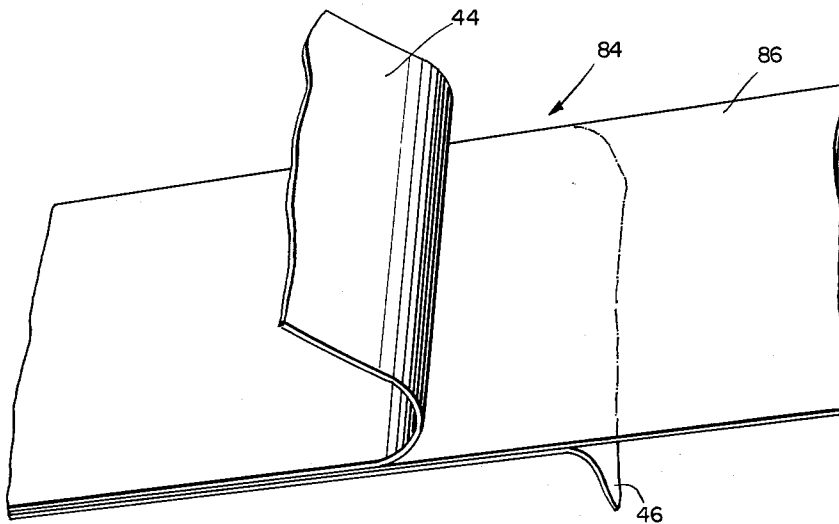


FIG. 4B

INVENTORS
JAMES T. WELCH
LOUIS R. BUSCHE
CHARLES E. LANYON
BY

Blair & Fuchs

ATTORNEYS

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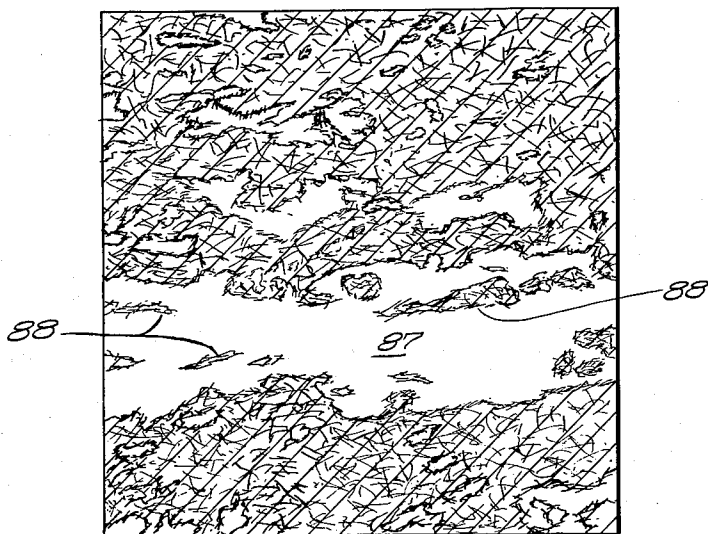


FIG. 5A



FIG. 5B

PRIOR ART

INVENTORS
JAMES T. WELCH
LOUIS R. BUSCHE
BY CHARLES E. LANYON

Blair & Buckles
ATTORNEYS

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3,256,138

APPLICATION OF RESIN PARTICLES TO A WET FIBROUS PLY IN FORMING A MULTI-PLY WATER-LAID WEB

James T. Welch, Loudonville, N.Y., Louis R. Busche, West Hartford, Conn., and Charles E. Lanyon, Troy, N.Y., assignors to John A. Manning Paper Co., Inc., Troy, N.Y.

Continuation of application Ser. No. 233,508, Oct. 25, 1962, which is a continuation of application Ser. No. 204,551, June 22, 1962. This application Feb. 8, 1965, Ser. No. 436,401

10 Claims. (Cl. 162—124)

This application is a continuation of application Serial No. 233,508, filed October 25, 1962, which is a continuation of application Serial No. 204,551, filed June 22, 1962, both now abandoned.

This invention relates to laminating and, more specifically, to multilayer, air-laid nonwoven or carded webs as well as to paper, board, and other waterlaid products, which include integral plastic layers, and to a process for making such products. The invention is applicable to fibrous products made from felted cellulosic fibers, synthetic fibers, and other organic and inorganic fibers, alone or in combination with each other or with other paper-making materials.

The use of resins and thermoplastics is common in the paper industry. For example, extrusion coating of polyethylene on paper and paperboard has gained wide acceptance in the food and packaging industries, largely because of the increased resistance to the passage of water, grease, or vapors which can be achieved through the combination of paper and plastics. Also, films such as Mylar, cellulose acetate, polyethylene, etc., are laminated to paper or board to improve electrical or physical properties. These have invariably been secondary converting operations requiring additional processing after the paper leaves the paper machine.

There are inherent economic and functional disadvantages in the prior methods of combining paper and paperboard with plastic materials. Inasmuch as these methods are not coextensive with papermaking, i.e., do not yield an integrally formed product on the paper machine, they require off-machine processing. This leads to wastage resulting from trimming of the material, as well as increased costs attendant on rehandling it. Further, in certain applications, the films on extrusion-coated products are susceptible to puncture, abrasion, and other damage, and difficulty may be encountered in gluing, printing, or laminating the coated products or the films themselves. Polyethylene, for example, has failed to reach its potential in the paper industry in spite of its low cost. Thermal and electrical oxidation of the polyethylene surface offer hope of overcoming difficulties in printing and gluing, but still another secondary treatment is required.

The principal object of the present invention is to incorporate into paper, paperboard, and other water-laid products, continuous films of resinous or plastic materials, preferably through the addition of such materials on the wet end of the paper machine.

It is another object of this invention to add the resin in such a way that the lamination can be completed continuously on the paper machine without the need for secondary converting operations.

A further object is to provide a laminate of resin and fibrous material having improved resistance to separation of the laminations.

Yet another object is to provide a paper, paperboard or

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other water-laid product having improved electrical properties, a high degree of resistance to the passage of fluids and improved wet strength.

A still further object is to provide a material of the above type characterized by toughness and substantial folding endurance and elongation.

Another object of the invention is to provide an improved method for producing materials of the above type.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the article which possesses the characteristics, properties and relation of elements, all as exemplified in the detailed disclosure hereinafter set forth, and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description, taken in connection with the accompanying drawings, in which:

FIG. 1 is a fragmentary sectional view of the initial stages of a papermaking machine operating according to the principles of our invention,

FIG. 2 is a schematic view of the final stages of the papermaking machine,

FIG. 3 is a chart showing the variations of viscosity of certain plastics with temperature,

FIGS. 4a and 4b are pictorial illustrations of paper-plastic laminates, showing the difference between a consolidated and an unconsolidated layer of plastic particles,

FIG. 5a is an enlarged pictorial representation of the cross section of a paper-plastic laminate made according to our invention, and

FIG. 5b is an enlarged pictorial representation of the cross section of a laminate made by use of prior techniques.

Our invention is based on the discovery that discrete resin particles can be incorporated in the surfaces of fibrous plies, for example, at the wet end of a paper machine, or elsewhere, in such manner that subsequent heating and calendering of the dried paper will result in the formation of a continuous film of the resin or plastic substantially integral with the fibrous plies adjacent thereto.

If the resin film is to be located between a pair of plies, finely divided, water insoluble resin particles can be applied to a wet web or paper which can then be used to couch a second wet web or ply of paper from the wire of the paper machine. In this way, an integral water-laid product is produced with a layer of discrete particles of resin between two wet plies. This is wet pressed and dried according to well-known papermaking operations. The dried composite, while still on the paper machine, is heated to a temperature previously determined to be adequate for softening and causing incipient flow in the particular resin used and is then immediately calendered. Thereupon, the resin undergoes plastic flow and forms a continuous film internally laminating the two paper plies with a bond strength exceeding the internal strength of the plies.

In practicing our invention it has been found unnecessary to alter the normal papermaking process. If the size of the resin particles is correctly chosen, the coating of discrete particles adheres remarkably well to the sheet of paper during its passage through the papermaking equipment, and the relatively uniform coating can be transformed into the desired continuous film. Moreover, where the film is disposed between two fibrous plies, the ply adhesion of the two integral wet webs is not greatly lowered by the interpositioning of the coating of discrete

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resin particles between the plies, and thus the sheet holds together in a satisfactory manner until it is heated and calendered. The proper selection of particle size also insures normal drainage and water removal at the presses so that machine speed is not limited by drying capacity and normal production rates can be maintained.

The discrete particles of finely divided resin are applied to the wet web either as a dry powder or as a dispersion in liquids such as water. If applied as a dry powder, they are wetted by the water in the web, and this causes the powder to adhere to the web. However, to obtain optimum uniformity of coverage, we prefer to apply the resin particles as a water dispersion. The dispersion may be applied by spraying, by a "lick" or "dandy" roll contacting the wet web and revolving in a trough containing resin particles dispersed in water, or by other means well known to those skilled in the art. Our preference as to means of applying the water dispersion depends upon operating conditions such as machine speed, etc. At speeds below 150 ft./min., we prefer the lick roll method, and at higher speeds we prefer a spraying technique, although we do not limit ourselves to these particular combinations of speeds and methods of application.

While the economies resulting from our process are more fully realized when it is incorporated into the papermaking operation, it will be apparent that the process provides material advantages over the prior use of preformed films even in off-machine operations.

It should be noted that the invention is applicable to thermosetting as well as thermoplastic materials, and the terms "plastic" and "resin," as used herein, include both types. "Plastic" and "resin" are used interchangeably herein because most plastics are resins. However, it will be understood that other materials having plastic properties, e.g., cellulose derivatives, are within the scope of the invention and are therefore included within these terms.

The two-mold cylinder machine shown in FIG. 1 is illustrative of the type of papermaking equipment suitable for the practice of this invention. Stock consisting of a dilute suspension 10 of papermaking fibers in water is introduced into a pair of vats 12 and 14 at inlets 16 and 18. It then flows through arcuate passageways 20 and 22 around cylinders 24 and 26 out through overflows 28 and 30. The cylinders, which are hollow and covered with fine wire mesh 32 and 34, turn with the flow of the stock.

The level 36 of water inside the cylinders is kept below the level 38 of the stock on the outside by means of outflow openings 40 and 42. Hence, a pressure gradient exists which forces the stock to flow from the outside of the cylinders to the inside. The fiber in the stock is trapped on the wire mesh forming layers or plies 44 and 46, which move out of the vats and are transferred to the underside of a traveling wet felt 48 by means of pressure rolls (couches) 50 and 52.

The resin dispersion is applied at point (X) by means of a dandy roll 54, which revolves in a trough 56 containing a dispersion of resin particles 58 in a suitable liquid, e. g., water. The roll 54 is turned by contact with the wet ply 44 (formed in the first vat 12) traveling on the underside of the felt 48. The amount of resin that is applied can be controlled by varying the concentration of the dispersion, by changing the characteristics of the dandy roll, or by other means obvious to those skilled in the art. The roll 54 ordinarily takes the form of a hollow cylinder whose surface is comprised of cylinder or Fourdrinier wire (30-80 mesh).

After the application of the resin particles 58, the ply 46 is added at the vat 14 to form a composite web 60. The web 60, in which the paper plies 44 and 46 sandwich a layer of the particles, then continues around the roll 52 and on to the subsequent papermaking operations.

The resin is still added at point X if the method of

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application is changed. For example, if it is added in the form of an aqueous dispersion, it can be sprayed onto the ply 44, with the sprays directed upward so that they impinge upon the underside of the ply. Resin particles of the proper size will adhere to the sheet against the force of gravity, and the concentration or pressure can be varied to control the pickup. The method of application is not critical. However, uniform coverage is necessary for good film formation.

As shown in FIG. 2, the composite web 60 passes through a wet press section 62 and a drier section 64. Because these are conventional papermaking equipment, they need not be described in detail. From the drier section the web passes around a guide roll 66, a heated drum 68, and another guide roll 70 to a calender stack 72. Heated air is blown through a hood 74 to heat the composite sheet. Infrared heaters 76 may be used for supplementary heating and to keep the web 60 from cooling while passing to the calender stack 72. The rolls 78 of the calender stack may be hollow, with a heating fluid passing into them to heat the web. Not all of the heating devices illustrated in FIG. 2 will be used in every case, as the temperature required to consolidate the layer of discrete resin particles into a continuous film is dependent on the softening point of the resin and to a lesser extent on the pressure obtainable in the calenders. Finally, the finished web leaving the calender stack is wound into rolls in a winder section 80.

Numerous variations of the apparatus illustrated in FIGS. 1 and 2 are possible. Thus, although we prefer to use a cylinder machine, our invention is not limited to this type of papermaking equipment. Any wet end such as a multi-head box Fourdrinier, wet machine, Inverformer, etc., wherein two or more independent wet plies are brought together, pressed and integrally combined before drying to form a multiply sheet can be used with our process. The best method of applying the discrete resin particles to the wet web will be governed by the type and details of the equipment used in each case.

Furthermore, we do not limit ourselves to the introduction of a single internal film when more than two plies are laminated together. A 5-vat cylinder machine, for example, produces a sheet composed of five independent plies, and this would make it possible to produce a finished product containing as many as four separate and distinct internal films. For reasons of economy, we prefer to heat and calendar immediately at the dry end of the paper machine, but this does not preclude the use of a secondary operation instead. Other modifications of the basic process and apparatus of our invention will be obvious to those skilled in the art.

The film should not be so thin as to be unduly susceptible to rupture or so thick as to cause undue stiffness in the finished sheet. A thickness range of from 0.5 to 5 mils is generally acceptable.

It should be noted that a process for the manufacture of waterproof paper containing a film of waterproof material interposed between certain plies of multiply paper has been known for a long time. Such a process is described, for example, in U.S. Patents Nos. 1,616,901 and 1,616,902, both issued to L. Kirschbraun; and U.S. Patent No. 2,622,491, issued to C. R. MacDonald. The waterproofing material normally utilized is an aqueous emulsion of pitch, bitumen or asphalt. The emulsion is applied at the wet end of the paper machine in a manner analogous to our application of the resin suspensions, but the underlying principles and mechanism of the subsequent film formation are entirely different.

More specifically, formation of films from asphalt and latex emulsions is thought to take place in a two-step process in which (1) the water is removed to a point where the particles come into irreversible contact and (2) the particles then fuse under surface tension forces. The second step occurs mainly in the drier section, where the moisture content of the paper is drastically

reduced, and the natural tackiness of asphalt and its propensity to fuse insure final consolidation and film formation.

In order to form a satisfactory film, most of the material interposed between the plies must remain at the ply interface. However, the dispersed phase of an aqueous emulsion normally contains particles with an average diameter less than 1 micron, and particles of this size are difficult or impossible to trap on a wet fibrous mat. The clay generally used as a dispersing agent in the asphalt and latex emulsions results in a gelatinous structure upon removal of the water, which helps retain the asphalt at the interface.

Our approach is fundamentally different in that we use a suspension of much larger, discrete, unemulsified particles, and this enables us to control the particle size accurately by grinding, screening or other mechanical means to achieve optimum results. For example, we have found that the particles should have an average effective diameter greater than 10 microns when simple mechanical filtration, rather than the effect of clay, is the retention mechanism. As a matter of fact, only about 50% of particles distributed in the 5-25 micron range are retained within the sheet, the remainder being wasted, and of the 50% retained, only a fraction are positioned at the ply interface. For this reason, we generally prefer to use somewhat larger particles, as set forth below in greater detail.

The relatively large particle size used in the practice of our method limits the importance of surface tension forces in bringing about film formation. These forces, while strong in the case of sub-micron particles, drop off rapidly as particle size increases and are insignificant in our preferred size range. Moreover, the plastics we prefer to use become tacky, and thus in condition for film formation, only near or above the boiling point of water. Therefore, almost all the water has been removed by the time coalescence of the particles is undertaken.

Accordingly, we utilize external forces to consolidate the resin particles. This can be done in several ways, including pressing or calendering. We prefer calendering, because, as pointed out below, it lends desirable properties to the product and offers economic advantages as well. The pressure requirements in the calendar stack depend upon the temperature and the temperature-viscosity characteristics of the resin. Although we do not limit ourselves to any particular conditions, the optimum loading at each nip in the calendar stack generally varies from 50 to 1000 lbs. per lineal inch.

The characteristics of the resins found suitable for our process have been studied in detail, and the importance of the particle size has been mentioned already. The particle size is not only important as a process variable, but it affects the nature of the final product. Particles which are too small are not held at the ply interface, and the resulting penetration into the wet web makes it difficult to form a uniform coating of discrete particles. This may lead to inefficient use of the resin and discontinuities in the film subsequently produced by calendering. Particles which are too coarse do not adhere as well to the web and hinder development of ply adhesion through the fiber-fiber bonding which is necessary to prevent ply separation during drying and before the resin is fused. In addition, resin particles that are too coarse are more difficult to disperse, cannot be sprayed as well, and do not flow out as readily under heat and pressure to develop a continuous film. There is also a tendency to get more uneven films and strike-through during calendering at the positions of the excessively large particles. A more uniform and satisfactory product is obtained if the effective particle size is controlled between roughly 10 and 500 microns, with the optimum range between 40 and 150 microns. The optimum range, therefore, corresponds to particles classified as 325 and 100 mesh.

Table I is a list of various resins, having different temperature-viscosity relationships, which were tested in connection with our process:

TABLE I

No.	Chemical Class	Manufacturer	Description
1	Polyethylene	Allied Chemical Corp.	Grade 6A; emulsifiable type; 50-150 mesh.
2	do.	U.S. Industrial Chemicals Co.	"Microthene 608"; density .916; melt index 22; 200 mesh.
3	do.	do.	"Microthene 620"; density .924; melt index 6; 200 mesh.
4	do.	Spencer Chemical Co.	"Polypro 5"; 50-150 mesh.
5	Copolymer of methyl methacrylate and high alkyl esters.	Rohm & Haas Co.	"Acryloid K-120 N"; 150-200 mesh.
6	Combination of poly (methyl methacrylate) copolymer with a synthetic rubber polymer.	do.	Acryloid KM-227; 50-150 mesh.
7	Linear polycarbonate formed by the direct phosphorylation of bisphenol A.	General Electric Co.	"Lexan"; 40-80 mesh.
8	Polystyrene	Dow Chemical Co.	"Styron 666-K27"; 100 mesh.
9	Epoxy	Hysol Corp.	"Hysol 4459"; 200 mesh.
10	Polychlorotrifluoroethylene.	Allied Chemical Corp.	"Halon VK"; 60 mesh.

The viscosity-temperature characteristic of these materials were investigated as follows. A small amount of each material, in powder form, was placed on an aluminum bar while the temperature was raised slowly. The temperature was monitored by placing a thermometer in a hole drilled in the bar so that the bulb of the thermometer was directly below the resin. Heat was supplied by resting the bar at one or both ends on hot plates controlled with a variable rheostat. The viscosity characteristics were determined visually and by moving and working the particles with a glass stirring rod. The resin is described as tacky when the particles would adhere to each other, as molten when extremely viscous but formable and usually having a tendency to pull out in a taffy-like fashion when touched with the glass rod, and as fluid when it will readily flow upon tilting the bar or otherwise tended to assume the viscosity characteristics normally associated with a liquid. These observations are portrayed graphically in FIG. 3.

The resins in Table I were investigated next for their suitability in our process. This is described in the following example:

Example I

A handsheet was made from an unbleached kraft pulp beaten to about 40 Slowness (3 grams Schopper-Riegler). When dried, this sheet would weight approximately 40 pounds (480 sheets, 24 inch x 36 inch). The wet sheet, containing 65-70% water, was sprayed on one side with an aqueous dispersion of resin, sufficient of which was applied to be the equivalent of 2 mils of film. This sprayed sheet was then used to couch a similar, unsprayed sheet from the handsheet mold, thereby forming a sandwich of two outside layers of kraft stock with the sprayed resin coating between. After wet pressing at 10 tons (8 inch x 8 inch) for 30 seconds, the composite was dried on a handsheet dryer at 175° F.

The above procedure was used with each of the resins listed in Table I. The resins were mixed with water at a 20% solids concentration, and a small amount of wetting agent was generally needed to obtain a satisfactory dispersion.

Each handsheet was pressed between hot platens in a laboratory press. The pressure and temperature were carefully regulated. The pressure was approximately 500

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pounds per square inch, and the platen temperature was varied from 100° C. to 200° C. the upper limit being in the region at which cellulose begins to degrade. The load was gradually applied over a period of 15 seconds and then maintained for an additional 15 seconds, at which time it was instantaneously released.

The hot-presser handsheets were examined for the formation of a continuous film between the plies. The usual criterion was resistance to passage of liquid water under a three-foot head for 24 hours. As a further check, the layers of paper were sometimes removed with acid or by mechanical abrasion after soaking in water, and the films were examined microscopically for the absence of pinholes. The data obtained in this study are presented in Table II.

TABLE II

Resin	Film Formation			
	100° C.	125° C.	150° C.	200° C.
1.....	No ¹	No ¹	No ¹	Yes.
2.....	No.....	Yes.....	Yes.....	Yes.
3.....	No.....	Yes.....	Yes.....	Yes.
4.....	No.....	No.....	No.....	Yes.
5.....	No.....	No.....	No.....	No.
6.....	No.....	No.....	Yes.....	Yes.
7.....	No.....	No.....	No.....	No. ²
8.....	No.....	No.....	Yes.....	Yes.
9.....	Yes.....	No ¹	No.....	Yes.
10.....	No.....	No.....	No.....	Yes.

¹ No—Strikes into sheet without forming film.

² No—Separating sheet indicates film formation about to start.

From FIG. 3 and Table II it is obvious that the temperature must be raised above that necessary for the resin to become tacky before film formation will occur with the aid of external pressure. (It will be noted that in some cases, e.g., Resin 2, film formation appears to take place at a lower temperature than the tackiness range of FIG. 3 would seem to indicate. This slight, apparent discrepancy is due to the effect of pressure on the material, which tends to lower the temperature at which it becomes tacky.) Resins which do not become tacky (e.g., Resin No. 5) are not readily used with this process. Resins which become fluid near or below the boiling point of water (e.g., Resin No. 1) are not so useful in on-machine processing either, because they will "strike-in" or penetrate the entire sheet when heated in the dryers during the paper-making operation. Resin No. 2 is similar to Resin No. 1 in that both become tacky near the boiling point of water, but of these two, only Resin No. 2 is practical, because it maintains its tacky or molten state over a wide temperature range. Resins with a relatively narrow tacky or molten workable range (e.g., Resin No. 9) have limited utility because of the difficulty encountered in controlling the temperature within this range in a commercial operation.

The effect of temperature on the process was investigated further in Example II:

Example II

Handsheets were prepared as described in Example I. The furnish, i.e., fiber makeup, was a mixture of 90% Manila hemp and 10% 9-micron glass fiber. The extrusion grade acrylic (Resin No. 6) was selected for this example because it showed a greater tendency to exhibit decreased viscosity and to become fluid at elevated temperatures. The resin application was increased to the equivalent of a 5 mil film between the two 40-pound plies. The pressure was maintained at about 500 p.s.i., and the temperature was increased to 235° C. at arbitrary intervals. Film formation and the tendency to strike through the plies is recorded in Table III.

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TABLE III

Temperature, °C.	Film Formation	Strike-through
125	No	None
150	Yes	None
170	Yes	None
190	Yes	None
210	Yes	Slight
235	Yes	Severe

Strike-through started about 210° C., close to the upper end of the region classified as tacky in the test described above. Increasing the temperature apparently magnifies the problem to the point where film formation is impaired. Optimum results are obtained by carefully regulating the temperature between 150–175° C. Temperature control is not as critical with Resins 2, 3 and 8, which are molten (as defined) over a wider temperature range.

Example III

Handsheets were prepared again as described in Example I. The furnish was a mixture of 80% ¼ inch 1.5 DPF Dacron polyester fiber and 20% modified polyester "201 Fibrid" (U.S. Patent No. 2,999,788). "Microthene 620" polyethylene resin (Resin No. 3) was sprayed to the equivalent of a 3-mil film between the plies. The sheets were pressed between the platens at 100° C. and 150° C. using pressures of approximately 100 p.s.i. and 1000 p.s.i. at each temperature. They were then tested for film formation and examined for strike-through with the following results:

TABLE IV

	Film Formation	Strike-through
100° C.:		
Pressure=100 p.s.i.....	No.....	No.
Pressure=1,000 p.s.i.....	No.....	No.
150° C.:		
Pressure=100 p.s.i.....	Yes.....	No.
Pressure=1,000 p.s.i.....	Yes.....	No.

The data in Table IV show that the pressure can be varied by as much as a factor of 10 without interfering with film formation. Increasing the pressure, however, will not compensate for a temperature which is too low. Thus, the pressure requirements of the process do not appear to be critical except that there must be adequate force applied to cause the resin to flow after elevation of the temperature to the point where it becomes tacky.

Combinations of resins such as nylon and polypropylene are known in extrusion coating to produce films with unique characteristics and may be used in our process. Another combination including epoxy resin, formed in accordance with our invention, is described in the following example.

Example IV

A rag stock beaten to about 80 Slowness (3 grams Schopper-Riegler) was used to prepare handsheets as described in Example I. A water dispersion of a 50/50 mixture of the epoxy resin (Resin No. 9) and Microthene 620 polyethylene resin (Resin No. 3) was sprayed to the equivalent of a 2 mil film between the plies. The sheets were pressed at 125° C. and 150° C. and 500 p.s.i. as described previously. A perfect film was obtained between the plies, and there was no evidence of strike-through. Removal of the outside plies revealed what appeared to be a uniform film with no indication of inhomogeneity which might be expected from the starting composition. The flexibility of the film appeared to be intermediate to that obtained from the two resins themselves.

Improved dimensional stability at elevated temperatures, better abrasion resistance and reduced cost are

advantages which can be realized through the use of a compounded and cross-linkable polyethylene in our process. This was investigated in Example V.

Example V

Handsheets were prepared as described in Example I. The furnish was a semibleached kraft beaten to approximately 40 Slowness (3 grams Schopper-Riegler) and containing about 5% Du Pont Neoprene latex which had been beater added and precipitated with alum in accordance with well-known papermaking procedure. The handsheets were sprayed to obtain the equivalent of a 3-mil film of 50-100 mesh "CAB-XL" (Cabot Corporation) modified polyethylene between the plies. The "CAB-XL" was grade LBD-6M, which contains approximately 60 parts of carbon black and 2.5 parts of dicumylperoxide per 100 parts of 0.92 low-density polyethylene. The handsheets were pressed at 135° C. and 500 p.s.i. to form an internal film.

One-half of the handsheets were cured at 175° C. for 20 minutes. The cured and uncured handsheets were heated and tested for ply adhesion at approximately 120° C. The cured sheets stuck together, whereas the uncured sheets came apart at the ply interface.

Although dicumylperoxide and other peroxides are decomposed by water, they can be used effectively with our process. Compounding distributes the peroxide uniformly through the resin, and the peroxide within the discrete resin particles appears to be protected when the particles are dispersed in water. This technique offers economic and functional advantages in designing products for specific end uses.

The extension of our basic process to papermaking materials other than fibrous structures is demonstrated in Example VI.

Example VI

An aqueous slurry was prepared which consisted of 15% bleached kraft beaten to 45 Slowness (3 grams Schopper-Riegler) and 85% Owens-Corning flakeglass. Handsheets were prepared in the usual way. "Microthene 620" polyethylene resin (Resin No. 3) was sprayed to the equivalent of 2-mil film between the plies. The sheets were pressed between the platens at 150° C. and 100 p.s.i. A perfect film was obtained and the resulting product was less brittle and more flexible than a similar 2-ply sheet without the internal film.

Differences between handsheets prepared in the laboratory and a product obtained on standard papermaking equipment might be expected. This was investigated in Example VII.

Example VII

A two-mold cylinder machine identical to that illustrated in FIG. 1 was used in this investigation. The deckle or width of the machine was approximately 20 inches and the machine speed was 20 ft./min. An unbleached kraft was beaten to 30 Slowness (3 grams Schopper-Riegler) and used to produce a 2-ply sheet with a combined basis weight of 54 pounds (480 x 24 x 36). A 20% aqueous slurry of "Microthene 608" polyethylene resin was applied at point X in FIG. 1 with a small air-operated spray gun. The spray was directed upward to obtain uniform coverage approximately 6 inches in width in the center of the 20-inch sheet. After passing through the dryer section in the usual way, the paper was conducted to a small calender stack where it went through a single nip with a loading of 50 pounds/lineal inch. Immediately before entering the calender stack, the sheet was passed under a gas-fired infrared heater which raised the temperature of the web to approximately 150° C. The finished product was next wound on the reel at the end of the paper machine in the usual way.

After sufficient paper was obtained as described above, the infrared heater was turned off and the paper was conducted directly to the reel, bypassing the calendar. A

portion of this uncalendered product containing particulate polyethylene between the plies was pressed in the laboratory between platens at 500 p.s.i. and 150° C.

The basis weights of the 3 distinct products were determined to be about 86 pounds (480 x 24 x 36) in each case. Subtracting the fiber weight (54 pounds) from the total weight (86 pounds) gives 32 pounds/ream of polyethylene, which is equivalent to about a 2.5-mil film. All three samples were checked for water penetration under a three-foot head for 24 hours and examined for film formation after dissolving the cellulosic outer plies with 72% sulfuric acid. The tensile strengths of the films obtained in this way were measured in the with-machine (L) and cross-machine (X) directions, and the results are summarized in Table V.

TABLE V

	Resistance to passage of Liquid Water	Film Formation	Film Tensile Strength, Pounds	
			X	L
Laminate not pressed or calendered.	No.....	No.....		
Laminate after pressing.	Yes.....	Yes.....	2.5	2.7
Laminate after calendering.	Yes.....	Yes.....	3.5	9.3

The differences in the products in Table V are shown schematically in FIGS. 4a and 4b. The laminate not pressed or calendered is illustrated at 82. The discrete resin particles 58 forming the uniform coating between the plies 44 and 46 were not coalesced when the paper was dried. The layer of particles is not resistant to passage of water through the composite web and no continuous film is left when the cellulosic plies 44 and 46 are dissolved with acid.

After pressing or calendering, the laminates in Table V are as shown at 84 in FIG. 4b, an interply film 86 having been formed by coalescing the resin particles. Although a film can be produced by calendering or pressing, the calendering operation allows formation of an oriented film. The oriented film is superior in that it is tougher and stronger as demonstrated by the data in Table V.

FIGS. 4a and 4b suggest that the plastic film 86 in the calendered laminate might be identical to an ordinary pre-formed film. This is not the case, as illustrated by the following example:

Example VIII

Handsheets were prepared from rag stock beaten to about 80 Slowness (3 grams Schopper-Riegler), each sheet having a weight of approximately 40 pounds/ream (480 x 24 x 36).

(A) In one case, wet (65-70% water) sheets were sprayed with a 20% aqueous dispersion of "Microthene 620" polyethylene (Resin No. 3). The pickup of plastic particles was equivalent to a 3-4 mil film. Second sheets were added and the composites were wet pressed and dried at about 100° C. on a laboratory handsheet drier.

The composites were then heated to roughly 125-135° C. and passed immediately through a single nip of a calender stack on a commercial paper machine. The stack load was between 100 and 300 pounds/lineal inch, and the speed was approximately 20 feet/minute.

(B) The other handsheets were pressed and dried separately without the application of resin particles. Films of 0.004 inch "T-4" polyethylene (Olin Mathieson Chemical Corp.), density 0.92, melt index 1.5-2.5, were cut to the size of the fiber handsheets. Composites were prepared with the film sandwiched between a pair of handsheets. Finally, the composites were heated and calendered in the same manner as the resin particle composites.

A comparison of the laminates produced in Example VIII(A) and (B) is illustrated in FIGS. 5a and 5b. FIG. 5a is a drawing of a microtome cross section of the cal-

entered laminate of our invention (VIII(A)). The fibers actually enter into and reinforce the plastic web 87 as indicated at 88. It is this phenomenon which imparts such excellent ply adhesion to the composite—a characteristic not generally associated with a hot-formed laminate. This should be contrasted with FIG. 5b, which shows a cross section of a laminate formed in accordance with prior techniques (Example VIII(B)). The paper fibers in the latter material do not enter the plastic web 87 therein.

The exceptional ply adhesion found with these laminates suggested that our process might be used also to overcome the problem of ply separation in a cylinder or multiply sheet in those cases where an impervious film is not necessary or perhaps not even desirable. This study is described in Example IX.

Example IX

Unbleached kraft pulp was beaten to 45 Slowness (3 grams Schopper-Riegler) and a 40-pound (480 x 24 x 36) handsheet was prepared. Having previously determined that an amount of resin equivalent to approximately 0.5 mil film is needed to obtain a continuous internal laminate, the wet handsheet was sprayed with a 5% dispersion of "Microthene 608" polyethylene (Resin No. 2) to obtain a pickup of 6 pounds/ream. This was equal to less than 0.5 mil of polyethylene and would not be expected to produce a continuous film. The sprayed handsheet was used to couch another 40-pound handsheet from the handsheet mold and the composite was pressed and dried in the usual manner. Another 2-ply handsheet was made at the same time without the polyethylene spray application in order to have a control.

The control and polyethylene sprayed laminates were pressed between platens at 150° C. and 500 p.s.i. They were then examined for ply adhesion and formation of an impervious film using impenetrability to liquid water as the criterion for such an internal film as opposed to a pervious film. The results are given in Table VI.

TABLE VI

	Impervious Internal Film	Ply Adhesion (gms./cm.) (ASTM Spec. D-825, Method A)	Ply Adhesion
Control-unsprayed laminate.	No.-----	40-50	Plies can be separated when dry. Readily separates between plies when wet.
Polyethylene sprayed laminate.	No.-----	100	Cannot be separated at ply even when wet, i.e., splits within the plies.

The data in Table VI demonstrate that even a small amount of resin used in accordance with the teachings of our invention will result in ply adhesion exceeding the internal strengths of the plies themselves. Thus, our basic process, used as an improvement to standard papermaking techniques, offers the opportunity of eliminating a major shortcoming of cylinder and multiply papers.

It will be appreciated that our invention is applicable to materials other than ordinary paper and paperboard. For example, its use in the nonwoven field is illustrated by the following:

Example X

A carded web comprising a major portion of 1¼ inch viscose fibers (regenerated cellulose) and a minor portion of 1 inch nylon fiber, containing a small amount of polyvinyl acetate as a binder and weighing 1.5 ounces per square yard, was uniformly coated, by dusting through a screen, with polyethylene particles finer than 150 mesh. In this case, the polyethylene used was marketed by United States Industrial Chemicals Co. under the trade

designation "Microthene 700." The amount applied weighed about 0.6 ounce per square yard. A similar carded web was carefully positioned over the coated web and the composite pressed for 15 seconds at a temperature of 175° C. and under a pressure of 100 pounds per square inch.

Because of the open structure of the carded web, some of the polyethylene particles penetrated into the web and increased the bond between the constituent fibers. However, sufficient resin was retained between the webs to form a continuous film when tested by the methods described above.

The examples, so far given, relate to a product with an interior resin film protected on either side by a fibrous ply. In other applications where the product may be used as a container for liquids or damp materials, such as raw meats, it may be expedient to dispense with one of the covering fibrous plies, allowing the resin film to contact directly the liquid or damp material.

An example of such a product is as follows:

Example XI

A handsheet which when dry would weigh 40 pounds per ream was made from well beaten rag pulp. The wet sheet, containing 68 percent water, was sprayed on one side with an aqueous dispersion of finely divided "Microthene M620" polyethylene. The aqueous dispersion consisted of 20 parts of polyethylene dispersed in 80 parts of water containing a small amount of Triton X-100, a wetting agent to aid dispersion.

The amount of polyethylene applied to the sheet was equivalent to 0.001 inch of film.

After pressing at 10 tons pressure, the 8 inch x 8 inch sheet was dried at 175° F., which is low enough to prevent the resin from unduly softening and adhering to the drier. It was then preheated under a gas fired infrared heater to approximately 300° F. and immediately passed through a single nip of a calender stack loaded to 300 pounds per inch at a speed of 150 feet per minute.

No sticking of the resin to the calender roll was experienced, and, from examination, the film was determined to be continuous and free from pinholes. Moreover, the paper fibers were found to penetrate into the resin film, so that the film and the paper formed an integral composite structure, as in the cases where the film is disposed between two fibrous plies.

It will be apparent that the invention is not limited to the resins mentioned above. For example, among the useful materials are polyester, polyvinyl chloride, polyvinyl chloride copolymer, polyvinyl acetate, polyvinyl acetate copolymer, polyvinylidene chloride, polyvinylidene chloride copolymer, acrylate copolymer, methacrylate and methacrylate copolymer resins as well as ethyl cellulose, cellulose acetate and other cellulose derivatives. In general, it is preferable that the plastic be a type which wets the material bonded thereto.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in the constructions set forth without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention, which, as a matter of language, might be said to fall therebetween.

We claim:

1. A process of manufacturing a fiber-resin film laminate comprising a resin film and a pair of water-laid fibrous plies, said process comprising the steps of bringing wet water-laid plies together in a face-to-face relation-

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ship at the wet end of a water-laid sheet-forming machine with a layer of resin particles between them, the bulk of said particles having an effective diameter from 10 to 500 microns and the quantity of said particles being equivalent to the thickness of said film, heating the composite of said plies and plastic particles to a temperature at which said particles are tacky and in condition for flow under pressure, and subjecting said composite to pressure to force said particles to flow together and form a continuous film between said plies.

2. The combination defined in claim 1 in which the bulk of said particles range in effective diameter from 40 to 150 microns.

3. In a process for the manufacture of paper on a paper machine arranged to form a multiply web and to press and dry the composite web, the improvement of adding water-insoluble resin particles with effective diameters ranging from 10 to 500 microns between the plies at the wet end of said paper machine and subjecting said web to pressure at the dry end of said machine to cause said particles to flow together at the interface between said plies and bond to said plies.

4. A process of manufacturing a laminate comprising a resin film and a water-laid fibrous ply, said process comprising the steps of applying a layer of resin particles to a face of a wet water-laid uncalendered ply, the bulk of said particles ranging in effective diameter from 10 to 500 microns and the quantity of said particles being equivalent to the thickness of said film, heating the composite of said ply and resin particles to a temperature at which said particles are tacky and in condition for flow under pressure, and subjecting said composite to pressure to force said particles to flow together and form a continuous film on said ply.

5. The combination defined in claim 4 in which the bulk of said particles range in effective diameter from 40 to 150 microns.

6. The process defined in claim 4 in which said particles are sprayed onto said ply in a liquid dispersion.

7. A process for manufacturing a water-laid product having an internal resin layer, said process comprising the steps of forming a first wet ply of papermaking fibers, distributing water-insoluble resin particles on said first ply prior to drying and calendering it, said particles having effective diameters substantially between 10 and 500 microns, said particles being of a resin that upon initial heating become tacky only at temperatures above a temperature useful for drying water from said plies, forming at least a second ply of wet papermaking fibers over said particles, drying the composite including said plies and said particles, and subjecting the composite to pressure to cause the resin particles to flow together among the fibers between said plies into a layer bonded to said plies.

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8. A process for producing a multiple ply water-laid product comprising the steps of water laying at least a first fibrous ply, applying an aqueous suspension of resin particles to a first surface of said first ply, said particles having an effective diameter substantially between 10 and 500 microns, said particles being of a resin that upon initial heating becomes tacky only at temperatures above the boiling point of water, water laying at least a second fibrous ply to cover the resin material on said first ply, wet pressing and drying the web comprising said first and second plies and said resin particles, said drying step being carried out at temperatures below the temperature at which said resin particles become tacky, heating said web to above the temperature at which said resin particles become tacky and calendering said heated web with sufficient pressure to form said particles into a resin layer bonded between said plies.

9. A process for manufacturing a fibrous product comprising the steps of spraying a distribution of resin particles onto a first wet uncalendered water-laid fibrous ply, said particles having an effective diameter substantially between 10 and 500 microns, applying a second wet water-laid uncalendered ply to cover the resin-sprayed surface of said first ply, and subjecting said particles to pressure so that they flow among the interface fibers of said plies.

10. In a process for the manufacture of paper on a paper machine arranged to form a fibrous ply and to press and dry the ply, the improvement of adding water-insoluble resin particles with effective diameters ranging from 10 to 500 microns to the face of a ply at the wet end of said paper machine, said particles being of resin that upon initial heating becomes tacky only at temperatures above a temperature useful for drying water from said ply, and calendering the composite of said ply and said resin at the dry end of said machine after raising the temperature of said particles at least to above the point at which they become tacky.

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DONALL H. SYLVESTER, *Primary Examiner*.
S. L. BASHORE, *Assistant Examiner*.