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THERMOPLASTIC PAPER

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This invention relates to moldable thermoplastic paper and to methods of manufacturing the same. More particularly, the present invention is concerned with moldable thermoplastic paper comprising mixtures of (a) wood pulp fibers, (b) synthetic fibers of a vinyl chloride-acrylonitrile copolymerization product and (c) synthetic fibers of a vinyl chloride-vinyl acetate copolymerization product, and to paper making methods of manufacturing thermoplastic paper therefrom.

It has been previously known to incorporate various synthetic fibers in paper making pulp fibers and to manufacture paper therefrom by paper making processes. Not all synthetic fibers, however, are amenable to such processing and the number of useful synthetic fibers for this purpose has been limited. For example, certain synthetic fibers have smooth surfaces and do not have the desired frictional or felting characteristics. As a consequence, they have not been satisfactorily adaptable to paper making techniques. Other synthetic fibers, due most likely to their physical characteristics, have clogged the openings in the Fourdrinier screen and have prevented suitable drainage. As a result, the useful life of such screens has been reduced and the use of such fibers has been halted. Other synthetic fibers possess high static electrical properties and have rendered the finish-processing difficult and the final products have been rough, uneven and unacceptable. Still other synthetic fibers, due either to surface tension characteristics or to their specific gravities have not been suitable to paper making processes and have separated from the wood pulp fibers, thus resulting in difficult handling and inferior products.

One synthetic fiber in common use is a vinyl resin copolymerization product of vinyl chloride and acrylonitrile (preferably in the range of 40–60 percent of one component and 60–40 percent of the other component). One specific example of such a fiber is "Dynel." This fiber is characterized by good dry and wet strength, dimensional stability, resilience, rapid drying, exceptional resistance to both combustion and chemical degradation, moth- and mildew-proofness and thermoplasticity at low temperatures with a softening point as low as about 220° F. (104° C.). Such a material is excellent for general molding purposes and methods for making thermoplastic paper therefrom are disclosed in my copending U.S. patent application, Serial No. 612,097, filed September 26, 1956.

These fibers of vinyl chloride and acrylonitrile are thermoplastic and are normally readily moldable upon the application of heat and pressure in standard molding apparatus into plates, bowls, cups, trays, and like articles. Unfortunately, these fibers have not completely satisfactorily responded in all cases as well to standard electronic high-frequency heat-sealing techniques and this failure of complete response in all cases has not been satisfactorily explained to date.

Another synthetic fiber in common use is a vinyl resin copolymerization product of vinyl chloride and vinyl acetate in which the monomeric proportions may range, respectively, from about 4:1 to about 40:1. One specific

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example of such a fiber is "Vinyon." This fiber is of marked versatility, having high strength, excellent water and chemical resistance, good moth- and mildew-proofness and thermoplasticity at low temperatures with a softening point as low as 149° F. (65° C.). Such a material is usually excellent for general heat and pressure molding purposes and many methods are known for making molded articles therefrom. These vinyl chloride-vinyl acetate fibers are normally readily moldable upon the application of heat and pressure in standard molding apparatus into curtains, place mats, screens, and like articles. Unfortunately, these fibers have also not responded in all cases as well to standard high-frequency electronic heat-sealing techniques and this failure of complete response has not been satisfactorily explained to date.

The third basic component of the products of the present invention is derived from wood pulp cellulosic fibers. Analysis of typical samples of wood pulp cellulosic fibers applicable to the present invention indicates that substantially all or at least the vast preponderance of fiber lengths of such materials are below one-quarter of an inch and that there is a substantial proportion below one-eighth of an inch, along with very short fibers and even some "fines." This is generally true for practically all raw wood pulp materials, whether made from wood or cellulosic vegetable pulps made by the mechanical method, soda method, sulfate method, sulfite method, kraft method, or combinations of these methods. It is also to be appreciated that other short cellulosic fibers having similar fiber lengths would also be applicable to the present invention. Among these other fiber sources would be cotton linters, macerated linen rags, comminuted paper or mixtures thereof.

When these three components are blended and processed in standard paper making equipment, such as described on page 373 of Modern Pulp and Paper Making, 2nd edition, by G. S. Witham, Sr. (1942), a number of unexpected problems arise. For example, a blend of 50% wood pulp, 25% vinyl chlorideacrylonitrile fibers (60% vinyl chloride and 40% acrylonitrile) and 25% vinyl chloride-vinyl acetate fibers (87% vinyl chloride and 13% vinyl acetate) does not fibrillate well, is not conducive to good sheet formation, and results in products which do not completely respond satisfactorily in all cases to high frequency electronic heat-sealing.

It has now been discovered that if the vinyl chloride-vinyl acetate fibers are modified by the addition of small amounts of a dibasic acid, or anhydride thereof, during the polymerization process and the resulting modified products are used in fibrous form or as small rods in these paper making mixtures, that fibrillation is improved, good sheet formation is effected, and products are obtained which respond very satisfactorily in substantially all cases to electronic heat sealing.

The dibasic acids, or anhydrides thereof, are preferably of the lower unsaturated aliphatic series and include, for example, maleic acid (cis-butenedioic acid), maleic anhydride and fumaric acid (trans-butenedioic acid). Other dibasic acids such as citraconic acid and mesaconic acid, for example, are also applicable to the present invention but, due to their increased cost and lack of ready commercial availability, are not as desirable as the acids and the anhydrides mentioned previously.

The amount of dibasic acid which is included in the polymerization process may range from as low as about 0.1% up to as high as 3% or more by weight, with preferred ranges being from about 0.5% to about 2% by weight.

The average fiber length of the modified vinyl chloride-vinyl acetate and the vinyl chloride-acrylonitrile fibers to be included with the cellulosic fibers in the paper making process is less than about one-quarter of an inch. Prefer-

ably, the average fiber length is less than about one-eighth of an inch. It is, of course, to be appreciated that a proportion of such fibers is of extremely short fiber length, such as about $\frac{1}{64}$ inch or less, and that a small proportion may even be "fines."

The amount of vinyl chloride-acrylonitrile fibers to be included in the mixture may be varied from as low as about 10 percent up to as high as about 60 percent by weight of the total mixture and preferably from about 20 percent to about 40 percent by weight, depending on the use and purpose for which the thermoplastic paper is intended.

The amount of modified vinyl chloride-vinyl acetate fibers to be included in the mixture may be varied from as low as about 20 percent up to as high as about 70 percent by weight and preferably from about 25 percent to about 50 percent by weight of the total mixture, depending on the use and purpose for which the thermoplastic paper is intended.

It is not essential that these modified vinyl chloride-vinyl acetate fibers be used directly in fibrous form. If desired, they can be initially in the form of small rods having a length of from about $\frac{1}{32}$ inch to about $\frac{1}{4}$ inch and preferably from about $\frac{1}{16}$ inch to about $\frac{1}{8}$ inch. The diameters of these small rods may similarly be varied depending primarily on their use and in the majority of cases, from about $\frac{1}{32}$ inch to about $\frac{1}{4}$ inch have been satisfactory, with from about $\frac{1}{16}$ inch to about $\frac{1}{8}$ inch being preferred.

When required for molding into plates and bowls of relatively shallow curvature, or other articles where a low degree of plasticity or plastic flow is required, lower percentages of such synthetic thermoplastic fibers are permitted. Where deeper articles of greater curvature or depth of draw are involved, or where a high degree of plasticity or plastic flow is desired, higher percentages are required.

The denier of the synthetic fibers in the ultimate product may range from an average as low as 2 or 3 or as high as 10 or 15. Such fibers need not necessarily be all of the same denier and mixtures are used satisfactorily.

The amount of wood pulp fibers which is present in the paper making mixture may range from as low as about 20 percent up to about 70 percent by weight, with the preferred ranges being from about 25 percent to about 60 percent by weight of the mixture.

The modified vinyl chloride-vinyl acetate and vinyl chloride-acrylonitrile fibers are preferably mixed with the wood pulp fibers in the beater and are usually beaten relatively hard in order to disperse the synthetic fibers substantially uniformly throughout the wood pulp. During the beating, the synthetic fibers are quite often broken and shortened in length so that, on occasion, synthetic fibers of slightly increased fiber length could be used as the raw material.

It is not essential that only one particular type of wood pulp or other cellulosic fiber be employed and it has been found quite advantageous, for example, to mix several types of wood pulp obtained from different sources or methods in with the synthetic fibers. In such mixtures, the proportion of the vinyl chloride-vinyl acetate fibers and the vinyl chloride-acrylonitrile fibers is still to be maintained in the same range of percent by weight, as previously indicated.

The temperature at which the thermoplastic paper softens and becomes moldable will vary, depending upon the relative proportions of the cellulosic fibers and the vinyl resin fibers, as well as the relative proportions of the individual polymerizable materials going into the synthesis of the vinyl resin fiber. It has been determined that temperatures as low as about 176° F. (80° C.) will result in sufficient thermoplasticity and plastic flow for certain types of the thermoplastic paper to be shaped under pressure in a mold. When more thermoplasticity and plastic flow are required, or where different propor-

tions of fibers are used, temperatures of up to 325° F. (163° C.) or more are utilized.

The invention will be further illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe in particular detail some of the more specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not to be construed as limited thereto.

Example I

High frequency electronically heat-sealable thermoplastic paper is produced as follows: one hundred grams of a rod-extruded material having a length of $\frac{1}{4}$ of an inch and a diameter of about $\frac{1}{16}$ inch and containing a mixture of (a) 80% by weight of a copolymer of 85% vinyl chloride, 14% vinyl acetate and 1% maleic acid with (b) 20% by weight (on the 100 grams) of polyethylene are placed in a beater approximately half full of water. After five minutes of beating, 100 grams of a fibrous copolymer consisting of about 60% vinyl chloride and about 40% acrylonitrile (shearings, average 3 denier) is added and the beating is continued for about five minutes. Two hundred grams of bleached Weyerhaeuser sulfate pulp is added, circulated and beaten for an additional ten minutes. The dispersion is then diluted with water to obtain proper consistency and is deposited on a screen and allowed to drain, thereby forming a paper sheet. The sheet is then dried in a mold. Fifteen sheets are prepared in this manner. To evaluate the electronic heat-sealing characteristics of the paper, ten sheets are charged to a die so constructed that electric current flows in multiple through 8 brass bars each $\frac{1}{16}$ of an inch wide which are in contact with the sheets of paper lying flat in a horizontal plane. For ten seconds, 2000 volts are applied at a frequency of 14-17 megacycles. The sheets laminate well, without arcing, and are moldable into plates, trays, bowls and the like.

Example II

The procedures set forth in Example I are followed substantially as set forth therein with the exception that 150 grams of the modified vinyl chloride-vinyl acetate fibrous materials (as 3 denier fibers average), 150 grams of vinyl chloride-acrylonitrile fibers (3 denier average) and 150 grams of wood pulp fibers are employed. The resulting product is very readily electronically heat-sealable and is moldable into deep bowls.

Example III

The procedures set forth in Example I are followed substantially as set forth therein with the exception that 150 grams of the modified vinyl chloride-vinyl acetate fibers (3-5 denier range), 150 grams of vinyl chloride-acrylonitrile fibers (3-5 denier range) and 100 grams of fibrous wood pulp are employed. The resulting thermoplastic paper laminates with ease without arcing and is moldable into cups and containers of considerable depth.

Example IV

The procedures set forth in Example I are followed substantially as set forth therein with the exception that the modified vinyl chloride-vinyl acetate fibers (3 denier) comprise 80% vinyl chloride, 19.3% vinyl acetate and 0.7% maleic acid, with the polyethylene being present on an 82:18 percent basis by weight. The resulting products are similar in nature to the products of Example I.

Example V

The procedures set forth in Example I are followed substantially as set forth therein with the exception that the modified vinyl chloride-vinyl acetate fibers comprise 80% of vinyl chloride, 18.7% vinyl acetate and 1.3% maleic anhydride, with the polyethylene being present on a 78:22 percent basis by weight. The resulting prod-

uct is moldable in similar fashion to the products of Example I.

Although several specific examples of the inventive concept have been described, the same should not be construed as limited thereby nor to the specific substances mentioned therein but to include various other compounds of equivalent constitution as set forth in the claims appended hereto. It is understood that any suitable changes, modifications and variations may be made without departing from the spirit and scope of the invention.

I claim:

1. Thermoplastic paper comprising from about 20 percent to about 70 percent by weight of cellulosic fibers, from about 60 percent to about 10 percent by weight of synthetic vinyl resin fibers, said vinyl resin being a copolymerization product of from about 40% to about 60% vinyl chloride and from about 60% to about 40% acrylonitrile, and from about 20 percent to about 70 percent by weight of a second vinyl resin, said second vinyl resin being a copolymerization product comprising vinyl chloride, vinyl acetate and a material selected from the group consisting of the lower aliphatic unsaturated dibasic acids and anhydrides thereof, said vinyl chloride and said vinyl acetate being in monomeric proportions of from about 4:1 to about 40:1 and said dibasic acids and anhydrides being present in an amount from about 0.1% to about 3% by weight.

2. Thermoplastic paper as defined in claim 1 wherein the dibasic acid is maleic acid.

3. Thermoplastic paper as defined in claim 1 wherein the dibasic acid anhydride is maleic anhydride.

4. Thermoplastic paper comprising from about 25 percent to about 60 percent by weight of cellulosic fibers, from about 40 percent to about 20 percent by weight of synthetic vinyl resin fibers, said vinyl resin being a copolymerization product of from about 40% to about 60% vinyl chloride and from about 60% to about 40% acrylonitrile and from about 20 percent to about 50 percent by weight of a second vinyl resin, said second vinyl resin being a copolymerization product comprising vinyl chloride, vinyl acetate and a material selected from the group consisting of the lower aliphatic unsaturated dibasic acids and anhydrides thereof, said vinyl chloride and said vinyl acetate being in monomeric proportions of from about 4:1 to about 40:1 and said dibasic acids and anhydrides being present in an amount from about 0.1% to about 3% by weight.

5. Thermoplastic paper as defined in claim 4 wherein the dibasic acid is maleic acid.

6. Thermoplastic paper as defined in claim 4 wherein the dibasic acid anhydride is maleic anhydride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,253,000	Francis	Aug. 19, 1941
2,526,125	Francis	Oct. 17, 1950