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[54] **PAPER AND PAPER-LIKE FIBROUS STRUCTURES FROM MIXTURES OF NATURAL, ARTIFICIAL AND SYNTHETIC FIBERS**

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[58] **Field of Search**.....162/157, 146

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

There are disclosed paper and paper-like fibrous structures comprising natural or artificial cellulose fibers and synthetic fibers which are fibers of a propylene polymer, such as polypropylene consisting essentially of isotactic polypropylene made up of isotactic macromolecules, and having a melt index of from 0.5 to 50, said propylene polymer fibers having a length not exceeding 20 mm and a count not greater than, and preferably lower than, 2.5 dtex. The fibrous structures may also comprise a polymeric binding agent, which can be a basic condensation polymer or copolymer of epichlorhydrin with at least one member selected from the group consisting of primary and secondary aliphatic amines, aromatic amines and heterocyclic amines.

9 Claims, No Drawings

PAPER AND PAPER-LIKE FIBROUS STRUCTURES FROM MIXTURES OF NATURAL, ARTIFICIAL AND SYNTHETIC FIBERS

In the following discussion, the term "paper and paper-like fibrous structures" is used to designate any type of paper, fibrous paper-like product, and analogous materials as prepared on conventional paper-making equipment.

THE PRIOR ART

It is known to prepare paper and paper-like structures, e.g., nonwoven fabrics, from cellulose and cellulose derivatives. It is also known to prepare paper and similar structures from synthetic polymers or mixtures thereof.

For instance, U.S. Pat. No. 2,971,858 describes a process in which synthetic paper is prepared by dissolving polypropylene in a suitable solvent, forming a film from the solution, and then evaporating the solvent under particular conditions.

Italian Pat. No. 632,085 describes another process for preparing synthetic paper involving the formation of a film or sheet by extruding a molten mixture of polypropylene consisting essentially of isotactic macromolecules and a mineral filler in the form of granules of special size.

Also known are papers or paperlike products obtained, by more or less conventional methods, from cellulosic natural or artificial fibers and from synthetic fibers such as fibers obtained from acrylonitrile polymers and copolymers, from polyamides, and from polyesters.

One of the more advanced modern techniques for the manufacture of paper from substantially synthetic fibers comprises the preparation of "fibrids" through the precipitation of fibrils from solutions of synthetic fibers as mentioned above, and transformation of the "fibrids" into "textrils" by special techniques, the "textrils" being similar to paper.

The various techniques and structures have been developed with the object of eliminating the drawbacks of traditional paper, particularly its low resistance to tearing, low bursting pressure, and the like, and in many cases, it was possible to improve the poor characteristics of conventional paper.

However, the products obtained by the techniques mentioned are not free from various drawbacks such as, for instance, low receptivity for inks and dyes, and the high costs resulting from the use of materials more expensive than cellulose which also entails resort to complex production and finishing operations.

THE PRESENT INVENTION

One object of the present invention was to provide a new kind of paper or paperlike product free from the prior art drawbacks and disadvantages, characterized by a combination of desirable physical characteristics and the manufacture of which does not require highly special and/or expensive processing and finishing operations.

This and other objects are accomplished by the invention in accordance with which paper and paperlike fibrous structures having particularly valuable properties are obtained from mixes consisting of from 1 to 60 percent by weight of fibers from propylene polymers, and from 35 to 99 percent by weight of fibers of cellulose or a cellulose derivative, and optionally, a polymeric binding agent,

The synthetic fibers from propylene polymers include polypropylene consisting essentially of isotactic macromolecules and thermoplastic block polymers formed substantially of units of propylene and containing units of at least one other monomer, preferably of ethylene and butene.

The mixture of fibers may comprise some which consist of a core and sheath, at least one of the core and sheath being formed of propylene polymers and the other being formed either of propylene polymers having different characteristics, or by polymers of other monomers.

The fiber-forming propylene polymers used preferably show a melt index of from 0.5 to 50. They may be modified by the inclusion of antioxidants, dulling agents, pigments, dyes, stabilizers, lubricants and other like additives.

The fibers are obtained by melt-spinning processes followed, preferably, by curing, stretching, crimping, dimensional stabilization, cutting, and other like operations.

For spinning the fibers of the propylene fibers there are preferably used spinnerets having holes with single diameters greater than 0.5 mm and a length/diameter ratio greater than 1.1, and preferably of from 10 to 30.

The spinneret holes may have a transverse cross-section showing either a circular or non-circular profile.

Polypropylenic fibers obtained by methods different from conventional methods involving spinning the polymer through a spinneret may also be used. More particularly, it has been found that there may be used, conveniently, fibers from propylene polymers obtained from fibers or sheets which have been stretched longitudinally and subjected, contemporaneously or not, to a fibrilation operation, especially fibers obtained by cutting fibrilated synthetic rafia.

The polypropylene fibers used in accordance with this invention have a length not greater than 20 mm and a count below 2.5 dtex.

As second component of the fiber mixture used in practicing the invention there may be used all fibers from cellulose, both natural and artificial, such as those obtained from wood pulp, from viscose rayon, from cotton linters, and the like.

As noted, the fiber mixture may comprise, as third component, a polymeric binding agent, Surprisingly, we have found that the preferred binding agent is a substantially amorphous propylene polymer (possibly modified) and/or a basic polymer or copolymer of epichlorhydrin.

Said substantially amorphous propylene polymers, modified or not, have an intrinsic viscosity of from 0.1 to 0.9, measured in tetrahydronaphthalene at 135° C. In a presently preferred embodiment, the substantially amorphous propylene polymers are modified, as described in U.S. Pat. No. 3,037,949 and U.S. Pat. No. 3,043,787 and in Italian patents Nos. 597,560 and 588,200, and contain from 2 to 40 percent by weight of chlorine and/or from 0.01 to 3 percent by weight of sulphur.

The amount of the substantially amorphous propylene polymers used in the fiber mix is from 0.3 to 15 percent by weight, based on the weight of the mixture.

As polymeric binding agent there may be used, instead of or in addition to the amorphous propylene polymers, a basic polymer or copolymer resulting from the condensation of epichlorohydrin with at least one primary and/or secondary aliphatic, aromatic or heterocyclic amine. In a presently preferred embodiment, said binding agent is the condensation product of epichlorohydrin and at least one amine selected from the group consisting of n-dodecylamine, n-octodecylamine, piperazine, and N,N'-dicyclohexamethylene diamine, the molar ratio between the epichlorohydrin and total amines being 1:1. Polymers and copolymers of this type are described in Italian Patent Nos. 611,258; 643,990; 682,346; 799,544 and 809,075. In the patents mentioned, and others the polymers and copolymers of epichlorohydrin with amines were incorporated, before spinning, in fiber--forming polymers and functioned as dyeing modifiers.

Surprisingly, we have found that the basic epichlorohydrin polymers have an excellent binding capacity in the mixtures based on cellulosic and polypropylenic fibers, without being incorporated into a fiber-forming polymer. The addition thereof to the present fiber mixtures, as binding agents, also substantially improves the receptivity of the final paper and paper-like products for inks and dyes and increases the relative resistance to moisture of the paper and paper-like structures of the invention.

The paper provided by the present invention is particularly desirable for use as book covers, lining paper in general, fine map paper, gasket paper and cardboards, as filter papers, paper for table cloths and napkins, as packing or wrapping paper, as paper for hygienic purposes, and for the production of laminates, felts, and the like. It may be subjected to all of the conventional finishing treatments.

The following examples are given to illustrate the invention, and are not intended to be limiting. In said examples, the resistance to bursting was measured by means of a Mullen burst-analyzer according to the procedures described in the Tappi T 40 m 53 test. The resistance to tearing was measured in an Elmendorf analyzer according to the Tappi T 414 m 49 test.

EXAMPLE I

A. Preparation of the polypropylene fibers.

Polyropylene fibers were prepared in the following way:

99.5 kg of polypropylene (with a melt index of 14, an ash residual content of 0.001 percent and a residue from an extraction with n-heptane 0.97 percent i.e., polypropylene consisting essentially of isotactic polypropylene made up of isotactic macromolecules), 0.25 kg of lauryl thiodipropionate and 0.25 kg of the phenolic antioxidant, 2,6-di-tert.butylparacresol, were mixed together.

The mix was then granulated in an extruder at 210° C in an oxygen-free atmosphere. The granulate was then spun in a melt-spinning equipment under the following conditions:

spinneret with 60 holes having an individual diameter of 0.6 mm and a capillary length of 15 mm:

temperature of extruding screw:	250° C
temperature of spinneret:	250° C
winding up speed;	400 mt/min.

The filaments thus obtained were stretched in vapor at 130° C with a stretch ratio of 1:5 and finally cut into short fibers having the following characteristics:

count	1.8 dtex/filament
length	5.0 mm

B Preparation of the paper:

5 kg of the polypropylene fibers thus prepared were mixed with 5 kg of cellulose bleached with sulphite, batched with 100 liters of water and preliminarily disintegrated.

The mix was then subjected to stirring for 1 hour in a conventional paper mixer to obtain a homogeneous suspension which was formed into a paper-like sheet by conventional procedures. After drying and a subsequent calendering for 5 seconds between calender cylinders heated at 155° C, the sheet showed the following characteristics:

weight	50.0	g/sq.mt
breaking load	0.42	kg/sq.mm
elongation at break	4.4	%
resistance to tearing	24.5	g/25μ
bursting pressure	1.5	kg/sq.cm

The paper thus obtained had an excellent receptivity for inks.

EXAMPLE 2

A. Preparation of the polypropylene fibers.

Polypropylene fibers were prepared as follows: 99.5 kg of polypropylene (having a melt index of 8, an ash residual content of 0.001 percent and a residue from an extraction with n-heptane of 97 percent i.e., consisting essentially of isotactic macromolecules), 0.25 kg of lauryl thiodipropionate and 0.25 kg of the phenolic antioxidant 4,4'thiobis-(6-tert. butyl-metacresol) were mixed together. The mix was then granulated in the extruder at 210° C in an oxygen-free atmosphere. The granulate was then spun in a melt-spinning equipment under the following conditions:

spinneret having 60 holes with an individual diameter of 0.6 mm and a capillary length of 16 mm.

temperature of the extruding screw:	250° C
temperature of the spinneret:	250° C
winding up speed:	400 mt/min.

the filaments thus obtained were stretched in vapor at 130° C with a stretch ratio of 1:5, and then cut to obtain short fibers having the following characteristics:

count	1.75	dtex/filament
length	5.0	mm

B. Preparation of the paper:

5 kg of the polypropylene fibers thus prepared were mixed with 5 kg of cellulose bleached with sulphite and, after preliminary disintegration, batched with 100 liters of water. This mix was kept under stirring for about 1 hour in a conventional paper mixer in order to obtain a homogeneous suspension, which was formed into a sheet of paper by conventional procedures. After drying and subsequent calendering for about 5 seconds between calendering cylinders heated at about 155° C, the sheet had the following characteristics:

weight	50 g/sq.mt
breaking load	0.45 kg/sq.mm
elongation at break	4.1 %
resistance to tearing	21.2 g/25μ
bursting pressure	1.51 kg/sq.cm

The pater thus obtained showed an excellent receptivity to inks.

EXAMPLE 3

A. Preparation of the polypropylene fibers:

The polypropylene fibers were prepared in the following manner:

99.5 kg of polypropylene (having a melt index of 14, an ash residual content of 0.001% and, after extraction with n-heptane, gave a residue of 97%). 0.25 kg of lauryl thiodipropionate, and 0.25 kg of the phenolic antioxidant, 2, 6-di-tert.butylparacresol, were mixed together.

This mixture was then granulated on an extruder at 210° C in an pxygen-free atmosphere. The granulate was then spun in a melt-spinning equipment, under the following conditions:

spinneret with 60 holes having an individual diameter of 0.6 mm and a capillary length of 15 mm.

temperature of the extruding screw:	250° C
temperature of	spinneret: 250° C
winding up speed:	400 mt/min.

The filaments thus obtained were stretched in vapor at 130° C with a stretch ratio of 1:5 and were then cut to obtain short fibers having the following characteristics:

count	1.85 dtex/filaments
length	5.0 mm

B. Preparation of the paper:

1 kg of the polypropylene fibers thus prepared were mixed with 9 kg of cellulose bleached with sulphite, and after having been disintegregated, batched with 10 liters of water.

This mixture was then stirred for about 1 hour in a conventional paper mixer to obtain a homogeneous suspension, which was then formed into a sheet of paper by conventional procedures. After drying, followed by calendering for 5 seconds between calendering cylinders, heated at about 165° C, the paper-like sheet had the following characteristics:

weight:	50.0	g/sq.mt
breaking load:	0.48	kg/sq.mm
elongation at break:	5.5	%
resistance to tearing:	25.0	g/25μ
bursting pressure:	1.5	kg/sq.cm

The paper thus obtained showed an excellent receptivity for inks.

EXAMPLE 4

4.65 kg of polypropylene fibers prepared as in example 1(A) and having a count of 1.7 dtex/filament and a length of 5 mm were mixed with 5.0 kg of cellulose bleached with sulphite, and, after disintegration, batched with 100 liters of water, and with 0.35 kg of amorphous, atactic polypropylene having an intrinsic viscosity (measured in tetralin at 135° C) of 0.35.

The amorphous polymer was added in the form of an aqueous emulsion. The mixture was kept under stirring for about 1 hour in a conventional paper mixer, in order to form a homogeneous suspension.

By means of conventional procedures there was obtained from said suspension a sheet of paper which, after being dried and calendered for 5 seconds between calendering cylinders heated at about 165° C, showed the following characteristics:

weight:	50 g/sq.mt
breaking load:	0.41 kg/sq.mm
elongation at break:	3.75 %
resistance to tearing:	23.0 g/25μ
bursting pressure:	1.49 kg/sq.cm

The paper thus obtained showed an excellent receptivity for inks. EXAMPLE 5

2.5 kg of the polypropylene fibers prepared as in example 1(A) but showing a count of 1.85 dtex/filament and a length of 6 mm were mixed together with 7.0 kg of cellulose bleached with sulphite, and, after disintegration, batched with 100 liters of water, and with 0.5 kg of amorphous atactic polypropylene having an intrinsic viscosity of 0.45, in an aqueous emulsion. The mix was then kept under stirring for about 1 hour in a conventional paper mixer, in order to form homogeneous suspension.

By conventional procedures there was then obtained from said suspension a sheet of paper which, after drying followed by a calendering for 5 sec. better calender cylinders heated to about 165° C, had the following characteristics:

weight:	50.0 g/sq.mt
breaking load:	0.4 kg/sq.mm
elongation at break:	3.5 %
resistance to tearing:	20.7 g/25μ
bursting pressure:	1.5 kg/sq.cm

The paper thus obtained showed an excellent receptivity for inks.

EXAMPLE 6

4.5 kg of polypropylene fibers prepared as in example 1(A) and having a count of 1.7 dtex/filament and a length of 6 mm were mixed together with 5 kg of cellulose bleached with sulphite, and after previous disintegration, batched with 100 liters of water, and with **0.5** kg of amorphous, atactic, polypropylene having an intrinsic viscosity of 0.4 and which had been subjected to a preliminary chlorination and contained 8% of combined chlorine. Said polymer was admixed in the form of an acetone solution. The mixture was kept under stirring for about 1 hour in a conventional paper mixer, to obtain a homogeneous suspension which was formed into a sheet by conventional paper-making procedures. After drying, followed by a calendering for 5 seconds between calendering cylinders heated at about 160° C, the sheet had the following characteristics:

weight:	50.0 g/sq.mt
breaking load:	0.35 kg/sq.mm
elongation at break:	5.2 %
resistance to tearing:	18 g/25μ
bursting pressure:	1.51 kg/sq.cm

The paper thus obtained showed an excellent receptivity for inks.

EXAMPLE 7

4.5 kg of polypropylene fibers prepared as in examples 1(A) and 2(A) and having a count of 1.7 dtex/filament and a length of 6 mm were mixed with 5 kg of cellulose pin wood pulp, batched with 100 liters of water and preliminarily disintegrated, and with 0.5 kg of a condensation copolymer of epichlorohydrin/n-octodecylamine/piperazine (molar ratios 1:0.2:0.8). The mixture was stirred for about 1 hour in a conventional stirrer for paper, in order to form a homogeneous suspension.

By conventional paper-making procedures, there was obtained from said suspension a sheet of paper which, after drying and subsequent calendering for 5 seconds between cylinders heated at about 155° C, had the following characteristics:

weight:	100.0 g/sq.mt.
breaking load:	0.43 kg/sq.mm
elongation at break:	4.2 %
tear resistance:	23.0 g/25
bursting pressure:	2.0 kg/sq/cm

The paper thus obtained showed an excellent receptivity for inks.

EXAMPLE 8

2.5 kg of the polypropylene fibers prepared as in example 3(A) but having a count of 1.75 dtex/filament and a length of 6 mm were mixed with 7.0 kg of cellulose bleached with sulphite, batched with 100 liters of water and previously disintegrated, and with 0.5 kg of an epichlorohydrin/piperazine condensation polymer (in a molar ratio equal to 1:1).

The mix was thereupon stirred for about 1 hour in a conventional paper mixer, in order to form a homogeneous suspension.

From this suspension there was obtained, by conventional paper-making procedures, a sheet of paper which, after drying followed by a calendering for 5 seconds between a set of cylinders heated at about 155° C, showed the following characteristics:

weight:	50.0 g/sq.mt
breaking load:	0.38 kg/sq.mm
elongation at break:	3.9 %
tearing resistance:	21.0 kg/25μ
bursting pressure:	1.5 kg/sq.cm

The paper thus obtained showed an excellent receptivity for inks.

EXAMPLE 9

5 kg of polypropylene fibers prepared as in one of the examples 1(A), 2(A) and 3(A) and having a count of 1.7 dtex/filament and a length of 6 mm were mixed with 4.5 kg of cellulose bleached with sulphite, batched with 100 liters of water, and preliminarily disintegrated, and with 0.5 kg of a condensation copolymer of epichlorohydrin piperazine and NN'-dicyclohexylhexamethylendiamine (in molar ratios equal to 1:0.75:0.25).

The mixture thus obtained was then stirred for about 1 hour in a conventional paper mixer, to obtain a homogeneous suspension.

Using conventional paper-making procedures, there was then obtained from the homogeneous suspension a sheet of paper which, after drying followed by calendering for 5 seconds at about 165° C between calendering cylinders, had the following characteristics:

weight:	100.0 g/sq.mt.
breaking load:	0.44 kg/sq.mm.
elongation at break:	4.7 %
tearing resistance:	20.5 g/25
bursting pressure:	2.0 kg/sq.cm

The paper thus obtained showed an excellent receptivity for inks.

The polypropylene used to obtain the synthetic fibers in the foregoing examples was a polypropylene consisting essentially of isotactic polypropylene made up of macromolecules having substantially isotactic structure and as described in U.S. Pat. No. 3,112,300. The amorphous polypropylene used as polymeric binder in the foregoing examples was a linear, head-to-tail atactic polypropylene as disclosed Natta et al., U.S. Pat. No. 3,438,956

As will be apparent some changes may be made in practicing the invention without departing from the spirit thereof. Therefore, we intend to include in the scope of the appended claims all modifications which will be obvious to those skilled in the art from the description and working examples given herein.

What is claimed is:

1. Paper and paper-like fibrous structures made from aqueous suspensions containing cellulosic fibers and synthetic fibers, said structures being characterized in containing from 1 to 50 percent by weight, based on the total solids weight, of fibers of a propylene polymer having a melt index of from 0.5 to 50, which fibers have a length not greater than 20 mm. and a count not greater than 2.5 dtex, from 40 to 98.9 percent by weight of cellulosic fibers, and, as a polymeric binding agent, from 0.1 to 10 percent by weight of a basic condensation polymer or copolymer of epichlorhydrin with at least one member selected from the group consisting of primary and secondary aliphatic amines, aromatic amines and heterocyclic amines.

2. Paper and paper-like fibrous structures according to claim 1, further characterized in that the propylene polymer is polypropylene consisting essentially of isotactic polypropylene made up of isotactic macromolecules.

3. Paper and paper-like fibrous structures according to claim 1, further characterized in that the propylene polymer is a thermoplastic fiber-forming block-polymer substantially formed of combined units of propylene alternated with combined units of at least one other monomer.

4. Paper and paper-like fibrous structures according to claim 1, further characterized in that the cellulosic fibers are natural fibers.

5. Paper and paper-like fibrous structures according to claim 1, further characterized in that the cellulosic fibers are artificial fibers.

6. Paper and paper-like fibrous structures according to claim 1, further characterized in that the synthetic fibers comprise a core and a sheath, one of the core and sheat being formed of one propylene polymer and the other being formed of another propylene polymer having different characteristics.

7. Paper and paper-like structures according to claim 1, further characterized in that the synthetic fibers comprise a core and sheath, one of the core and sheath being formed of a propylene polymer and the other being formed of a polymer of a different monomer.

8. Paper and paper-like fibrous structures according to claim 1, further characterized in that the polymeric binding agent is a condensation polymer or copolymer of epichlorhydrin and at least one amine selected from the group consisting of n-dodecylamine, n-octodecylamine, piperazine, N,N'-dicyclohexylhexamethylenediamine.

9. Paper and paper-like fibrous structures according to claim 1, further characterized in that the epichlorhydrin to total amines molar ratio is 1:1.

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