

PATENT SPECIFICATION

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(54) PROCESS FOR THE MANUFACTURE OF A PAPER SUBSTITUTE

(71) We, UOB, of 4 Chaussée de Charle-
 roi, Saint-Gilles-lez-Bruxelles, Belgium, (a
 Société Anonyme) organised under the laws of
 Belgium, do hereby declare the invention, for
 which we pray that a patent may be granted
 to us, and the method by which it is to be
 performed to be particularly described in and
 by the following statement:—

The present invention is concerned with a
 paper substitute and with processes for the
 manufacture thereof.

When the properties of an ordinary cellulose
 paper are compared with those of any film of
 synthetic materials, for example of polyethyl-
 ene, polypropylene, polyvinyl chloride, poly-
 styrene or the like, it is found that the cellulose
 paper is characterised by lower specific
 strengths and elongations at break and and by
 greater rigidity. Furthermore, the resistance to
 tearing of cellulose paper is relatively poor and
 practically equal in both directions of the
 plane of the paper. Apart from these mea-
 surable properties, cellulose paper is charac-
 terised by some specific properties, namely:

1. appearance;
2. touch;
3. permanent deformation after folding;
4. absence of or a low static electricity charge;
5. ability to be written on by a pencil, pen, ballpen and the like; and
6. ability to be printed on by various processes, such as letterpress, offset, photo-gravure and the like.

If it is desired to produce a substitute
 resembling cellulose paper, it is, therefore,
 necessary to provide the specific properties

characterising the latter. At the same time, the
 paper substitutes may provide additional pro-
 perties not possessed by cellulose paper, such
 as impermeability to water vapour and gases,
 resistance to greases, dimensional stability
 under various atmospheric conditions and seal-
 ability.

Various means have already been adopted in
 attempts to imitate cellulose paper.

Some have attempted to imitate appearance
 alone, by surface treatment. A synthetic film
 may, for example, be treated by one of the
 following processes:

- a. sand blasting;
- b. passing over a rough heated roller;
- c. chemical treatment: passing the film
 through a bath of solvent, followed by passage
 through a bath containing a non-solvent for
 the polymer which is, however, miscible with
 the first solvent;
- d. coating the film with a highly pig-
 mented layer;
- e. extrusion by a specific method.

These surface treatments result in the
 opaqueness and the feel of paper being ob-
 tained. The base polymer in the film pro-
 vides the mechanical properties. This film
 may or may not be oriented.

By chemical treatment with a system com-
 prising the solvent and the non-solvent, it is
 also possible to obtain a certain porosity but
 an important advantage of plastics paper, i.e.
 its impermeability and resistance to liquids, is
 then partly lost.

One of the first attempts to make a paper
 substitute consisted in producing a porous
 film by incorporating, during extrusion, an ex-

pansion agent which forms cavities in the film (for example, expanded polystyrene). However, this film is difficult to print on and it suffers both from poor impermeability and from poor resistance to liquids (spongy effect).

There are also so-called "paper-like" films, which are simple films, the paper-like feel of which is obtained by a controlled melt fracture phenomenon during extrusion. These films are normally manufactured to form a film-imitating tissue paper.

So-called "spun-bonded" paper substitutes also exist, which are papers manufactured with synthetic fibres instead of cellulose fibres. These papers may also be subsequently coated.

Another type of paper substitute is obtained from a composition containing at least one high density polyethylene, a copolymer of ethylene and a vinyl compound (for example, vinyl acetate, acrylic ester or the like), mineral fillers and unmodified polystyrene. This mixture must first be calendered before extrusion thereof.

More recently, a paper substitute has been proposed comprising (a) olefinic resins, (b) resins of the group comprising styrene resins, acrylic resins, acetal resins and phenol resins, (c) fillers and (d) optionally a synthetic elastomer, this mixture also being calendered, extruded and then additionally subjected to biorientation.

Without prejudging the quality of the various paper substitutes obtained by the processes mentioned above, it will be noted that the cost of manufacture is burdened by operations such as calendering, which consumes a large amount of energy, and biorientation, which requires special equipment and an elaborate technique.

An important technical and economic improvement would be made if it were possible to manufacture a paper substitute having the maximum resemblance to cellulose paper, while the cost of manufacture is reduced to a minimum. In other words, it would, in particular, be necessary to be able to develop a paper substitute composition permitting the direct production of the desired paper substitute by simply mixing the components and by simple extrusion, without calendering or biorientation. The present invention relates to the solution of this problem.

The process according to the present invention for the manufacture of a paper substitute requiring neither calendering nor biorientation is characterised in that a composition containing the following is homogenised in a conventional rotary mixer:

30—94.8% by weight of at least one rigid polyolefin (A) selected from the homopolymers and copolymers of ethylene, propylene and butylene and also mixtures thereof, having a melt index of at most 1 decigramme per minute;

0.1 to 35% by weight of at least one polymer (B) which is incompatible with the rigid

polyolefin (A) and which, when extruded by itself, produces a brittle film and which has a melt index of less than 10 decigrammes/minute, the polymer (B) being selected from the homopolymers and copolymers containing a preponderant amount of a polymerisable, ethylenically-unsaturated monomer, containing a terminal vinylidene group $\text{CH}_2=\text{C}<$, selected from styrene, styrene halo- or alkyl-substituted in the side chain or in the nucleus, vinyl chloride, vinylidene chloride, acrylic esters and methacrylic esters of alkanols containing up to 3 carbon atoms;

0.1 to 35% by weight of a macromolecular material (C) producing compatibility between (A) and (B), selected from (1) copolymers of at least one monomer selected from ethylene, propylene and butylene, and at least one monomer selected from isobutylene, butadiene and isoprene; and (2) a mixture previously prepared from at least one homopolymer of ethylene, propylene or butylene and at least one homopolymer of isobutylene, butadiene and isoprene, the macromolecular material having a melt index of at most 2 dg/minute;

5—45% by weight of a mineral filler (D) having a particle size of less than 50 microns;

0 to 10% by weight of adjuvants (E) selected from anti-oxidising agents, heat stabilisers, optical bleaching agents, pigments, colouring agents, antistatic agents and/or lubricants, and the mixture thus homogenised is subjected to extrusion in order to obtain a paper substitute, the paper substitute thus obtained being optionally subjected to surface treatment.

By rigid polyolefin (A), there is to be understood a high density polyethylene, an isotactic polypropylene or an isotactic polybutene which has a melt index (M.I.) of at most 1 decigramme/minute, preferably lower than 0.2 decigramme per minute, measured according to ASTM D 1238/57T. However, the rigid polyolefin (A) may also consist of a physical mixture of these homopolymers with one another or of copolymers obtained from ethylene, propylene and/or butene.

In the form of a film, the polyolefin (A) has a modulus of elasticity higher than 2000 kg per cm^2 , measured according to ASTM D 882/61T. The polyolefin (A) is used in the composition according to the present invention in an amount of 30—94.8% by weight, preferably of from 40 to 80% by weight: it provides the paper substitute of the present invention with rigidity and constitutes its framework.

The polymer (B), which is incompatible with the rigid polyolefin (A) and which, when extruded by itself, gives a brittle, hard, fragile film, is obtained by polymerisation of a preponderant quantity of a polymerisable, ethylenically-unsaturated monomer having a terminal $\text{CH}_2=\text{C}$ group, selected particularly from styrene, styrene halo- and alkyl-substituted on

the side chain or in the nucleus, vinyl chloride, vinylidene chloride, acrylic and methacrylic esters of alkanols containing 1 to 3 carbon atoms and the like. In the composition of the present invention, the polymer (B) imparts hardness and tearability to the paper substitute manufactured from the composition. Nevertheless, the properties of the polymer (B) may be modified by the concurrent use of minor amounts of olefinic or diolefinic elastomers, derived, for example, from isobutylene, butadiene, isoprene or the like in an amount of at most 49% by weight of the polymer (B).

Thus, polymer (B) is preferably either a mixture containing a major amount of a homopolymer obtained by polymerisation of an ethylenically-unsaturated polymerisable monomer having a terminal vinylidene group, selected from styrene, styrene halo- or alkyl-substituted in the side chain or on the nucleus, vinyl chloride, vinylidene chloride and acrylic and methacrylic esters of alkanols containing up to 3 carbon atoms, and a minor amount of a homopolymer obtained by polymerisation of an olefinic compound selected from isobutylene, butadiene and isoprene; or is a copolymer obtained by copolymerisation of a major amount of an ethylenically-unsaturated polymerisable monomer having a terminal vinylidene group, selected from styrene, styrene halo- or alkyl-substituted in the side chain or on the nucleus, vinyl chloride, vinylidene chloride, acrylic esters and methacrylic esters of alkanols containing up to 3 carbon atoms, and a minor amount of a polymerisable olefinic monomer selected from isobutylene, butadiene and isoprene.

It is also possible to modify the polymer (B) by external plastification with conventional plasticisers for vinyl resins, for example with dioctyl phthalate or tricresyl phosphate, in an amount of from 0.1 to 30% by weight, of the polymer (B). The melt index of the polymer (B) must be less than 10 decigrammes per minute and is preferably less than 5. The polymer (B) is used in an amount from 0.1 to 35% by weight, preferably from 5 to 30% by weight, of the total composition of the present invention.

The macromolecular material (C) provides compatibility in the molten state between the polyolefin (A) and the polymer (B). It is obtained in one of two ways: (1) by copolymerisation of two monomers, one of which is compatible with the polyolefin (A), for example, ethylene, propylene or butylene, and the other is compatible with the polymer (B), for example isobutylene, butadiene or isoprene; or (2) by preliminary mixing of a polymer compatible with the polyolefin (A) and a polymer compatible with the polymer (B). As examples of macromolecular materials (C), there may be mentioned a 50/50 by weight ethylene/isobutylene

copolymer, and a 75/25 by weight ethylene-butadiene copolymer; as examples of mixtures of a polymer compatible with (A) and of another polymer compatible with (B), there may be mentioned a mixture of high or low density polyethylene and polyisobutylene in a 50/50 by weight ratio, a mixture of high or low density polyethylene and polybutadiene in a 75/25 by weight ratio, a 70/30 by weight mixture of high density polyethylene and butyl rubber or the like. The presence of the macromolecular material (C) (copolymer or mixture of polymers) makes it possible to obtain a homogeneous composition according to the present invention, without using calendering, the homogeneity of the composition of the present invention being simply obtained in the mixer and the extruder itself. The melt index of the macromolecular material (C) must be at most 2 decigrammes per minute and preferably at most 1 decigramme per minute. It is used in the composition of the present invention at a rate of 0.1 to 35% by weight of the total mixture, preferably at a rate of 0.1 to 25% by weight.

The mineral filler (D) is selected from mineral substances which impart opaqueness and a suitable surface structure to the paper substitute of the present invention. It may be, for example, talc, titanium dioxide, kaolin, a zeolite, silica, zinc oxide, natural or precipitated calcium carbonate, magnesium carbonate, barytine or the like.

The maximum particle size of the mineral filler is 50 microns. Particle sizes higher than this are disadvantageous because of the formation of grains which are detrimental to the uniformity of the paper substitute. The amount of mineral filler added constitutes from 5 to 45% by weight of the total composition of the paper substitute of the present invention and preferably from 5 to 25% by weight thereof.

The adjuvants (E) are:

a. thermal stabilisers, such as diphenyl-thiourea, α -phenylindole, barium, cadmium or zinc palmitate or stearate, tris-nonylphenyl phosphite or the like;

b. anti-oxidising agent, such as 4,4'-thio-bis-(6-*t*-butyl-*m*-cresol), 4,4'-methylene-bis-(2,6-di-*t*-butyl-phenol), butylated hydroxytoluenes or the like;

c. optical bleaching agents, such as sulphonated derivatives of stilbene;

d. organic colouring agents, such as phthalocyanines, disazoic colouring agents, chlorinated inanthrenes or the like;

e. mineral pigments, such as zinc chromate, cadmium sulphide, iron oxide or the like;

f. lubricants, such as magnesium or calcium stearate, paraffin oil or the like, and

g. anti-static agents, such as C_{12} - C_{18} alkylamines.

These adjuvants (E) are added to the com-

position of the paper substitute according to the present invention in an amount of from 0 to 10% by weight.

5 The components (A), (B), (C), (D) and (E) are mixed together in a mixer of conventional construction, preferably in an ordinary rotary mixer. Therefore, the composition of the present invention makes it possible to eliminate
10 calendaring and subsequent granulation before extrusion, which constitutes a considerable saving in manufacturing costs.

A suitable way of preparing this mixture consists in introducing components (A), (B) and (C), together with a liquid
15 lubricant (E) (for example paraffin oil), into a rotary mixer and then adding to the resulting mixture the components (D) and the other adjuvants (E), which are in the form of a powder. This technique is
20 not necessary if the components (D) and (E) are added in the form of a master batch. As a rule, the length of the operation of mixing in the rotary mixer is at most 60 minutes and is preferably from 10 to 45 minutes, at ambient
25 temperature.

The homogeneous mixture thus obtained is subjected to extrusion in an apparatus of conventional design, in which the mixture is brought to a temperature of at most 290°C.
30 The extrusion temperature may vary between 100°C. and 290°C., depending upon the composition of the mixture. Furthermore, while remaining within the temperature limits specified above, temperature gradients may exist
35 from the supply zone of the extruder to the end zone of the extrusion die.

The extruder may contain one or more extrusion screws; it is merely important, in each case, that the composition obtained should be
40 perfectly homogeneous at the outlet of the die.

The die should, in turn, be constructed so that the extruded film has a regular final calibre.

45 If desired, the properties of the paper substitute obtained at the outlet of the die are such that subsequent biorientation is unnecessary which provides a second, considerable saving in the manufacturing process according to the present invention.

50 The paper substitute according to the present invention may then undergo surface treatment to improve subsequent printability. This

treatment, which is well known in the field of plastics, may consist in subjecting the paper to the action of a flame, corona effect, oxidising chemical agents or the like. 55

If desired, the surface treatment of the paper substitute as described above may be preceded by an operation for embossing its surface, in which the film passes between profiled heated rollers, thus making it possible to impart to the film a grained appearance, a linen paper appearance or any other appearance desired.

The following Examples are given for the purpose of illustrating the present invention: — 65

Example 1.

The following are mixed in a rotary mixer:

50% by weight of a high density polyethylene having a melt index of 1 dg/min (component A); 70

15% by weight of a mixture of the impact polystyrene type containing 90% polystyrene and 10% polybutadiene, with a melt index of 3 dg/min., under a pressure of 100 psi (7 kg/cm²) (component B); 75

20% by weight of a 50/50 mixture of polyethylene and polyisobutylene with a melt index of 0.2 g/min (component C);

10% by weight of titanium dioxide passing through a 50 micron screen (component D); 80

4% by weight of precipitated calcium carbonate passing through a 50 micron screen (component D); and

1% by weight of paraffin oil (component E). 85

Components (A), (B) and (C) are wetted with component (E), before incorporating filler (D), and the ingredients are mixed for 35 minutes at ambient temperature. The mixture obtained in this manner is then passed into a laboratory extruder of the type L=20 D, with a round die, at a temperature of 235°C.; the bubble is blown to three times the dimension of the die. After passing between pressing rollers, the film obtained is wound up. The film is then subjected to a corona treatment on one surface. The final paper substitute obtained in this manner has the appearance of a glazed cellulose paper on which it is possible to write with a pencil, pen or ballpen. 95

The properties of the paper substitute obtained in this Example are given in the following Table I: 100

TABLE I

Thickness of paper		microns	150
Density of paper			1
Breaking load	SM	kg/cm ²	190
(ASTM D 882/61T)	ST		115
Elongation at break	SM	%	13
(ASTM D 882/61T)	ST		11
Apparent elastic limit	SM	kg/cm ²	nil
(ASTM D 882/61T)	ST		
Modulus of elasticity	SM	kg/cm ²	7,600
(at a traction speed of 10 mm/min)	ST		7,400
Resistance to tearing	SM	g/sheet	67
(ASTM D 1922/61T)	ST		74
Resistance to bursting		kg	1.85
(Mullen Burst, ASTM D 774/67)		sag mm	3.7
Impact resistance (ASTM D 1709/67)		g	50 to 90
Rigidity	SM	mg/sheet	87
(ASTM D 747/63)	ST		113
Coefficient of friction		static	0.5
film on film (ASTM D 1894/63)		dynamic	0.3
Permeability to water vapour		g/m ² /24h	2
(ASTM E 96/66)			
Permeability to air(*)		ml/m ² /atm/24h	90
(ASTM D 1434/58)			
Dimensional variations in %	SM	75°C.	+ 0.04
at the temperature of	ST		+ 0.17
	SM	100°C.	- 1.23
	ST		- 0.16
Softening temperature	Start	°C.	121°
	Total		133°
Dimensional variations in	SM		0%
% in 24 hr. in water at 20°C.	ST		0%

Footnotes to Table I.

SM = machine direction

ST = transversal direction

(*) number of ml. of air passing through a 1 m² film, with a pressure difference of 1 atmosphere between the faces of the film, in 24 hours.

In this Table I, the properties of tearability, impact resistance, rigidity and permeabilities are properties which depend on the thickness of the paper substitute, while the breaking load, elongation at break and modulus of elasticity are properties independent of the thickness of the paper substitute.

This Table I shows that the paper substitute according to the present invention possesses mechanical properties similar to those of a cellulose paper and that, in this regard, it is very different from an ordinary film of plastics material. In addition, foldability and tearability are also of the same kind as those of glazed paper. Nevertheless, the paper substitute of the present invention has the advantage over cellulose paper of possessing better impermeability to water vapour and air and of having remarkable dimensional stability under variable climatic conditions. Furthermore, unlike ordinary paper, it withstands water perfectly.

Example 2.

The following are mixed in an ordinary rotary mixer:

35% by weight of a high density polyethylene having a melt index of 0.4 dg/min (component A);

14% by weight of a styrene-butadiene (90/10) copolymer having a melt index of 3.5 dg/min under a pressure of 100 psi (7 kg/cm²) (component B);

20% by weight of an ethylene-isobutylene (50/50) copolymer having a melt index of 0.2 dg/min (component C);

20% by weight of a master batch of titanium dioxide and of high density polyethylene (60/40) having a melt index of 8 dg/min (components A and D);

10% by weight of a master batch of calcium carbonate and of high density polyethylene (50/50) having a melt index of 4 dg/min (components A and D); and

1% by weight of antistatic agent (component E) consisting of a mixture of C₁₂—C₁₈ alkylamines;

at ambient temperature for a period of 25 minutes. The homogenised mixture obtained in this manner is extruded in the same extruder and under the same operating conditions as in Example 1.

The paper substitute obtained in this manner possesses characteristics similar to those of the paper substitute prepared in Example 1.

Example 3.

The following are mixed in a rotary mixer:

12% by weight of isotactic polypropylene having a melt index equal to 1 dg/min and 39% by weight of high density polyethylene having a melt index equal to 1 dg/min (component A);

10% by weight of a mixture of polystyrene and polybutadiene (80/20) having a melt index equal to 4 dg/min under a pressure of 300 psi (21 kg/cm²) (component B);

23% by weight of a mixture of high density polyethylene and butyl rubber (70/30) with a melt index equal to 2 dg/min (component C);

10% by weight of a master batch consisting of a 50/50 mixture of titanium dioxide and high density polyethylene with a melt index equal to 5 dg/min (component A+D);

5% by weight of precipitated calcium carbonate (component D);

0.9% by weight of paraffin oil (component E), and

0.1% by weight of optical bleaching agent (component E), at ambient temperature for a period of 35 minutes. The homogenised mixture obtained in this manner is extruded in the same extruder and under the same operating conditions as in Example 1.

The properties of the paper substitute obtained are similar to those of the paper substitute prepared in Example 1.

The paper substitute of the present invention can be printed, in particular, by the following processes: offset, litho, letterpress, gravure, flexography and silk screen; it can be impulse or heat sealed, it can be stuck on to ordinary paper with glues normally suitable for polyethylene, it can be laminated on to different types of film or on to "Cellophane" ("Cellophane" is a Registered Trade Mark) with the use of standard glues, and it is thermoformable, so that embossing can be carried out and any desired surface structures obtained by simply passing over heated rollers.

The paper substitute manufactured according to the present invention can be used for making maps of any kind: tourist maps, topographical maps, road maps or the like for printing instructions on official documents (driving licences, hunting permits, fishing permits), for forms, catalogues or the like.

The paper substitute according to the present invention can also be used for any artistic

printing application and for posters displayed outdoors.

It can also be used for printing children's books because the pages can be washed with water. Since the paper substitute of the present invention does not form dust, it is recommended for special applications in certain industries (for example, for the manufacture of transistors) where the presence of dust is not allowable.

The paper substitute of the present invention is very particularly recommended for use in places where oil or grease is found, for example as manuals for the greasing of cars, machines or the like and as self-adhesive labels resistant to oils, greases and the like.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a paper substitute requiring neither calendering nor biorientation, wherein there is homogenised, in a conventional rotary mixer, a composition containing:

30 to 94.8% by weight of at least one rigid polyolefin (A) selected from the homopolymers and copolymers of ethylene, propylene and butylene, and also mixtures thereof and having a melt index of at most 1 decigramme per minute; 0.1 to 35% weight of at least one polymer (B) which is incompatible with the rigid polyolefin (A) and which, when extruded by itself, produces a brittle film and which has a melt index of less than 10 decigrammes per minute, the polymer (B) being selected from the homopolymers and copolymers containing a preponderant amount of an ethylenically-unsaturated polymerisable monomer having a terminable vinylidene group, selected from styrene, styrene halo- or alkyl-substituted in the side chain or in the nucleus, vinyl chloride, vinylidene chloride, acrylic esters and methacrylic esters of alkanols containing up to 3 carbon atoms.

0.1 to 35% by weight of a macromolecular material (C) producing compatibility between (A) and (B), selected from:

(1) copolymers of at least one monomer selected from ethylene, propylene and butylene, and at least one monomer selected from isobutylene, butadiene and isoprene, and

(2) a mixture previously prepared from at least one homopolymer of ethylene, propylene or butylene, and at least one homopolymer of isobutylene, butadiene or isoprene, the macromolecular material having a melt index of at most 2 dg/minute; 5 to 45% by weight of a mineral filler (D) having a particle size of less than 50 microns; and 0 to 10% by weight of adjuvants (E) selected from anti-oxidising agents, thermal stabilisers, optical bleaching agents, pigments, colouring materials, antistatic agents and/or lubricants, the mixture thus homogenised being extruded to give a paper substitute and the paper substitute thus obtained optionally subjected to surface treatment.

2. A process according to claim 1, wherein the polyolefin (A) is selected from high density polyethylene, isotactic polypropylene and isotactic polybutene.

3. A process according to claim 1, wherein the polyolefin (A) is a physical mixture of at least two polyolefins selected from high density polyethylene, isotactic polypropylene and isotactic polybutene.

4. A process according to claim 1, wherein the polyolefin (A) is a copolymer obtained from at least two olefins selected from ethylene, propylene and butylene.

5. A process according to any of the preceding claims, wherein the polymer (B) is a mixture containing a major amount of a homopolymer obtained by polymerisation of an ethylenically-unsaturated polymerisable monomer having a terminal vinylidene group, selected from styrene, styrene halo- or alkyl-substituted in the side chain or the nucleus, vinyl chloride, vinylidene chloride and acrylic or methacrylic esters of alkanols containing up to 3 carbon atoms, and a minor amount of a homopolymer obtained by polymerisation of an olefinic compound selected from isobutylene, butadiene and isoprene.

6. A process according to any of claims 1—4, wherein the polymer (B) is a copolymer obtained by copolymerisation of a major amount of an ethylenically-unsaturated polymerisable monomer having a terminal vinylidene group, selected from styrene, styrene halo- or alkyl-substituted on the side chain or the nucleus, vinyl chloride, vinylidene chloride, acrylic esters and methacrylic esters of alkanols containing up to 3 carbon atoms, and a minor amount of a polymerisable olefinic monomer selected from isobutylene, butadiene and isoprene.

7. A process according to any of the preceding claims wherein the polymer (B) is plasticised with 0.1 to 30% by weight of a plasticiser.

8. A process according to any of the preceding claims, wherein the macromolecular material (C) is a 50/50 by weight ethylene-isobutylene copolymer or a 75/25 by weight ethylene-butadiene copolymer.

9. A process according to any of claims 1—7, wherein the macromolecular material (C) is a 50/50 by weight mixture of high density polyethylene and polyisobutylene, a 50/50 by weight mixture of low density polyethylene and polyisobutylene, a 75/25 by weight mixture of high density polyethylene and polybutadiene, a 75/25 by weight mixture of low density polyethylene and polybutadiene or 70/30 by weight mixture of high density polyethylene and butyl rubber.

10. A process according to any of the preceding claims, wherein the mineral filler (D) is selected from talc, titanium dioxide, kaolin, zeolites, silica, zinc oxide, natural or precipi-

printing application and for posters displayed outdoors.

It can also be used for printing children's books because the pages can be washed with water. Since the paper substitute of the present invention does not form dust, it is recommended for special applications in certain industries (for example, for the manufacture of transistors) where the presence of dust is not allowable.

The paper substitute of the present invention is very particularly recommended for use in places where oil or grease is found, for example as manuals for the greasing of cars, machines or the like and as self-adhesive labels resistant to oils, greases and the like.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a paper substitute requiring neither calendering nor biorientation, wherein there is homogenised, in a conventional rotary mixer, a composition containing:

30 to 94.8% by weight of at least one rigid polyolefin (A) selected from the homopolymers and copolymers of ethylene, propylene and butylene, and also mixtures thereof and having a melt index of at most 1 decigramme per minute; 0.1 to 35% weight of at least one polymer (B) which is incompatible with the rigid polyolefin (A) and which, when extruded by itself, produces a brittle film and which has a melt index of less than 10 decigrammes per minute, the polymer (B) being selected from the homopolymers and copolymers containing a preponderant amount of an ethylenically-unsaturated polymerisable monomer having a terminable vinylidene group, selected from styrene, styrene halo- or alkyl-substituted in the side chain or in the nucleus, vinyl chloride, vinylidene chloride, acrylic esters and methacrylic esters of alkanols containing up to 3 carbon atoms.

0.1 to 35% by weight of a macromolecular material (C) producing compatibility between (A) and (B), selected from:

(1) copolymers of at least one monomer selected from ethylene, propylene and butylene, and at least one monomer selected from isobutylene, butadiene and isoprene, and

(2) a mixture previously prepared from at least one homopolymer of ethylene, propylene or butylene, and at least one homopolymer of isobutylene, butadiene or isoprene, the macromolecular material having a melt index of at most 2 dg/minute; 5 to 45% by weight of a mineral filler (D) having a particle size of less than 50 microns; and 0 to 10% by weight of adjuvants (E) selected from anti-oxidising agents, thermal stabilisers, optical bleaching agents, pigments, colouring materials, antistatic agents and/or lubricants, the mixture thus homogenised being extruded to give a paper substitute and the paper substitute thus obtained optionally subjected to surface treatment.

2. A process according to claim 1, wherein the polyolefin (A) is selected from high density polyethylene, isotactic polypropylene and isotactic polybutene.

3. A process according to claim 1, wherein the polyolefin (A) is a physical mixture of at least two polyolefins selected from high density polyethylene, isotactic polypropylene and isotactic polybutene.

4. A process according to claim 1, wherein the polyolefin (A) is a copolymer obtained from at least two olefins selected from ethylene, propylene and butylene.

5. A process according to any of the preceding claims, wherein the polymer (B) is a mixture containing a major amount of a homopolymer obtained by polymerisation of an ethylenically-unsaturated polymerisable monomer having a terminal vinylidene group, selected from styrene, styrene halo- or alkyl-substituted in the side chain or the nucleus, vinyl chloride, vinylidene chloride and acrylic or methacrylic esters of alkanols containing up to 3 carbon atoms, and a minor amount of a homopolymer obtained by polymerisation of an olefinic compound selected from isobutylene, butadiene and isoprene.

6. A process according to any of claims 1—4, wherein the polymer (B) is a copolymer obtained by copolymerisation of a major amount of an ethylenically-unsaturated polymerisable monomer having a terminal vinylidene group, selected from styrene, styrene halo- or alkyl-substituted on the side chain or the nucleus, vinyl chloride, vinylidene chloride, acrylic esters and methacrylic esters of alkanols containing up to 3 carbon atoms, and a minor amount of a polymerisable olefinic monomer selected from isobutylene, butadiene and isoprene.

7. A process according to any of the preceding claims wherein the polymer (B) is plasticised with 0.1 to 30% by weight of a plasticiser.

8. A process according to any of the preceding claims, wherein the macromolecular material (C) is a 50/50 by weight ethylene-isobutylene copolymer or a 75/25 by weight ethylene-butadiene copolymer.

9. A process according to any of claims 1—7, wherein the macromolecular material (C) is a 50/50 by weight mixture of high density polyethylene and polyisobutylene, a 50/50 by weight mixture of low density polyethylene and polyisobutylene, a 75/25 by weight mixture of high density polyethylene and polybutadiene, a 75/25 by weight mixture of low density polyethylene and polybutadiene or 70/30 by weight mixture of high density polyethylene and butyl rubber.

10. A process according to any of the preceding claims, wherein the mineral filler (D) is selected from talc, titanium dioxide, kaolin, zeolites, silica, zinc oxide, natural or precipi-



- tated calcium carbonate, magnesium carbonate and barytine.
11. A process according to any of the preceding claims, wherein the adjuvant (E) is a thermal stabiliser selected from diphenyl-thiourea, α - phenyl - indole, barium palmitate, cadmium palmitate, zinc palmitate, barium stearate, cadmium stearate, zinc stearate and tris - nonylphenyl phosphite.
12. A process according to any of the preceding claims, wherein the adjuvant (E) is an antioxidantising agent selected from 4,4' thio - bis - (6 - *t* - butyl - *m* - cresol), 4,4' - methylene - bis - (2,6 - di - *t* - butyl phenol) and butylated hydroxytoluenes.
13. A process according to any of the preceding claims, wherein the adjuvant (E) is an optical bleaching agent which is a sulphonated derivative of stilbene.
14. A process according to any of the preceding claims, wherein the adjuvant (E) is an organic colouring agent selected from the phthalocyanines, disazoic colouring agents and chlorinated indanthrenes.
15. A process according to any of the preceding claims, wherein the adjuvant (E) is a mineral pigment selected from zinc chromate, cadmium sulphide and iron oxide.
16. A process according to any of the preceding claims, wherein the adjuvant (E) is a lubricant selected from magnesium stearate, calcium stearate and paraffin oil.
17. A process according to any of the preceding claims, wherein the mixing of the components A, B, C, D and E in the rotary mixer is effected at ambient temperature.
18. A process according to any of the preceding claims, wherein the extrusion is effected at a temperature between 100 and 290°C.
19. A process according to any of the preceding claims, wherein the surface treatment to which the paper substitute is subjected is a flame treatment.
20. A process according to any of claims 1—18, wherein the surface treatment to which the paper substitute is subjected is a treatment by corona effect.
21. A process according to any of claims 1—18, wherein the surface treatment to which the paper substitute is subjected is a treatment by oxidising agents.
22. A process according to any of the preceding claims, wherein the paper substitute is subjected to an embossing operation.
23. A process according to claim 1 for the manufacture of a paper substitute, substantially as hereinbefore described and exemplified.
24. A composition for the manufacture of paper substitute as defined in claim 1.
25. A paper substitute, whenever obtained by the process according to any of claims 1—23.

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