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(54) Abstract Title  
**Calcium carbonate filler in stretched polyolefin film**

(57) A ground particulate calcium carbonate material having a  $d_{50}$  of less than 1.0  $\mu\text{m}$  is used as a mineral filler in a stretched thermoplastic polyolefin film, for the purpose of increasing the moisture vapour permeability of said film.

Also disclosed is a method of increasing the moisture vapour permeability of a stretched, mineral-filled thermoplastic polyolefin film which method comprises using, as the mineral filler, a ground calcium carbonate having a  $d_{50}$  of less than 1.0  $\mu\text{m}$ . The calcium carbonate may be treated with a hydrophobic agent, such as an aliphatic carboxylic acid, preferably stearic acid. The polyolefin film is preferably a polyethylene such as LLDPE or LDPE.

**GB 2 383 046 A**

DESCRIPTION OF THE INVENTIONField of the invention

The present invention relates to a breathable film,  
5 and its uses and preparation thereof.

Background of the Invention

Alkaline earth metal carbonates, particularly  
calcium carbonates are used as the particulate filler in  
10 end products comprising compositions incorporating  
thermoplastic polymers, such as breathable film  
products. Such films are manufactured for a number of  
consumer products such as backing materials, plastic  
paper, house wrap, roofing membranes, grocery sacks,  
15 diapers, bandages, training pants, sanitary napkins,  
surgical drapes, and surgical gowns. The compositions  
from which these films are made may include two basic  
components, the first being a thermoplastic polymer,  
usually a predominantly linear polyolefin polymer such  
20 as a linear low density polyethylene and the second  
being an inorganic particulate filler such as calcium  
carbonate. A third component, namely a bonding or  
tackifying agent may often be present. These components  
are mixed and compounded together to form a compound or  
25 concentrate which is formed (usually in a subsequent  
process) into a film layer using any one of a variety of  
film-producing processes known to those of ordinary  
skill in the film making art including casting or  
blowing. Alternatively, the film may be laid down on a  
30 substrate such as paper or board in a process known as  
extrusion coating.

After the film is fabricated into its desired form, to make a porous breathable film, the film is then stretched, uniaxially or biaxially, by any of the well-known techniques in the art including by hydraulics, by  
5 pinch rolls moving at different rates, by interdigitating rolls or by tentering.

Nago et al ((1992); Journal of Applied Polymer Science, Vol. 45, 1527-1535 discloses the preparation of microporous polypropylene sheets by biaxially stretching  
10 polypropylene sheets containing a calcium carbonate filler content of 59 % by weight, the calcium carbonate having a particle size of 0.08 - 3.0 %.

#### Summary of the Invention

15 According to one aspect of the present invention, there is provided the use of a ground particulate calcium carbonate material having a  $d_{50}$  of less than 1.0  $\mu\text{m}$  as a mineral filler in a stretched thermoplastic polyolefin film, for the purpose of increasing the  
20 moisture vapour permeability of said film.

According to another aspect of the present invention, there is provided a method of increasing the moisture vapour permeability of a stretched, mineral-filled thermoplastic polyolefin film which method  
25 comprises using, as the mineral filler, a ground calcium carbonate having a  $d_{50}$  of less than 1.0  $\mu\text{m}$  .

#### DESCRIPTION OF THE INVENTION

The purpose of the present invention is to increase  
30 the moisture vapour permeability (or "breathability") of stretched, mineral-filled polyolefin films. This is

achieved in accordance with the invention by using, as the mineral filler, a ground calcium carbonate filler, having a  $d_{50}$  of less than 1.0  $\mu\text{m}$ . It has been found that, when such a ground calcium carbonate is used, the  
5 breathability of the stretched polyolefin film is increased compared with conventional mineral filled polyolefin films in which the mineral filler has a  $d_{50}$  which is greater than 1.0  $\mu\text{m}$ .

The " $d_{50}$ " of the mineral filler used herein is  
10 defined as the particle size value less than about which there are 50% by weight of the particles.

For the purposes of the present invention, a film is "breathable" if it has a moisture vapour transmission rate (MVTR) of at least 100  $\text{g}/\text{m}^2/24$  hours as calculated  
15 using the test method described in US Patent No. 5,695,868.

In this specification, "film" means a sheet or layer of material having a median thickness of no more than about 250  $\mu\text{m}$ . Typical thickness sizes and  
20 properties of films are described later. The film of the present invention is a breathable film, i.e. having microscopic interconnecting pores not greater than about 30  $\mu\text{m}$  in size (usually much less). Such a film allows for example water vapor in the atmosphere on one side of  
25 the film to permeate to the atmosphere on the other side without liquid water being transmitted through the film.

The calcium carbonate used in the present invention may comprise a carbonate obtained from a mineral source and processed by refining and treatment processes  
30 including grinding to obtain a suitable particle size distribution. The grinding process may be carried out

either in a dry state, typically in the absence of added hygroscopic or hydrophilic chemicals or in a wet state in an aqueous medium in which any dispersant employed is minimized and/or subsequently removed from the filler in a known manner. Wet ground material is subsequently dried to an extent such that the particulate material has an appropriate moisture content. The particles of the particulate product according to the present invention are treated (coated) with one of the aliphatic carboxylic acid hydrophobizing surface treatment agents conventionally employed to coat carbonates.

The calcium carbonate used in the present invention may be obtained from a natural source, e.g. marble, chalk or limestone. Desirably, at least 95%, preferably at least 99%, by weight of the calcium carbonate filler comprises the carbonate itself although minor additions of other mineral additives, e.g. one or more of kaolin, calcined kaolin, wollastonite, bauxite, talc or mica, could also be present together with the carbonate. At least 95% to 99% by weight may be calcium carbonate which may be obtained in a well known way by processing naturally occurring calcium carbonate obtained from a mineral source.

The particulate product according to the present invention preferably has one or more of the following particle size properties:

- i. a top cut (the particle size value less than about which at least 99% by weight of the particles of the material have a size) of less than about  $10\mu\text{m}$ , desirably less than about  $8\mu\text{m}$ ;

ii. a moisture pick up of less than about 0.35% by weight, more preferably less than about 0.2 % by weight, and most preferably less than about 0.1% by weight;

All particle size values as specified herein are  
5 measured by the well known conventional method employed in the art of sedimentation of the particles in a fully dispersed state in an aqueous medium using a SEDIGRAPH 5100 machine as supplied by Micromeritics Corporation, USA.

10 The ground calcium carbonate filler used in the present invention may have a  $d_{50}$  of at least 0.3  $\mu\text{m}$ , and for example may have a  $d_{50}$  which is greater than 0.5  $\mu\text{m}$ . Further, the calcium carbonate may have  $d_{50}$  which is less than 0.8  $\mu\text{m}$ .

15 The calcium carbonate used in the present invention preferably has a total surface moisture content which is preferably less than about 0.1% by weight even after exposure for 40 hours at 20°C to a moist atmosphere having a relative humidity of 80%. Desirably, the  
20 surface moisture content is less than about 0.1% by weight even after exposure for 40 hours at 20°C to an atmosphere having a relative humidity of 97.

The calcium carbonate filler used in the present invention is ground to obtain a suitable particle size  
25 distribution. The grinding process may be carried out either in a dry state in the absence of added hygroscopic or hydrophilic chemicals or in a wet state in an aqueous medium in which any dispersant employed is minimized and/or subsequently removed from the filler in  
30 a known manner. Wet ground material is subsequently

dried to an extent such that the particulate material has an appropriate moisture content.

The calcium carbonate used in the invention may have been processed, e.g. by known purification, 5 comminution and particle size classification procedures to have a suitable form prior to use to form the particulate product according to the present invention. However, following such processing the amount of hygroscopic or hydrophilic additives present is 10 preferably minimized, as described earlier, e.g. by removing any such additives used by a washing process.

The calcium carbonate used in the present invention is treated with a hydrophobizing surface treatment agent and the treatment may be carried out prior to use by 15 addition to thermoplastic polymeric material.

Alternatively, the hydrophobizing agent, sometimes referred to as antagonizing agent, may be added directly to the thermoplastic polymer with which the calcium carbonate is to be compounded, before, during or after 20 addition of the particulate product according to the present invention. For maximizing the effect of the hydrophobizing agent, complete surface treatment of the calcium carbonate is preferred prior to addition to the thermoplastic polymer.

25 Where the calcium carbonate filler used in the invention is surface treated, the  $d_{50}$  of the filler after treatment (which may differ slightly from the  $d_{50}$  before such treatment) should be in the ranges defined above.

30 Use of surface treatment agents, which, when added to the inorganic particulate material which is dry,

facilitate dispersion of the inorganic particulate material in hydrophobic polymeric material are well known. Suitable surface treatment agents are known to include aliphatic carboxylic acids having from 10 to 30  
5 carbon atoms in their chain, including but not limited to, stearic acid, behenic acid, palmitic acid, arachidic acid, montanic acid, capric acid, lauric acid, myristic acid, isostearic acid and cerotic acid and mixtures thereof.

10 Further details concerning the surface treatment of calcium carbonate fillers for polymer compositions may be found in WO 99/61521, the contents of which are incorporated herein by reference for all purposes.

The production route employed for producing the  
15 calcium carbonate used in the present invention can be selected from the many procedures known to those skilled in the art. Further details regarding the production of suitable particulate calcium carbonate minerals for use in the invention may be found in WO 99/61521, the  
20 contents of which are incorporated herein by reference for all purposes.

The polymeric material to which the particulate calcium carbonate is added to form a composition may comprise, for example, a continuous thermoplastic  
25 polyolefin polymer matrix.

The particulate calcium carbonate may be incorporated in an application composition (to form an intermediate product which is then stretched to form the stretched end product) together with a thermoplastic  
30 polyolefin material and other optional conventional additives, e.g. a bonding or tackifying agent.



The process employed to form the intermediate product, and subsequently the stretched polyolefin film, from the thermoplastic material and the particulate calcium carbonate may be one or more of the methods well known in the art as described later.

In the intermediate film product and the subsequent stretched product, the thermoplastic polyolefin polymer may form from 20% to 80% by weight and the filler will form from 30% to 80% by weight of the composition, i.e. combination of the polymer plus filler. More preferably, the thermoplastic polymer forms from about 30% to about 55% by weight of the composition and the filler forms from about 45% to about 65% by weight of the composition.

The preferred thermoplastic polymer for us in the invention is a thermoplastic polyolefin, for example one which comprises more than about 50% by weight of olefin units and is referred to as polyolefin resin.

The polyolefin polymers (or resins) which can be used to provide the polyolefin resin, for example, include mono-olefin polymers of ethylene, propylene, butene or the like, or copolymers thereof as a main component. Typical examples of the polyolefin resin include polyethylene resins such as a low-density polyethylene, linear low-density polyethylene (ethylene- $\alpha$ -olefin copolymer), middle-density polyethylene and high-density polyethylene; polypropylene resins such as polypropylene and ethylene-polypropylene copolymer; poly(4-methylpentene); polybutene; ethylene-vinyl acetate copolymer; and mixtures thereof. These polyolefin resins may be obtained by polymerization in a

known way, e.g. by the use of a Ziegler catalyst, or obtained by the use of a single site catalyst such as a metallocene catalyst. Above all, polyethylene resins are preferable, and linear low-density polyethylene  
5 (ethylene- $\alpha$ -olefin copolymer) and low-density polyethylene are most preferable. Furthermore, in view of the moldability, the stretchability and the like of the film, the melt index of the polyolefin resin is preferably in the range of about 0.5 to 5 g/10 min.

10 Other thermoplastic polymers which may be used in the practice of the present invention are thermoplastic elastomers, such as SBS.

Desirably, the filler includes at least 50% by weight, e.g. from 80% to 99% by weight of the calcium  
15 carbonate where one or more other fillers are employed together with the particulate product according to the present invention.

Examples of the other fillers include calcium carbonate (not in accordance with the invention), barium  
20 sulphate, calcium sulphate, barium carbonate, magnesium hydroxide, aluminum hydroxide, zinc oxide, calcium oxide, magnesium oxide, titanium oxide, silica and talc. The average particle diameter of the other filler is preferably 20  $\mu\text{m}$  or less, preferably 10  $\mu\text{m}$  or less,  
25 preferably in the range of 0.5 to 5  $\mu\text{m}$ . In order to improve the dispersibility of the other filler in the polyolefin resin, the other filler may be subjected to a surface treatment to render its surfaces hydrophobic, may be used. Examples of suitable surface treatment  
30 agents include the fatty acids such as stearic acid, specified earlier.

The composition ratio between the thermoplastic polymer and the calcium carbonate filler has an influence on the moldability and the stretchability of the film as well as the breathability and the moisture vapor transmission of the obtained film. If the amount of the filler is insufficient, adjacent micropores, which are required to be obtained by the interfacial separation of the polymer and the calcium carbonate filler from each other, are not continuous, so that a porous film having the good gas breathability and moisture vapor transmission cannot be obtained. On the contrary, if the amount of the calcium carbonate filler is excessive, defective molding occurs during the film forming process and the stretchability deteriorates, so that the sufficient stretching cannot be carried out. In view of these limiting factors, the composition ratio between the polymer and the calcium carbonate filler may be from 25 to 70 parts by weight of the polymer with respect to from 75 to 30 parts by weight of the calcium carbonate filler, e.g. from 30 to 60 parts by weight of the polymer with respect to 70 to 40 parts by weight of the calcium carbonate filler.

In the manufacture of a breathable film according to the present invention a concentrate or masterbatch of the thermoplastic polyolefin polymer resin and the calcium carbonate filler may first be produced by mixing and compounding prior to the film production stages.

The mixture of ingredients to be blended by compounding may include in addition to the polymer and the filler other known optional ingredients conventionally employed in thermoplastic films, e.g. one

or more of bonding agents, plasticisers, lubricants, anti-oxidants, ultraviolet absorbers, dyes, colorants. A bonding or tackifying agent, where employed, may facilitate bonding of the film after formation to  
5 another member, e.g. a non-woven fibrous layer, or one or more non-porous layers.

The thermoplastic polymer, the filler and, if necessary, other optional additives, may be mixed by the use of a suitable compounder/mixer e.g. a Henschel  
10 mixer, a super mixer, a tumbler type mixer or the like, and kneaded and may be pelletized, e.g. by the use of a single screw extruder or a twin-screw extruder which forms strands which may be cut or broken into pellet.

The masterbatch or concentrate, e.g. in the form of  
15 pellets, is melted and molded or shaped into the intermediate film (i.e. the film before stretching) by the use of a molding and film forming machine, as well known in the art. . Normally, the masterbatch, prior to the film forming step is "let down" to a suitable  
20 calcium carbonate content, using a polymer which may be the same as or different from the polymer of the masterbatch. For example, the masterbatch may be formed at a mineral filler content of the order of 70 wt.% which is let down to a mineral filler content of, for  
25 example, 55 wt.%

The intermediate may be a blown film, cast film or extruded film. Other types of films are also considered to be within the scope of the present invention provided the forming technique is compatible with filled films.  
30 Appropriate methods for producing the films according to

the present invention will be readily apparent to the skilled artisan.

The intermediate film is then heated, e.g. to a temperature of about 5°C less than about the melting  
5 point of the thermoplastic polymer or more, and then stretched to at least about 1.2 times, preferably at least 2.5 times, its original length to thin the film and render it porous.

An additional feature of the thinning process is  
10 the change in opacity of the film. As formed, the film is relatively transparent but after stretching, it becomes opaque. In addition, while the film becomes orientated during the stretching process, it also becomes softer. Taking all these factors into  
15 consideration, and the desire to have a water vapor transmission rate of at least 100 grams per square meter per 24 hours, the film may, for example, be thinned to such an extent that it has a weight per unit area of less than about 35 grams per square meter for personal  
20 care absorbent article applications and a weight per unit area of less than about 18 grams per square meter for certain other applications.

The molding and film forming machine may for  
example comprise, as in the prior art, an extruder  
25 equipped with a T-die or the like or an inflation molding machine equipped with a circular die. The film production may be carried out at some time after the masterbatch production, possibly at a different manufacturing plant. In some cases, the masterbatch can  
30 directly be formed into the film without producing an intermediate product.

The film can be stretched in at least a uniaxial direction at a temperature of from room temperature to the softening point of the thermoplastic polymer in a known manner such as a roll method, an interdigitizing  
5 method, or a tenter method to bring about the interfacial separation of the polymer and the inorganic filler from each other, whereby a porous film can be prepared. The stretching may be carried out by one step or by several steps. Stretch magnification determines  
10 film breakage at high stretching as well as breathability and the moisture vapor transmission of the obtained film, and so excessively high stretch magnification and excessively low stretch magnification are desirably avoided. The stretch magnification is  
15 preferably in the range of 1.2 to 5 times, more preferably 1.2 to 4 times in at least a uniaxial direction. If biaxial stretching is carried out, it is possible that for example stretching in a first direction is applied in the machine direction or a  
20 direction perpendicular thereto, and stretching in a second direction is then applied at right angles to the first direction. Alternatively, the biaxial stretching may be carried out simultaneously in the machine direction and the direction perpendicular thereto. Any  
25 method known in the art or after developed can be applied in making the film in the method according to this aspect of the present invention.

After the stretching, a heat setting treatment may be carried out if required in order to stabilize the  
30 shape of obtained voids. The heat setting treatment may be, for example, a heat setting treatment at a

temperature in the range of from the softening point of the resin to a temperature less than about the melting point of the resin for a period of 0.1 to 100 seconds.

No particular restriction is put on the thickness of a breathable film produced of the present invention. The thickness should be such as to obtain film unlikely to tear or break and which has appropriate softness and good feel. Usually, the thickness of the breathable film is in the range of 5  $\mu\text{m}$  to 100  $\mu\text{m}$ , preferably 10  $\mu\text{m}$  to 70  $\mu\text{m}$ .

Generally, once the film is formed, it will have a weight per unit area of less than about 100 grams per square meter and after stretching and thinning its weight per unit area will be less than about 35 grams per square metre and more desirably less than about 18 grams per square metre.

The breathable film can be suitably utilized in applications requiring softness, for example, as the backing sheet of disposable diapers.

"Porous" as used in the present application includes but is not coextensive with "breathable" films.

A breathable film of the present invention having such properties may have a suitable breathability, moisture vapor transmission and feeling as well as excellent mechanical properties and long-term adhesive properties to be suitably used in products such as disposable diapers, body fluid absorbing pads and bed sheets; medical materials such as surgical gowns and base materials for hot compress; clothing materials such as jumpers, rainwear; building materials such as wallpapers and waterproof materials for roofs and house

wraps; packaging materials for packaging desiccants, dehumidifying agents, deoxidizers, disposable body warmers; packaging materials for keeping the freshness of various articles and foods; separators for the cells; 5 and the like. The breathable film is particularly desirable as a material used in products such as disposable diapers and body fluid absorbing pads. The breathable film may in such products be formed into a composite or laminate in one of the ways well known in 10 the art with one or more other layers, e.g. a non-woven fibrous layer, e.g. by an adhesive or bonding agent.

Embodiments of the present invention will now be described, by way of example only, and with reference to the following Examples.

15

**EXAMPLE 1**

A chemical-free, ground calcium carbonate was used, produced by a low-solids sand-milling route. The calcium carbonate had a nominal  $d_{50}$  of  $0.6\mu\text{m}$ .

A 3 tonne (dry weight) sample of the carbonate was 20 dewatered, dried and stearate coated by the addition of a stearate dose of 2.1 wt% (equivalent to 1 wt% per  $4.5\text{m}^2.\text{g}^{-1}$  of surface area). To ensure the product was free from oversize aggregates, the coated material was then passed through a Nisshin air-classifier to remove 25 any material present with a  $d_{50}$  exceeding  $10\mu\text{m}$ .

Two tonnes of a coated final product were produced. The physical analyses of the uncoated and coated product are shown below in Tables 1 and 2 respectively. The physical analysis of the coated product was for three 30 representative samples collected from the 2 tonne bulk sample.



**Table 1**  
**Physical Analysis of Uncoated Product**

Sedigraph Particle Size Analysis						Surface area (m <sup>2</sup> .g <sup>-1</sup> )	distribution steepness
+10um	-2um	-1um	-0.5um	0.25um	d <sub>50</sub>		
2.7	92.2	73.4	35.7	9.4	0.65	9.7	46

5

**Table 2**  
**Physical Analysis of Coated Product (Carbonate A)**

Mastersizer Particle Size Analysis						LOI (wt%) H <sub>2</sub> O pickup (wt%)
+10um	-2um	-1um	-0.5um	0.25um	d <sub>50</sub>	
1.2	82.6	62.8	34.6	8.7	0.72	2.1/0.19
Not measured						2.2/0.16
Not measured						2.6/0.14

The performance of a sample of the coated calcium carbonate material referred to above (hereafter Carbonate A) and a sample of a commercially available calcium carbonate having a d<sub>50</sub> of 1.27 (hereafter Carbonate B) were compared in a variety of LLDPE resins of differing densities at 65% filler (also containing 1500ppm of Irganox 1010 antioxidant).

The following masterbatch compositions were produced as shown in Table 3 which also indicates the single point viscosity (MI) and stiffness (density) of the resins employed (prior to the addition of any processing additive):

20

**Table 3**

Compound	Carbonate	MI of PE	Density of PE
A	B	2.3	0.917
B	B	2.5	0.935

C	A	2.3	0.917
D	B	2.3	0.917
E	A	2.3	0.917
F	A	3.3	0.917
G	A	4.0	0.916
H	A	6.0	0.919
I	A	5.4	0.921
J	A	9.5	0.920

The LLDPE used in Compounds D and E contained 10% by weight of a polyethylene wax processing additive.

These compositions were compounded on a Werner and Pfleiderer ZSK40 compounder operating at an extruder speed of 300rpm and a throughput of 80kg.h<sup>-1</sup> with a die temperature of 220 °C

The compounds containing the polyethylene wax processing additive (Compounds D and E) were prepared on a Baker-Perkins MP2030 compounder operating at an extruder speed of 300rpm, a throughput of 5kg.h<sup>-1</sup> and a die temperature of 220°C.

The resulting masterbatch samples were then let down to nominal 50 or 55% calcium carbonate content and then extruded in a cast-film pilot line having 5 heating zones maintained at the following temperatures: 190°C, 200°C, 200°C, 210°C, 220°C and a die temperature of 220°C, and subsequently stretched in machine direction. Extruder feed rates and speed of the stretching rollers were chosen to produce stretched films with a nominal thickness of 25µm.

The results obtained are set out in Table 4 below. The Moisture Vapour Transmission Rates (MVTR), measured in  $\text{g.H}_2\text{O.m}^{-2}.\text{day}^{-1}$ , of the films were measured as duplicate samples (using micropore membranes as controls) according to ASTM E - 96 (weight loss method) at 37°C. The  $\text{CaCO}_3$  content of the film was measured by ashing at 450°C for 1 hour. The comments refer to the quality of the film produced in terms of its uniformity of thickness and ability to resist tearing.

10

Table 4

Film	Compound (filler content: stretch ratio)	$\text{CaCO}_3$ content	MVTR	Comments
1	control	49.9	2501	control film
2	A (50: x4)	50.6	2174	Pass
3	A (50: x3)			Fail
4	C (50: x4)	52.1	1999	Pass
5	C (50: x3)			Fail
6	B (50: x4)			Fail
7	B (50: x5)			Fail
8	J (50: x4)	48.5	496	Fail
9	J (50: x3)			Fail
10	H (50: x4)			Fail
11	H (50: x5)	50.5	2918	Fail
12	F (50: x4)	50.5	1705	Fail
13	F (50: x5)	48.8	2169	Pass
14	I (50: x4)	49.8	654	Fail
15	I (50: x5)	48.1	2052	Pass
16	G (50: x4)	52.2	2049	Fail
17	G (50: x5)	51.3	3195	Pass
18	E (50: x4)	45.8	40	Fail
19	E (50: x5)	44.6	21	Fail
20	G (55:x4)	54.5	3029	Fail
21	G (55: x5)	55.3	3478	Pass
22	C (55: x4)	54.0	2438	Fail
23	C (55: x5)	54.2	3277	Pass
24	A (55: x4)	56.4	3673	Pass
25	A (55: x5)	54.6	3147	-
26	B (55: x4)			Fail

Film	Compound (filler content: stretch ratio)	CaCO <sub>3</sub> content	MVTR	Comments
27	B (55: x5)	55.0	3679	Fail
28	J (55: x4)			Fail
29	J (55: x5)			-
30	H (55: x4)			Fail
31	H (55: x5)	54.2	4137	Fail
32	F (55: x4)	51.9	1853	Fail
33	F (55: x5)	51.7	2981	Pass
34	I (55: x4)			Fail
35	I (55: x5)	52.3	2339	Fail
36	E (55: x4)			Fail
37	E (55: x5)	57.7	1329	Fail

A number of the films obtained were not uniform, principally as a result of limitations in the stretching equipment employed, and are thus marked "failed".

- 5 Although some of these films were sampled for MVTR, the results obtained for these films are of limited comparative value.

#### Example 2

10 A chemical-free, ground calcium carbonate was used, produced by low-solids sand-milling route. The slurry was hydrocycloned to eliminate coarse material, dewatered, dried and stearate treated by the addition of a stearate dose of 1.25wt % (equivalent to 1 wt% per 4.5m<sup>2</sup>g<sup>-1</sup> of surface area). The product had a d<sub>50</sub> of 0.81  
15 μm as measured by Sedigraph (subsequently referred to as Carbonate C).

The performance of Carbonate C in an LLDPE resin at various filler level contents was compared to that of a commercially available calcium carbonate having a d<sub>50</sub> of  
20 1.27 (hereafter Carbonate D).

60 weight % (of filler) masterbatches of carbonates C and D were prepared on a Werner and Pfleiderer ZSK40 twin screw extruder. The equipment was operated at a feed rate of 100 kg masterbatch hr<sup>-1</sup> with barrel temperatures of 170°C, 190°C, 200°C, 210°C, and a die temperature of 220°C, and a drive torque of 50%. Masterbatches also contained 1500 ppm of Irganox 1010.

The resulting masterbatches were let down with virgin LLDPE to attain required nominal levels of 45, 50 or 55 weight % filler and extruded in a cast-film pilot line with 5 heating barrels maintained at temperatures of 190°C, 200°C, 200°C, 210°C, 220°C, respectively, and a die maintained at a temperature of 220°C. The extruded film was subsequently stretched in the machine direction. Extruder rates and the speed of stretching rollers were chosen to produce microporous films with a nominal thickness of 25µm.

The Moisture Vapour Transmission Rates (MVTR), in g.H<sub>2</sub>O.m<sup>-2</sup>.day<sup>-1</sup>, of the films were measured as duplicate samples (using micropore membranes as controls) according to ASTM E-96 (weight loss method) at 37°C. Results are shown in Table 5. The actual percentage of filler in the films was measured by loss on ignition at 400 °C. It is therefore possible to normalise all MVTR values to nominal filler loading levels of 45, 50, and 55 weight %. These values are shown in Table 5.

Table 5

Film Description	% Filler	MVTR	MVTR corrected
Carbonate C, 45 wt.%, x4 stretch	43.7	925	--

Carbonate C, 45 wt.%, x5 stretch	43.7	799	1209
Carbonate C, 45 wt.%, x6 stretch	43.7	460	--
Carbonate C, 50 wt.%, x4 stretch	50.4	2378	--
Carbonate C, 50 wt.%, x5 stretch	50.4	2598	2516
Carbonate C, 50 wt.%, x6 stretch	50.4	2365	--
Carbonate C, 55 wt.%, x4 stretch	55.5	3302	--
Carbonate C, 55 wt.%, x5 stretch	55.5	3464	3402
Carbonate C, 55 wt.%, x6 stretch	55.5	3778	--
Carbonate D, 45 wt.%, x4 stretch	44.3	741	--
Carbonate D, 45 wt.%, x5 stretch	44.3	792	975
Carbonate D, 45 wt.%, x6 stretch	44.3	1181	--
Carbonate D, 50 wt.%, x4 stretch	47.9	1501	--
Carbonate D, 50 wt.%, x5 stretch	47.9	1710	2264
Carbonate D, 50 wt.%, x6 stretch	47.9	1510	--
Carbonate D, 55 wt.%, x4 stretch	53.9	3068	--
Carbonate D, 55 wt.%, x5 stretch	53.9	3295	3610
Carbonate D, 55 wt.%, x6 stretch	53.9	3534	--

Reference to Table 5 shows that for most stretching ratios and filler loadings Carbonate C gives rise to higher breathability than Carbonate D.

**CLAIMS**

1. The use of a ground particulate calcium carbonate material having a  $d_{50}$  of less than  $1.0 \mu\text{m}$  as a mineral filler in a stretched thermoplastic polyolefin film, for the purpose of increasing the moisture vapour permeability of said film.

2. The use as claimed in claim 1, wherein the particulate calcium carbonate material has a  $d_{50}$  greater than  $0.3 \mu\text{m}$ .

3. The use as claimed in claim 2, wherein the particulate calcium carbonate material has a  $d_{50}$  greater than  $0.5 \mu\text{m}$ .

4. The use as claimed in claim 1, 2 or 3, wherein the particulate calcium carbonate material has a  $d_{50}$  less than  $0.8 \mu\text{m}$ .

5. The use as claimed in any preceding claim, wherein the calcium carbonate has been surface treated with a hydrophobizing agent.

6. The use as claimed in claim 5, wherein the hydrophobizing agent is an aliphatic carboxylic acid having from 10 to 30 carbon atoms.

7. The use as claimed in claim 6, wherein the hydrophobizing agent is stearic acid.

8. The use as claimed in any preceding claim, wherein the polyolefin is polyethylene.

9. The use as claimed in claim 8, wherein the polyethylene is linear low-density polyethylene or low-density polyethylene.

10. A method of increasing the moisture vapour permeability of a stretched, mineral-filled thermoplastic polyolefin film which method comprises

using, as the mineral filler, a ground calcium carbonate having a  $d_{50}$  of less than 1.0  $\mu\text{m}$ .

11. A method according to claim 10, wherein the particulate calcium carbonate material has a  $d_{50}$  greater than 0.3  $\mu\text{m}$ .

12. A method as claimed in claim 11, wherein the particulate calcium carbonate material has a  $d_{50}$  greater than 0.5  $\mu\text{m}$ .

13. A method as claimed in claim 10, 11 or 12, wherein the particulate calcium carbonate material has a  $d_{50}$  less than 0.8  $\mu\text{m}$ .

14. A method as claimed in any one of claims 10 to 13, wherein the calcium carbonate has been surface treated with a hydrophobizing agent.

15. A method as claimed in claim 14, wherein the hydrophobizing agent is an aliphatic carboxylic acid having from 10 to 30 carbon atoms.

16. A method as claimed in claim 15, wherein the hydrophobizing agent is stearic acid.

17. A method as claimed in any one of claims 10 to 16, wherein the polyolefin is polyethylene.

18. A method as claimed in claim 17, wherein the polyethylene is linear low-density polyethylene or low-density polyethylene.





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Application No: GB 0129701.9  
Claims searched: 1 to 18

Examiner: Matthew Clarke  
Date of search: 4 April 2002

### Patents Act 1977 Search Report under Section 17

#### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T): C3K (KEB, KGG) C3L (LDA, LDB, LDR)

Int Cl (Ed.7): C08J (5/10) C08K (3/26)

Other: Online: WPI, EPODOC, PAJ

#### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 1002826 A1 (TOKUYAMA CORP) see page 3 lines 25 to 33, page 4 lines 21 to 30 and page 4 lines 55 to 58	1-18
X	WO 99/61521 A1 (ECC INTERNATIONAL) see page 9 lines 13 to 17, page 17 lines 11 to 22 and page 23 lines 1 to 5	1-18
X	US 5489471 A (INOUE et al) see column 1 line 63 to column 2 line 58	1-4, 8, 9-13, 17, 18
X	US 4921652 A (TSUJI et al) see column 2 lines 8 to 23	1-4, 8, 9-13, 17, 18
X	JP 080225680 A (MITSUI TOATSU) see enclosed WPI Abstract Accession No.1996-451002 [51]	1-4, 8, 9-13, 17, 18
X	JP 630162729 A (MITSUI TOATSU) see enclosed WPI Abstract Accession No.1988-230514 [33]	1-8, 10-17

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.