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<p>(54) Title: MULTILAYER ARTICLE OF MICROPOROUS AND SUBSTANTIALLY NONPOROUS MATERIALS</p> <p>(57) Abstract</p> <p>A multilayer article comprises at least one layer of substantially nonporous material fusion bonded in the absence of extrinsic intervening adhesive to at least one layer of microporous material comprising a matrix consisting essentially of linear ultrahigh molecular weight polyolefin, a large proportion of finely divided, water-insoluble filler at least about 50 percent of which is siliceous, and interconnecting pores.</p>		

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MULTILAYER ARTICLE OF MICROPOROUS  
AND SUBSTANTIALLY NONPOROUS MATERIALS

2

4           This Application is a continuation-in-part of Application  
Serial No. 169,654, filed March 18, 1988, which is a  
6 continuation-in-part of Application Serial No. 138,980, filed  
December 29, 1987.

8           The present invention is directed to multilayer articles  
comprising microporous material characterized by a matrix consisting  
10 essentially of essentially linear ultrahigh molecular weight  
polyolefin, a very large proportion of finely-divided particulate  
12 filler, and a high void content, bonded to substantially nonporous  
material.

14           Accordingly, one embodiment of the invention is a  
multilayer article comprising material which is impervious to the  
16 passage of gas and bacteria fusion bonded in the absence of  
extrinsic intervening adhesive to microporous material comprising  
18 (a) a matrix consisting essentially of essentially linear ultrahigh  
molecular weight polyethylene having an intrinsic viscosity of at  
20 least about 18 deciliters/gram, essentially linear ultrahigh  
molecular weight polypropylene having an intrinsic viscosity of at  
22 least about 6 deciliters/gram, or a mixture thereof, (b) finely  
divided particulate substantially water-insoluble siliceous filler  
24 distributed throughout the matrix, the filler constituting from  
about 50 percent to about 90 percent by weight of the microporous  
26 material, and (c) a network of interconnecting pores communicating  
throughout the microporous material, the pores before fusion bonding  
28 constituting at least about 35 percent by volume of the microporous  
material.

30           Another embodiment of the invention is a multilayer  
article comprising at least one layer of substantially nonporous  
32 material fusion bonded in the absence of extrinsic intervening  
adhesive to at least one layer of microporous material comprising  
34 (a) a matrix consisting essentially of essentially linear ultrahigh  
molecular weight polyolefin which is essentially linear ultrahigh

molecular weight polyethylene having an intrinsic viscosity of at least about 18 deciliters/gram, essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least about 6 deciliters/gram, or a mixture thereof, (b) finely divided particulate substantially water-insoluble filler, of which at least about 50 percent by weight is siliceous, distributed throughout the matrix, the filler constituting from about 50 percent to about 90 percent by weight of the microporous material, and (c) a network of interconnecting pores communicating throughout the microporous material, the pores before fusion bonding constituting at least about 35 percent by volume of the microporous material.

The thickness across the microporous material may vary widely, but usually it is in the range of from about 0.03 to about 4 millimeters. In many cases it is in the range of from about 0.07 to about 1.5 millimeters. From about 0.18 to about 0.6 millimeter is preferred.

Inasmuch as ultrahigh molecular weight (UHMW) polyolefin is not a thermoset polymer having an infinite molecular weight, it is technically classified as a thermoplastic. However, because the molecules are essentially very long chains, UHMW polyolefin, and especially UHMW polyethylene, softens when heated but does not flow as a molten liquid in a normal thermoplastic manner. The very long chains and the peculiar properties they provide to UHMW polyolefin are believed to contribute in large measure to the desirable properties of the microporous material.

As indicated earlier, the intrinsic viscosity of the UHMW polyethylene is at least about 18 deciliters/gram. In many cases the intrinsic viscosity is at least about 19 deciliters/gram.

Although there is no particular restriction on the upper limit of the intrinsic viscosity, the intrinsic viscosity is frequently in the range of from about 18 and 39 deciliters/gram. An intrinsic viscosity in the range of from about 18 to about 32 deciliters/gram is preferred.

Also as indicated earlier the intrinsic viscosity of the UHMW polypropylene is at least about 6 deciliters/gram. In many

cases the intrinsic viscosity is at least about 7 deciliters/gram.  
2 Although there is no particular restriction on the upper limit of  
the intrinsic viscosity, the intrinsic viscosity is often in the  
4 range of from about 6 to about 18 deciliters/gram. An intrinsic  
viscosity in the range of from about 7 to about 16 deciliters/gram  
6 is preferred.

As used herein and in the claims, intrinsic viscosity is  
8 determined by extrapolating to zero concentration the reduced  
viscosities or the inherent viscosities of several dilute solutions  
10 of the UHMW polyolefin where the solvent is freshly distilled  
decahydronaphthalene to which 0.2 percent by weight,  
12 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid, neopentetetrayl  
ester [CAS Registry No. 6683-19-8] has been added. The reduced  
14 viscosities or the inherent viscosities of the UHMW polyolefin are  
ascertained from relative viscosities obtained at 135°C using an  
16 Ubbelohde No. 1 viscometer in accordance with the general procedures  
of ASTM D 4020-81, except that several dilute solutions of differing  
18 concentration are employed. ASTM D 4020-81 is, in its entirety,  
incorporated herein by reference.

20 The nominal molecular weight of UHMW polyethylene is  
empirically related to the intrinsic viscosity of the polymer  
22 according to the equation:

$$M = 5.37 \times 10^4 [\eta]^{1.37}$$

24 where M is the nominal molecular weight and  $[\eta]$  is the intrinsic  
viscosity of the UHMW polyethylene expressed in deciliters/gram.

26 Similarly, the nominal molecular weight of UHMW polypropylene is  
empirically related to the intrinsic viscosity of the polymer

28 according to the equation:

$$M = 8.88 \times 10^4 [\eta]^{1.25}$$

30 where M is the nominal molecular weight and  $[\eta]$  is the intrinsic  
viscosity of the UHMW polypropylene expressed in deciliters/gram.

32 The essentially linear ultrahigh molecular weight  
polypropylene is most frequently essentially linear ultrahigh  
34 molecular weight isotactic polypropylene. Often the degree of  
isotacticity of such polymer is at least about 95 percent, while

preferably it is at least about 98 percent.

2           Sufficient UHMW polyolefin should be present in the matrix  
to provide its properties to the microporous material. Other  
4 thermoplastic organic polymer may also be present in the matrix so  
long as its presence does not materially affect the properties of  
6 the microporous material in an adverse manner. The amount of the  
other thermoplastic polymer which may be present depends upon the  
8 nature of such polymer. In general, a greater amount of other  
thermoplastic organic polymer may be used if the molecular structure  
10 contains little branching, few long sidechains, and few bulky side  
groups, than when there is a large amount of branching, many long  
12 sidechains, or many bulky side groups. For this reason, the  
preferred thermoplastic organic polymers which may optionally be  
14 present are low density polyethylene, high density polyethylene,  
poly(tetrafluoroethylene), polypropylene, copolymers of ethylene and  
16 propylene, copolymers of ethylene and acrylic acid, and copolymers  
of ethylene and methacrylic acid. If desired, all or a portion of  
18 the carboxyl groups of carboxyl-containing copolymers may be  
neutralized with sodium, zinc, or the like. It is our experience  
20 that usually at least about 50 percent UHMW polyolefin, based on the  
weight of the matrix, will provide the desired properties to the  
22 microporous material. Often at least about 70 percent by weight of  
the matrix is UHMW polyolefin. In many cases the other  
24 thermoplastic organic polymer is substantially absent.

The finely divided substantially water-insoluble siliceous  
26 filler used in the present invention is particulate. As present in  
the microporous material, the siliceous filler may be in the form of  
28 ultimate particles, aggregates of ultimate particles, or a  
combination of both. In most cases, at least about 90 percent by  
30 weight of the siliceous filler used in preparing the microporous  
material has gross particle sizes in the range of from about 5 to  
32 about 40 micrometers as determined by use of a Model TAI1 Coulter  
counter (Coulter Electronics, Inc.) according to ASTM C 690-80 but  
34 modified by stirring the filler for 10 minutes in Isoton II  
electrolyte (Curtin Matheson Scientific, Inc.) using a four-blade,

4.445 centimeter diameter propeller stirrer. Preferably at least  
2 about 90 percent by weight of the siliceous filler has gross  
particle sizes in the range of from about 10 to about 30  
4 micrometers. It is expected that the sizes of filler agglomerates  
will be reduced during processing of the ingredients to prepare the  
6 microporous material. Accordingly, the distribution of gross  
particle sizes in the microporous material may be smaller than in  
8 the raw siliceous filler itself. ASTM C 690-80 is, in its entirety,  
incorporated herein by reference.

10 Examples of suitable siliceous fillers include silica,  
mica, montmorillonite, kaolinite, asbestos, talc, diatomaceous  
12 earth, vermiculite, natural and synthetic zeolites, cement, calcium  
silicate, aluminum silicate, sodium aluminum silicate, aluminum  
14 polysilicate, alumina silica gels, and glass particles. Silica and  
the clays are the preferred siliceous fillers. Of the silicas,  
16 precipitated silica, silica gel, or fumed silica is most often used.

In addition to the siliceous filler, finely divided  
18 particulate substantially water-insoluble non-siliceous fillers may  
also be employed. Examples of such optional non-siliceous fillers  
20 include carbon black, charcoal, graphite, titanium oxide, iron  
oxide, copper oxide, zinc oxide, antimony oxide, zirconia, magnesia,  
22 alumina, molybdenum disulfide, zinc sulfide, barium sulfate,  
strontium sulfate, calcium carbonate, magnesium carbonate, magnesium  
24 hydroxide, and finely divided particulate substantially  
water-insoluble flame retardant filler such as  
26 ethylenebis(tetrabromophthalimide), octabromodiphenyl oxide,  
decabromodiphenyl oxide, and ethylenebisdibromonorbornane  
28 dicarboximide.

The finely divided substantially water-insoluble  
30 non-siliceous filler used in the present invention is particulate.  
As present in the microporous material, the non-siliceous filler may  
32 be in the form of ultimate particles, aggregates of ultimate  
particles, or a combination of both. In most cases, at least about  
34 75 percent by weight of the non-siliceous filler used in preparing  
the microporous material has gross particle sizes in the ranges of

from about 0.1 to about 40 micrometers as determined by use of a  
2 Micromeritics Sedigraph 5000-D (Micromeritics Instrument Corp.) in  
accordance with the accompanying operating manual. The preferred  
4 ranges vary from filler to filler. For example, it is preferred  
that at least about 75 percent by weight of antimony oxide particles  
6 be in the range of from about 0.1 to about 3 micrometers, whereas it  
is preferred that at least about 75 percent by weight of barium  
8 sulfate particles be in the range of from about 1 to about 25  
micrometers. It is expected that the sizes of filler agglomerates  
10 will be reduced during processing of the ingredients to prepare the  
microporous material. Therefore, the distribution of gross particle  
12 sizes in the microporous material may be smaller than in the raw  
non-siliceous filler itself.

14           The particularly preferred finely divided particulate  
substantially water-insoluble siliceous filler is precipitated  
16 silica. Although both are silicas, it is important to distinguish  
precipitated silica from silica gel inasmuch as these different  
18 materials have different properties. Reference in this regard is  
made to R. K. Iler, The Chemistry of Silica, John Wiley & Sons, New  
20 York (1979), Library of Congress Catalog No. QD 181.S6144, the  
entire disclosure of which is incorporated herein by reference.  
22 Note especially pages 15-29, 172-176, 218-233, 364-365, 462-465,  
554-564, and 578-579. Silica gel is usually produced commercially  
24 at low pH by acidifying an aqueous solution of a soluble metal  
silicate, typically sodium silicate, with acid. The acid employed  
26 is generally a strong mineral acid such as sulfuric acid or  
hydrochloric acid although carbon dioxide is sometimes used.  
28 Inasmuch as there is essentially no difference in density between  
the gel phase and the surrounding liquid phase while the viscosity  
30 is low, the gel phase does not settle out, that is to say, it does  
not precipitate. Silica gel, then, may be described as a  
32 nonprecipitated, coherent, rigid, three-dimensional network of  
contiguous particles of colloidal amorphous silica. The state of  
34 subdivision ranges from large, solid masses to submicroscopic  
particles, and the degree of hydration from almost anhydrous silica



to soft gelatinous masses containing on the the order of 100 parts  
2 of water per part of silica by weight, although the highly hydrated  
forms are only rarely used in the present invention.

4           Precipitated silica is usually produced commercially by  
combining an aqueous solution of a soluble metal silicate,  
6 ordinarily alkali metal silicate such as sodium silicate, and an  
acid so that colloidal particles will grow in weakly alkaline  
8 solution and be coagulated by the alkali metal ions of the resulting  
soluble alkali metal salt. Various acids may be used, including the  
10 mineral acids and carbon dioxide. In the absence of a coagulant,  
silica is not precipitated from solution at any pH. The coagulant  
12 used to effect precipitation may be the soluble alkali metal salt  
produced during formation of the colloidal silica particles, it may  
14 be added electrolyte such as a soluble inorganic or organic salt, or  
it may be a combination of both.

16           Precipitated silica, then, may be described as  
precipitated aggregates of ultimate particles of colloidal amorphous  
18 silica that have not at any point existed as macroscopic gel during  
the preparation. The sizes of the aggregates and the degree of  
20 hydration may vary widely.

Precipitated silica powders differ from silica gels that  
22 have been pulverized in ordinarily having a more open structure,  
that is, a higher specific pore volume. However, the specific  
24 surface area of precipitated silica as measured by the Brunauer,  
Emmet, Teller (BET) method using nitrogen as the adsorbate, is often  
26 lower than that of silica gel.

Many different precipitated silicas may be employed in the  
28 present invention, but the preferred precipitated silicas are those  
obtained by precipitation from an aqueous solution of sodium  
30 silicate using a suitable acid such as sulfuric acid, hydrochloric  
acid, or carbon dioxide. Such precipitated silicas are themselves  
32 known and processes for producing them are described in detail in  
the United States Patent No. 2,940,830 and in United States Patent  
34 No. 4,681,750, the entire disclosures of which are incorporated  
herein by reference, including especially the processes for making

precipitated silicas and the properties of the products.

2           In the case of the preferred filler, precipitated silica,  
the average ultimate particle size (irrespective of whether or not  
4 the ultimate particles are agglomerated) is less than about 0.1  
micrometer as determined by transmission electron microscopy. Often  
6 the average ultimate particle size is less than about 0.05  
micrometer. Preferably the average ultimate particle size of the  
8 precipitated silica is less than about 0.03 micrometer.

The finely divided particulate substantially  
10 water-insoluble filler constitutes from about 50 to 90 percent by  
weight of the microporous material. Frequently such filler  
12 constitutes from about 50 to about 85 percent by weight of the  
microporous material. From about 60 percent to about 80 percent by  
14 weight is preferred.

At least about 50 percent by weight of the finely divided  
16 particulate substantially water-insoluble filler is finely divided  
particulate substantially water-insoluble siliceous filler. In many  
18 cases at least about 65 percent by weight of the finely divided  
particulate substantially water-insoluble filler is siliceous.  
20 Often at least about 75 percent by weight of the finely divided  
particulate substantially water-insoluble filler is siliceous.  
22 Frequently at least about 85 percent by weight of the finely divided  
particulate water-insoluble filler is siliceous. In many instances  
24 all of the finely divided particulate water-insoluble filler is  
siliceous.

26           Minor amounts, usually less than about 5 percent by  
weight, of other materials used in processing such as lubricant,  
28 processing plasticizer, organic extraction liquid, surfactant,  
water, and the like, may optionally also be present. Yet other  
30 materials introduced for particular purposes may optionally be  
present in the microporous material in small amounts, usually less  
32 than about 15 percent by weight. Examples of such materials include  
antioxidants, ultraviolet light absorbers, reinforcing fibers such  
34 as chopped glass fiber strand, dyes, pigments, and the like. The  
balance of the microporous material, exclusive of filler and any

impregnant applied for one or more special purposes is essentially  
2 the thermoplastic organic polymer.

On an impregnant-free basis, pores constitute at least  
4 about 35 percent by volume of the microporous material. In many  
instances the pores constitute at least about 60 percent by volume  
6 of the microporous material. Often the pores constitute from at  
least about 35 percent to about 95 percent by volume of the  
8 microporous material. From about 60 percent to about 75 percent by  
volume is preferred. As used herein and in the claims, the porosity  
10 (also known as void volume) of the microporous material, expressed  
as percent by volume, is determined according to the equation:

$$12 \quad \text{Porosity} = 100[1 - d_1/d_2]$$

where  $d_1$  is the density of the sample which is determined from the  
14 sample weight and the sample volume as ascertained from measurements  
of the sample dimensions and  $d_2$  is the density of the solid portion  
16 of the sample which is determined from the sample weight and the  
volume of the solid portion of the sample. The volume of the solid  
18 portion of the same is determined using a Quantachrome  
stereopycnometer (Quantachrome Corp.) in accordance with the  
20 accompanying operating manual.

The volume average diameter of the pores of the  
22 microporous material is determined by mercury porosimetry using an  
Autoscan mercury porosimeter (Quantachrome Corp.) in accordance with  
24 the accompanying operating manual. The volume average pore radius  
for a single scan is automatically determined by the porosimeter.  
26 In operating the porosimeter, a scan is made in the high pressure  
range (from about 138 kilopascals absolute to about 227 megapascals  
28 absolute). If about 2 percent or less of the total intruded volume  
occurs at the low end (from about 138 to about 250 kilopascals  
30 absolute) of the high pressure range, the volume average pore  
diameter is taken as twice the volume average pore radius determined  
32 by the porosimeter. Otherwise, an additional scan is made in the  
low pressure range (from about 7 to about 165 kilopascals absolute)  
34 and the volume average pore diameter is calculated according to the  
equation:

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$$d = 2 \left( \frac{v_1 r_1}{w_1} + \frac{v_2 r_2}{w_2} \right)$$

where  $d$  is the volume average pore diameter,  $v_1$  is the total volume of mercury intruded in the high pressure range,  $v_2$  is the total volume of mercury intruded in the low pressure range,  $r_1$  is the volume average pore radius determined from the high pressure scan,  $r_2$  is the volume average pore radius determined from the low pressure scan,  $w_1$  is the weight of the sample subjected to the high pressure scan, and  $w_2$  is the weight of the sample subjected to the low pressure scan. Generally the volume average diameter of the pores is in the range of from about 0.02 to about 50 micrometers. Very often the volume average diameter of the pores is in the range of from about 0.04 to about 40 micrometers. From about 0.05 to about 30 micrometers is preferred.

In the course of determining the volume average pore diameter of the above procedure, the maximum pore radius detected is sometimes noted. This is taken from the low pressure range scan if run; otherwise it is taken from the high pressure range scan. The maximum pore diameter is twice the maximum pore radius.

Microporous material may be produced according to the general principles and procedures of United States Patent No. 3,351,495, the entire disclosure of which is incorporated herein by reference, including especially the processes for making microporous materials and the properties of the products.

Preferably filler, thermoplastic organic polymer powder, processing plasticizer and minor amounts of lubricant and antioxidant are mixed until a substantially uniform mixture is obtained. The weight ratio of filler to polymer powder employed in forming the mixture is essentially the same as that of the microporous material to be produced. The mixture, together with additional processing plasticizer, is introduced to the heated barrel of a screw extruder. Attached to the extruder is a sheeting die. A continuous sheet formed by the die is forwarded without

drawing to a pair of heated calender rolls acting cooperatively to  
2 form continuous sheet of lesser thickness than the continuous sheet  
exiting from the die. The continuous sheet from the calender then  
4 passes to a first extraction zone where the processing plasticizer  
is substantially removed by extraction with an organic liquid which  
6 is a good solvent for the processing plasticizer, a poor solvent for  
the organic polymer, and more volatile than the processing  
8 plasticizer. Usually, but not necessarily, both the processing  
plasticizer and the organic extraction liquid are substantially  
10 immiscible with water. The continuous sheet then passes to a second  
extraction zone where the residual organic extraction liquid is  
12 substantially removed by steam and/or water. The continuous sheet  
is then passed through a forced air dryer for substantial removal of  
14 residual water and remaining residual organic extraction liquid.

From the dryer the continuous sheet, which is microporous material,  
16 is passed to a take-up roll.

The processing plasticizer has little solvating effect on  
18 the thermoplastic organic polymer at 60°C, only a moderate solvating  
effect at elevated temperatures on the order of about 100°C, and a  
20 significant solvating effect at elevated temperatures on the order  
of about 200°C. It is a liquid at room temperature and usually it  
22 is processing oil such as paraffinic oil, naphthenic oil, or  
aromatic oil. Suitable processing oils include those meeting the  
24 requirements of ASTM D 2226-82, Types 103 and 104. Preferred are  
those oils which have a pour point of less than 22°C according to  
26 ASTM D 97-66 (reapproved 1978). Particularly preferred are oils  
having a pour point of less than 10°C. Examples of suitable oils  
28 include Shellflex® 412 and Shellflex® 371 oil (Shell Oil Co.) which  
are solvent refined and hydrotreated oils derived from naphthenic  
30 crude. ASTM D 2226-82 and ASTM D 97-66 (reapproved 1978) are, in  
the entireties, incorporated herein by reference. It is expected  
32 that other materials, including the phthalate ester plasticizers  
such as dibutyl phthalate, bis(2-ethylhexyl) phthalate, diisodecyl  
34 phthalate, dicyclohexyl phthalate, butyl benzyl phthalate, and  
ditridecyl phthalate will function satisfactorily as processing  
36 plasticizers.

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There are many organic extraction liquids that can be used. Examples of suitable organic extraction liquids include 1,1,2-trichloroethylene, perchloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, methylene chloride, chloroform, 1,1,2-trichloro-1,2,2-trifluoroethane, isopropyl alcohol, diethyl ether and acetone.

In the above described process for producing microporous material, extrusion and calendaring are facilitated when the substantially water-insoluble filler carries much of the processing plasticizer. The capacity of the filler particles to absorb and hold the processing plasticizer is a function of the surface area of the filler. It is therefore preferred that the filler have a high surface area. High surface area fillers are materials of very small particle size, materials having a high degree of porosity or materials exhibiting both characteristics. Usually the surface area of at least the siliceous filler is in the range of from about 20 to about 400 square meters per gram as determined by the Brunauer, Emmett, Teller (BET) method according to ASTM C 819-77 using nitrogen as the adsorbate but modified by outgassing the system and the sample for one hour at 130°C. Preferably the surface area is in the range of from about 25 to 350 square meters per gram. ASTM C 819-77 is, in its entirety, incorporated herein by reference.

Preferably, but not necessarily, the surface area of any non-siliceous filler used is also in at least one of these ranges.

Inasmuch as it is desirable to essentially retain the filler in the microporous material, it is preferred that the substantially water-insoluble filler be substantially insoluble in the processing plasticizer and substantially insoluble in the organic extraction liquid when microporous material is produced by the above process.

The residual processing plasticizer content is usually less than 5 percent by weight of the microporous sheet and this may be reduced even further by additional extractions using the same or a different organic extraction liquid.

Pores constitute from about 35 to about 80 percent by  
2 volume of the microporous material when made by the above-described  
process. In many cases the pores constitute from about 60 to about  
4 75 percent by volume of the microporous material.

The volume average diameter of the pores of the  
6 microporous material when made by the above-described process, is  
usually in the range of from about 0.02 to about 0.5 micrometers.  
8 Frequently the average diameter of the pores is in the range of from  
about 0.04 to about 0.3 micrometers. From about 0.05 to about 0.25  
10 micrometers is preferred.

The microporous material produced by the above-described  
12 process may be used for producing multilayer articles of the present  
invention. However, it may optionally be stretched and the  
14 stretched microporous material used for producing such multilayer  
articles. When such stretching is employed, the product of the  
16 above-described process may be regarded as an intermediate product.

It will be appreciated that the stretching both increases  
18 the void volume of the material and induces regions of molecular  
orientation in the ultrahigh molecular weight (UHMW) polyolefin. As  
20 is well known in the art, many of the physical properties of  
molecularly oriented thermoplastic organic polymer, including  
22 tensile strength, tensile modulus, Young's modulus, and others,  
differ considerably from those of the corresponding thermoplastic  
24 organic polymer having little or no molecular orientation. Although  
it is not desired to be bound by any theory, it is believed that the  
26 properties of the UHMW polyolefin, the regions of molecular  
orientation, the high levels of filler loading, and the high degrees  
28 of porosity cooperate to provide many of the desirable properties  
characteristic of the stretched microporous material used in the  
30 present invention.

Stretched microporous material may be produced by  
32 stretching the intermediate product in at least one stretching  
direction above the elastic limit. Usually the stretch ratio is at  
34 least about 1.5. In many cases the stretch ratio is at least about

1.7. Preferably it is at least about 2. Frequently the stretch ratio is in the range of from about 1.5 to about 15. Often the stretch ratio is in the range of from about 1.7 to about 10.  
4 Preferably the stretch ratio is in the range of from about 2 to about 6. As used herein, the stretch ratio is determined by the  
6 formula:

$$S = L_2/L_1$$

8 where S is the stretch ratio,  $L_1$  is the distance between two reference points located on the intermediate product and on a line  
10 parallel to the stretching direction, and  $L_2$  is the distance between the same two reference points located on the stretched microporous  
12 material.

The temperatures at which stretching is accomplished may  
14 vary widely. Stretching may be accomplished at about ambient room temperature, but usually elevated temperatures are employed. The  
16 intermediate product may be heated by any of a wide variety of techniques prior to, during, and/or after stretching. Examples of  
18 these techniques include radiative heating such as that provided by electrically heated or gas fired infrared heaters, convective  
20 heating such as that provided by recirculating hot air, and conductive heating such as that provided by contact with heated  
22 rolls. The temperatures which are measured for temperature control purposes may vary according to the apparatus used and personal  
24 preference. For example, temperature-measuring devices may be placed to ascertain the temperatures of the surfaces of infrared  
26 heaters, the interiors of infrared heaters, the air temperatures of points between the infrared heaters and the intermediate product,  
28 the temperatures of circulating hot air at points within the apparatus, the temperature of hot air entering or leaving the  
30 apparatus, the temperatures of the surfaces of rolls used in the stretching process, the temperature of heat transfer fluid entering  
32 or leaving such rolls, or film surface temperatures. In general, the temperature or temperatures are controlled such that the  
34 intermediate product is stretched about evenly so that the variations, if any, in film thickness of the stretched microporous



material are within acceptable limits and so that the amount of  
2 stretched microporous material outside of those limits is acceptably  
low. It will be apparent that the temperatures used for control  
4 purposes may or may not be close to those of the intermediate  
product itself since they depend upon the nature of the apparatus  
6 used, the locations of the temperature-measuring devices, and the  
identities of the substances or objects whose temperatures are being  
8 measured.

In view of the locations of the heating devices and the  
10 line speeds usually employed during stretching, gradients of varying  
temperatures may or may not be present through the thickness of the  
12 intermediate product. Also because of such line speeds, it is  
impracticable to measure these temperature gradients. The presence  
14 of gradients of varying temperatures, when they occur, makes it  
unreasonable to refer to a single film temperature. Accordingly,  
16 film surface temperatures, which can be measured, are best used for  
characterizing the thermal condition of the intermediate product.  
18 These are ordinarily about the same across the width of the  
intermediate product during stretching although they may be  
20 intentionally varied, as for example, to compensate for intermediate  
product having a wedge-shaped cross-section across the sheet. Film  
22 surface temperatures along the length of the sheet may be about the  
same or they may be different during stretching.

24 The film surface temperatures at which stretching is  
accomplished may vary widely, but in general they are such that the  
26 intermediate product is stretched about evenly, as explained above.  
In most cases, the film surface temperatures during stretching are  
28 in the range of from about 20°C to about 220°C. Often such  
temperatures are in the range of from about 50°C to about 200°C.  
30 From about 75°C to about 180°C is preferred.

Stretching may be accomplished in a single step or a  
32 plurality of steps as desired. For example, when the intermediate  
product is to be stretched in a single direction (uniaxial  
34 stretching), the stretching may be accomplished by a single  
stretching step or a sequence of stretching steps until the desired

final stretch ratio is attained. Similarly, when the intermediate product is to be stretched in two directions (biaxial stretching), the stretching can be conducted by a single biaxial stretching step or a sequence of biaxial stretching steps until the desired final stretch ratios are attained. Biaxial stretching may also be accomplished by a sequence of one or more uniaxial stretching steps in one direction and one or more uniaxial stretching steps in another direction. Biaxial stretching steps where the intermediate product is stretched simultaneously in two directions and uniaxial stretching steps may be conducted in sequence in any order.

Stretching in more than two directions is within contemplation. It may be seen that the various permutations of steps are quite numerous. Other steps, such as cooling, heating, sintering, annealing, reeling, unreeling, and the like, may optionally be included in the overall process as desired.

Various types of stretching apparatus are well known and may be used to accomplish stretching of the intermediate product. Uniaxial stretching is usually accomplished by stretching between two rollers wherein the second or downstream roller rotates at a greater peripheral speed than the first or upstream roller.

Uniaxial stretching can also be accomplished on a standard tentering machine. Biaxial stretching may be accomplished by simultaneously stretching in two different directions on a tentering machine. More commonly, however, biaxial stretching is accomplished by first uniaxially stretching between two differentially rotating rollers as described above, followed by either uniaxially stretching in a different direction using a tenter machine or by biaxially stretching using a tenter machine. The most common type of biaxial stretching is where the two stretching directions are approximately at right angles to each other. In most cases where continuous sheet is being stretched, one stretching direction is at least approximately parallel to the long axis of the sheet (machine direction) and the other stretching direction is at least approximately perpendicular to the machine direction and is in the plane of the sheet (transverse direction).

After stretching has been accomplished, the microporous material may optionally be sintered, annealed, heat set, and/or otherwise heat treated. During these optional steps, the stretched microporous material is usually held under tension so that it will not markedly shrink at the elevated temperatures employed, although some relaxation amounting to a small fraction of the maximum stretch ratio is frequently permitted.

Following stretching and any heat treatments employed, tension is released from the stretched microporous material after the microporous material has been brought to a temperature at which, except for a small amount of elastic recovery amounting to a small fraction of the stretch ratio, it is essentially dimensionally stable in the absence of tension. Elastic recovery under these conditions usually does not amount to more than about 10 percent of the stretch ratio.

The stretched microporous material may then be further processed as desired. Examples of such further processing steps include reeling, cutting, stacking, treatment to remove residual processing plasticizer or extraction solvent, impregnation with various materials, and fabrication into shapes for various end uses.

Stretching is preferably accomplished after substantial removal of the processing plasticizer as described above. For purposes of this invention, however, the calendered sheet may be stretched in at least one stretching direction followed by substantial removal of the processing plasticizer by extraction and substantial removal of the residual organic extraction liquid. It will be appreciated that as stretching may be accomplished in a single step or a plurality of steps, so likewise extraction of the processing plasticizer may be accomplished in a single step or a plurality of steps and removal of the residual organic extraction liquid may be accomplished in a single step or a plurality of steps. The various combinations of the steps stretching, partial stretching, processing plasticizer extraction, partial plasticizer extraction, removal of organic extraction liquid, and partial removal of organic extraction liquid are very numerous, and may be

accomplished in any order, provided of course, that a step of  
2 processing plasticizer extraction (partial or substantially  
complete) precedes the first step of residual organic extraction  
4 liquid removal (partial or substantially complete). It is expected  
that varying the orders and numbers of these steps will produce  
6 variations in at least some of the physical properties of the  
stretched microporous product.

8 In all cases, the porosity of the stretched microporous  
material is, unless impregnated after stretching, greater than that  
10 of the intermediate product. On an impregnant-free basis, pores  
usually constitute more than 80 percent by volume of the stretched  
12 microporous material. In many instances the pores constitute at  
least about 85 percent by volume of the stretched microporous  
14 material. Often the pores constitute from more than 80 percent to  
about 95 percent by volume of the stretched microporous material.  
16 From about 85 percent to about 95 percent by volume is preferred.

Generally the volume average diameter of the pores of the  
18 stretched microporous material is in the range of from 0.6 to about  
50 micrometers. Very often the volume average diameter of the pores  
20 is in the range of from about 1 to about 40 micrometers. From about  
2 to about 30 micrometers is preferred.

22 The microporous material, whether or not stretched, may be  
printed with a wide variety of printing inks using a wide variety of  
24 printing processes. Both the printing inks and the printing  
processes are themselves conventional. Printing may be accomplished  
26 before assembly of the microporous material into multilayer articles  
of the present invention or after assembly of such multilayer  
28 articles.

There are many advantages in using the microporous  
30 material described herein as a printing substrate.

One such advantage is that the substrate need not be  
32 pretreated with any of the pretreatments customarily used to improve  
adhesion between the printing ink and polyolefin substrate such as  
34 flame treatment, chlorination, or especially corona discharge

treatment which is most commonly employed. This is surprising  
2 inasmuch as untreated polyolefins such as polyethylene and  
polypropylene cannot ordinarily be successfully printed because of a  
4 lack of adhesion between the polyolefin printing ink and the  
polyolefin substrate. The microporous material substrates used in  
6 the present invention may be pretreated to further improve  
ink-substrate adhesion, but commercially satisfactory results can  
8 ordinarily be attained without employing such methods.

Another advantage is that the microporous material  
10 substrates accept a wide variety of printing inks, including most  
organic solvent-based inks which are incompatible with water,  
12 organic solvent-based inks which are compatible with water, and  
water-based inks.

14 Yet another advantage is very rapid drying of most inks to  
the tack-free state upon printing the microporous material  
16 substrates. This advantage is quite important in high speed press  
runs, in multicolor printing, and in reducing or even eliminating  
18 blocking of stacks or coils of the printed substrate.

A further advantage is the sharpness of the printed image  
20 that can be attained. This is especially important in graphic arts  
applications where fine lines, detailed drawings, or halftone images  
22 are to be printed. Halftone images printed on the microporous  
material substrates ordinarily exhibit high degrees of dot  
24 resolution.

Ink jet printing, especially when a water-based ink jet  
26 printing ink is used, is particularly suitable for printing bar  
codes on microporous material substrates. The resulting bars are  
28 sharp and of high resolution, which are important factors in  
reducing errors when the codes are read by conventional methods and  
30 equipment. The ink dries very rapidly when applied, thereby  
minimizing loss of bar resolution due to smearing in subsequent  
32 handling operations.

Microporous material substrate, after being printed with  
34 water-based printing ink, has been washed and dried using a  
conventional household washer and a conventional household drier.

It was observed upon completion of the washing and drying operations  
2 that the printed colors held fast with no significant fading.

Printing processes, printing equipment, and printing inks  
4 have been extensively discussed and documented. Examples of  
reference works that may be consulted include L. M. Larsen,  
6 Industrial Printing Ink, Reinhold Publishing Corp., (1962);  
Kirk-Othmer, Encyclopedia of Chemical Technology, 2d Ed., John Wiley  
8 & Sons, Inc., Vol. 11, pages 611-632 (1966) and Vol. 16, pages  
494-546 (1968); and R. N. Blair, The Lithographers Manual, The  
10 Graphic Arts Technical Foundation, Inc., 7th Ed. (1983).

For a more detailed description of printing on microporous  
12 material of the kind frequently employed in the present invention,  
see Application Serial No. 238,684, filed August 30, 1988, which is  
14 a continuation-in-part of Application Serial No. 42,404, filed April  
24, 1987, the entire disclosures of which are incorporated herein by  
16 reference.

The microporous material is fusion bonded to at least one  
18 layer of substantially nonporous material in the absence of  
extrinsic intervening adhesive. Substantially nonporous materials  
20 are those which are generally impervious to the passage of liquids,  
gases, and bacteria. On a macroscopic scale, substantially  
22 nonporous materials exhibit few if any pores, viz., minute openings  
through which matter passes. These materials include those  
24 customarily recognized and employed for their barrier properties.  
Examples of suitable materials include substantially nonporous  
26 thermoplastic polymeric sheet or film, substantially nonporous  
metalized thermoplastic polymeric sheet or film, substantially  
28 nonporous thermoset polymeric sheet or film, substantially nonporous  
elastomeric sheet or film, and substantially nonporous metal sheet  
30 or foil. Although the substantially nonporous material is most  
often in the form of sheet, film, or foil, other shapes may be used  
32 when desired, such as for example, plates, bars, rods, tubes, and  
forms of more complex shape. Examples of thermoplastic polymeric  
34 materials which are suitable for use include high density  
polyethylene, low density polyethylene, polypropylene, poly(vinyl

chloride), saran, polystyrene, high impact polystyrene, the nylons,  
2 the polyesters such as poly(ethylene terephthalate), copolymers of  
ethylene and acrylic acid, and copolymers of ethylene and  
4 methacrylic acid. If desired, all or a portion of the carboxyl  
groups of carboxyl-containing copolymers may be neutralized with  
6 sodium, zinc, or the like. Examples of substantially nonporous  
thermoplastic sheets or films include extruded substantially  
8 nonporous thermoplastic sheet or film, coextruded substantially  
nonporous thermoplastic sheets or films of differing thermoplastic  
10 polymers, and substantially nonporous sheets or films coated with  
one or more differing thermoplastic polymers, and substantially  
12 nonporous thermoplastic sheets or films laminated to other  
thermoplastic sheets or films. An example of a metalized  
14 thermoplastic polymeric material is aluminized poly(ethylene  
terephthalate). Examples of thermoset polymeric materials include  
16 thermoset phenol-formaldehyde resin and thermoset  
melamine-formaldehyde resin. Examples of elastomeric materials  
18 include natural rubber, neoprene, styrene-butadiene rubber,  
acrylonitrile-butadiene-styrene rubber, elastomeric polyurethanes,  
20 and elastomeric copolymers of ethylene and propylene. Examples of  
metals include iron, steel, copper, brass, bronze, chromium, zinc,  
22 die metal, aluminum, nickel, and cadmium. Most often the metals  
employed are alloys.

24           The multilayer article of the present invention may be  
constructed by fusion bonding at least one layer of microporous  
26 material to at least one layer of substantially nonporous material  
in the absence of extrinsic intervening adhesive. The microporous  
28 material usually has, on a macroscopic scale, generally opposed  
major surfaces such as are characteristic of sheets, films, foils,  
30 and plates. The multilayer article may comprise one layer or more  
than one layer of microporous material and one layer or more than  
32 one layer of the substantially nonporous material in the absence of  
extrinsic intervening adhesive. Most often, but not always, at  
34 least one exterior layer is microporous material.

Fusion bonding may be made by conventional techniques such

as for example sealing through use of heated rollers, heated bars,  
2 heated plates, heated bands, heated wires, flame bonding, radio  
frequency (RF) sealing, and ultrasonic sealing. Heat sealing is  
4 preferred. Solvent bonding may be used where the substantially  
nonporous material is soluble in the applied solvent at least to the  
6 extent that the surface becomes tacky. After the microporous  
material has been brought into contact with the tacky surface, the  
8 solvent is removed to form the fusion bond. Foamable compositions  
may be foamed in contact with the microporous material to form a  
10 fusion bond between the resulting closed cell foam and the  
microporous material. Films or sheets of thermoplastic may be  
12 extruded and while still hot and tacky, brought into contact with  
the microporous material to form a fusion bond.

14           The fusion bond may be permanent or peelable, depending  
upon the bonding technique and/or the nature of the substantially  
16 nonporous material employed.

The microporous material may be substantially continuously  
18 fusion bonded to the substantially nonporous material, as is usually  
preferred; or it may be discontinuously fusion bonded to the  
20 substantially nonporous material. Examples of discontinuous bonds  
include bonding areas in the form of one or more spots, patches,  
22 strips, stripes, chevrons, undulating stripes, zigzag stripes,  
open-curved stripes, closed-curved stripes, irregular areas, and the  
24 like. When patterns of bonds are involved, they may be random,  
repetitive, or a combination of both.

26           The microporous material employed in the present invention  
is particularly useful for fusion bonding to polyolefins such as  
28 polyethylene and polypropylene by heat sealing in the absence of  
extrinsic intervening adhesive. The fusion bond obtained is  
30 ordinarily quite strong which is surprising inasmuch as the  
lamination of materials to polyolefins is usually difficult unless  
32 special adhesives are used. This property of the microporous  
material used in the present invention makes it especially useful  
34 for the in-mold labeling of polyolefin containers and other items  
manufactured by the blow molding process. In this procedure, labels



(usually preprinted) are placed against the sides of the opened  
2 mold, the mold is closed, the polyolefin parison is blown to form  
the labeled container, the mold is opened, and the labeled container  
4 is ejected. Similar in-mold labeling techniques may be used with  
the bag molding, compression molding, and injection molding of  
6 polyolefins. While polyethylene (usually low density polyethylene)  
is most often used in in-mold labeling procedures, the process is  
8 applicable to a wide variety of other thermoplastic polymers as well.

The multilayer articles of the present invention have many  
10 and varied uses including gaskets, cushion assemblies, signs,  
printing substrates, substrates for pen and ink drawings, maps  
12 (particularly maritime maps), book covers, book pages, wall  
coverings, and seams, joints, and seals of breathable packages.

14 The invention is further described in conjunction with the  
following examples which are to be considered illustrative rather  
16 than limiting.

18

#### EXAMPLES

20

##### Microporous Material Formation

22 The preparation of the above described materials is  
illustrated by the following descriptive examples. Processing oil  
24 was used as the processing plasticizer. Silica, polymer, lubricant,  
and antioxidant in the amounts specified in Table I were placed in a  
26 high intensity mixer and mixed at high speed for 30 seconds to  
thoroughly blend the dry ingredients. The processing oil needed to  
28 formulate the batch was pumped into the mixer over a period of 2-3  
minutes with low speed agitation. After the completion of the  
30 processing oil addition a 2 minute low speed mix period was used to  
distribute the processing oil uniformly throughout the mixture.

Table I  
Formulations

Example No.	1	2	3	4	5	6	7	8	9	10
<u>Ingredient</u>										
UHMWPE										
(1), kg	5.67	9.98	4.25	8.57	6.12	9.98	3.49	5.73	11.84	4.54
Polypropylene										
(2), kg	0	0	1.42	0	0	0	0	0	0	0
Polyethylene										
(3), kg	0	0	0	0	0	0	0	0	0	4.54
Precipitated										
Silica (4),kg	19.96	19.96	19.96	19.96	13.02	9.98	19.96	20.17	20.87	19.96
Silica Gel, kg	0	0	0	0	6.49	0	0	0	0	0
Clay, kg	0	0	0	9.98	0	0	0	0	0	0
Lubricant (5), g	100	100	100	100	100	50	100	100	100	100
Antioxidant (6), g	100	100	100	100	100	50	100	100	100	100
Processing Oil										
(7), kg	31.21	31.21	31.21	37.58	33.44	16.89	31.72	31.29	34.13	31.11
in Batch	13.61	41.59	30.39	28.60	~ 14	18.72	13.61	~ 10.96	~ 51.93	~ 16.61
at Extruder										

- (1) UHMWPE = Ultrahigh Molecular Weight Polyethylene, Himont 1900, Himont, U.S.A., Inc.
- (2) Profax® 6801, Himont U.S.A., Inc.
- (3) Alathon L-5005, high density, E.I. du Pont de Nemours & Co., Inc.
- (4) HiSil® SBG, PPG Industries, Inc.
- (5) Petrac® CZ81, Desoto, Inc., Chemical Speciality Division
- (6) Irganox® B-215, Ciba-Geigy Corp.
- (7) Shellflex® 412, Shell Chemical Co.

The batch was then conveyed to a ribbon blender where usually it was mixed with up to two additional batches of the same composition. Material was fed from the ribbon blender to a twin screw extruder by a variable rate screw feeder. Additional processing oil was added via a metering pump into the feed throat of the extruder. The extruder mixed and melted the formulation and extruded it through a 76.2 centimeter x 0.3175 centimeter slot die. The extruded sheet was then calendered. A description of one type of calender that may be used may be found in the United States Patent No. 4,734,229, the entire disclosure of which is incorporated herein by reference, including the structures of the devices and their modes of operation. Other calenders of different design may alternatively be used; such calenders and their modes of operation are well known to the art. The hot, calendered sheet was then passed around a chill roll to cool the sheet. The rough edges of the cooled calendered sheet were trimmed by rotary knives to the desired width.

The oil filled sheet was conveyed to the extractor unit where it was contacted by both liquid and vaporized 1,1,2-trichloroethylene (TCE). The sheet was transported over a series of rollers in a serpentine fashion to provide multiple, sequential vapor/liquid/vapor contacts. The extraction liquid in the sump was maintained at a temperature of 65-88°C. Overflow from the sump of the TCE extractor was returned to a still which recovered the TCE and the processing oil for reuse in the process. The bulk of the TCE was extracted from the sheet by steam as the sheet was passed through a second extractor unit. A description of these types of extractors may be found in United States Patent No. 4,648,417, the entire disclosure of which is incorporated herein by reference, including especially the structures of the devices and their modes of operation. The sheet was dried by radiant heat and convective air flow. The dried sheet was wound on cores to provide roll stock for further processing.

The microporous sheets, as well as the hereinafter described biaxially stretched microporous sheets produced therefrom,

were tested for various physical properties. Table II identifies 2 the properties with the methods used for their determination. The various ASTM test methods and Method 502 C, referenced in Table II, 4 are, in their entireties, incorporated herein by reference. The results of physical testing of the unstretched microporous sheets 6 are shown in Table III.

Property values indicated by MD (machine direction) were 8 obtained on samples whose major axis was oriented along the length of the sheet. TD (transverse direction; cross machine direction) 10 properties were obtained from samples whose major axis was oriented across the sheet.

12

14

Table II

16

Physical Test Methods

18

Property	Test Method
20 Tensile Strength and Elongation	ASTM D 412-83.
22 Porosity	As described in the text above.
24 Matrix Tensile Strength	Tensile Strength determined in accordance with ASTM D 412-83 multiplied by the quantity 100/(100-Porosity).
28 Tear Strength, Die C	ASTM D 624-81.
32 Processing Oil Content	Method 502 C in "Standard Methods for the Examination of Water and Wastewater", 14th Ed., APHA-AWWA-WPCF (1975).
36 Maximum Pore Diameter	Mercury Porosimetry, as described in the text above.
40 Volume Average Pore Diameter	Mercury Porosimetry, as described in the text above.
42 Gurley Air Flow	ASTM D 726-58(reapproved 1971),Method A.
44	

Table II (Continued)

<u>Physical Test Methods</u>	
<u>Property</u>	<u>Test Method</u>
2	
4	
6	
8	
10	
12	
14	
16	
18	
20	
22	
24	
Mullens Hydrostatic Resistance	ASTM D 751-79, Sec. 30-34, Method A.
MVTR (Moisture Vapor Transmission Rate)	ASTM E 96-80.
Methanol Bubble Pressure	ASTM F 316-80, using methanol.
Maximum Limiting Pore Diameter	ASTM F316-80, using methanol where $c\gamma = 22.34 (\mu\text{m})(\text{kPa})$ .
Heat Shrinkage	ASTM D 1204-84, using 15.24 cm x 20.32 cm sample, 1 hr at 100°C.
Strip Tensile Strength and Elongation	ASTM D 828-60.
Breaking Factor and Elongation	ASTM D 882-83.

Table III  
Physical Properties of Microporous Sheet

Example No.	1	2	3	4	5	6	7	8	9	10
Thickness, mm	0.229	0.279	0.229	0.381	0.483	0.254	0.229	0.356	0.305	0.305
Matrix Tensile Strength, MPa										
MD	23.82	34.33	25.66	27.79	29.21	70.47	20.35	31.90	51.37	16.98
TD	9.94	14.91	10.38	19.05	15.55	26.39	5.97	15.82	21.25	9.85
Elongation at break, %										
MD	250	279	227			14	110	264		371
TD	108	140	112	546	470	482	214	466		99
Tear Strength, kN/m										
MD	36.25	61.47	47.81	56.39	57.09	93.34	24.52	53.06	87.04	82.66
TD	18.04	39.93	23.12	39.75	32.22	89.66	7.36	32.57	56.39	44.83
Porosity, vol %	71	66	68	57.9	59.3	58.9	77	66	66.9	62.0
Processing Oil Content, wt%	4.1	2.7	2.4				2.7	2.4		3.1
Maximum Pore Diameter, $\mu\text{m}$	0.86	0.30	0.28	1.34	6.11	0.16				
Volume Average Pore Diameter, $\mu\text{m}$	0.11	0.065	0.069	0.099	0.111	0.12				
Gurley Air Flow, sec/100cc	904	1711	955			4098	422	1757	1792	1447

Biaxial Stretching of Microporous Sheet

2           Portions of the microporous materials produced in Examples  
3 1-3 were unwound from cores and biaxially stretched by first  
4 uniaxially stretching in the machine direction using a single stage  
5 roll-to-roll machine direction stretching (MDS) unit and then  
6 essentially uniaxially stretching in the transverse direction using  
7 a moving clip tenter frame as a transverse direction stretching  
8 (TDS) unit. A preheat roll was employed with the MDS unit to heat  
9 the sheet prior to stretching. In the TDS unit, the sheet was  
10 heated by banks of infrared radiant heaters. The Preheat and  
11 Stretch I Zones of the TDS Unit each contained both upper and lower  
12 banks of such heaters. The upper banks were located about 10.16  
13 centimeters above the precursor microporous material while the lower  
14 banks were located about 15.24 centimeters below the intermediate  
15 product. Electrical power to the heaters of each lower bank was  
16 controlled by an on-off controller in response to the difference  
17 between a set point and the signal provided by a thermocouple  
18 mounted in one heater of the bank. Autotransformers were used to  
19 adjust electrical power to the heaters of the upper banks. The  
20 Stretch II, Stretch III, Sinter I, and Sinter II Zones each  
21 contained upper banks of infrared radiant heaters located about  
22 10.16 centimeters above the intermediate product. There were no  
23 lower banks in these zones. Electrical power to the heaters of each  
24 upper bank was controlled as described in respect of the heaters of  
25 each lower bank in the Preheat and Stretch I Zones. For a  
26 description of a typical TDS unit, see Figure 2 and column 2, lines  
27 43-69, of United States Patent No. 2,823,421, the entire disclosure  
28 of which is incorporated herein by reference.

29           The MDS stretch ratio was varied by controlling the  
30 relative peripheral speeds of the feed rolls and the takeoff rolls  
31 of the MDS unit. The chain track positions in the tenter frame were  
32 set to achieve the desired stretch ratio and then to essentially  
33 maintain that stretch ratio during sintering. For each of the  
34 Examples 11-32, the settings of one of the last four vertical  
columns in Table IV were employed. The correct column may be

ascertained by matching up the TD stretch ratio of the example with 2 the final stretch ratio of the column.

4

Table IV

Transverse Direction Stretching

6

8 Zone Cumulative Distance from Beginning of Oven, meters Approximate Transverse Stretch Ratio

10	0	1	1	1	1
Preheat					
12	2.794	1	1	1	1
Stretch I					
14	4.318	1.33	1.44	1.65	1.87
Stretch II					
16	8.890	2.31	2.75	3.62	4.49
Stretch III					
18	9.779	2.5	3	4	5
Sinter I					
20	11.430	2.5	3	4	5
Sinter II					
22	13.716	2.5	3	4	5
24	_____				

26

The microporous sheet stock of Examples 1-3 was fed over 28 the preheat roll of the MDS unit which was heated to the temperature indicated in Tables V-VII. The sheet was then stretched to the 30 indicated stretch ratio by maintaining the relative peripheral speeds of the second and first stretch rolls at essentially the same 32 ratio as the stretch ratio. The line speed given in Tables V-VII is the output speed of the MDS unit and the machine direction speed of 34 the TDS unit. The linear feed rate from the roll stock of microporous material to the MDS unit was set at a value given by the



line speed divided by the MDS stretch ratio. Thus, with a line speed of 24 m/min and a MDS stretch ratio of 2, the linear feed rate from the roll stock of the MDS unit would be 12 m/min. The properties of several representative examples of biaxially stretched sheets are given in Tables V-VII.

Table V  
Properties of Biaxially Stretched Microporous Sheets  
Produced from Microporous Sheet of Example 1

Example No.	11	12	13	14	15	16	17	18	19
Thickness, mm	0.178	0.152	0.127	0.076	0.076	0.102	0.127	0.102	0.076
Stretch Ratio									
MD	2	2	2	2	3	3	3	3	3
TD	3	3	3	4	5	3	3	3	3
4									
Line Speed m/min	48.8	24.4	24.4	24.4	24.4	24.4	24.4	24.4	24.4
MDS Preheat Temp., °C	79	79	79	79	79	79	79	79	79
TDS Average Zonal Set Point Temps., °C Preheat (lower banks)	149	177	177	149	149	149	177	149	177
Stretch I (lower banks)	149	177	177	149	149	149	177	149	177
Stretch II	189	171	171	189	189	189	171	189	171
Stretch III	149	142	142	149	149	149	142	149	142
Sinter I	149	144	144	149	149	149	144	149	144
Sinter II	204	227	227	204	149	204	227	260	227
Weight, g/m <sup>2</sup>	27	24	17	14	14	10	14	14	10
Porosity, vol%	91	90	92	90	89	93	93	93	91

Table V (continued)  
Properties of Biaxially Stretched Microporous Sheets  
Produced from Microporous Sheet of Example 1

Example No.	11	12	13	14	15	16	17	18	19
Matrix Tensile Strength, MPa									
MD	53.70	32.96	40.25	25.30	29.52	62.74	67.77	41.96	56.69
TD	40.14	29.30	65.76	46.54	61.99	45.41	43.93	57.62	55.77
Elongation at break, %									
MD	57	56	60	67	26	23	34	18	33
TD	27	41	13	9	23	27	30	31	12
Gurley Air Flow, sec/100cc	47	45	40	29	32	28	37	28	36
Tear Strength, kN/m									
MD	9.28	5.78	7.01	3.85	2.28	5.08	6.30	5.60	5.08
TD	4.90	4.90	7.01	8.23	7.53	1.93	4.38	4.55	4.73
Mullens Hydrostatic, kPa 483	434	490	448	476	503	496	434	510	
MVTR, g/m <sup>2</sup> day	935							963	
Methanol Bubble Point Pressure, kPa	290	276	296	234	145	276	324	55	317
Maximum Limiting Pore Diameter, μm	0.077	0.081	0.075	0.095	0.154	0.081	0.069	0.404	0.070
Maximum Pore Diameter, μm								155	

Table V (continued)  
Properties of Biaxially Stretched Microporous Sheets  
Produced from Microporous Sheet of Example 1

Example No.	11	12	13	14	15	16	17	18	19
Volume Average Pore Diameter, $\mu\text{m}$						17.92			
Heat Shrinkage after 1 hr at 100°C, %									
MD	19.0		9.4	12.0		19.3	24.1	21.2	
TD	23.2		22.5	28.3		25.7	29.1	30.8	

The biaxially stretched microporous sheet of Example 17 was  
2 examined by scanning electron microscopy at a magnification of  
430X. A section taken in a plane perpendicular to the sheet surface  
4 (viz., looking into the thickness) and along the machine direction  
showed substantial pore elongation. A section taken in a plane  
6 perpendicular to the sheet surface and along the transverse  
direction showed pore elongation which was not as pronounced as  
8 along the machine direction. A view of the sheet surface (not  
sectioned) showed that large void structures were not as numerous as  
10 in views of either of the sections looking into the thickness.

Table VI  
 Properties of Biaxially Stretched Microporous Materials  
 Produced from Microporous Sheet of Example 2

Example No.	20	21	22	23	24	25	26	27	28
Thickness, mm	0.203	0.152	0.178	0.127	0.152	0.127	0.102	0.076	0.178
Stretch Ratio									
MD	2	2	2	2	2	3	3	3	3
TD	2.5	3	3	3	4	3	3	3	4
Line Speed m/min	24.4	24.4	15.2	24.4	15.2	24.4	15.2	24.4	15.2
MDS Preheat Temp., °C	104	104	121	79	121	104	121	79	121
TDS Average Zonal Set Point Temps., °C Preheat (lower banks)	177	177	149	149	149	177	149	149	149
Stretch I (lower banks)	177	177	149	149	149	177	149	149	149
Stretch II	171	171	188	188	188	171	188	188	188
Stretch III	142	142	144	149	144	142	144	149	144
Sinter I	144	144	200	149	144	144	144	149	144
Sinter II	227	227	255	316	255	227	255	316	255
Weight, g/m <sup>2</sup>	44	24	24	24	24	17	14	14	31
Porosity, vol%	86	90	90	90	90	92	90	90	90
Matrix Tensile Strength, MPa									
MD	52.94	61.50			36.61	96.18		73.91	37.51
TD	44.47	67.98			109.49	54.38		75.01	117.21

Table VI (continued)  
Properties of Biaxially Stretched Microporous Materials  
Produced from Microporous Sheet of Example 2

Example No.	20	21	22	23	24	25	26	27	28
Elongation at break, %									
MD	58	54	161	41	87	31	13	19	111
TD	51	39	15	16	9	42	16	16	7
Tear Strength, kN/m									
MD	20.31	12.61	17.51	6.13	13.13	12.26	8.41	5.95	18.56
TD	13.31	12.78	21.02	7.18	11.03	9.11	5.25	7.53	19.44
Gurley Air Flow, sec/100cc	81	40			46	45			52
Mullens Hydrostatic, kPa	745	689	676	496	745	717	641	503	703
MVTR, g/m <sup>2</sup> day			868	761		947	913	827	
Methanol Bubble Point Pressure, kPa	290	303			303	365			290
Maximum Limiting Pore Diameter, μm	0.077	0.074			0.074	0.061			0.077
Maximum Pore Diameter, μm			111			>146			
Volume Average Pore Diameter, μm			7.13						4.70

Table VI (continued)  
Properties of Biaxially Stretched Microporous Materials  
Produced from Microporous Sheet of Example 2

Example No.	20	21	22	23	24	25	26	27	28
Heat Shrinkage after 1 hr at 100°C, %									
MD	11.7		3.8	7.1	12.3		15.3	6.3	7.7
TD	24.4		23.6	11.8	22.0		34.1	18.9	21.5



The biaxially stretched microporous sheet of Example 25 was examined by scanning electron microscopy at a magnification of 430X. A section taken in a plane perpendicular to the sheet surface and along the transverse direction showed pore elongation which was not as pronounced as that seen in a similar section taken along the machine direction. A view of the sheet surface (not sectioned) showed that large void structures were not as numerous as in views of either of the sections looking into the thickness.

10

12 Table VII  
 13 Properties of Biaxially Stretched Microporous Sheets  
 14 Produced from Microporous Sheet of Example 3

16 Example No.	29	30	31	32
18 Thickness, mm	0.178	0.102	0.127	0.102
20 Stretch Ratio				
20 MD	2	2	3	3
20 TD	3	3	3	4
22 Line Speed				
24 m/min	24.4	24.4	24.4	24.4
26 MDS Preheat				
26 Temp., °C	79	79	79	79
28 TDS Average				
30 Zonal Set				
30 Point Temps., °C				
32 Preheat				
34 (lower banks)	177	149	177	177
36 Stretch I				
36 (lower banks)	177	149	177	177
38 Stretch II	171	188	171	171
40 Stretch III	142	149	142	142
42 Sinter I	144	149	144	144
44 Sinter II	227	260	227	227
46 Weight, g/m <sup>2</sup>	27	14	20	14

Table VII (continued)  
 Properties of Biaxially Stretched Microporous Sheets  
 Produced from Microporous Sheet of Example 3

Example No.	29	30	31	32
6 Porosity, vol %	90	91	90	92
8 Matrix Tensile				
10 Strength, MPa				
MD	29.58	52.94	77.84	109.89
12 TD	122.73	44.43	32.96	39.90
14 Elongation at break, %				
16 MD	90	47	27	17
TD	9	24	32	30
18 Tear Strength,				
20 kN/m				
MD	15.41	10.51	15.24	7.18
22 TD	21.02	5.43	4.20	3.50
24 Gurley Air Flow,				
26 sec/100cc	56	33		36
28 Mullens Hydrostatic,				
30 kPa	552	655	641	586
32 MVTR, g/m <sup>2</sup> day	843	815	862	982
34 Methanol				
36 Bubble Point Pressure, kPa	303	276		317
38 Maximum				
40 Limiting Pore Diameter, $\mu$ m	0.074	0.081		0.070
42 Heat Shrinkage				
44 after 1 hr. at 100°C, %				
46 MD	24.1	16.5	26.4	
TD	40.1	31.4	34.8	
48				

EXAMPLE 33

2           Microporous material was taken from a different roll of  
3           microporous material produced during the same production run as the  
4           microporous material of Example 8. Two sheets 10.2 centimeters wide  
5           and several centimeters long were cut from the microporous  
6           material. A polyethylene bag which was about 15.2 centimeters wide  
7           when flat, was procured. The bag was cut along the width to provide  
8           a polyethylene loop which was about 1.6 centimeters wide and about  
9           15.2 centimeters long. The loop was slipped over the end of one of  
10          the microporous sheets such that it encircled the microporous sheet  
11          across the width dimension near the end of the sheet. The looped  
12          portion of the microporous sheet was then superimposed on the end  
13          portion of the other microporous sheet. The superimposed layers of  
14          the resulting sandwich were therefore in the order: polyethylene -  
15          microporous material - polyethylene - microporous material. A PAC  
16          Model 24PI Impulse Sealer (Packaging Aids Corporation) fitted with  
17          top and bottom heater bands 6.35 millimeters wide was used as a heat  
18          sealing unit. The surfaces of the heater bands were covered with  
19          polytetrafluoroethylene film to prevent sticking. This unit is an  
20          impulse sealer which clamps the heater bands around the package  
21          opening with full power to the heater bands for 1.5 seconds. The  
22          clamping force is then maintained for 9.5 seconds while the heater  
23          bands cool to about ambient temperature. The air pressure setting  
24          for providing clamping pressure was 413.7 kilopascals. The sandwich  
25          was processed in the heat sealer to form a lap seam. Half of the  
26          heat sealed material was processed in the heat sealer a second  
27          time. There was in both cases some penetration of polyethylene into  
28          the pores of the microporous sheets, but the polyethylene layers  
29          still retained their integrity as films. After cooling, the  
30          microporous sheets of both samples were pulled in opposite  
31          directions perpendicular to the length of the seams to test the  
32          seams. In both cases the microporous material drew and eventually  
33          broke in the drawn area without failure of the seam. In destructive  
34          testing of the seams themselves, the microporous sheet could be  
            peeled away from the polyethylene by pulling parallel to the length

of the seam. The surface of the top polyethylene layer showed a  
2 whitish cast where some of the microporous material was embedded in  
the surface. The center polyethylene strip was less well bonded.

4 This Example establishes that the hot melt concept of heat  
sealing to polymer which melts or flows more readily at or below the  
6 flow temperature of the polymer of the microporous material,  
produces successful laminations.

8

EXAMPLE 34

10 The procedure of Example 33 was repeated except that the  
microporous material used was that of Example 10. Upon pulling the  
12 microporous sheet from the polyethylene, the surface of the  
polyethylene was whiter than was observed in Example 33, thereby  
14 indicating a deeper penetration of polyethylene into the microporous  
sheet than in Example 33.

16

EXAMPLE 35

18 A sample of film about 0.051 millimeter thick which had  
been produced by the Reynolds Metals Company was obtained. The film  
20 was a two-layer composite of Surlyn® thermoplastic polymer and  
aluminum. Squares measuring about 5.1 centimeters on a side were  
22 cut from the film and from microporous material. The microporous  
material was from the same source as that used in Example 33. The  
24 squares were superimposed with the Surlyn® thermoplastic polymer  
side of the composite film adjacent the microporous material, and  
26 the sandwich was placed in a 30.5 centimeters by 30.5 centimeter  
Pasadena press at 105°C to 110°C for 30 seconds under essentially no  
28 pressure. The film successfully laminated to the microporous  
material. Attempts to peel the film from the microporous material  
30 produced a pull-out of silica onto the polymer side of the composite  
film, thereby demonstrating that the bond was stronger than the  
32 microporous material itself.

EXAMPLE 36

2           An electrically heated rod was fabricated by inserting a  
400 watt quartz heater into a 21 centimeter length of stainless  
4 steel tubing having an outside diameter of 12.7 millimeters. The  
heater was held coaxially within the tubing by wrapping several  
6 turns of glass fiber cloth tape 12.7 millimeters wide around each  
end of the heater prior to insertion. The rod was held in a  
8 horizontal position by two asbestos covered clamps which engaged the  
ends of the rods. The electrical leads from the quartz heater were  
10 connected to the secondary of a variable autotransformer. The  
primary of the autotransformer was connected to standard 110 volt,  
12 60 hertz alternating current. The temperature of the heated rod was  
measured by holding a dial thermometer in contact with the outside  
14 surface of the rod using glass fiber cloth tape. Strips measuring  
about 2.54 centimeters by about 20.32 centimeters were cut from  
16 microporous material and two-layer Surlyn® thermoplastic polymer and  
aluminum composite film. The microporous material was from the same  
18 source as that used in Example 33 and the two-layer composite film  
was from the same source as that used in Example 35. The strips  
20 were superimposed with the Surlyn® thermoplastic polymer side of the  
composite film adjacent the microporous material to form a  
22 sandwich. The electrically heated rod was heated to about 150°C and  
the sandwich was slowly drawn by hand over the heated rod with the  
24 aluminum side next to the surface of the rod. A paper towel folded  
four times was used to apply pressure to the sandwich and against  
26 the rod as the drawing was performed. A good wrinkle-free, uncurled  
laminate, having no entrapped air bubbles, was obtained. After  
28 cooling it was attempted to peel a portion of the composite film  
from the microporous material. A uniform white coloration on the  
30 film side indicated good, uniform adhesion. The white coloration  
was silica which had been pulled out of the microporous material.

32           Samples of the microporous material and composite film were  
taken from the same general regions of the stock from which the  
34 strips had been cut and their thicknesses were measured. The

thickness of the laminate was also measured. The results were as follows:

	Microporous Material	0.37084 millimeter
4	Composite Film	0.0508 millimeter
	Laminate	0.381 millimeter

6 The laminate is therefore 0.04064 millimeter thinner than the sum of the thicknesses of the layers from which it was produced.

8 Circles of 17.78 millimeter diameter were die cut from the materials and these were weighed. The results were as follows:

10	Microporous Material	0.0492 gram
	Composite Film	0.0160 gram
12	Laminate	0.0632 gram

The surface areas of the various materials were determined according to the BET method described in ASTM C 819-77 using nitrogen as the adsorbate but modified by outgassing the system and sample for one hour at 130°C. The results were as follows:

	Microporous Material	136	m <sup>2</sup> /g
18	Composite Film	5	m <sup>2</sup> /g
	Laminate	51	m <sup>2</sup> /g

20 If it is assumed that there was no weight loss of composite film during lamination, then the surface area of the microporous material of the laminate is  $(51)(0.0632)/(0.0632-0.0160)=68 \text{ m}^2/\text{g}$ .

If it is alternatively assumed that the BET surface area of the composite film did not change during lamination, then the surface area of the microporous material portions of the laminate is  $[(51)(0.0632)-(5)(0.0160)]/[0.0632-0.0160]=67 \text{ m}^2/\text{g}$ . Based on these data, it is believed that a loss of about half of the BET surface area of the microporous material during lamination was due to a penetration of the Surlyn® thermoplastic polymer into about half of the thickness of the microporous material used to form the laminate.

### 32 Microporous Material Formation

Larger batch mixing equipment was employed than was used for Examples 1-10. Processing oil was used as the processing plasticizer. Silica, polymer, lubricant, and antioxidant in the

amounts specified in Table VIII were placed in a high intensity 2 mixer and mixed at high speed for 6 minutes. The processing oil needed to formulate the batch was pumped into the mixer over a 4 period of 12-18 minutes with high speed agitation. After completion of the processing oil addition a 6 minute high speed mix period was 6 used to complete the distribution of the processing oil uniformly throughout the mixture.

8

Table VIII

10

Formulations

12

Example No.	37	38	39
16 <u>Ingredient</u>			
18 UHMWPE (1), kg	24.04	17.24	17.24
20 HDPE (2), kg	0.00	6.80	6.80
22 Precipitated			
Silica (3), kg	59.87	59.87	59.87
24 Lubricant (4), g	300.0	300.0	600.0
26 Antioxidant (5) g	300.0	300.0	0.0
28                   (6) g	0.0	0.0	100.0
30 Processing Oil (7), kg			
in Batch	91.63	91.63	91.63
32      at Extruder	~35.14	~35.14	~35.14

34

(1) UHMWPE=Ultrahigh Molecular Weight Polyethylene, Himont 1900, Himont, U.S.A., Inc.

36

(2) HDPE=High Density Polyethylene Hostalen® GM 6255, Hoechst Celanese Corp.

38

(3) HiSil® SBG, PPG Industries, Inc.

40

(4) Petrac® CZ81, Desoto, Inc., Chemical Speciality Division

(5) Irganox® B-215, Ciba-Geigy Corp.

42

(6) Irganox® 1010, Ciba-Geigy Corp.

(7) Shellflex® 371, Shell Chemical Co.

44

The batch was then processed according to the general procedures described in respect of Examples 1-10 to form microporous sheets.

The microporous sheets, as well as the hereinafter described biaxially stretched microporous sheets produced therefrom, were tested for various physical properties. Table II identifies the properties with the methods used for their determination. The results of physical testing of the unstretched microporous sheets are shown in Table IX. The abbreviations MD and TD have the same meanings previously discussed.

Table IX

Physical Properties of Microporous Sheet

Example No.	37	38	39
<u>Ingredient</u>			
Thickness, mm	0.267	0.254	0.255
Strip Tensile Strength, kN/m			
MD	3.42		
TD	1.52		
Breaking Factor, kN/m			
MD		3.44	3.23
TD		1.42	1.52
Elongation at break, %			
MD	391	477	688
TD	448	451	704
Processing Oil Content, wt %	2.8	3.3	3.1

Biaxial Stretching of Microporous Sheet

Portions of the microporous materials produced in Examples 37 and 38 were unwound from cores and biaxially stretched by first



uniaxially stretching in the machine direction using a single stage 2 roll-to-roll MDS unit and then essentially uniaxially stretching in the traverse direction using a moving clip tenter frame as a TDS 4 unit.

Operation of the MDS unit can be characterized by the 6 temperatures and line speeds shown in Table X.

8

Table X

10

MDS Unit Parameters

	<u>Roll No.</u>	<u>Function</u>	<u>Diameter, mm</u>	<u>Temperature, °C</u>	<u>Peripheral Speed, m/min</u>
14	1	Preheat	305	116	3.84
	2	Preheat	305	116	3.84
16	3	Stretching	152	127	3.84
	4	Stretching	152	127	11.52
18	5	Annealing	305	79	11.53
	6	Cooling	305	38	11.53

20

22 The gap between the slow and fast stretching rolls (Rolls 3 and 4, respectively) was 0.533 millimeter.

24 The TDS unit was a typical chain and clip tenting frame machine. It comprised three contiguous heating zones, each 2.54 26 meters in length where the beginning of the first heating zone coincided with the entrance to the TDS unit. The microporous sheet 28 was heated by recirculating hot air in the heating zones. The heating zone temperatures are indicated in Table XI, where heating 30 zone numbers increase in the direction of sheet travel.

32

Table XI2                                    Heating Zone Temperature

4	<u>Heating Zone</u>	<u>Temperature, °C</u>
	1	107
6	2	116
	3	121

8

Stretching was controlled by positioning the tracks in  
 10 which the chains holding the gripping clips rode. Microporous  
 sheets, which had been uniaxially stretched in the machine direction  
 12 as described above, were introduced to the TDS unit which had the  
 track geometry shown in Table XII.

14

Table XII16                                    Track Geometry of TDS Unit

18	<u>Distance from Entrance, meters</u>	<u>Width, meters</u>
	-0.30	0.53
20	+1.22	0.53
	2.01	0.53
22	2.74	0.74
	3.51	0.97
24	4.27	1.17
	5.03	1.38
26	5.79	1.60
	7.32	1.60
28	7.92	1.57

30                    The properties of representative samples of biaxially  
 stretched microporous sheets are given in Table XIII.

32

Table XIII

<u>Properties of Biaxially Stretched Microporous Sheets</u>		
<u>Example No.</u>	<u>40</u>	<u>41</u>
2		
4		
6		
8		
10		
12		
14		
16		
18		
20		
22		
24		
26		
28		
30		
32		
34		
36		

38

EXAMPLE 42

40 Stretched microporous material was taken from a roll of stretched microporous material produced in Example 40 and

42 polyethylene was taken from a polyethylene bag. The stretched microporous material was superimposed on aluminum foil and the

44 resulting two-layer assembly was trimmed to form a 21.59 centimeters by 27.94 centimeter rectangle which was then folded in the middle to

46 form a 13.97 centimeter by 21.59 centimeter rectangular four-layer assembly with the layers superimposed in the order aluminum foil -

- 50 -

stretched microporous material - stretched microporous material -  
2 aluminum foil. The polyethylene was trimmed to form a 12.7  
centimeter by 20.32 centimeter rectangular panel which was inserted  
4 between the two stretched microporous material layers of the  
four-layer assembly. The layers of the resulting five-layer  
6 assembly were in the order: aluminum foil - stretched microporous  
material - polyethylene - stretched microporous material - aluminum  
8 foil. A 30.48 centimeter Graphic III Laminator (Spiral Binding  
Company, Inc., Clifton, New Jersey), modified by removing the two  
10 rolls of plastic sheeting ordinarily employed for laminating  
documents, was used as a heat sealer. The two heat shoes of the  
12 Graphic III Laminator were heated to 160°C. The five-layer assembly  
was passed over one of the heat shoes while applying pressure with a  
14 leather-palm glove to assure good contact with the heat shoe,  
through the nip of a pair of laminating rolls, and then through the  
16 nip of a pair of rubber pull rolls. When the resulting laminate had  
cooled, the two layers of aluminum foil were peeled off, leaving as  
18 the product a three-layer laminate in which the order of the layers  
were: stretched microporous material - polyethylene - stretched  
20 microporous material. In destructive testing of the product,  
adhesion was tested by attempting to forcibly delaminate the layers  
22 by pulling them apart. It was found that failure occurred in the  
stretched microporous material itself rather than at a polyethylene  
24 - stretched microporous material interface. This indicated that the  
adhesive bond between layers was stronger than the stretched  
26 microporous material.

28

EXAMPLE 43

The procedure of Example 42 was repeated except that the  
30 stretched microporous material used was that produced in Example  
41. The results were essentially the same as in Example 42.

32 Although the present invention has been described with  
reference to specific details of certain embodiments thereof, it is  
34 not intended that such details should be regarded as limitations  
upon the scope of the invention except insofar as they are included  
36 in the accompanying claims.

CLAIMS

2

1. A multilayer article comprising material which is  
4 impervious to the passage of gas and bacteria fusion bonded in the  
absence of extrinsic intervening adhesive to microporous material  
6 comprising:

8 (a) a matrix consisting essentially of essentially linear  
ultrahigh molecular weight polyolefin which is  
essentially linear ultrahigh molecular weight  
10 polyethylene having an intrinsic viscosity of at  
least about 18 deciliters/gram, essentially linear  
12 ultrahigh molecular weight polypropylene having an  
intrinsic viscosity of at least about 6  
14 deciliters/gram, or a mixture thereof.

16 (b) finely divided particulate substantially  
water-insoluble siliceous filler distributed  
throughout said matrix, said filler constituting from  
18 about 50 percent to about 90 percent by weight of  
said microporous material, and

20 (c) a network of interconnecting pores communicating  
throughout said microporous material, said pores  
22 before fusion bonding constituting at least about 35  
percent by volume of said microporous material.

24

2. The multilayer article of claim 1 wherein

26 (a) said essentially linear ultrahigh molecular weight  
polyolefin is essentially linear ultrahigh molecular  
28 weight polyethylene having an intrinsic viscosity of  
at least about 18 deciliters/gram,

30 (b) said siliceous filler is precipitated silica, and

32 (c) said pores before fusion bonding constitute from  
about 35 percent to about 80 percent by volume of  
said microporous material.

34

3. The multilayer article of claim 2 wherein said

material which is impervious to the passage of gas and bacteria is  
2 polyethylene.

4           4.    The multilayer article of claim 3 wherein said  
polyethylene is heat sealed to said microporous material.

6

5.    A multilayer article comprising at least one layer of  
8 substantially nonporous material fusion bonded in the absence of  
extrinsic intervening adhesive to at least one layer of microporous  
10 material comprising:

(a) a matrix consisting essentially of essentially linear  
12 ultrahigh molecular weight polyolefin which is  
essentially linear ultrahigh molecular weight  
14 polyethylene having an intrinsic viscosity of at  
least about 18 deciliters/gram, essentially linear  
16 ultrahigh molecular weight polypropylene having an  
intrinsic viscosity of at least about 6  
18 deciliters/gram, or a mixture thereof.

(b) finely divided particulate substantially  
20 water-insoluble filler, of which at least about 50  
percent by weight is siliceous, distributed  
22 throughout said matrix, said filler constituting from  
about 50 percent to about 90 percent by weight of  
24 said microporous material, and

(c) a network of interconnecting pores communicating  
26 throughout said microporous material, said pores  
before fusion bonding constituting at least about 35  
28 percent by volume of said microporous material.

30           6.    The multilayer article of claim 5 wherein said  
microporous material has a thickness in the range of from about 0.03  
32 to about 4 millimeters.

34           7.    The multilayer article of claim 5 wherein said  
substantially nonporous material is thermoplastic polymeric sheet or  
36 film.

2           8. The multilayer article of claim 5 wherein said  
substantially nonporous material is metalized thermoplastic  
4 polymeric sheet or film.

6           9. The multilayer article of claim 5 wherein said  
substantially nonporous material is thermoset polymeric sheet or  
8 film.

10          10. The multilayer article of claim 5 wherein said  
substantially nonporous material is elastomeric sheet or film.  
12

14          11. The multilayer article of claim 5 wherein said  
substantially nonporous material is metal sheet or foil.

16          12. The multilayer article of claim 5 wherein said  
essentially linear ultrahigh molecular weight polyolefin is  
18 essentially linear ultrahigh molecular weight polyethylene having an  
intrinsic viscosity of at least about 18 deciliters/gram.  
20

22          13. The multilayer article of claim 12 wherein said  
ultrahigh molecular weight polyethylene has an intrinsic viscosity  
in the range of from about 18 to about 39 deciliters/gram.  
24

26          14. The multilayer article of claim 12 wherein said  
filler constitutes from about 50 percent to about 85 percent by  
weight of said microporous material.  
28

30          15. The multilayer article of claim 12 wherein at least  
about 85 percent by weight of said filler is siliceous.

32          16. The multilayer article of claim 12 wherein all of  
said filler is siliceous.  
34

36          17. The multilayer article of claim 12 wherein said  
siliceous filler is silica.

2           18. The multilayer article of claim 12 wherein said  
siliceous filler is precipitated silica.

4

19. The multilayer article of claim 18 wherein said  
6 precipitated silica has an average ultimate particle size of less  
than about 0.1 micrometer.

8

20. The multilayer article of claim 12 wherein the volume  
10 average diameter of said pores as determined by mercury porosimetry  
is in the range of from about 0.02 to about 50 micrometers.

12

21. The multilayer article of claim 12 wherein said pores  
14 constitute from at least about 35 percent to about 95 percent by  
volume of said microporous material.

16

22. The multilayer article of claim 12 wherein said pores  
18 constitute from about 35 percent to about 80 percent by volume of  
said microporous material.

20

23. The multilayer article of claim 12 wherein said pores  
22 constitute from more than 80 percent to about 95 percent by volume  
of said microporous material.

24

24. The multilayer article of claim 5 wherein said layer  
26 of microporous material is heat sealed to said layer of  
substantially nonporous material.

28

25. The multilayer article of claim 5 wherein said layer  
30 of microporous material is discontinuously fusion bonded to said  
layer of substantially nonporous material.

32

26. The multilayer article of claim 5 wherein said layer  
34 of microporous material is essentially continuously fusion bonded to  
said layer of substantially nonporous material.



2           27. The multilayer article of claim 5 wherein other  
thermoplastic organic polymer is present in said matrix and wherein  
4 at least about 50 percent by weight of said matrix is said  
essentially linear ultrahigh molecular weight polyolefin.

6

          28. The multilayer article of claim 27 wherein said other  
8 thermoplastic organic polymer is polypropylene.

10           29. The multilayer article of claim 27 wherein said other  
thermoplastic organic polymer is high density polyethylene.

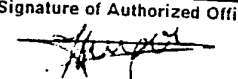
12

          30. The multilayer article of claim 5 wherein other  
14 thermoplastic organic polymer is present in said matrix and wherein  
at least about 70 percent by weight of said matrix is said  
16 essentially linear ultrahigh molecular weight polyolefin.

18           31. The multilayer article of claim 5 wherein other  
thermoplastic organic polymer is substantially absent from said  
20 matrix.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/03773

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <b>IPC5: B 32 B 5/18</b>		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC5	B 32 B; C 08 J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>*</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US, A, 4861644 (YOUNG ET AL) 29 August 1989, see column 1, line 15 - line 32; claims 1-10  --	1-31
Y	US, A, 4582753 (GARY L. DUNCAN) 15 April 1986, see column 1, line 28 - line 49; column 5, line 35 - line 41; column 6, line 1 - line 25  --	1-31
Y	US, A, 3799828 (MASANORI TAKASHI ET AL) 26 March 1974, see column 2, line 36 - line 50; column 3, line 48 - line 50; column 4, line 19  --	1-31
<p><sup>*</sup> Special categories of cited documents:<sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
24th April 1990		04 MAY 1990
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		 <b>Mme N. KUIPER</b>

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	<p>Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 88-365642/51, Toa Nenryo Kogyo KK: "Polyolefin based laminate for cell separator, filter etc. - consists of ultrahigh mol.wt. microporous film and porous reinforcing layer", JP 63276533,A, 881114, 8851 (Basic)</p> <p style="text-align: center;">-- -----</p>	1-31

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 89/03773

SA 31112

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on 30/03/90  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4861644	29/08/89	EP-A- 0289859 JP-A- 1070538	09/11/88 16/03/89
US-A- 4582753	15/04/86	US-A- 4702954	27/10/87
US-A- 3799828	26/03/74	DE-A-B- 1914972 FR-A-B- 2004775 GB-A- 1268823 US-A- 3841943 US-A- 4075050 US-A- 4318950	16/10/69 28/11/69 29/03/72 15/10/74 21/02/78 09/03/82

For more details about this annex: see Official Journal of the European patent Office, No. 12/82