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Australia

Patents Act 1990

Patent Request: Standard Patent

We, the Applicant/Nominated Person specified below, request we be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant/Nominated Person:

Atochem, a French Body Corporate, of 4 & 8 Cours Michelet, La Defense 10, 92800 Puteaux, France.

[54] Invention Title:

Barrier Film Consisting of an Alloy Based on an Ethylene-Vinyl Alcohol Copolymer, its Preparation, its use Especially in Packaging.

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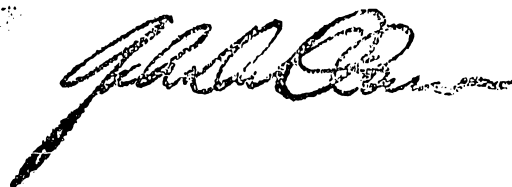
Basic Convention Application Details

[31] Application No	[33] Country	[32] Date of Application
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Atochem



Registered Patent Attorney



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1 of 1

AM 0395

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

DECLARATION IN SUPPORT OF CONVENTION OR
NON-CONVENTION APPLICATION FOR A PATENT
OR PATENT OF ADDITION

Insert title of invention

Insert full name(s) and address(es)
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Cross out whichever of paragraphs
1(a) or 1(b) does not apply

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Insert place and date of signature.

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Note: Initial all alterations.

In support of the Application made for a patent ~~patent of addition~~ for an invention
entitled:

Barrier Film Consisting of an Alloy Based on an Ethylene-
Vinyl Alcohol Copolymer, its Preparation, its use Especially in
Packaging We, Pierre POISSON

of: ATOCHEM, a French Body Corporate of:

of: 4 & 8 Cours Michelet, La Defense 10, 92800 PUTEAUX,
France.

do solemnly and sincerely declare as follows:-

1. (a) ~~I am~~ the applicant..... for the ~~patent~~
~~We are~~ ~~patent of addition~~

or (b) I am authorized by

ATOACHEM,

the applicant..... for the ~~patent~~
~~patent of addition~~ to make this declaration on its behalf.

2. (a) ~~I am~~ the actual inventor..... of the invention
~~We are~~

or (b) RICHARD AUDRY and PIERRE NOGUES,

of: rue Hervieu Deschenes, 27170 BEAUMONT LE ROGER, France:
and Le Bourg, Saint-Aubin le Vertueux, 27300 BERNAY, France.

(respectively)

~~is~~ the actual inventor..... of the invention and the facts upon which the applicant
~~is~~ ~~are~~ entitled to make the application are as follows:-

"The applicant would, if a patent were granted upon
an application made by the inventors, be entitled to
have the patent assigned to it".

3. The basic application..... as defined by Section 141 of the Act ^{was} made ^{were}
in FRANCE: NO. 90.00384 on the 15th January, 1990
by ATOCHEM
in on the
by
in on the
by

4. The basic application..... referred to in paragraph 3 of this Declaration ^{was}
the first application..... made in a Convention country in respect of the invention ^{were} the subject
of the application.

Declared at Puteaux
Pierre POISSON

this 15th day of January 1991

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-69355/91
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(54) Title
BARRIER FILM CONSISTING OF AN ALLOY BASED ON AN ETHYLENE-VINYL ALCOHOL
COPOLYMER, ITS PREPARATION, ITS USE ESPECIALLY IN PACKAGING

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(56) Prior Art Documents
AU 637821 62347/90 C08L 29/04 23/12
AU 645622 86936/91
US 5061751

(57) Claim

1. A method of packaging food which method comprises packaging the food in a film which comprises a blend of at least one ethylene-vinyl alcohol (EVOH) copolymer, at least one propylene polymer and at least one compatibilising agent.

The present invention relates to the field of films and more particularly so-called barrier films which resist hot water and superheated steam and are intended for food packaging.

5 To ensure preservation of food products it is necessary to ensure not only protection against dust but also against moisture, against some gases such as oxygen and carbon dioxide and against odours.

Polymeric resins are employed for this purpose; these are known as barrier resins, which have gas and water vapour permeability properties, that is to say they are more or less permeable to gases and to water vapour.

The films generally consist of one or more layers consisting of polymers which are impervious to gases and of polymers which are impervious to water vapour.

Thus, when permeability to oxygen must be low, use is made of polymers whose barrier properties in respect of this gas are very high, such as ethylene-vinyl alcohol (EVOH) copolymers, which are recognised as being excellent

20

materials in this respect.

If a sufficient protection against water vapour is to be obtained, a barrier layer consisting of polyolefins such as polypropylene is employed.

5 Since the requirements of imperviousness to gases and to water vapour vary from one form of packaging to another and from one food product to another, the films employed may consist of one or more polymer layers which have different gas and water vapour permeability properties.

10 To improve the quality of "fresh" food products and to increase their preservation time, the food products must be packaged aseptically. Many processes exist for this purpose. For example, pasteurisation and sterilisation may be mentioned.

15 In these processes the packaging - or the packaged food product - is subjected to the action of hot water (85°C-100°C) or to the action of superheated steam for periods ranging from a few seconds to several hours. For example, in the case of sterilisation the temperature
20 reaches 121°C or even 135°C-140°C. It is then necessary for the packaging consisting of a film which has one or more barrier layers to withstand mechanically the combined action of water and of temperature, as well as the pressures, which may reach 3 to 4 bars.

25 It has been found that at the time of the sterilisation or under the effect of hot water, certain films, especially those based on EVOH, undergo degradation,

which is seen as creasing of the affected layer or even a total delamination of the multilayer film.

A film which has an improved resistance to hot water and to superheated steam has now been found, according to the present invention, which is characterised in that it consists wholly or partially of an alloy (or blend) comprising at least one ethylene-vinyl alcohol (EVOH) copolymer, at least one propylene polymer and at least one compatibilising agent.

10 According to the present invention there is provided a method of packaging food which method comprises packaging the food in a film which comprises a blend of at least one ethylene-vinyl alcohol (EVOH) copolymer, at least one propylene polymer and at least one compatibilising agent.

15 The film used according to the invention is generally characterised in that the alloy contains at least 30% by weight of EVOH. Among these films preference will be given to those made from alloys comprising:

- 42.5% to 99.5% by weight of EVOH
- 20 - 42.5% to 0.4% by weight of propylene polymer
- 0.1% to 15 % by weight of compatibilising agent.

The EVOH composition of the alloy is characterised by the fact that the matrix or dispersing phase is EVOH. The propylene polymer may be dispersed in the form of more or

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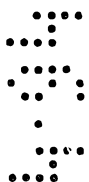
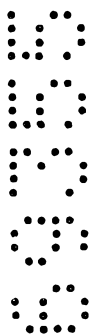


3A

less spherical nodules or of small cylindrical rods.

The adhesion between the phases is preferably ensured by a graft copolymer based on an α -monoolefin referred to as a compatibility agent, which is described in European Patent Application No. 0,342,066.

5 Among the compatibilising agents mentioned in the



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European patent application mentioned as reference above,
preference is given to the compatibilising agents of formula
AMXP:

- AM denotes a backbone copolymer obtained by
5 copolymerising propylene and one or more α -olefins,

- X is chosen from the group consisting of
citraconic anhydride, fumaric acid, mesaconic acid, the
anhydride of 3-allylsuccinic acid and maleic anhydride, -

P denotes a polyamide oligomer derived from
10 caprolactam, 11-aminoundecanoic acid or dodecalactam.

The EVOH is a copolymer consisting essentially of
ethylene and vinyl alcohol units and may contain small
quantities of other monomer units, in particular of vinyl
ester units. These copolymers may be obtained by
15 saponification or partial or complete alcoholysis of
ethylene-vinyl ester copolymer. Among the vinyl esters,
vinyl acetate is the preferred monomer. The degree of
saponification or of alcoholysis is desirably at least 90
mol% and is preferably from 94 to 99.5 %. The molar
20 proportion of ethylene in the EVOH is desirably from 3 to
75 % and preferably from 10 to 50 %.

The propylene polymer (hereafter referred to simply
as "polypropylene") is a polymer consisting essentially of
propylene units. It may contain quantities (generally not
25 exceeding 40 mol%) of another monomer unit, in particular
ethylene and/or one or more α -olefins containing 4 to 6
carbon atoms. In particular, a homopolypropylene or a block

propylene copolymer with 0.5 to 30 mol% of ethylene, or a random copolymer of propylene and ethylene containing 0.1 to 30 mol% of ethylene is employed.

Small quantities of other compounds of the
5 stabiliser, antistatic agent or lubricant type and other polymeric compounds may be optionally added to three main constituents, which are EVOH, polypropylene and the compatibilising agent.

Since the constituents are generally in the form of
10 powder or granules, the preparation of the blend/alloy can be carried out in solution or in the molten state by means of a conversion machine of the single-screw or counter- or corotative twin-screw extruder type or a roll mill.

Monolayer films^{used} according to the invention will
15 generally consist wholly of the alloy.

Multilayer films^{used} consist of at least one layer of alloy, the other layer or layers usually consisting of polyethylene (PE), polypropylene (PP), polyamide (PA), polyethylene terephthalate (PET) and polycarbonate (PC).

20 A coextrusion binder, which ensures better adhesion between the layers must be employed in the case of some polymers.

In the multilayer films^{used} according to the invention the alloy layer may be external or internal.



The following films may be mentioned as examples of multilayer films^{Used} according to the invention:

- PP/alloy/PP
- PP/coextrusion binder/alloy
- 5 - PP/coextrusion binder/alloy/coextrusion binder/PP
- PA/alloy.

The films^{Used} according to the invention may be obtained by flat extrusion or by film blowing at temperatures of, say, 200°C to 260°C.

10 Apart from the coextrusion techniques using a flat die or an annular die, the films in accordance with the invention can be processed by techniques such as extrusion coating and extrusion lamination, the latter technique making it possible, for example, to combine a film and a

15 sheet of metal such as aluminium.

The films^{Used} according to the invention which are produced from the alloy exhibit an improved resistance to hot water and to superheated steam.

20 Thus, the single-layer or multilayer films subjected to superheated steam at temperatures of 100°C to 140°C at pressures from 1 to 4 bars, retain their transparency and have a virtually intact surface appearance, whereas the same films consisting wholly or partially of EVOH become opaque and are striated, distorted or

25 delaminated.

The films^{used} according to the invention consisting



wholly or partially of the alloy can be used in the form of pouches, flexible envelopes, small tubs or pots.

The following Examples further illustrate the present invention.

- Tests 1 to 5

a) Five compositions are produced with the aid of a corotative twin-screw extruder with the following proportions of the constituents:

10 - EVOH: 99.3% hydrolysed ethylene-vinyl acetate copolymer containing 32 mol% of ethylene with a melt index of 3.2 g/10 minutes measured at 210°C under 2.16 kg,

- PP: random ethylene-propylene copolymer containing 3% by weight of ethylene of MI 2 g/10 minutes, measured at 15 230°C under 2.16 kg,

- compatibilising agent: graft copolymer as shown in Table I, prepared according to Example 1 of European Patent Application No. 0,342,066.

In this table:

20 A is a unit derived from propylene
M is a unit derived from ethylene



X is a unit derived from maleic anhydride

P is a caprolactam oligomer of molecular mass 2,700, determined by potentiometric determination of the end amine functional groups.

- 5 b) These compositions are then extruded in the form of a 20- μ m thick film by means of a single-screw extruder at a temperature ranging from 210°C to 230°C.

10 These films are inspected using a scanning electron microscopy (SEM) after cryogenic fracture. (see Table I).

15 Because of the orientation due to the film extrusion, the disperse phase is in the form of small rods which are oriented in the extrusion direction: the size of the small rods is measured on the fractures after dissolving the disperse phase in xylene.

 The assessment of the adhesion between phases is made qualitatively on the fractures.

TABLE I

5	TESTS	COMPOSITION OF THE ALLOY (% by weight)			SEM INSPECTION OF THE ALLOY AS 20- μ m THICK FILM
		EVOH	PP	COMPATIBILI- SING AGENT	
10	1 com- parative	85	15	0	The PP is distri- buted in the EVOH matrix in the form of small cylindrical rods from 0.7 to 5 μ m in cross- section. No adhesion between phases.
15	2 com- parative	80.75	14.25	$A_{663}M_{136}$ $X_{0.65} : 4$ EVOH cont. 29 mol% of ethy- lene: 1	5 The PP is distri- buted in the EVOH matrix in the form of small cylindrical rods from 0.5 to 3 μ m in cross- section. A weak adhesion exists between phases.
20					
25	3	80.75	14.25	$A_{663}M_{136}X_{2.91}$ $P_{0.87} : 5$	The PP is distributed in the EVOH matrix in the form of small cylin- drical rods from 0.1 to 2 μ m in cross-section. A strong adhesion exists between phases.
30	4	85.5	9.5	$A_{663}M_{136}X_{2.91}$ $P_{0.87} : 5$	The PP is distributed in the form of the EVOH matrix in small cylin- drical rods from 0.05 to 1.5 μ m in cross- section. A strong adhesion exists between phases.
35	5 com- parative	9.5	85.5	$A_{663}M_{136}X_{2.91}$ $P_{0.87} : 5$	The EVOH is distributed in the PP matrix in the form of small cylin- drical rods from 0.1 to 2 μ m in cross-section. A strong adhesion exists between phases.
40					
45					

c) Hot water resistance of single-layer films1) Film composition- Example 1 (Comparative)

Composition of the single-layer film: 100 %

5 of ethylene-vinyl alcohol copolymer containing 32 % of ethylene (melt index: 3.2 g/10 minutes, measured at 210°C under 2.16 kg)

- Example 2

Composition of the single-layer film

10 according to the invention: 100 % of the alloy which has the following composition by weight:

EVOH of Example 1: 80.75 %

PP: random ethylene-propylene copolymer
containing 3 % of ethylene (MI: 10-230°C/2.16 kg): 14.25 %
15 compatibilising agent $A_{663}M_{136}X_{2.91}P_{0.87}$: 5 %

- Example 3 (Comparative)

Composition of the single-layer film: 100 %

of ethylene-vinyl alcohol copolymer containing 44 mol% of ethylene (MI: 3.5-210/2.16 kg).

20 - Example 4

Composition of the single-layer film

according to the invention: 100 % of the alloy which has the following weight composition:

EVONH of Example 3 : 80.75 %
 polypropylene of Example 2 : 14.25 %
 compatibilising agent of
 Example 2 : 5 %

5

- Example 5

Film which has the composition of the film of Example 2, but obtained by blow extrusion.

2) Conditions of the hot water behaviour tests

10 The films are stretched in a transparency frame and are then immersed for 30 minutes in a bath of distilled water at constant temperature and gently stirred using a bar magnet.

- Assessment of the results

15 At the end of the test, film appearance and transparency are assessed according to the following arbitrary classification:

<u>Appearance:</u>	A : unchanged	<u>Transparency</u>
	B : streaked	from 1: unchanged
	C : creased	to
	D : holed	4: opaque

20

Thus a film which is unchanged in appearance and opaque will be classified as A4.

The results are listed in Table II

5	<u>EXAMPLES</u>	<u>Water temperature</u> (under 1 bar)	80°C	90°C	95°C
	1 (Comparative)	A1	D4	D4	
	2	A1	B3	C3	
10	3 (Comparative)	A1	A1	D4	
	4	A1	A2	B2	
15	5	A1	A1	A2	

TABLE II

The single-layer films according to the invention - Examples 2, 4 and 5 - exhibit a better behaviour towards hot water than the single-layer films based on EVOH - Examples 1 and 3. The best results are obtained with the alloy based on EVOH containing 32 mol% of ethylene (Example 5).

d) Superheated steam (sterilisation) resistance1) Film composition- Example 6 (Comparative)

Composition of the single-layer film: as

5 Example 1.

- Example 7

Composition of the single-layer film: as

Example 2.

2) - Conditions of the superheated steam10 behaviour tests

The tests carried out at a temperature equal to or higher than 100°C were performed in an autoclave.

The films, stretched in a stainless steel frame (5 x 5 cm), are arranged in the autoclave and
15 subjected for 30 minutes to the test conditions which may take place either in saturated steam or in superheated water.

In the case where the test is carried out using superheated water the water, is preheated in a storage
20 vessel adjoining the autoclave and is then quickly introduced into the autoclave by means of a device designed for this purpose.

In the case of the tests carried out with superheated steam the pressures range from 1 to 3 bars.

25 - Assessments of the results

The arbitrary classification mentioned above in the case of the hot water behaviour tests is employed.

Results

- Temperature of the superheated steam: 120°C

- Example 6 (Comparative) D4

- Example 7 B1

5 e) Resistance of three-layer films to superheated steam

1) Film composition

10 Three-layer films whose composition and thicknesses are listed in Table III are obtained by blow coextrusion.

LAYER COMPOSITION	EXAMPLES	
	8	9
Layer 1 : copolymer X	40 μm	40 μm
Layer 2 : EVOH of Example 3	10 μm	
Layer 2 : alloy of Example 2		10 μm
Layer 3 : copolymer X	40 μm	40 μm

TABLE III

25 In this table, copolymer X denotes a coextrusion binder (propylene-ethylene copolymer grafted with maleic anhydride).

These tests were carried out on a three-layer blow coextrusion equipment.

2) Coextrusion conditions

- Extruder 1 (copolymer X)

5 temperature: 210°C - 230°C

screw speed: 132 rev/min

- Extruder 2 (copolymer X)

temperature: 210°C - 230°C

screw speed: 122 rev/min

10 - Extruder 3 (alloy or EVOH)

temperature: 210°C - 230°C

- Die:

diameter : 150 mm

blow ratio : 8.12

15 temperature : 220°C

- Draw speed: 8.83 m/min

The results are collated in Table IV.

EXAMPLES	Temperature of the superheated steam	120°C	133°C
8		A4	A4
25 9		A2	A3

TABLE IV

f) Resistance of five-layer films to superheated

steam

1) Film composition

Five-layer films whose composition and thicknesses are collated in Table V are obtained by flat coextrusion.

LAYER COMPOSITION	EXAMPLES		
	10	11	12
Layer 1: PP	75 μm	50 μm	50 μm
Layer 2: coextrusion binder	20 μm	10 μm	10 μm
Layer 3: alloy of Example 2	20 μm	10 μm	
Layer 3: EVOH cont. 38 mol% of ethylene			10 μm
Layer 4: coextrusion binder	20 μm	10 μm	10 μm
Layer 5: PP	75 μm	50 μm	50 μm

TABLE V

2) - Coextrusion conditions

These tests were carried out on a five-layer coextrusion equipment.

- Extruder (PP)

temperature: 200°C - 245°C

5

- Extruder (coextrusion binder)

temperature: 220°C - 245°C

- Extruder (EVOH or alloy)

temperature: 215°C - 245°C

- Die

10

gap: 0.7 mm, width 2 m

temperature: 250°C

The results are collated in Table VI.

15	TEMPERATURE OF THE SUPERHEATED STEAM		130°C
	EXAMPLES		
		10	A1
		11	A1
20		12	C4

TABLE VI

The claims defining the invention are as follows:

1. A method of packaging food which method comprises packaging the food in a film which comprises a blend of at least one ethylene-vinyl alcohol (EVOH) copolymer, at least one propylene polymer and at least one compatibilising agent.

2. A method according to claim 1 in which the blend comprises at least 30% by weight of EVOH.

3. A method according to claim 1 or 2 in which the blend comprises:

42.5% to 99.5% by weight of EVOH

0.2% to 42.5% by weight of propylene polymer

0.1% to 15% by weight of compatibilising agent.

4. A method according to any one of claims 1 to 3 in which the compatibilising agent is a graft copolymer of formula AMXP in which:

AM denotes units of a backbone copolymer obtained by copolymerising propylene and one or more α -olefins,

X denotes units derived from citraconic anhydride, fumaric acid, mesaconic acid, the anhydride of 3-allylsuccinic acid or maleic anhydride, and

P denotes units of a polyamide oligomer derived from caprolactam, 11-aminoundecanoic acid or dodecalactam.

5. A method according to any one of claims 1 to 4 in which the molar proportion of ethylene in the EVOH is from 3% to 75%.



6. A method according to claim 5 in which the molar proportion of ethylene in the EVOH is from 10% to 50%.

7. A method of packaging food which comprises packaging the food in a multilayer film comprising at least 5 one layer which is a film as defined in any one of claims 1 to 6.

8. A method according to claim 7 in which the other layer or layers of the film consist of polyethylene, polypropylene, polyamide, polyethylene terephthalate or 10 polycarbonate.

9. A method according to any one of claims 1 to 8 which further comprises subjecting the packaged food to the action of water at 85°C to 100°C or of superheated steam.

10. A method according to claim 1 or 7 wherein 15 the film used is substantially as described in any one of Examples 2, 4, 5 and 7 to 12.

11. Food whenever packaged by the method claimed in any one of claims 1 to 10.

Dated 5 April, 1994
Atochem

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

