

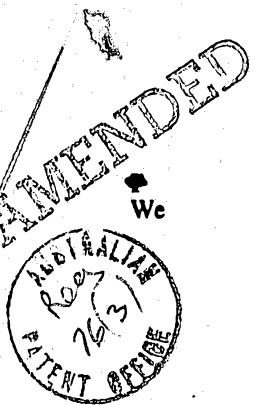
71500/87

COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

607907



We
W. R. Grace & Co.-Conn., of
1114 Avenue of the Americas,
New York,
New York 10036,
United States of America,

hereby apply for the grant of a Standard Patent for an invention entitled:

"MULTILAYER PACKAGING FILM"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

Number

Convention Country

Date

861051993

Europe

15 April, 1986

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 21.12.90

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 22nd day of June, 19 89.

To: THE COMMISSIONER OF PATENTS

Keith Collison
.....
(a member of the firm of DAVIES &
COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
DECLARATION IN SUPPORT OF CONVENTION OR
NON-CONVENTION APPLICATION FOR A PATENT

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

MULTILAYER PACKAGING FILM

I, JULES H. STEINBERG, of W. R. GRACE & CO., of 1114 Avenue of the Americas, New York, New York, 10036, U.S.A., do solemnly and sincerely declare as follows:

1. (a) I am authorized by W. R. GRACE & CO., the applicant for the patent to make this declaration on its behalf.

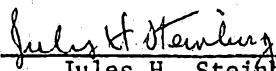
(b) Paolo Botto, Viale Romagna 10, Milano, Italy,
Claudio Freschi, Via Milano 1, Cassina de Pecchi, Milano, Italy
is/~~are~~ the actual inventor... of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The said applicant is the assignee of the
said actual inventors... in respect of the
invention.

2. The basic application... as defined by Section 141 of the Act was made in Europe (EPO) on the 15th April 1986 by W. R. Grace & Co.

3. The aforesaid basic application was/~~was~~ the first application... made in a Convention country in respect of the invention the subject of the application.

Declared at New York, New York, this 17th day of March, 1987.


Jules H. Steinberg
Assistant Secretary

(12) PATENT ABRIDGMENT (11) Document No. AU-B-71500/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 607907

(54) Title
MULTILAYER PACKAGING FILM

International Patent Classification(s)
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(71) Applicant(s)
W. R. GRACE & CO.-CONN.

(72) Inventor(s)
PAOLO BOTTO; CLAUDIO FRESCHI

(74) Attorney or Agent
DAVIES & COLLISON, 1 Little Collins Street, MELBOURNE VIC 3000

(56) Prior Art Documents
AU 37382/85 B32B 27/32
AU 34995/84 B32B 27/32
AU 27775/84 B32B 27/32

(57) Claim

1. A vacuum packaging film comprising at least two coextruded layers of which:

(a) a bonding layer comprises a material selected from the group consisting of olefinic homopolymers and copolymers and ionomers; and

(b) a complementary layer comprises an ethylene vinyl acetate copolymer, wherein the vinyl acetate content is in the 15% to 26% range, by weight, the remainder being ethylene, said film being cross-linked by radiation.

COMMONWEALTH OF AUSTRALIA.

PATENT ACT 1952

COMPLETE SPECIFICATION

(Original)

FOR OFFICE USE

607907

Class

Int. Class

Application Number: 71500/87
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

This document contains the
amendments made under
Section 49 and is correct for
printing.

Name of Applicant: W.R. GRACE & CO. - CONN

Address of Applicant: 1114 Avenue of the Americas,
New York,
New York, 10036,
UNITED STATES OF AMERICA.

Actual Inventor(s): Paolo BOTTO
Claudio FRESCHI

Address for Service: DAVIES & COLLISON, Patent Attorneys,
1 Little Collins Street, Melbourne, 3000.

Complete Specification for the invention entitled:

"MULTILAYER PACKAGING FILM"

The following statement is a full description of this invention,
including the best method of performing it known to us

"MULTILAYER PACKAGING FILM"

This invention relates to a multilayer packaging film for generic use and in particular for vacuum packaging food products.

5 A method of vacuum packaging food products, exemplary of the inventive film application, is the one disclosed in Italian Patent No. 937,557, corresponding to UK Patent No. 1,307,054, or the one disclosed in Italian Patent No. 1,001,879, corresponding to UK Patent No. 1,404,417.

10 Known are multilayer films for packaging food products, in particular from US Patent No. 3,741,253, granted on June 26, 1973, which discloses a film comprising a first layer of a radiated ethylene vinyl acetate copolymer, bonded to an intermediate layer of
15 vinylidene chloride, and a third layer bonded directly to the intermediate layer and formed from a copolymer of ethylene vinyl acetate.

That film cannot, however, be radiated because the intermediate layer of vinylidene chloride tends to
20 release gas while being radiated, and the layer comprised of the ethylene vinyl acetate polymer must be radiated separately from the other layers.

The film is suitable for use in making bags typically utilized to receive food products thereinto,
25 thereafter a vacuum is formed within the bag and clip applied to close it, the filled bag being then immersed in a hot water bath at a temperature approximating the temperature at which the film was stretched.

One of the problems encountered is the unreliable

closure provided by the clip, particularly as the film shrinks around the food product under the heat applied, and the clip tends to be pulled away.

5 US Patent No. 4,469,742 discloses a multilayer film, (inner) A/B/C/D/C/E (outer), where A is a bonding layer comprising an ethylene-propylene copolymer; B is a shrinking layer which may be formed from an ethylene vinyl acetate copolymer having a vinyl acetate content in the range of 6% to 12% by weight, preferably of 6%:
10 C are adhesive layers effective to join the barrier layer D to the remainder of the film. The layer D is formed from a copolymer of ethylene vinyl acetate hydrate (EVOH). The outer layer E isolates the barrier layer against contact with outside moisture and
15 comprises an ethylene vinyl acetate copolymer having a vinyl acetate content ranging from 5% to 12%, preferably of 6%, by weight.

It has been ascertained in actual practice that in the course of the vacuum packaging process,
20 conventional films tend to be broken when subjected to high stretch ratios at particular projections or recesses randomly arranged on the material being packaged.

~~Accordingly, an object of this invention is to~~
25 provide a suitable film for vacuum packaging food products, which exhibits high mechanical strength properties even at high stretch ratios, thereby it can conform to the shape of the product being packaged by deformation without breaking.

~~Another object of the invention is to provide a~~



The present invention provides a vacuum packaging film comprising at least two coextruded layers of which:

(a) a bonding layer comprises a material selected from the group consisting of olefinic homopolymers and copolymers and ionomers; and

(b) a complementary layer comprises an ethylene vinyl acetate copolymer, wherein the vinyl acetate content is in the 15% to 26% range, by weight, the remainder being ethylene, said film being cross-linked by radiation.

Preferably said bonding layer comprises a material selected from the group consisting of low density polyethylene, high density polyethylene, linear low density polyethylene, ethylene vinyl acetate copolymer with a vinyl acetate content of 3% to 9% by weight, ionomer, and mixtures thereof.

Of preference, that bonding layer is selected from low-density polyethylene, high-density polyethylene, and a mixture thereof.

More preferably, the bonding layer is formed essentially from low-density polyethylene.

In a first embodiment, the film comprises two coextruded layers only: the bonding layer and the complementary layer, and is intended for use in packaging food products which require no oxygen barrier.

In a variation of the first embodiment, the film comprises an outer layer coextruded with the bonding layer and the complementary layer, said outer layer being provided outwardly on the remote side from said bonding layer, said outer layer comprising a material selected from the group consisting of low density polyethylene, high density polyethylene, linear low density polyethylene, ethylene vinyl acetate copolymer with a vinyl acetate content of 3% to 9% by weight, ionomer, and mixtures thereof.

Of preference, the outer layer comprises a material



selected from: low-density polyethylene, high-density polyethylene, and a material yielded by mixing them together.

5 More preferably, the outer layer is formed essentially from low-density polyethylene.

10 In a second embodiment, the film comprises an oxygen barrier layer. That second embodiment is specially suitable for packaging applications with food products which require preservation against the oxidizing action of air oxygen.

15 In particular, the barrier layer is placed between the complementary layer and the outer layer, and is joined to the nearby layers by two adhesive layers. The barrier layer preferably comprises an ethylene-vinyl alcohol copolymer.

20 This second embodiment envisages preferably a double complementary layer. In this case, the sequence for the co-extruded layers would be, from the inside out: a bonding layer, a complementary layer, an adhesive layer, a barrier layer, an adhesive layer, a complementary layer, an outer layer.

25 The adhesive layers are preferably formed in general from an ethylene vinyl acetate copolymer suitable for cross-linking by radiation and being chemically modified to accept functional groups having great affinity for the ethylene-vinyl alcohol copolymer that forms the barrier layer. Suitable commercially available adhesives are identified by the trade names of Bynel 3095, Plexar PX3.

30 Accordingly, the present invention also provides a vacuum packaging film comprising the following successive coextruded layers;

(a) a bonding layer comprising a material selected from the group consisting of olefinic homopolymers and copolymers and ionomers;

35 (b) a complementary layer comprising an ethylene vinyl acetate copolymer wherein the vinyl acetate content



is in the 9% to 26% range, by weight, the remainder being ethylene said Film being cross-linked by radiation;

(c) an adhesive layer;

(d) an oxygen barrier layer;

5 (e) a second adhesive layer;

(f) a second complementary layer comprising an ethylene vinyl acetate copolymer wherein the vinyl acetate content is in the 9% to 26% range, by weight, the remainder being ethylene; and

10 (g) an outer layer comprising a material selected from the group consisting of low density polyethylene, high density polyethylene, linear low density polyethylene, ethylene vinyl acetate copolymer with a vinyl acetate content of 3% to 9% by weight, ionomer, and
15 mixtures thereof.

Irrespective of the embodiment of choice, the combined thickness of the stretched layer or layers will preferably be 35% to 75% of the overall thickness of the film and more preferably from 50% to 65% of the overall
20 film thickness. The film overall thickness ranges from 50 μ to 300 μ , preferably from 80 to 200 μ , and still better from 120 μ to 150 μ .

The thickness of the bonding layer and/or thickness of the outer layer preferably amount to $3\frac{1}{10}$ to 25% of the
25 overall thickness of the film.

The bonding layer and/or outer layer are preferably formed from low-density polyethylene and preferably have a thickness dimension amounting to $3\frac{1}{10}$ to 10% of the overall
30 thickness of the film.

The film according to the invention can be obtained by a method which allows to improve the formability and abuse resistance of a known multi-layer, coextruded, thermoplastic packaging film, which has layers of ionomer, EVOH, low density polyethylene and high density
35 polyethylene. Such improvement is obtained replacing the low density polyethylene layers with ethylene vinyl



acetate copolymer layers having a vinyl acetate content in the range of 12% to 26%.

5 The entire coextruded multi-layer film is then irradiated with ionizing radiation to induce cross-linking in the ethylene polymers and copolymers.

The radiation level is preferably lower than 20 MRads, more preferably is in the 8 to 16 MRad range, and most preferably in the 12 to 14 MRad range.



of the film.

The film according to the invention is obtained by a method which allows to improve the formability and abuse resistance of a known multi-layer, coextruded, thermoplastic packaging film, which has layers of ionomer, EVOH, low density polyethylene and high density polyethylene. Such improvement is obtained replacing the low density polyethylene layers with ethylene vinyl acetate copolymer layers having a vinyl acetate content in the range of 12% to 26%.

The entire coextruded multi-layer film is then irradiated with ionizing radiation to induce cross-linking in the ethylene polymers and copolymers.

The radiation level is lower than 20 MRads, preferably is in the 8 to 16 MRad range, still better preferably in the 12 to 14 MRad range.

The invention will be more clearly understood from the Examples and the drawing herewith, given by way of illustration and not of limitation of this invention.

Table 1 shows examples 1-8, wherein examples 1 and 2 are conventional comparative Examples and Examples 3-8 illustrate the inventive film. Abbreviations are standard in the art, as follows.

LDPE = Low-Density Polyethylene:

HDPE = High-Density Polyethylene:

LLDPE = Linear Low-Density Polyethylene; and

EVA = Ethylene Vinyl Acetate Copolymer.

The last column in the Table (Hole Area) relates to the results of a specially meaningful test to an understanding of this invention objectives. The holes



whose areas have been set forth therein are shown in Figure 1, which depicts a wooden block 1, drilled and vacuum packaged. The film 6 completely envelops the block 1, and of course, also covers the ports of the circular holes 2,3,4, and 5. The depth dimension is the same for all the holes but the area of each hole port increases progressively.

During the packaging tests with the wooden block 1, the film tends to undergo a stretching stress which is the higher the larger is the area of a hole. In the Example considered in Figure 1, the film 7,8,9 stretches without breaking over the holes 2,3 and 4, but breaks in 10, over the largest area hole 5. The area of the largest hole before the film becomes broken is entered, therefore, in the last column of Table 1, and is highly representative of the film packaging ability.

The packaging tests on the block 1 were conducted throughout examples 1-8 on a Cryovac VS44 machine equipped with a rotary vacuum pump and a serially connected auxiliary pump. The temperature under the heater bell was of 200°C, and the films were infrared pre-heated up to 70-80°C. The level of the vacuum provided varied between 3 and 6 millibars.

As can be taken from Table 1, with specific reference to examples 5,6,7 and 8, the inventive film affords breakage-free packaging of holes having a section area which is about seven times as large as those of the comparative films in Examples 1 and 2.

EXAMPLE	bonding layer Thickness in microns	Stretched layer Thickness in microns	Adhesive layer Thickness in microns	Barrier layer Thickness in microns	Adhesive layer Thickness in microns	Stretched layer Thickness in microns	Outer layer Thickness in microns	Overall Thickness (microns)	Radiation (MRad)	Hole area (mm ²)
1 Comparison	Ionomer — 18	LDPE — 29	Modified EVA — 5	Ethylene- -Vinyl Alcohol Copolymer — 7	Modified EVA — 5	LDPE — 29	HDPE — 7	100	12	50,3
2 Comparison	Ionomer 27	LDPE 47	Mod.EVA 7	do. 11	Mod.EVA 7	LDPE 40	HDPE 11	150	12	50,3
3	Ionomer (surlyn 1702) — 18	EVA 9% VA — 30	Mod.EVA — 5	do. — 7	Mod.EVA — 5	EVA 9% VA — 30	HDPE — 7	102	12	153,9
4	Ionomer (surlyn 1702) — 18	EVA 18% VA — 30	Mod.EVA — 5	do. — 7	Mod.EVA — 5	EVA 18% VA — 30	HDPE — 7	102	12	201
5	Ionomer (surlyn 1702) — 7	EVA 18% VA — 52	Mod.EVA — 5	do. — 9	Mod.EVA — 5	EVA 18% VA — 26	HDPE — 26	130	12	380,1

TABLE 1

14 00 71000

Sample	Bonding Layer Thickness in microns	Stretched Layer Thickness in microns	Adhesive Layer Thickness in microns	Barrier Layer Thickness in microns	Adhesive Layer Thickness in microns	Stretched Layer Thickness in microns	Outer Layer Thickness in microns	Overall Thickness (Microns)	Radiation (MRad)	Hole Area (mm ²)
6	LDPE — 8	EVA 18% VA — 59	Mod.EVA — 3	do. — 7	Mod.EVA — 3	EVA 18% VA — 45	HDPE — 25	— 150	— 12	— 380,1
7	HDPE — 25	EVA 18% VA — 45	Mod.EVA — 3	Ethylene-Vinyl Alcohol Copolymer — 7	Mod.EVA — 3	EVA 18% VA — 59	Ionomer — 8	— 150	— 12	— 314,2
8	LDPE — 25	EVA 18% VA — 45	Mod.EVA — 3	do. — 7	Mod.EVA — 3	EVA 18% VA — 59	LDPE — 8	— 150	— 12	— 380,1

TABLE 1 (Cont.)

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A vacuum packaging film comprising at least two coextruded layers of which:

(a) a bonding layer comprises a material selected from the group consisting of olefinic homopolymers and copolymers and ionomers; and

(b) a complementary layer comprises an ethylene vinyl acetate copolymer, wherein the vinyl acetate content is in the 15% to 26% range, by weight, the remainder being ethylene, said film being cross-linked by radiation.

2. The film according to claim 1, characterised wherein said bonding layer comprises a material selected from the group consisting of low density polyethylene, high density polyethylene, linear low density polyethylene, ethylene vinyl acetate copolymer with a vinyl acetate content of 3% to 9% by weight, ionomer, and mixtures thereof.

3. The film according to claim 1, further comprising an outer layer coextruded with the bonding layer and the complementary layer, said outer layer being provided outwardly on the remote side from said bonding layer, said outer layer comprising a material selected from the group consisting of low density polyethylene, high density polyethylene, linear low density polyethylene, ethylene vinyl acetate copolymer with a vinyl acetate content of 3% to 9% by weight, ionomer, and mixtures thereof.

4. The film according to claim 3, wherein an oxygen barrier layer is provided between said complementary layer and said outer layer.



5. The film according to claim 3, wherein said barrier layer is joined to the complementary and outer layers by means of two adhesive layers.

6. A vacuum packaging film comprising the following successive coextruded layers;

(a) a bonding layer comprising a material selected from the group consisting of olefinic homopolymers and copolymers and ionomers;

(b) a complementary layer comprising an ethylene vinyl acetate copolymer wherein the vinyl acetate content is in the 9% to 26% range, by weight, the remainder being ethylene said film being cross-linked by radiation;

(c) an adhesive layer;

(d) an oxygen barrier layer;

(e) a second adhesive layer;

(f) a second complementary layer comprising an ethylene vinyl acetate copolymer wherein the vinyl acetate content is in the 9% to 26% range, by weight, the remainder being ethylene; and

(g) an outer layer comprising a material selected from the group consisting of low density polyethylene, high density polyethylene, linear low density polyethylene, ethylene vinyl acetate copolymer with a vinyl acetate content of 3% to 9% by weight, ionomer, and mixtures thereof.

7. A vacuum packaging film substantially as hereinbefore described with reference to the Examples 3 to 8 and/or accompanying drawings.



- 12 -

8. A method for the production of a vacuum packaging film substantially as hereinbefore described with reference to the Examples 3 to 8 and/or accompanying drawings.

DATED this 16th day of October, 1990.

W.R.GRACE & CO.-CONN

By its Patent Attorneys:

DAVIES & COLLISON



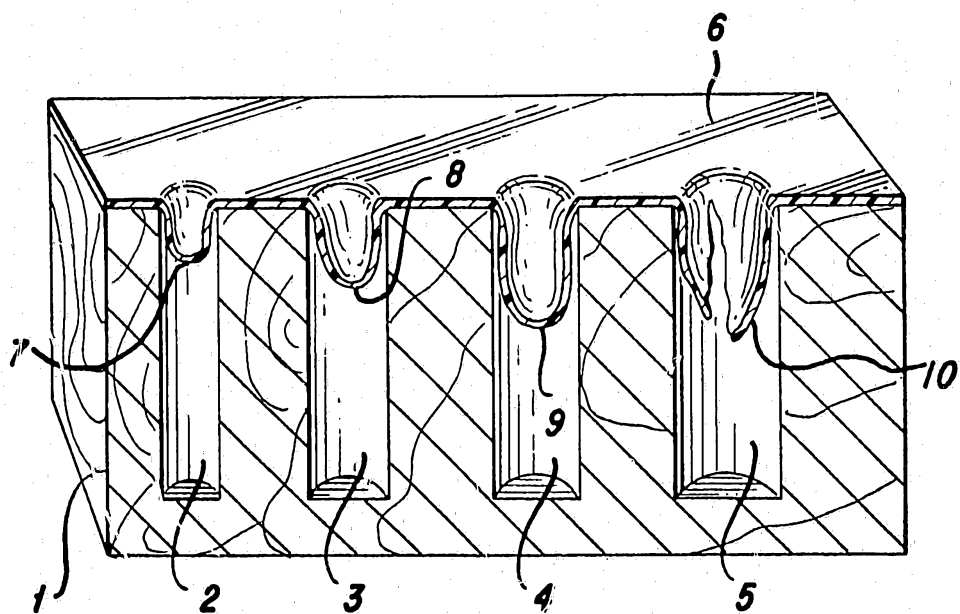


Fig. 1