INSTRUCTIONS

(a) If Convention application insert "Convention"

67 6004 (a) CONVENTION

AUSTRALIA

Patents Act 1990

REQUEST FOR A (b) STANDARD/~~PETTY~~ PATENT

(b) Delete one

(c) Insert FULL name(s) of applicant(s)

I/We being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying Standard/~~Petty~~ Complete Patent Specification.

I ~~am~~/We are (b) not an opponent or eligible person described in Sections 33-36 of the Act.

[70,71] Applicant and Nominated Person (c): EMS-INVENTA AG

(d) Insert FULL address(es) of applicant(s)

of (d) Selnaustrasse 16, CH-8001 Zurich, Switzerland

(e) Insert TITLE of invention

[54] Invention Title (e) ~~BARRIER LAYER OF TRANSPARENT~~ COPOLYAMIDE FOR USE IN A BARRIER LAYER.

(f) Insert Names of actual Inventors.

[72] Names of Actual Inventors (f)

Ulrich Presenz

Manfred Hewel

[74] Address for Service: PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia 3000
Attorney Code: PO

(Note: The following applies only to Convention applications)

Basic Convention Application Details

(g) Insert number, country and filing date for the/or each basic application

(g)	[31] Application No.	[33] Country	Country Code	[32] Date of Application
	P 43 09 534.8	Germany	DE	24 March 1993

(h) Signature of applicant(s) (For body corporate see headnote*)

(i) Insert date of signing

(j) Corporate seal if any

(j)

Note: No legalization or other witness required

SCHULZE, Dr. Walter-Joachim ENZINGER Hans Ulrich
Holder of procuration (h) Signature of Applicant President (i) Date Zürich, Febr. 28. 1994

PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia

DB 4447 230394

P17/5/91

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

INSTRUCTIONS
(a) Name of person making statement.

I (a) SCHULZE, Dr. Walter-Joachim
Enzinger, Hans-Ulrich

(b) Position of that person.

(b) Holder of procuration
President

(c) Name of applicant

of (c) Ems-INVENTA AG

(d) Address of applicant

of (d) Selnaustrasse 16
CH-8001 Zürich

State the following:-

(e) Delete as necessary

1. The nominated person (applicant) is entitled to the grant of a patent
(e) (i) as assignee of the actual inventor(s)
~~(ii) by contract of employment of the actual inventor(s)~~
or (iii) (f)

(f) Insert details if not covered by (i) or (ii)

(g) Delete as necessary

2. The nominated person (applicant) is entitled to claim priority from the basic convention application(~~s~~).
(g) (i) as applicants of the said application(~~s~~)
~~(ii) as the assignees of the applicants of the said application(s)~~
~~(iii) with the consent of the applicants of the said application(s)~~

(h) Delete for non-convention applications

3. The basic convention application(~~s~~) was/~~were~~ the first made in a Convention country in respect of the invention the subject of the application. (h)

(i) Insert DATE of signing

Dated (i)

(j) Zürich, February,28 1994

(j) Signature(s) of person making statement

SCHULZE, Dr. Walter-Joachim ENZINGER Hans-Ulrich

Note: No legalization or other witness required

To: The Commissioner of Patents

PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia

P18/3/91

AU9457995

(12) PATENT ABRIDGMENT (11) Document No. AU-B-57995/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 676004

(54) Title
COPOLYAMIDE FOR USE IN A BARRIER LAYER

International Patent Classification(s)
(51)[5] C08G 069/26

(21) Application No. : 57995/94 (22) Application Date : 23.03.94

(30) Priority Data

(31) Number	(32) Date	(33) Country
4309534	24.03.93	DE GERMANY

(43) Publication Date : 29.09.94

(44) Publication Date of Accepted Application : 27.02.97

(71) Applicant(s)
EMS-INVENTA AG

(72) Inventor(s)
ULRICH PRESENZ; MANFRED HEWEL

(74) Attorney or Agent
PHILLIPS ORMONDE & FITZPATRICK , 367 Collins Street, MELBOURNE VIC 3000

(56) Prior Art Documents
EP 409660
EP 457958

(57) It is the object of this invention to overcome the disadvantages of prior art. A special barrier characteristic is additionally required for barrier substances used in the field of cheese packaging. The ratio of carbon dioxide barrier to oxygen barrier must lie in the range of 3:1 to 5:1 or higher.

These objects are attained by means of the copolymers of the prese it invention, barrier layers made from said copolymers and multi-layer structures including such barrier layers.

An inherent property of the copolyamide of this invention is that it has a ratio of carbon dioxide to oxygen barrier values of at least 3:1. The copolyamide may be used in a barrier layer which may be advantageously employed in the food industry in multi-layer structures ~~compounds~~ such as multi-ply films for packaging cheese and products containing cheese.

Claim

1. A copolyamide for barrier layers consisting of the following components:

I Between 15-75 mol% of hexamethylenediamine and adipic acid;

II Between 15-65 mol% of

(a) hexamethylenediamine and azelaic acid; or

(b) hexamethylenediamine and sebacic acid;

. . ./2

or a combination thereof; and

III Between 10-70 mol% of

(a) hexamethylenediamine and isophthalic acid; or

(b) hexamethylenediamine and terephthalic acid;

or a combination thereof,

with the total quantity of the components I, II and III being 100 mol% and wherein the ratio of the diamine and acid in each component is approximately equimolar.

5. A barrier layer structure suitable for multi-ply ~~compounds~~ structures characterised in that it includes a copolyamide according to any one of claims 1 to 4~~, and has a carbon dioxide to oxygen barrier ratio of at least 3:1~~.

6. A multi-layer structure including a barrier layer according to claim 5.

AUSTRALIA

Patents Act

COMPLETE SPECIFICATION
(ORIGINAL)

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority

Related Art:

Name of Applicant:

Ems-Inventa AG

Actual Inventor(s):

Ulrich Presenz
Manfred Hewel

Address for Service:

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne 3000 AUSTRALIA

Invention Title:

~~**BARRIER LAYER OF TRANSPARENT**~~ A **COPOLYAMIDE** FOR USE IN A BARRIER LAYER

Our Ref : 359733
POF Code: 3856/3856

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

The subject matter of the present invention is a barrier layer of transparent copolyamide, which is used in multi-layer structures, such as multi-ply films useful for cheese packaging.

Multi-layer structures containing polyvinylidene compounds are currently prevalent in the packaging industry. Examples that might be cited are: European Patent 369,808, US Patent 4,424,243 and US 4,801,486. The main drawback of polyvinylidene chloride, in addition to being difficult to process and having a strong corroding effect on processing machines, is the environmental impact its disposal has due to the release of chloride and the possible formation of dioxins.

European Patent Application 409660 claims copolyamide compositions polymerized from isophthalic acid, adipic acid, alternatively terephthalic acid, hexaminethylene diamine and m-xylylene diamine having good gas-barrier properties. Nevertheless the specification does not show how a carbon dioxide barrier to oxygen barrier ratio higher than 3:1 can be achieved and how the effect of humidity on these resistances can be minimised.

According to EP 457,598, the use of a copolyamide 6/12 has also become known recently. One great disadvantage of this material relates to its oxygen barrier ability, which is affected by environmental humidity and decreases as the humidity increases.

However, the field of packaging is in need of a barrier substance that demonstrates good processing properties, does not have any corrosive properties, is halogen free, and whose capability as a barrier does not deteriorate if moisture is absorbed.

Blends having three or more components, and preferably, partly aromatic polyamides, allow relatively good barrier properties to be obtained. The disadvantages of the blends by comparison with copolyamides are problems with granulation, the great expense of testing each separate component, and the additional extrusion step, which increases production cost considerably, adding to the significantly higher costs of raw material.

It is the object of this invention to overcome the disadvantages of prior art. A special barrier characteristic is additionally required for barrier substances used in the field of cheese packaging. The ratio of carbon dioxide barrier to oxygen barrier must lie in the range of 3:1 to 5:1 or higher.

These objects are attained by means of the copolymers of the present invention, barrier layers made from said copolymers and multi-layer structures including such barrier layers.

An inherent property of the copolyamide of this invention is that it has a ratio of carbon dioxide to oxygen barrier values of at least 3:1. The copolyamide may be used in a barrier layer which may be advantageously employed in the food industry in multi-layer structures ~~compounds~~ such as multi-ply films for packaging cheese and products containing cheese.

~~of cheese packaging. The ratio of carbon dioxide barrier to~~ oxygen barrier must lie in the range of 3:1 to 5:1 or ~~higher~~.

These objects are attained by means of the copolymers of the present invention, barrier layers made from said copolymers and multi-ply films including such barrier layers.

The object is especially attained by means of a barrier layer whose ratio ~~of~~ carbon dioxide to oxygen barrier values is at least 3:1 and which may be advantageously employed in the ~~food~~ industry in multi-ply compounds for packaging cheese ~~and products containing cheese.~~

The barrier layers according to the invention are copolyamide films characterized by good biaxial stretchability, high shrinkage of the stretched material, a high degree of transparency, sufficient flexibility and compatibility. They may be produced without problems by coextrusion in combination with other layers of thermoplastically processable polymers, for example, supporting layers, sealing layers or protective layers, and may be used as multi-ply ~~compounds~~ structures.

In accordance with the present invention there is provided a copolyamide for barrier layers including the following components:

I Between 15-75 mol% of hexamethylenediamine and adipic acid;

II Between 15-65 mol% of

(a) hexamethylenediamine and azelaic acid; or

(b) hexamethylenediamine and sebacic acid;

or a combination thereof; and

III Between 10-70 mol% of

(a) hexamethylenediamine and isophthalic acid; or

(b) hexamethylenediamine and terephthalic acid;

or a combination thereof,

with the total quantity of the components being 100 mol% and wherein the ratio of the diamine and acid in each component is approximately equimolar.

A preferred composition comprises

15-60 mol% of I;

15-55 mol% of IIa and/or IIb;

10-45 mol% of IIIa and/or IIIb

More preferably the composition comprises

35 to 55 mol% of I;

15 to 55 mol% of IIa or IIb;

10 to 30 mol% of IIIa or IIIb.

The components add up to a total of 100 mol%, respectively. As the person of skill in the art knows, acid and diamine must be present at a nearly equimolar ratio.

The copolyamides according to the invention may contain, among others, common prior art additives such as chain regulators, stabilisers, anti-foaming agents, crystallisation accelerators.

The production of copolyamides according to the invention is accomplished in a known manner using the melt-condensation method.

Depending on use, the preferred range of relative viscosity of the copolyamide according to the invention (measured as a 0.5% solution in m-cresol at 20°C) lies between 1.75 and 2.50. However, both higher and lower degrees of viscosity may be used without problems.

The production of barrier layers, for example, for testing and examination purposes is accomplished in a known manner by means of film-blowing extrusion.

If required, different prior art barrier layers and a plurality of further prior art polymer layers may be used for a multi-layer structure incorporating a layer according to the present invention. Other preferred polymer layers are prior art protective and supporting layers which give defined functional characteristics to the multi-layer structure. Known sealing layers may be used in order to render the multi-layer structure sealable by means of hot sealing. Known layers of adhesion promotors may also be used advantageously.

Preferred polymers for protective and supporting layers are those made of polyamides, polyolefins or polyesters.

Advantageous adhesion promotor layers are functionalised polyolefins, ie., they are provided with functional groups. Preferred sealing layers consist of low-melting polymers. So called ionomers are preferred. Multi-layered structures that may include a barrier layer of this invention include:-

Multi-layered packaging films;

Multi-layered bags;

Multi-layered shrink bags;

Multi-layered bottles;

Multi-layered cardboard;

Multi-layered cups;

Multi-layered trays;

Multi-layered containers.

Such multi-layered structures can be formed by:-

Injection moulding;

Extrusion to films, sheets, tubes;

Blow moulding (extrusion, injection or injection stretch blow moulding);

Deep drawing;

Lamination;

Coating;

or other common processing methods used in the production of thermoplastic material.

The Examples ~~elucidate~~ illustrate the invention without limiting it.

Table 1:

The composition of the barrier layers in Examples 1-3.

Composition of Copolyamides in Barrier Layers				
Example No.	I Mol%	IIa Mol%	IIIa Mol%	IIIb Mol%
1	38	52	10	--
2	55	15	30	--
3	38	52	--	10

IIIa hexamethylenediamine and isophthalic acid;

IIIb hexamethylenediamine and terephthalic acid.

Table 2:

Barrier behavior at 0 and 85% relative humidity

Example No.	Environ. Humidity	Barrier Behavior*		Ratio ***
		Oxygen**	Carbon dioxide**	
1	0% rH	65	204	3.1
	85% rH	40	469	11.7
2	0% rH	48	144	3.0
	85% rH	24	209	8.7
3	0% rH	75	228	3.0
	85% rH	45	363	8.1
Comparative Example	0% rH	120	400	3.3
	85% rH	200	800	4.0

* Blown film thickness 50 µm

** cm^3/m^2 day bar

Measuring devices: 85% rH Mocon Oxtran Twin

0% rH Lissy L 100

*** Ratio of carbon dioxide to oxygen barrier

(rH: relative humidity)

Comparative Example:

Copolyamide CF 6S (Ems-Chemie AG, Zurich) a copolyamide on a Caprolactam and Laurinlactam base.

The barrier layers according to the invention in Example 1-3 are significantly improved oxygen barriers with respect to the comparative example and have essentially better carbon dioxide to oxygen barrier ratios.

In the field test packaged cheese was stored in a cooling chamber and packaged in a film material. The film material containing the copolyamide from Example No. 1 proved to be most successful. After six months' storage, no mildew formed and no swelling occurred due to the carbon dioxide formed during ripening of cheese.

Table 3 is a comparison of a commercially used cheese package having polyvinylidene chloride as a barrier layer and a multi-layer structure according to the invention containing the copolyamide from Example No. 1 as a barrier layer in combination with an inner ionomer sealing layer, an outer protective layer of polyolefin, and two adhesive layers surrounding the barrier layer.

Table 3:

Multi-layer packaging films:

Barrier Layer		Barrier Behaviour		Ratio
Type	Thickness µ	Oxygen**	Carbon-dioxide **	***
PVDC	10	160/175	800/800	5 to 4.6
Example 1	10	208/207	1323/26100	6.4 to 12.6

** cm^3/m^2 day bar
0% rH /85 % rH
Measuring devices: 85% rH Mocon Oxtran Twin
0% rH Lissy L 100

*** Ratio of carbon dioxide to oxygen barrier.

The multi-layer structure having the copolyamide barrier according to the invention is a sufficient oxygen barrier and has an excellent barrier ratio of carbon dioxide to oxygen.

\ special advantage of using copolyamides as barrier substances compared to compounds containing polyvinylidene chloride is that their oxygen barrier capabilities are not affected by environmental humidity. Further advantages are good flexibility, the lack of corrosive properties and, above all, freedom from release of halogens.

The oxygen barrier capabilities of the copolyamide barrier layers according to the invention may be further improved in the dry state by adding known nucleation substances, for example, polyamide 22 or mineral nucleation substances such as talc. The commonly known nucleation substances are used in commonly known concentrations. Moreover, due to this measure, a stable barrier level is more rapidly obtained after film extrusion.

The claims defining the invention are as follows:

1. A copolyamide for barrier layers consisting of the following components:

I Between 15-75 mol% of hexamethylenediamine and adipic acid;

II Between 15-65 mol% of

(a) hexamethylenediamine and azelaic acid; or

(b) hexamethylenediamine and sebacic acid;

or a combination thereof; and

III Between 10-70 mol% of

(a) hexamethylenediamine and isophthalic acid; or

(b) hexamethylenediamine and terephthalic acid;

or a combination thereof,

with the total quantity of the components I, II and III being 100 mol% and wherein the ratio of the diamine and acid in each component is approximately equimolar.

2. A copolyamide according to claim 1, characterized in that the copolyamide consists of the following components:

15 to 60 mol % of component I;

15 to 55 mol % of component II; and

10 to 45 mol % of component III.

3. A copolyamide for barrier layers according to claim 2, characterized in that the copolyamide consists of the following components:

35 to 55 mol % of component I;

15 to 55 mol % of component II consisting of either (a) or (b); and

10 to 30 mol % of component III consisting of either (a) or (b).

4. A copolyamide according to any one of claims 1 to 3 characterized in that said copolyamide has a relative viscosity between 1.75 and 2.50 measured as a 0.5 % solution in m-cresol at 20°C.

5. A barrier layer structure suitable for multi-ply ~~compounds~~ structures characterised in that it includes a copolyamide according to any one of claims 1 to 4~~, and has a carbon dioxide to oxygen barrier ratio of at least 3:1.~~

6. A multi-layer structure including a barrier layer according to claim 5.

7. A multi-layer structure according to claim 6 produced by means of coextrusion.

8. A multi-layer structure according to claims 6 or 7 characterized in that at least one barrier layer is combined with at least one further polymer layer selected from adhesive layers, supporting layers, protective layers and sealing layers.

9. A multi-layer structure according to any one of claims 6 to 8 including at least one further supporting layer selected from polyamide, polyolefin, ionomer polyolefin and polyester groups.

10. A multi-layer structure according to any one of claims 6 to 9 wherein the multi-layer structure is a film.

11. A copolyamide according to claim 1 substantially as herein before described with reference to the examples.

12. A multi-layer structure according to claim 6 substantially as hereinbefore described with reference to the examples.

DATED: 19 July, 1996

PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

EMS-INVENTA AG

ABSTRACT

The invention relates to a barrier layer for multi-layer compounds characterized in that it is made of a transparent copolyamide consisting of the following components:

I Between 15-75 mol% of hexamethylenediamine and adipic acid;

II Between 15-65 mol% of

(a) hexamethylenediamine and azelaic acid; or

(b) hexamethylenediamine and sebacic acid;

or a combination thereof; and

III Between 10-70 mol% of

(a) hexamethylenediamine and isophthalic acid; or

(b) hexamethylenediamine and terephthalic acid;

or a combination thereof,

with the total quantity of the components being 100 mol%. The ratio of the barrier effects in the barrier layer of the present invention with respect to carbon dioxide and oxygen is at least 3:1.