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(21) International Application Number: PCT/EP91/01443 (22) International Filing Date: 1 August 1991 (01.08.91) (30) Priority data: 67634 A/90 9 August 1990 (09.08.90) IT (71) Applicant: BUTTERFLY S.R.L. [IT/IT]; Via XIII Giugno, 8, I-48100 Ravenna (IT). (72) Inventors: BASTIOLI, Catia ; Via della Noce, 63, I-28100 Novara (IT). BELLOTTI, Vittorio ; Via Mora e Gibin, 9, I-28010 Fontaneto d'Agogna (IT). ROMANO, Giancarlo ; Via Rosmini, 18, I-28100 Novara (IT). TOSIN, Maurizio ; Via San Giacomo, 6, I-13037 Serravalle Sesia (IT).		(74) Agents: RAMBELLI, Paolo et al.; Jacobacci-Casetta & Perani S.p.A., Via Alfieri, 17, I-10121 Torino (IT). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), + NO, SE (European patent), SU. Published <i>With international search report.</i>
(54) Title: A LAMINATED FILM WITH A STARCHY MATRIX AND LOW PERMEABILITY AND METHODS FOR ITS PRODUCTION (57) Abstract A laminated film including at least one first layer of a polymeric material which has a starchy matrix and is insoluble in water or at most expands in water, constituted by destructured starch and an olefinic copolymer and a second layer of a hydrophobic material adhering to the first. Applications are for the packaging of food products and for colostomy containers, for which a very effective barrier against gases and vapours is needed.		

+ DESIGNATIONS OF "SU"

It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

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A laminated film with a starchy matrix and low permeability and methods for its production

The present invention relates in general to biodegradable films based on starchy materials and in particular to a film which is substantially insoluble in water and suitable for forming an effective barrier against liquids, gases and vapours, at least for a certain period of time, and which at the same time is rapidly biodegradable after use.

Patent application No. EP-A-0 327 505 describes polymeric materials based on destructured starch and a synthetic thermoplastic polymeric material, which are useful, in particular, for the production of moulded articles having better dimensional stability after exposure to moisture than corresponding articles made of starch alone.

More specifically, as regards the production of films, self-supporting and biodegradable flexible films formed from compositions including starchy substances and an ethylene-acrylic acid copolymer are known from EP-A-0 032 802.

The Applicant's European patent No. 90011070.1 describes biodegradable films formed from compositions including starchy substances and an ethylene-vinyl alcohol copolymer.

These films have good resistance to tearing and to dissolving in the presence of water and can thus be used to replace conventional, non-biodegradable synthetic plastics materials for a wide range of applications. In the presence of water, however, the films tend to swell so that their properties as barriers against the diffusion of gases and vapours are seriously compromised, precluding

their use in some applications for which this property is important.

It has been found that films with starchy matrices of the type mentioned above can be coated with a hydrophobic material which forms an effective barrier and that the layers of starch-based and hydrophobic materials show good mutual adhesion. It is thus possible to produce a laminated film which is suitable for applications in which an effective barrier against gases and liquids is of critical importance.

A first subject of the invention is a laminated film, characterised in that it includes at least one first layer of a polymeric material which has a starchy matrix and is substantially insoluble in water or at most expands in water, and a second layer of a hydrophobic material adhering to the first.

A polymeric material which has a starchy matrix and is substantially insoluble in water but which at most expands in water, is intended to mean a material which can absorb quantities of water of no more than 40g per 100g of the material itself at ambient temperature without dissolving.

Materials suitable for use as the first layer with a starchy matrix include polymeric blends which are obtainable by the fusion of a starch and a synthetic thermoplastic polymer in the presence of water or a plasticiser with a high boiling point under temperature and pressure conditions suitable for producing a homogeneous melt which can be processed as a thermoplastic material.

The synthetic polymeric component includes polymers and

copolymers of at least one ethylenically insaturated monomer, the polymer or copolymer having repeating units provided with at least a polar group such as hydroxy, alkoxy, carboxy, carboxyalkyl, alkyl carboxy and acetal.

Preferred polymeric components include polyvinyl alcohol and copolymers of an olephin selected from ethylene, propylene, isobutene and styrene with acrylic acid, vinyl alcohol and/or vinyl acetate and mixtures thereof.

The preferred synthetic polymers are ethylene copolymers selected from the group consisting of ethylene-vinyl alcohol, ethylene-acrylic acid, ethylene-vinyl acetate, terpolymers of ethylene-vinyl acetate and vinyl alcohol which can be produced, for example, by the partial hydrolysis of ethylene-vinyl acetate and ethylene-vinyl alcohol copolymers modified by the partial replacement of the functional alcohol groups by oxo or alkylcarbonyl groups.

Preferred ethylene-vinyl alcohol copolymers have ethylene contents of from 10 to 90% by weight, preferably from 10 to 40% by weight (15-50% in moles) and most preferably from 30 to 45% in moles, with a melt flow index between 2 and 50 and preferably between 6 and 20 (210°C, 2.16 Kg). Further preferred characteristics of the polymers are:

- | | |
|--|-----------|
| - intrinsic viscosity (in DMSO at 30°C) | 0.50-0.9 |
| and preferably | 0.65-0.80 |
| - molecular weight distribution Mw/Mn | 1.3-4 |
| - molecular weight distribution (GPC in tetrahydrofuran) | |
| - melting point | <180°C |
| and preferably | 160-170°C |
| - degree of hydrolysis* | 90-99.9% |

* basic hydrolysis and titration of the residual base with acid.

In order to improve their biodegradability, the copolymers may be modified by the replacement of some, preferably from 0.1 to 5% in moles, of their functional alcohol groups by oxo groups or alkylcarbonyl groups in which the alkyl groups contain from 1 to 4 carbon atoms. These modified polymers can be produced from the corresponding ethylene-vinyl alcohol copolymers by known methods.

The ethylene-vinyl acetate polymers used within the scope of the present invention preferably have molar contents of vinyl acetate of from 5 to 90%, preferably from 12 to 80% and the corresponding copolymers modified by the hydrolysis of the acetate group preferably have from 5 to 90% of acetate and hydrolysed groups.

The ethylene-acrylic acid copolymers used may be those described in patent No. EP-A-0 032 802.

It is intended that mixtures of the copolymers indicated above may be used as the polymeric material of the first layer.

The film constituting the first layer of the laminate preferably has a water content due to the intrinsic water content of the starch or to water added during the destructuring stage, of less than 6% and preferably less than 2% by weight (as extruded, before conditioning).

If water has been added in order to facilitate the formation of a fused material which can be processed in an extruder it is necessary, therefore, to reduce the water content by degassing in an intermediate stage of the

extrusion, upstream of the filming.

The film constituting the first layer may contain destructured starch and the synthetic polymer in a ratio of from 1:9 to 9:1, preferably from 1:4 to 4:1, but the use of compositions with higher starch contents, in which the synthetic polymer constitutes from about 20 to 40% by weight of the sum of the synthetic polymer and starch is preferred.

The films may include a plasticiser with a high boiling point (boiling point above 150°C), such as polyethylene glycol, ethylene glycol, propylene glycol, glycerine, polyglycerol, polyethylene glycol sorbitol, mannitol, their acetate, ethoxilate or propoxylate derivatives and mixtures thereof in quantities from 0.05 to 100% and preferably from 0.5 to 30% of the weight of the starch. The presence of the plasticiser is useful both during the destructuring of the starch, particularly with the use of ethylene-vinyl alcohol copolymers, and as regards specific characteristics of the film constituting the first layer.

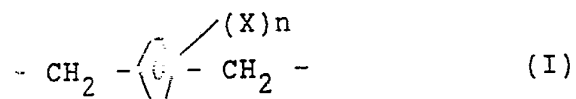
The nature of the starch used in the material constituting the first layer is not particularly critical and either native starches or physically or chemically modified starches such as starch ethoxylates, starch acetates, cationic starches, oxidised starches and cross-linked starches may be used.

The method of preparing the films constituting the first layer are described in Italian applications Nos. IT 67691-A/89, 67692-A/89, 67413-A/89 and 67666-A/89, the contents of which are intended to be incorporated in the present description by reference.

In a preferred embodiment of the invention, the hydrophobic material constituting the second layer consists essentially of a polymeric coating of polyparaxylylene and/or substitution derivatives thereof, deposited on the film constituting the first layer by the chemical deposition of the vapour phase. The thickness of the second layer may vary within wide limits and, according to the desired barrier properties to be obtained, thicknesses of about 0.01 μm to about 40 μm are preferred, preferably from 0.1 to 10 μm .

The technology of the application of polymeric polyparaxylylene coatings is known and is described, for example, in patent application No. EP-A-0 302 457, but with reference to substrates of a definitely hydrophobic nature.

The paraxylylene radical used corresponds to the formula:



in which:

- X is a C₁-C₆ alkyl group, a C₆-C₁₀ aryl group, a C₇-C₁₆ arylalkyl group, a haloalkyl or haloarylalkyl group, an acetoxy group, an aminoalkyl group, an arylamino group, a cyrano group, an alkoxy group, a hydroxy group, a nitro group, a halogen atom, a sulphonic radical, a sulphonic ester radical, a phosphorus-based substituent, a sulphide group, an alkylsulphoxide group or a hydrogen atom, and

- n is 0 or a whole number from 1 to 4.

Since their reactivity causes great difficulties in their

storage and handling, for practical applications, the preferred starting compounds are the dimers of paraxylylene or (2,2)-paracyclophane and of their derivatives conforming to the possible substitutions indicated above.

The dimers of paraxylylene are in fact stable crystalline solids at ambient temperature and can easily be stored and handled. The dimers can be prepared by conventional methods, for example, by the pyrolysis of paraxylylene or from the corresponding paramethylbenzyl trimethylammonium hydroxide by Hofmann degradation.

During the application of the polymeric coating by vapour deposition under vacuum, the paraxylylene dimers are subjected to pyrolytic cracking under vacuum at temperature higher than 400°C to give reactive radicals of formula (I) which are made to condense on the surface of the substrate producing homopolymers or copolymers of paraxylylene according to the dimer used.

Small quantities of other monomers such as maleic anhydride or chloroprene which polymerise on the surface of the film of material with a starchy matrix may be used with (2,2)-paracyclophane and its derivatives. The bivalent paraxylylene radicals condense and polymerise almost instantaneously on the surface of the first layer forming a compact polymer.

The structural principles of devices for the deposition of vapours of bivalent reactive paraxylylene radicals are known and are described, for example, in Kirk-Othmer Encyclopaedia of Chemical Technology, Third Ed., Volume 24, pages 746-747. Such a device includes an evaporation-cracking furnace in which the

(2,2)-paracyclophane or a derivative thereof is inserted, and which is in communication with a deposition chamber which is kept a temperature lower than the condensation temperature of the specific paraxylylene derivative.

The deposition chamber may conveniently be modified for the purposes of the present application to enable the continuous or semi-continuous deposition of the polymeric coating.

The application of a paraxylylene monomer is compatible with the optional use of agents such as, for example, siloxane compounds or derivatives of phosphorus usually used in the deposition under vacuum technique for promoting adhesion.

By way of example, preferred paraxylylene monomers are chloroparaxylylene, dichloroparaxylylene, cyanoparaxylylene, iodoparaxylylene, fluoroparaxylylene, hydroxymethylparaxylylene, ethylparaxylylene, methylparaxylylene, carbomethoxyparaxylylene and mixtures thereof.

In alternative embodiment of the invention, the hydrophobic material used for the second layer is a polymer containing free acid groups, preferably an ethylene-acrylic acid, or an ethylene-acrylic acid-alkyl acrylate copolymer.

For its application to the first layer with a starchy matrix, the polymer is salified by a base, preferably ammonium hydroxide, and is thus made soluble in water. Surfactants, emulsified waxes, silica, polyoxyethylene, polyacrylic acids, polyvinylpyrrolidone, polyvinyl alcohol, etc. may be added to the solution to increase its

ability to wet the starchy film and to reduce the stickiness of the coating. The solution thus obtained is spread on the first layer by a technique similar to varnishing or spray-coating and undergoes heat treatment at a temperature and for a period of time sufficient to remove the aqueous solvent and eliminate the salifying groups thus producing a polymeric coating which is insoluble in water.

In a further embodiment of the invention, the hydrophobic material used for the second layer is constituted by a polyhydroxyalkanoate polymer, particularly PHB (polyhydroxybutyrate), PHB/V (polyhydroxybutyrate/valerate) lactic acid homopolymers and lactic acids copolymerised with glycolic acids or with ϵ -caprolactone, polyethylene-vinyl alcohol, or polyethylene-vinyl acetate.

The coating can be achieved by coextrusion by blowing or casting technology.

These embodiments also produced hydrophobic coatings with good barrier properties and good adhesion to the starchy substrate.

In a further embodiment of the invention the second layer consists of a copolymer of polyvinylpyrrolidone (PVP) or PVP ester with butylacrylate, butyl amylate/methyl methacrylate (85:15 - 15:85% wt/wt) diethylamminomethyl methacrylate, vinylacetate, vinylacrylate, acrylic acid or acrylic acid polymer, inorganic or organic esters, particularly ammonium salts of acrylic acid or acrylic acid polymer.

Preferably the molar ratio of PVP with respect to the comonomer is from 5 to 60% molar.

The coating is obtained from an aqueous solution or emulsion of the copolymer which is dried to provide a water insoluble film which exhibits good adhesion to the starchy based first layer.

The laminated film according to the invention is particularly suitable for producing containers for faeces, for example, of the type used for colostomy care, in which case, the layer of hydrophobic material prevents unpleasant smells from escaping for at least several hours, and for the packaging of foods with high water contents in general.

The laminated film according to the invention will be described further with reference to the following examples.

Example 1: Preparation of the first starchy layer.

A composition having the following composition was prepared:

- 42% by weight of Globe 03401 Cerestar (registered trade mark) starch which had not been dried and had an intrinsic water content of 11% by weight,
- 39% by weight of an ethylene-vinyl alcohol copolymer with a molar ethylene content of 42%, intrinsic viscosity (DMSO, 30°C) 0.39, Mw/Mn 3.6, melting point 164°C, degree of hydrolysis 99.3, melt flow index (230°C, 2.16 kg) 20;
- 12.8% by weight of glycerine,
- 3.2% by weight of water,

- 3% by weight of EAA 5981 copolymer (Dow Chemical).

The components were supplied by a gravimetric batching plant to a Baker Perkins MPC/V-30 extruder with a double-screw unit divided into two regions with a screw diameter of 30 mm and a screw-length/diameter ratio (L/D) of 10:1 connected to a single-screw diameter of 30 mm and an L/D ratio of 8:1, divided into three regions. The capillary nozzle had a diameter of 4.5 mm. The extrusion temperature was kept within the range from 120-180°C in the double-screw region of the extruder and within the range from 170 to 140°C in the single-screw region.

The extrusion produced was transformed into pellets and processed by blow extrusion at about 160°C to produce a film.

Example 2-3

A piece of the film produced according to Example 1 having dimensions of 30 cm x 30 cm was inserted in the deposition chamber of a commercially-available laboratory deposition plant. 0.4 grams of dichloro-di-p-xylylene were loaded into the evaporation section. The dichloro-di-p-xylylene was evaporated under vacuum at a pressure of 0.05 mm Hg at 220°C.

The divalent chloro-p-xylylene radical was kept at 680°C and then allowed to polymerise on the cold surface of the film for two different periods, producing the thicknesses given in the Table:

Example	Thickness of the coating (μm)	Permeability* to water vapour
1	0	1800
2	1.5	102
3	2	43

* Permeability expressed in g per $30 \mu\text{m}^2$ per 24 h, determined at 30°C and 90% relative humidity.

Example 4

A 10% aqueous solution of ethylene-acrylic acid (20% acrylic acid) was prepared and its pH was brought to 10 in the presence of ammonia.

A sample of the film of Example 1 with dimensions of 10 cm x 20 cm x $60 \mu\text{m}$ was immersed in the solution for 10' and then dried at ambient temperature for 2 hours. The permeability of this film at 38°C and 90% relative humidity was 390 g per $30 \mu\text{m}^2$ per 24 h against 1800 g per $3 \mu\text{m}^2$ per 24 h for the untreated film.

This treatment also makes the film more transparent.

CLAIMS

1. A laminated film, characterised in that it includes at least one first layer of polymeric material which has a starchy matrix and is insoluble in water or at most expands in water and a second layer of hydrophobic material adhering to the first.

2. A laminated film according to claim 1 wherein the polymeric material consists of a composition including destructured starch and a synthetic thermoplastic polymer wherein said synthetic thermoplastic polymer is a copolymer of at least one thyleneically insaturated monomer, said polymer having repeating units provided with at least a polar group, selected from the group consisting of hydroxy, alkoxy, carboxy, carboxyalkyl, alkyl carboxy and acetal.

3. A polymeric blend according to claim 2, wherein said polymer is selected from the group consisting of polyvinylalcohol and copolymers of an olephin selected from the group consisting of ethylene, propylene, isobutene and styrene with acrylic acid, vinyl alcohol or vinyl acetate.

4. A laminated film according to claim 1, wherein the polymeric material with a starchy matrix is constituted by a composition including destructured starch and an ethylene copolymer selected from the group consisting of ethylene-vinyl alcohol, ethylene-vinyl alcohol modified by the replacement of some of the hydroxyl groups by oxo or alkyl carbonyl groups, ethylene-acrylic acid, ethylene-vinyl acetate, termopolymers of ethylene-vinyl alcohol-vinyl acetate and mixtures thereof.

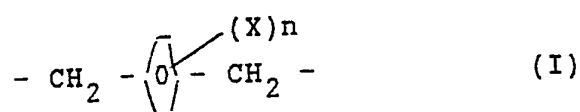
5. A laminated film according to claim 4, wherein the ethylene copolymer is ethylene-vinyl alcohol with an ethylene content of from 15 to 50% in moles, preferably from 30 to 45% in moles.

6. A laminated film according to claim 2, characterised in that the ethylene copolymer comprises ethylene-vinyl acetate having a molar content of vinyl acetate of from 12 to 80%.

7. A laminated film according to claim 1, in which the first layer comprises starch and an ethylene copolymer in a ratio by weight of from 1:4 to 4:1.

8. A laminated film according to claim 7, in which the polymeric material constituting the first layer includes a high boiling plasticiser and has a water content of no more than 6% by weight (as extruder before conditioning).

9. A laminated film according to claim 1, wherein the second layer is formed by a polymer or a copolymer of a paraxylylene monomer having the formula:



in which:

- X represents a C₁-C₆ alkyl group, a C₆-C₁₀ aryl group, a C₇-C₁₆ arylalkyl group, a haloalkyl or haloarylaklyl group, an acetoxy group, an aminoalkyl group, an arylamino group, a cyrano group, an alkoxy group, a hydroxy group, a nitro group, a halogen atom, a sulphonic radical, a sulphonic ester radical, a phosphorus-based substituent, a sulphide group, an alkylsulphoxide group or a hydrogen

atom, and

- n is 0 or a whole number from 1 to 4.

10. A laminated film according to claim 9, wherein the paraxylylene monomer is selected from the group consisting of chloroparaxylylene, dichloroparaxylylene, cyanoparaxylylene, iodoparaxylylene, fluoroparaxylylene, hydroxymethylparaxylylene, ethylparaxylylene, methylparaxylylene, aminomethylparaxylylene, carbomethoxyparaxylylene and mixtures thereof.

11. A laminated film according to claim 1 wherein the hydrophobic material of the second layer is a polymer containing free acid groups.

12. A laminated film according to claim 9 wherein the polymer including free acid groups is an ethylene-acrylic acid or an ethylene-acrylic acid-alkylacrylate copolymer.

13. A laminated film according to claim 1 wherein the hydrophobic material of the second layer is a polyhydroxyalkanoate polymer, a lactic acid homopolymer, a copolymer of lactic acids copolymerised with glycolic acids or with ϵ -caprolactone, polyethylene-vinyl alcohol, or polyethylene-vinyl acetate.

14. A laminated film according to claim 1 wherein the second layer comprises a copolymer of polyvinylpyrrolidone (PVP) or PVP ester with butylacrylate, butylacrylate/methylmethacrylate, diethylamminomethyl methacrylate, vinylacetate, acrylic acid or acrylic acid polymer, esters of acrylic acid or esters of acrylic acid polymer.

15. A container for faeces produced from a laminated film

according to claim 1.

16. Packaging for food products including a laminated film according to claim 1.

17. A method of producing a laminated film according to claim 1 wherein the layer of hydrophobic material is applied to the substrate with a starchy matrix by the deposition of the reactive vapours of a monomer of paraxylylene or derivatives thereof in the vapour state under vacuum and the condensation of the vapours on the substrate constituted by the film of starchy material.

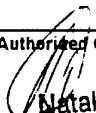
18. A method of producing a laminated film according to claim 11 comprising the steps of:

- salifying the polymer containing free acid groups with a base, preferably ammonium hydroxide, to produce an aqueous solution of the polymer,
- depositing the solution in a thin layer on at least one surface of the starch-based layer, and
- applying external heat to a temperature and for a period of time such as to evaporate the solvent and remove the basic groups from the polymer so as to make it insoluble in water.

19. A method according to claim 18, in which additives selected from surfactants, emulsified waxes, silica, polyxyethylene, polyacrylic acids, polyvinylpyrrolidone, polyvinyl alcohol and mixtures thereof are added to the aqueous solution of the polymer.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/01443

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: B 32 B 9/02, C 08 L 3/02						
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black;">Classification System</th> <th style="border: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: 1px solid black; vertical-align: bottom;">C 08 L; B 32 B</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 08 L; B 32 B
Classification System	Classification Symbols					
IPC5	C 08 L; B 32 B					
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹						
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³				
Y	GB, A, 2214918 (WARNER-LAMBERT COMPANY) 13 September 1989, see abstract, page 2, last paragraph - page 3, first paragraph, page 13, lines 5-16 --	1-8				
Y,P	WO, A1, 9014938 (GOODMAN FIELDER WATTIE AUSTRALIA LIMITED) 13 December 1990, see abstract, page 2, last line - page 3, first paragraph, page 15, line 18 - page 16, line 8 --	1-8				
A	WO, A1, 8500176 (UNITED STATES OF AMERICA, REPRESENTED BY THE SECRETARY, UNITED STATES DEPARTMENT OF COMMERCE) 17 January 1985, see the whole document --	1-18				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</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> </div> <div style="width: 45%;"> <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>"&" document member of the same patent family</p> </div> </div>						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search 15th October 1991		Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">25. 11. 91</div>				
International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>		Signature of Authorized Officer <div style="text-align: center;">  Natalie Weinberg </div>				

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/EP 91/01443**

SA 49841

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 30/08/91
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
GB-A- 2214918	13/09/89	AU-D-	2887689	03/08/89
		EP-A-	0327505	09/08/89
		JP-A-	2014228	18/01/90

WO-A1- 9014938	13/12/90	NONE		

WO-A1- 8500176	17/01/85	EP-A-B-	0132299	30/01/85
		JP-T-	60501645	03/10/85
		US-A-	4454268	12/06/84

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