

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) **EP 0 698 563 A1** 

(12)

## **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

28.02.1996 Bulletin 1996/09

(51) Int CI.6: **B65D 77/20**, B65D 81/26

(21) Application number: 95305625.6

(22) Date of filing: 11.08.1995

(84) Designated Contracting States:

AT BE CH DE DK ES FR GB GR IE IT LI LU NL
PT SE

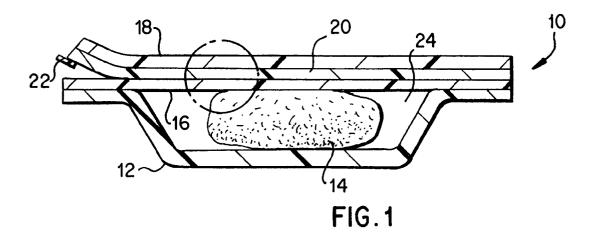
(30) Priority: 23.08.1994 US 295177

(71) Applicant: W.R. GRACE & CO.-CONN. New York, New York 10036-7794 (US) (72) Inventors:

- Mize, James Akers, Jr.
   Simpsonville, South Carolina 29681 (US)
- Stockley, Henry Walker, III
   Spartanburg, South Carolina 29301 (US)
- Logan, Robin Hill Spartanburg, South Carolina 29301 (US)
- Miranda, Nathanael Rustia
   Gastonia, North Carolina 28054 (US)
- (74) Representative: Barlow, Roy James London WC1R 5LX (GB)

# (54) Peelable package with oxygen scavenging layer

(57) A package 10 includes a product 14, a bottom 12 which supports the product, a non-barrier layer 16 sealed to the bottom which encloses the product, a peelable barrier layer 18 peelably disposed on the non-barrier layer and an oxygen scavenger layer 20, disposed between the non-barrier layer and the barrier layer. The peelable barrier layer and the oxygen scavenger layer are substantially impervious to oxygen and, when the peelable barrier layer and the oxygen scavenger layer are removed, the non-barrier layer which is substantially pervious to oxygen is exposed.



20

25

35

#### Description

#### BACKGROUND OF THE INVENTION

The invention relates to packages for products such as fresh red meat products and, specifically, to a peelable barrier package having an oxygen scavenging layer.

In U.S. Pat. No. 3,574,642 which issued on Apr. 13, 1971 to Carl Frederick Weinke, a package and a method for packaging meats is disclosed. The package includes an inner oxygen-permeable member which may be gas flushed or evacuated. The package preserves the freshness of the meat until the meat is ready to be marketed to the consumer. For marketing, the outer wrapper is removed and the inner package is displayed to the consumer. Being oxygen-permeable, the inner wrapper admits oxygen to the interior of the package causing the fresh meat product to change to a bright red color which the consumer associates with freshness. The inner pouch of the Weinke package may consist of polyethylene film and the outer pouch may be cellophane film with a coating of saran (vinylidene chloride copolymer.) Another patent showing portions of fresh meat individually packaged in oxygen permeable plastic film and inserted into an outer container of impermeable film is U.S. Pat. No. 3,681,092 which issued to Oliver R. Titchenal et al, on Aug. 1, 1972.

Another prior art package is described is U.S. Pat. No. 3,713,849 which issued to Paul E. Grindrod et al. on Jan 30, 1973. In the Grindrod et al. patent a fresh meat package having an outer oxygen impermeable lamina which is readily and entirely peelable from an inner oxygen-permeable lamina is disclosed. The package includes means for initiating the peeling separation along an edge of the package. The outer oxygen barrier maintains meats in well preserved condition in spite of the purplish color which has low consumer appeal. Shortly prior to display for sale to the consumer the outer lamina is removed by the retailer and the product develops a healthy, bright red "bloom" due to the high oxygen through-put of the inner remaining film package. The material disclosed in Grindrod et al. is a laminate of PVC/Saran and EVA/Saran. (EVA designates ethylene/vinylacetate copolymer and PVC designates polyvinyl-chloride.) The EVA and PVC layers are the inner layers and at the periphery of the package they are sealed together. The saran layers can be readily peeled from the respective EVA or PVC layers with gripping tabs that are provided.

Yet another peelable package is shown in U.S. Pat. No. 4,055,672 which issued on Oct. 25, 1977 to Arthur Hirsch et al. In the Hirsch et al. patent a semi-rigid Preformed tray of oxygen impermeable material is formed, a meat product placed therein, and then the tray is sealed around its upper periphery or flange area by a composite lid which has an inner layer of oxygen permeable material, an adhesive layer, and an outer layer of oxygen impermeable material. When the package is ready for retail

display, in order that oxygen can reach the fresh meat packaged within permeable material, the outer, impermeable lid is peeled away so that the oxygen can penetrate through the remaining portion of the lid.

A problem which arises with the foregoing is that the outer barrier layer typically still allows permeation of small amounts of oxygen which may shorten the shelf life of the package. This is particularly true of packages having an ethylene vinyl alcohol copolymer (EVOH) barrier layer which can lose some of its oxygen barrier properties when subjected to very high moisture conditions.

It is a primary object of the invention to provide a peelable package as above wherein the package includes an oxygen scavenger layer which serves both to scavenge oxygen trapped in the interior of the package during packaging and which also serves to enhance the effectiveness of the barrier layer by trapping or capturing oxygen which permeates the barrier layer so as to provide an "active" barrier to oxygen.

The use of oxygen scavenger materials in permanent or non-peelable layers of packaging is known. See, for example, European Patent Application No. EP 507207 A2. In end uses contemplated in the present application, however, the transparency of the oxygen scavenger layer is often important because it remains in place during display to the consumer.

It is a further object of the invention to utilize oxygen scavenger materials as a layer or component of a peelable barrier film package with good transparency.

Other objects and advantages will appear hereinbelow.

## SUMMARY OF THE INVENTION

The foregoing objects and advantages are readily attained by the present invention.

In accordance with the invention, a package having a peelable barrier layer which has an oxygen scavenger layer is disclosed which comprises a product, a bottom web which supports the product, a non-barrier layer sealed to the bottom web which encloses the product, a peelable barrier layer peelably disposed on the non-barrier layer, and means for scavenging oxygen, disposed between the non-barrier layer and the barrier layer. The peelable barrier layer and the scavenging means are substantially impervious to oxygen and, when the peelable barrier layer and the scavenging means are removed, the non-barrier layer which is substantially pervious to oxygen is exposed.

The package in accordance with the invention also preferably includes means for peeling the barrier layer from the non-barrier layer whereby the barrier layer and the oxygen scavenger layer are removed and oxygen permeates the non-barrier layer.

### BRIEF DESCRIPTION OF THE DRAWINGS

A detailed description of preferred embodiments of

the invention follows, with reference to the attached drawings, wherein:

Fig. 1 is a side schematic view of a package in accordance with the invention;

Fig. 2 is an enlarged portion of Fig. 1;

Fig. 3 is a similar view to Fig. 2, illustrating an alternative embodiment of the invention;

Fig. 4 is a side schematic view of a package according to an alternative embodiment of the invention;

Fig. 5 illustrates a partially peeled portion of a package according to the invention; and

Figs. 6 and 7 are side schematic views of a package according to other embodiments of the invention.

### **DETAILED DESCRIPTION**

The invention relates to a peelable barrier package for oxygen sensitive products such as fresh red meats. With reference to Fig. 1, a package in accordance with the invention is generally indicated by reference numeral 10. In accordance with the invention, package 10 includes an oxygen scavenger component which improves the characteristics of the package. As used herein, the term "oxygen scavenger" refers to a composition, layer, article, coating, sachet, or the like which consumes, reacts with, depletes or reduces the amount of oxygen in a given environment.

Package 10 includes a bottom web or support member 12 for supporting a product 14, an oxygen permeable non-barrier layer 16 enclosing product 14 on bottom web 12 and sealed thereto, an oxygen impermeable, peelable barrier layer 18 disposed over non-barrier layer 16, and an oxygen scavenger member or layer 20 disposed between non-barrier layer 16 and barrier layer 18. Package 10 also preferably includes a member such as pull tab 22 for use in initiating peel of barrier layer 18 and preferably of oxygen scavenger layer 20 from package 10. Figs. 2 and 3 illustrate an enlarged portion corresponding to the circled section of Fig. 1 to more clearly illustrate the invention.

In accordance with the invention, oxygen scavenger layer 20 serves to scavenge oxygen from within package 10, and also to enhance the barrier nature of barrier layer 18 by trapping or scavenging oxygen which permeates barrier layer 18 from outside the package. In this manner, product 14 has enhanced shelf life due to increased protection from oxygen. Furthermore, because oxygen scavenger layer 20 would in use typically be removed prior to display to the consumer, the appearance of oxygen scavenger layer 20 is sometimes of less importance.

When it is desired to display package 10 for sale,

tab 22 or any other suitable mechanism can be used to peel and remove barrier layer 18 and scavenger layer 20 so that oxygen is allowed to permeate non-barrier layer 16 and oxygenate product 14 so as to provide product 14 with a bright red "bloom" (in the case where the product is fresh red meat) which the consumer associates with freshness.

In accordance with the invention, non-barrier layer 16 is substantially pervious to oxygen and preferably allows an oxygen transmission of at least about 2000, and more, preferably at least about 5000 cc O2 per square meter over a 24 hour period at 73°F and one atmosphere. Such an oxygen transmission rate allows a rapid "bloom" of a fresh red meat product so that barrier layer 18 need be removed only a short time prior to placement of the package on display for the consumer. Numerous suitable materials are known for use in providing non-barrier layer 16. Examples of suitable materials include polyvinyl-chloride (PVC), ethylene/vinylacetate copolymers (EVA), ethylene butyl acrylate copolymer (EBA), and polyolefins such as polyethylene. Those skilled in the act will understand that other suitable materials are available for layer 16.

Barrier layer 18 preferably allows an oxygen transmission of less than or equal to about 1000, more preferably less than or equal to about 500 and most preferably less than about 100 cc  $O_2$  per square meter over a 24 hour period at 73°F at one atmosphere. Barrier layer 18 thereby serves to inhibit oxygen transmission so as to extend shelf life of product 14 in package 10. Barrier layer 18 also serves, as will be further described below, to limit the contact of oxygen from the surrounding atmosphere with oxygen scavenger layer 20 so that the scavenging capacity of oxygen scavenger layer 20 is not prematurely or rapidly exhausted by oxygen from outside the package.

Numerous materials are known for providing desired oxygen barrier characteristics of barrier layer 18. Examples of suitable materials include but are not limited to ethylene/vinyl alcohol copolymer (EVOH), silica (SiO<sub>2</sub>) coating, amorphous nylon, polyester, liquid crystalline polymer, and saran (vinylidine chloride copolymer or PVDC).

The optimal combination of oxygen transmission of both the barrier layer 18 and non-barrier layer 16 will depend on a variety of factors, including the nature of product 14, the packaging and storage temperatures, thickness of the respective layers, desired shelf life, etc.

Oxygen scavenger layer 20 serves to scavenge oxygen which may remain inside package 10 after packaging, and also serves to capture oxygen which may permeate barrier layer 18. In this regard, oxygen scavenger layer 20 and barrier layer 18 serve to provide an active barrier which is substantially impervious to oxygen. Numerous oxygen scavenging materials are known in the art. In accordance with the invention, ethylenically unsaturated hydrocarbon resins have an excellent capacity for reaction with oxygen. The ethylenically unsaturated

5

15

25

35

45

hydrocarbon may be substituted or unsubstituted.

An unsubstituted ethylenically unsaturated hydrocarbon has at least one aliphatic carbon-carbon double bond and comprises 100% by weight carbon and hydrogen.

Preferred examples of unsubstituted ethylenically unsaturated hydrocarbons include, but are not limited to, diene polymers such as polyisoprene, (e.g., transpolyisoprene), polybutadiene (especially 1,2-polybutadienes, which are defined as those polybutadienes possessing greater than or equal to 50% 1,2 microstructure), and copolymers thereof, e.g. styrene-butadiene. Such hydrocarbons also include polymeric compounds such as polypentenamer, polyoctenamer, and other polymers prepared by olefin metathesis; diene oligomers such as squalene; and polymers or copolymers derived from dicyclopentadiene, norbornadiene, 5-ethylidene-2-norbornene, or other monomers containing more than one carbon-carbon double bond (conjugated or non-conjugated). These hydrocarbons further include carotenoids such as β-carotene.

A substituted ethylenically unsaturated hydrocarbon as used herein is one which has at least one aliphatic carboncarbon double bond and comprises about 50% - 99% by weight carbon and hydrogen.

Preferred substituted ethylenically unsaturated hydrocarbons include, but are not limited to, those with oxygen-containing moieties, such as esters, carboxylic acids, aldehydes, ethers, ketones, alcohols, peroxides, and/or hydroperoxides. Specific examples of such hydrocarbons include, but are not limited to, condensation polymers such as polyesters derived from monomers containing carbon-carbon double bonds; unsaturated fatty acids such as oleic, ricinoleic, dehydrated ricinoleic, and linoleic acids and derivatives thereof, e.g. esters. Such hydrocarbons also include polymers or copolymers derived from (meth)allyl (meth)acrylates.

Of course, scavenger layer 20 may also comprise a mixture of any number of the foregoing materials.

The ethylenically unsaturated hydrocarbon preferably has two or more ethylenically unsaturated groups per molecule, and more preferably is a polymeric compound having three or more ethylenically unsaturated groups and an average molecular weight of at least about 1000.

In further accordance with the invention, oxygen scavenger layer 20 may preferably include a catalyst to accelerate the scavenging rate of the oxygen scavenging material.

Transition metal catalysts are preferred, preferably in the form of a transition metal salt. Suitable transition metals include but are not limited to metals selected from the first, second or third transition series of the Periodic Table such as, for example, manganese II or III, iron II or III, cobalt II or III, nickel II or III, copper I or II, rhodium II, III or IV, and ruthenium. The metal is further preferably iron, nickel or copper, more preferably manganese and most preferably cobalt.

Suitable counterions of the metal salt include but are

not limited to chloride, acetate, stearate, palmitate, 2-ethylhexanoate, neodecanoate or naphthenate. Particularly preferable salts include cobalt (II) 2-ethylhexanoate and cobalt II neodecanoate.

When incorporated into scavenger layer 20, the catalyst accelerates scavenging of oxygen so as to render scavenger layer 20 more effective.

Support member 12 may be any suitable tray (e.g. foamed polystyrene tray) or bottom material on which product 14 rests. In keeping with the barrier nature of package 10, of course, support member 12 should be made from a barrier material or contain a layer, film, laminate, coating or the like of an oxygen or gas barrier material.

As set forth above, package to is peelable in that barrier layer 18 is peelable or removable from the package to provide bloom when desired. Oxygen scavenger layer 20 is preferably also removed along with barrier layer 18. In this regard, oxygen scavenger layer 20 and barrier layer 18 can together comprise a composite or multi-layer film or laminate so that they are peeled together. Alternatively, oxygen scavenger layer 20 could be provided in the form of a packet or sachet positioned between non-barrier layer 16 and barrier layer 18 so that removal of peelable barrier layer 18 allows the packet to be removed as well.

The oxygen scavenger can be provided as a coating on the interior (i.e. towards the product) surface of barrier layer 18. The oxygen scavenger can also comprise a sachet or packet 20a (see Fig. 6).

In another embodiment (Fig. 7), a single film 16 comprising an oxygen permeable material can be sealed to an inner flange 30 of tray 12, and a second, barrier/scavenging film can be sealed to an outer flange 32 of the same tray 12.

Either or both of the barrier layer 18, and non-barrier layer 16, can be monolayer or multilayer construction. Barrier layer 18 can be directly adhered to oxygen scavenging layer 20, or indirectly adhered by one or more adhesive or other layers. The drawings generally show monclayer construction for purposes of clarity. Figures 2 and 3 show a barrier layer 18 which actually includes three layers, 15, 17, and 19, any one or more of which comprise the oxygen barrier materials referred to herein.

Numerous approaches are used and well known in the art for peeling barrier layer 18. Tab 22 as shown in the drawings is one way of initiating the peel. It is also known to perforate or score an edge of package 10 and provide a pull tab for peeling both layers 16, 18. Such a configuration is illustrated in Fig. 5. Perforations shown at 28 cause the rupture of non-barrier layer 16 and allow barrier layer 18 and oxygen scavenger layer 20 to be peeled as shown while the remainder of non-barrier layer 16 is left in place on package 10 and still enclosing product 14. In accordance with the invention, numerous other mechanisms may of course be utilized to provide peeling of barrier layer 18.

Scavenger layer 20 may be attached or adhered to

10

15

barrier layer 18 and thereby peels simultaneously therewith, or may be removed separately after peeling of barrier layer 18.

7

It should be noted that the application of non-barrier layer 16 and barrier layer 18 can be carried out in accordance with any of numerous conventional processes such as stretch wrapping, heat shrinking, vacuum skin or differential pressure, or any other suitable procedure. In some of these procedures, such as stretch wrapping, some oxygen may remain in an inner space 24 of package 10 (Fig. 1). In this instance, oxygen scavenger layer 20 serves both to supplement the oxygen barrier characteristics of barrier layer 18 and also to remove the remaining oxygen. In this regard, it may be desirable to provide non-barrier layer 16 with perforations 26 (Fig. 3) for increasing oxygen transmission or permeability of non-barrier layer 16. Perforations 26 serve to increase the access of scavenger layer 20 to gases in inner space 24 and thereby help to provide a rapid scavenging of remaining oxygen from inner space 24.

Further, non-barrier layer 16 can be applied together with barrier layer 18 and scavenger layer 20, or may be applied first, before application of barrier layer 18 and scavenger layer 20. In this regard, non-barrier layer 16 may be applied in the same or a different manner than barrier layer 18. For example, non-barrier layer 16 may be a vacuum skin wrap with barrier layer 18 stretch wrapped over non-barrier layer 16.

Of course, if both layers 16, 18 are applied under vacuum conditions (i.e., as skin wraps, see Fig. 4), it is less likely that space 24 will contain oxygen, and inner space 24 may not be formed at all. In such packages, the primary function of oxygen scavenger layer 20 is to enhance and supplement the barrier nature of barrier layer 18.

Thus disclosed is a package containing a peelable oxygen barrier layer and an oxygen scavenger layer whereby the package has enhanced shelf life. The oxygen scavenger layer advantageously serves to render the barrier layer more effective and thereby create an "active" oxygen barrier. The oxygen scavenger also serves to remove oxygen from within the package, which is necessary to preserve a deoxymyoglobin color of fresh meat, so that the meat will adequately oxygenate to oxymyoglobin color upon removal of the barrier layer. The peelable nature of the package, in accordance with the invention, allows removal of the barrier layer and oxygen scavenger so that the remaining non-barrier layer allows oxygen to permeate and "bloom" the product contained in the package.

It is to be understood that the invention is not limited to the illustrations described and shown herein, which are deemed to be merely illustrative of the best modes of carrying out the invention, and which are susceptible of modification of form, size, arrangement of parts and details of operation. The invention rather is intended to encompass all such modifications which are within its spirit' and scope as defined by the claims.

#### Claims

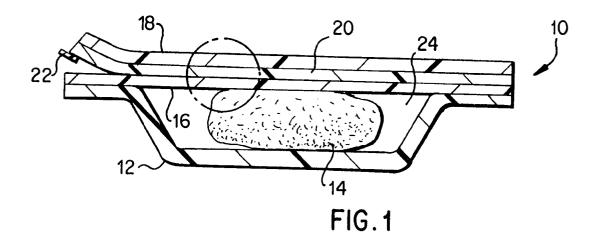
- 1. A package, comprising:
  - a product:
  - a bottom web which supports the product;
  - a non-barrier layer sealed to the bottom web which encloses the product;
  - a peelable barrier layer peelably disposed on the non-barrier layer; and
  - means for scavenging oxygen disposed between the non-barrier layer and the barrier layer.
- 2. A package according to claim 1 wherein the peelable barrier layer and the scavenging means are substantially impervious to oxygen and, when the peelable barrier layer and the scavenging means are removed, the non-barrier layer which is substantially pervious to oxygen is exposed.
- 20 3. A package according to claim 1 or 2, wherein the barrier layer and the scavenging means are layers of a peelable composite film peelably disposed on the non-barrier layer.
- 25 4. A package according to claim 1, 2 or 3 wherein the non-barrier layer includes oxygen passage means, preferably perforations, for allowing the scavenging means to scavenge oxygen from within the package.
- 30 5. A package according to any one of claims 1 to 4, wherein the scavenging means comprises an ethylenically unsaturated hydrocarbon polymer.
- 6. A package according to claim 5, wherein the ethylenically unsaturated hydrocarbon polymer has at least two ethylenically unsaturated groups per molecule, and preferably has at least three ethylenically unsaturated groups per molecule and a molecular weight of at least about 1000.
  - **7.** A package according to claim 5 or 6, wherein the ethylenically unsaturated hydrocarbon polymer further includes a transition metal catalyst.
- 45 8. A package according to claim 7, wherein the transition metal catalyst comprises a metal salt, preferably of cobalt, manganese or a mixture thereof.
- 9. A package according to any one of claims 1 to 4, wherein the scavenging means is a layer, or a coating, or a sachet, of oxygen scavenger material and is disposed between the barrier layer and the non-barrier layer.
  - 10. A package according to any one of claims 1 to 9, further including means for peeling the barrier layer from the non-barrier layer whereby the barrier layer and the scavenging means are removed and oxygen

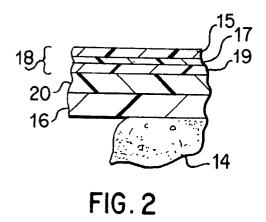
permeates the non-barrier layer.

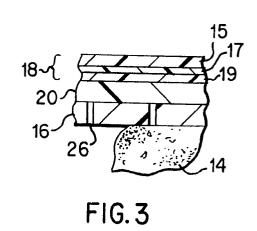
11. A package according to any one of claims 1 to 10, wherein the barrier layer is selected from the group consisting of ethylene/vinyl alcohol copolymers, silica coating, amorphous nylon, polyester, liquid crystalline polymer, vinylidene chloride copolymers and mixtures thereof.

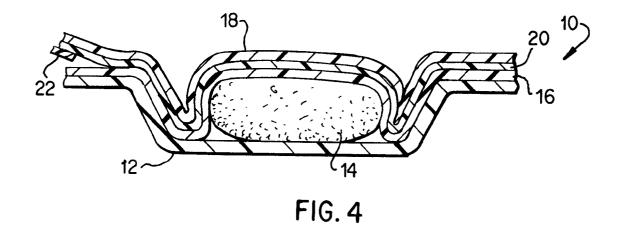
p |- *5* |-

12. A package according to any one of claims 1 to 11, wherein the non-barrier layer and the support member define an inner space of the package, and wherein the non-barrier layer has perforations for increasing oxygen transmission through the non-barrier layer.









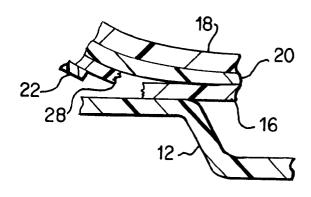
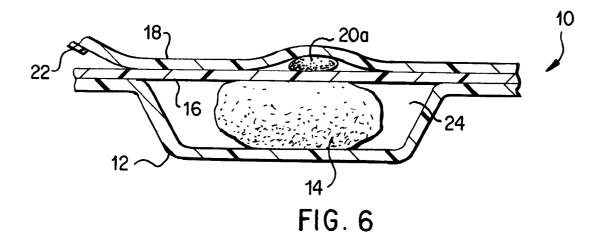


FIG. 5



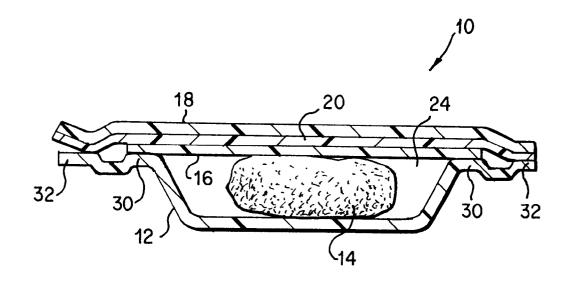


FIG. 7



# **EUROPEAN SEARCH REPORT**

Application Number EP 95 30 5625

ategory	Citation of document with indication of relevant passages	on, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
۸,D	US-A-4 055 672 (HIRSCH * the whole document *	ET AL.)	1	B65D77/20 B65D81/26
	WO-A-93 09946 (SHIRAT ) * page 11, paragraph 2 paragraph 2; figure 4B	- page 12,	1	
	EP-A-O 368 632 (MITSUBI * claim 1 *	SHI) 	1	
				TECHNICAL FIELDS SEARCHED (Int.Cl.6)
				B65D
	The present search report has been dra	wn up for all claims		
Place of search THE HAGUE		Date of completion of the search 29 November 199	Date of completion of the search Examiner 29 November 1995 Bridault, A	
X : part Y : part doct	CATEGORY OF CITED DOCUMENTS  icularly relevant if taken alone icularly relevant if combined with another ument of the same category inological background	T : theory or prin E : earlier patent after the filin D : document cite L : document cite	ciple underlying the document, but publ g date ed in the application d for other reasons	invention ished on, or

EPO FORM 1503 03.82 (P04C01)