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"FOODSTUFF PACKAGING MATERIALS"

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The present invention relates to packages for foodstuffs, suitable inter alia for commercial sterilization.

Heat sealed sheet or film food packages are used
5 for foods which are preserved by refrigeration as well as for dried foods. The film or sheet structure used for these purposes must at least have a heat sealable inside surface. The film or sheet must be relatively impervious to oxygen and moisture, and have an outside
10 surface of sufficient durability to protect the integrity of the package. The materials must not adversely affect the food product, of course.

The ability to hot fill sheet or film food packages, or to process them in a sterilizing retort, permits the
15 foods to be stored without refrigeration. Commercial sterilization by hot filling or retorting imposes several additional restrictions on the choice of materials for the sheet or film packaging structure. Heat seals must survive commercial sterilization temperatures of over
20 180°F (82°C) or typical retort conditions of steam or water at 250°F (121°C) or more under pressure for half an hour or more. The said structure must not delaminate, shrink, or wrinkle as a result of sterilization. The oxygen and water barrier properties
25 must not be adversely affected permanently by the

conditions of commercial sterilization. The structure must be strong enough to permit handling of the package while still hot. The requirements imposed by hot filling or by retorting prevent the use of many of the materials and structures commonly used for non-retorted film or sheet food packages.

Retortable sheet or film packages have been tried in which the oxygen and moisture impervious barrier layer is aluminium foil. Suitable materials for the inside and outside surfaces are bonded to the foil. The aluminium-containing laminate cannot be made in a single step, unlike multi-layer all polymeric structures which can be made in a single coextrusion operation, and this is a substantial drawback. Another drawback resides in the aluminium-containing laminate being opaque, so that purchasers cannot inspect the contents of the package visually. Moreover, microwave oven cooking of the packaged food cannot be accomplished when an electrically conductive material (the aluminium) is present.

An object of the present invention is to provide food packages in a variety of forms which can withstand commercial sterilization conditions, and which preferably employ transparent, or semi-transparent sheet or film structure. Preferably, packages according to the invention should be suited to microwave cooking by the

consumer.

According to B.P. 1,567,280 saponified ethylene-vinyl acetates cannot withstand water at elevated temperatures, even when sandwiched between protective olefinic resin layers. We share this conclusion. In the description which follows we describe such a structure (our control structure) and its unsatisfactory behaviour. The aforementioned patent specification teaches that satisfactory performance upon sterilisation can only be attained if the saponification product, ethylene-vinyl alcohol copolymer (EVOH), is acetalized. To the contrary, we have found that there is no need to resort to the extra complication of acetalizing, provided moisture which enters during sterilizing is allowed to escape subsequently, which it cannot do from the sandwiched structure noted above. Surprisingly, the oxygen barrier properties of a vinyl alcohol polymer are regained when we provide for escape moisture. Such behaviour would be wholly unexpected from a reading of B.P.1,567,280. Unlike B.P. 1,567,280, therefore, the present invention makes it possible to utilise a commercially available polymeric vinyl alcohol oxygen barrier without acetalization, and the term "vinyl alcohol polymer" used herein - after and in the claims is to be understood to mean the unacetalized polymer.

According to the present invention, there is provided a heat sealed package, for commercial heat sterilization and unrefrigerated storage of food products, made of multi-layer polymeric material having a first layer, which forms the outside surface of the package, that is relatively permeable to moisture at temperatures of unrefrigerated storage, to allow moisture present in the multi-layer material to escape out therefrom; a second layer

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which forms the inside surface of the package that is substantially impermeable to moisture at the temperatures of unrefrigerated storage but permeable to moisture at temperatures of commercial sterilization, and is a heat sealable polymer capable of providing a package-closing seal which will withstand commercial heat sterilization temperatures; and an interior oxygen barrier layer made of a vinyl alcohol polymer as hereinbefore defined.

- 10 The invention also provides a package for commercial heat sterilization and unrefrigerated storage of food products, made of multi-layer polymeric material, comprising the following layers, in order: a first layer on the outside surface of the package
- 15 which is permeable to moisture at temperatures of unrefrigerated storage, a second, oxygen barrier layer made of a vinyl alcohol polymer as hereinbefore defined, a third layer permeable to moisture at temperatures of unrefrigerated storage, a fourth
- 20 layer of polymeric material adherent to both the third layer and a fifth, heat sealing layer forming the inside surface of the package, the fifth layer being substantially impermeable to moisture at temperatures of unrefrigerated storage but permeable
- 25 to moisture at temperatures of commercial heat sterilization.

The present invention will now be described in more detail by way of example only with reference to the accompanying drawings, in which:

Figure 1 is a perspective view of a packaging
5 pouch according to the present invention,

Figure 2 is a perspective view of a covered tray
according to the present invention,

1 Figure 3 is an enlarged cross-sectional view of
the film or sheet material used in packages according
10 to the invention,

Figure 4 is a graph showing oxygen permeability of
ethylene-vinyl alcohol copolymer film as a function of
moisture content,

Figure 5 is a comparative graph showing oxygen
15 permeability as a function of time for a film according
to the invention and for a similar film constituting
a control which is not according to the invention, and

Figure 6 is a comparative graph showing the
moisture content as a function of time for the film
20 of a package according to the invention with a similar,
control film not according to the invention.

In practising the invention as will now be
described, each of the several layers of the sheet or
film structure employed serves particular purposes and
25 must satisfy particular requirements. Certain requirements

are shared in common by all layers. All the layers must be of sufficiently flexible materials to result in a flexible structure which will not fracture or crack in use. For economical manufacture, the materials from which all layers are made should be coextrusible, that is, the rheology of the materials in the molten state should allow them all to be extruded simultaneously to join in producing an integrated, multi layer film structure. To produce an inexpensive film structure, each material must be relatively inexpensive as measured by the relative amount of that material incorporated in the finished structure. Since the structure overall should be capable of being reasonably transparent to microwaves in an oven, and in some cases transparent visually i.e. see-through each layer must be similarly transparent. The choice of a particular material for one layer affects the choice of materials for the other layers. The following description of requirements and preferred materials begins with the interior barrier layer.

The barrier layer must provide a sufficient barrier to oxygen to provide adequate shelf-life for the packaged food. In the thickness required for adequate barrier properties, the material must not be expensive. Ethylene-vinyl alcohol copolymer (EVOH) provides superior oxygen impermeability when compared with other polymeric

materials such as Saran (Registered Trade Mark) and acrylonitrile which have been employed in packages for oxygen barrier qualities. A very thin layer of EVOH will provide an adequate barrier to oxygen. Extrusible grades of EVOH are available under the name EVAL from Kuraray Co. Ltd. of Japan. The oxygen barrier quality of EVOH is adversely affected by the presence of water therein, and a small quantity of water will raise the moisture content of a thin layer of EVOH to such an extent that the oxygen barrier quality of the layer is severely affected. The oxygen barrier quality of EVOH is restored when the moisture is removed, however.

Polyolefins such as polyethylene, polypropylene, and blends and copolymers of the two are considered to be excellent moisture barriers. Polyolefins are heat sealable. High density polyethylene, polypropylene, and blends and copolymers of polypropylene and polyethylene melt at temperatures sufficiently high to provide heat seals able to survive hot filling at temperatures in the neighborhood of 190°F (88°C) or retorting at up to 260°F (126°C). Such polymeric materials seal at temperatures between 350°F and 400°F (176°C to 204°C) which are attainable with existing heat seal equipment at normal sealing pressures and times. Consequently, high melting temperature polyolefins are suitable for use as an inside heat seal layer.

The permeability of polyolefins

to water is greatly increased at the elevated temperatures encountered in commercial sterilization. Thus, a polyolefin layer could permit intrusion of water into the EVOH oxygen barrier layer during hot filling or retorting. Since polyolefins become relatively impermeable to water again upon cooling, moisture in the EVOH layer cannot escape through a polyolefin layer. Thus, we have concluded that the layer or layers which are on the outside of the EVOH layer must be relatively permeable to moisture under normal storage conditions to permit escape of moisture in the EVOH layer, and hence the aforementioned polyolefins could not be used outside the EVOH layer.

A suitable polymeric material for the outside layer of the packages according to the invention is nylon. Nylon is sufficiently permeable to moisture to permit escape of moisture from an inner EVOH layer to restore the oxygen barrier quality of the latter, yet is sufficiently waterproof to permit the package to be accidentally wetted without harm. Nylon possesses all of the other desired properties for the outside of the package. It is tough, flexible, not greatly affected by heat or cold, is abrasion resistant, transparent, and can be printed upon for labeling. Nylon is not expensive and is one of the few polymers to which EVOH will

adequately adhere. Nylon can be coextruded with EVOH and with polyolefins. Thus, nylon is well suited for use as an outside surface layer overlying the EVOH barrier layer.

5 Polyolefins do not adhere well to EVOH, so steps must be taken to achieve adequate adhesion and prevent delamination of the film structure. An interlayer of a polymeric material adherent to EVOH and to polyolefins may be used between the inside, polyolefin heat sealable
10 layer and the EVOH oxygen barrier layer.

Where the inside heat sealable high melting polyolefin layer is high density polyethylene, suitable adherent, extrusible polymeric materials for the interlayer are those sold under the name Plexar by Chemplex Company
15 of Rolling Meadows, Illinois, U.S.A. These materials are blends of a polyolefin such as ethylene vinyl acetate with a graft copolymer of high density polyethylene and an unsaturated fused ring carboxylic acid anhydride.

Where the inside polyolefin layer is polypropylene
20 or a blend of polypropylene and polyethylene or a copolymer of propylene and ethylene, suitable adherent, extrusible polymeric materials for the interlayer are acid anhydride grafted polyolefins such as those sold under the name Admer by Mitsui Petrochemical Company of Japan.

25 The adherent polymeric materials sold under the

names Plexar and Admer also adhere well to nylon.

Since EVOH adheres well to nylon, a further interlayer of nylon on the inside face of the EVOH layer may be used. The adherent polymer is then located between that
5 nylon interlayer and the polyolefin inside layer.

Figure 1 shows a heat sealed food pouch according to the invention. The pouch is formed by two overlying rectangles or squares of film as described above, their heat sealable, high temperature polyolefin layers
10 confronting each other. The nylon surface layers of the two films are on the outside. A conventional heat seal bar is used to weld the films autogenously together along a seal line 12 extending along three of four side flanges 14. After the food product is placed in the pouch,
15 the fourth side flange is heat sealed.

After filling and sealing the fourth side, the pouch is ready for retorting. Filled pouches are loaded in a pressure cooker or retort and cooked under pressure in water or steam at temperatures up to about 260°F
20 (126°C) for times extending up to two hours. The times and temperature are related such that higher temperatures generally require shorter times. Many food products require about one-half hour at about 250°F (121°C). Other commercial sterilization techniques such as
25 microwave or hot air heating can be employed.

The illustrated pouch can be hot filled with certain food products which do not require high temperature processing to achieve commercial sterility for adequate storage life. Examples of such foods are sugar syrups, ketchup, fruit juices, jellies and preserves, and high acidity foods. Hot filling is usually done at temperatures in excess of 180°F (82°C). The pouch may be immersed in a hot water bath during or after filling and sealing for a period of time sufficient to assure the destruction of molds and yeasts.

Figure 2 shows a covered tray embodying the invention. The tray 20 is thermoformed from relatively thick sheet stock which may be formed by extrusion coating the polyolefin side of the multi-layer film structure described above with an additional thickness of polyolefin on the inside surface of the tray. The nylon surface is on the outside of the tray. After deposit of the food product in the tray 20, a cover 26 of the multi-layer film is positioned over the tray with the heat sealable polyolefin surface of the film confronting the polyolefin surface of the tray, the latter surface being uppermost on the flanges 24 which form the periphery of the tray. Conventional heat sealing bars are used to heat seal the cover sheet to

the tray flanges 24 along seal lines 22. The trays can be hot filled or retorted as described above.

Figure 3 is an enlarged cross-sectional view of a film structure according to the invention. The face of the film to form the outside of the package is the nylon layer, and the barrier layer is the oxygen impermeable material which preferably consists of a layer of ethylene-vinyl alcohol copolymer (EVOH). The film face to form an inside surface of the package is the heat sealable layer, preferably a polyolefin which heat seals at a temperature higher than that encountered in hot filling or retorting.

Between the barrier layer and the heat seal layer is an interlayer whose function is to bond the EVOH layer securely to the polyolefin heat seal layer. As illustrated, the interlayer is actually comprised of two layers: a nylon layer and an adhesive polymer such as the modified polyolefins e.g. Plexar or Admer. The nylon of the interlayer bonds well to EVOH and the adhesive polymer bonds well both to the polyolefin layer and to the nylon. This structure can be simultaneously coextruded in a single step to produce a packaging film economically. Typically, suitable films are from 3 to 12 mils in thickness.

Figure 4 shows the effect moisture in the EVOH

barrier layer has on its oxygen permeability. At high water contents the oxygen barrier quality of EVOH is seriously degraded. Removal of moisture from the EVOH layer restores the oxygen barrier quality. Since hot filling and retorting occur at temperatures of 190°F (88°C) or higher, the good moisture barrier properties of polyolefins are impaired until lower temperatures are restored. During the time a package is exposed to hot filling or pre-cooking temperatures, moisture can migrate through the polyolefin layer into the EVOH barrier layer. Return of the package to room temperature causes the moisture in the EVOH to result in a relatively high relative humidity which impairs the oxygen barrier quality. Restoration of moisture impermeability of the polyolefin at room temperature prevents escape of the moisture.

Figure 5 compares a film according to the invention with a control film which was a similar film to which a further layer of modified HDPE (Plexar II) was added outside the nylon layer. The film according to the invention was 7.5% nylon/20% EVOH/7.5% nylon /10% Plexar III/55% HDPE. The control film was 32.5% HDPE/7.5% nylon/20% EVOH/7.5% nylon/32.5% HDPE. The films were made into pouches which were filled and subjected to retorting. Figure 5 shows that oxygen barrier quality improved because the nylon outside

layer of the film of the invention permitted moisture entrapped in the EVOH layer to escape. The oxygen barrier quality of the film improved from a permeability of 650 cc/m²/day to about 20 cc/m²/day within 6 hours after retorting, whereas the control film which had a further layer of HDPE over the nylon only dropped from about 400 cc/m²/day to about 300 cc/m²/day in 24 hours. After a full day the control film still was 15 times more permeable to oxygen than the film of the invention. The HDPE outer layer of the control film prevented the escape of moisture from the EVOH barrier layer. The continued presence of moisture degraded the oxygen barrier quality of the control film.

Figure 6 compares the relative weight as a function of time of a package in accordance with the invention with a control package having a layer of HDPE over the nylon layer outside the EVOH barrier layer. The films used were the same as those used in Figure 5. The relative weight plotted is a measure of the percentage change in weight of water in the film. The relative weight is:

$$\frac{\text{weight at time } t - \text{original weight}}{\text{original weight}} \times 100$$

The packages were in the form of pouches filled with tomato paste. The packages were weighed to establish

the original weight. The packages were then retorted at 250°F for half an hour. The retorted pouches were then weighed and weighed again on the 1st., 2nd., 3rd., 6th, 7th, 10th, 13th and 15th day following retorting.

5 It is apparent that packages according to the invention initially gained more weight during retorting than did the control packages. After one day the packages according to the invention had less moisture in the film than did the control packages. For the
10 next two weeks the packages according to the invention continued to dry out more rapidly than the control packages and at all times following the first few hours contained less moisture than the control packages. The control packages were substantially unchanged in moisture
15 content, always remaining at an unacceptably high moisture content as is reflected by the high oxygen permeability shown for the control packages in Figure 5.

Transparent films according to the invention, and comprising a coextruded structure of 7.5% nylon/20%
20 EVOH/ 7.5% nylon/10% Plexar III/55% HDPE having thicknesses between 4.5 and 6 mils were formed into pouches which were filled with potatoes, tomatoes, corn, carrots, beef stew, and green beans. Each of the packages was subjected to retorting at temperatures of at least
25 250°F for at least half an hour. The packages were

successful.

Films similar to those above were used for hot fill packaging of syrup and tomato paste. These packages were also successful.

- 5 Foodstuffs contained in pouches, bags or trays as illustrated in Figs. 1 and 2 can be conveniently cooked by the consumer by boiling or microwave cooking in situ, i.e. before extracting from the package.

- 10 "ADMER" referred to in this specification is a Registered Trade Mark.

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Claims:

1. A heat sealed package, for commercial heat sterilization and unrefrigerated storage of food products, made of multi-layer polymeric material having a first
5 layer, which forms the outside surface of the package, that is relatively permeable to moisture at temperatures of unrefrigerated storage, to allow moisture present in the multi-layer material to escape out therefrom; a second layer which forms the inside
10 surface of the package that is substantially impermeable to moisture at the temperatures of unrefrigerated storage but permeable to moisture at temperatures of commercial sterilization, and is a heat sealable polymer capable of providing a package-closing seal
15 which will withstand commercial heat sterilization temperatures; and an interior oxygen barrier layer made of a vinyl alcohol polymer as hereinbefore ^{defined} ~~described~~.

2. A package for commercial heat sterilization and unrefrigerated storage of food
20 products, made of multi-layer polymeric material, comprising the following layers, in order: a first layer on the outside surface of the package which is permeable to moisture at temperatures of unrefrigerated storage, a second, oxygen barrier layer made of a
25 vinyl alcohol polymer as hereinbefore defined, a third



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layer permeable to moisture at temperatures of unrefrigerated storage, a fourth layer of polymeric material adherent to both the third layer and a fifth, heat sealing layer forming the inside surface of the package, the fifth layer being substantially impermeable to moisture at temperatures of unrefrigerated storage but permeable to moisture at temperatures of commercial heat sterilization.

3. The package according to claim 1 or claim 2 wherein the first layer which forms the outside surface of the package comprises nylon.

4. The package according to claim 1 or claim 2, wherein the oxygen barrier layer is sandwiched between two nylon layers, one of which constitutes the first layer permeable to moisture at temperatures of unrefrigerated storage, and the other of which has the heat sealable second layer bonded thereto.

5. The package according to claim 1, 2, 3 or 4, wherein the multi-layer polymeric material includes a polymeric layer adherent to the heat sealable second layer and to the oxygen barrier vinyl alcohol layer between these two layers.

6. The package according to claim 5, wherein the heat sealable second layer is a polyolefinic material and the adherent polymeric layer comprises a modified polyolefin.



7. The package according to any of claims 1 to 5, wherein the heat sealable second layer comprises a polyolefin polymer or copolymer.

8. The package according to claim 7, wherein
5 the polyolefinic layer comprises a polyolefin selected from high density polyethylene, polypropylene, copolymers of propylene and ethylene, and blends of polypropylene and polyethylene.

9. The package according to any of claims 1 to 8,
10 wherein the heat sealable second layer is high density polyethylene, and an adherent polymeric layer comprising a polyolefin blended with a graft copolymer of polyethylene and an unsaturated fused ring
15 carboxylic acid anhydride bonds the second layer and oxygen barrier layer together.

10. The package according to any of claims 1 to 8, wherein the inside layer is polypropylene or a polypropylene blend or propylene copolymer and an adherent layer comprising an acid anhydride grafted
20 polyolefin bonds the inside layer and oxygen barrier layer together.

11. The package according to any of claims 1 to 8, wherein the multilayer polymeric material comprises, in order, an outside surface layer of nylon,
25 the oxygen barrier layer, another layer of nylon, an adherent layer and an inside, heat sealable layer of



high density polyethylene, the adherent layer being a polyolefin blended with a graft copolymer of polyethylene and an unsaturated fused ring carboxylic acid anhydride.

5 12. The package according to any of claims 1 to 8, wherein the multilayer polymeric material comprises, in order, an outside layer of nylon, the oxygen barrier layer, another layer of nylon, an adherent layer and an inside, heat sealable layer
10 composed of polypropylene or a polypropylene blend or a polypropylene copolymer, the adherent layer being an acid anhydride grafted polyolefin.

 13. The package according to claim 10 or claim 11, wherein the inside, high density
15 polyethylene layer is extrusion coated with additional high density polyethylene, and the multi-layer material has the form of a tray which is covered by a film of the multi-layer sheet material.

 14. A package according to any of the
20 preceding claims, which is a pouch made from two sheets of the multi-layer polymeric material having an opening between a portion of their confronting margins for filling the package, the remainder of their confronting margins being heat sealed together.

25 15. A package for food products substantially as herein described with reference to and as shown in Figs. 1 to 3 of the accompanying drawings.