USE OF A POLYOLEFIN-POLYTERPENE BLEND FILM AS A FLAVOR AND ODOR BARRIER

VERWENDUNG EINES FILMS AUS EINEM POLYOLEFIN-POLYTERPEN-GEMISCH ALS AROMA- UND GERUCHSPERRFILM

EMPLOI D’UN FILM D’UN MELANGE DE POLYOLEFINE ET DE POLYTERPENE COMME BARRIERE ANTI-AROME ET ANTI-ODEUR

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

STETTER, Eileen A.
Rochester, New York 14623 (US)

Representative:
Lawrence, Peter Robin Broughton et al
GILL JENNINGS & EVERY,
Broadgate House,
7 Eldon Street
London EC2M 7LH (GB)

References cited:
EP-A- 0 079 520
EP-A- 0 406 642
US-A- 4 293 608

DATABASE WPI Week 8526, Derwent
DATABASE WPI Week 8901, Derwent

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).
The present invention is concerned with the overwrapping of products which can be adversely affected from a quality standpoint with the infusion of unwanted odors and unwanted flavors or by the loss of characteristic, desired aromas and flavors.

A constant problem in the packaging of commercial products, particularly those for human consumption, is now to protect the integrity of these products so that their desired flavor and aroma are not lost and unwanted odors and unpleasant flavors are not permitted to be transmitted into the product.

It is an object of the present invention to use a packaging film material to retain the integrity of the flavor and aroma of a packaged product and exclude unwanted odors and flavors from being transmitted to the product.

The present invention relates to the use of an oriented film which comprises a blend of:

(i) one or more polymers of an acyclic α-mono olefin;
(ii) one or more polymers of a natural or synthetic d-limonene and/or β-pinene

as a barrier for reducing the migration to a product of aromatic oils which provide unwanted odors and flavors.

The package preferably employs an oriented film of a blend of polypropylene and a member selected from the group consisting of polymerized d-limonene, polymerized beta-pinene, or a polymerized synthetic approximation of d-limonene and beta-pinene and mixtures thereof, to exclude unwanted odors or flavors and to retain those that are desirable.

It is preferred that the film structures identified above include a heat-sealable skin layer comprising a polyolefin of comparatively low stereoregularity on at least one surface thereof.

The present invention is broadly directed to the improvement in the flavor or aroma barrier properties of polypropylene films. It has been discovered that the admixture of certain polyterpenes identified above, into polypropylene polymers will effectively block the transmission of flavors and odors through polypropylene polymer blend while other polyterpene admixtures are comparatively ineffective. An example of a polymerized polyterpene which has given ineffective results is polymerized alpha-pinene.

This is a surprising result in the face of past general teachings regarding the moisture barrier and gas barrier benefits that can arise from the use of the broad general class of polyterpenes and their blends with polypropylene.

Past disclosures have taught improvements in gas barrier characteristics, which pertain to the minimization of non-condensable gases; such as oxygen, nitrogen, and carbon dioxide, through the film. These are useful in such applications as gas flushing with nitrogen or carbon dioxide to protect the product inside a package from oxidizing and becoming stale.

Past disclosures have also taught improvements in moisture barrier which pertain to the migration of water and water vapor through the film. These are useful in the packaging of dry foods, such as crackers and potato chips and to maintain texture.

What we have discovered is that application to pungent, aromatic oils is not encompassed in the past teaching. We have discovered a comparative few compounds which are effective in reducing the migration of aromatic oils when used in an admixture with polypropylene polymers. Oriented films made from these blends of polymers effectively prevent, for example, cigarette packages that are sold in gasoline station displays from picking up hydrocarbon odors, lemon-flavored cookies from losing their fresh-baked, lemon flavor and scent, etc. Oriented films with good moisture barrier and good gas barrier have not met these needs.

The base film of the present odor and flavor barrier structure is preferably comprised of a combination of a homopolymer polypropylene, which is of comparatively high stereoregularity having a melting point range of from 161° to 167°C (325° to 333°F), interblended suitably with from 1 to 20% by weight of the polyterpene used in the present invention. A preferred range is from 10 to 15% by weight of the added polyterpene. The basic structure of the aroma and flavor barrier film can be the same or similar to that described in U.S. Patent 4,911,976. In this patent the oriented multi-layer film structure comprises coextruded layers of (a) a base layer comprising polypropylene of comparatively high stereo regularity and (b) a heat-sealable skin layer comprising a polyolefin of comparatively low stereo regularity on at least one surface of (a). The skin layers can contain a slip additive and/or an antiblock material chosen from those suitable for such products. The skin layer can range from 0.5 to 5 μm. The preferred polypropylenes for the base layer are formed by polymerizing propylene in the presence of a stereo specific catalyst system. They can have a melt flow rate, measured by the ASTM-1238 technique, ranging from about 1 to about 25, preferably 2 - 4. The crystalline melting point is 161°C to 167°C (325° to 333°F). The average molecular weight range is from about 25,000 to about 100,000. The density is from 0.90 to 0.92.

The comparatively low stereo regular polyolefin polymers contemplated as the skin materials of the multi-layer system include, for example, ethylene-propylene-butene-1 terpolymers. Preferred terpolymers are ethylene-propylene-butene-1 terpolymers having 1-5 w% ethylene and 1-15 w% butene-1. The preferred polyterpenes have a molecular weight of from about 800 to about 15,000Mn.

The multi-layer films used in the present invention can be prepared employing commercially available systems for coextruding resins. The polypropylene homopolymer of comparatively high stereo regularity...
blended with the selected polyterpene can be coextruded with an ethylene-propylene-butene-1 terpolymer. The polymers can be brought to the molten state and coextruded from a conventional extruder through a flat sheet die, the melt streams being combined in an adapter prior to being extruded from the die. After leaving the die orifice, the multi-layer film structure is chilled and the quenched sheet then reheated and stretched, e.g., 4-6 times in the machine direction (MD), and subsequently, for example, 4-12 times in the transverse direction (TD). The edges of the film can be trimmed and the film wound onto a core.

The following Examples illustrate the invention.

EXAMPLE 1

A polypropylene homopolymer of comparatively high stereo regularity, i.e., Exxon PLTD745, was melt-blended with 15% by weight of Piccolyte C115 obtainable from Hercules Corporation. This material comprises polymerized d-limonene. This blend was coextruded with Sumitomo WS 709N which is an ethylene-propylene-butene-1 terpolymer containing 14% by weight butene-1 and 1.5% ethylene. This combination was coextruded and oriented so as to have outer skin layer dimensions of 0.6 μm and a core layer dimension of 20 μm. In order to test the effectiveness of this film in excluding deleterious odors and flavors from a package susceptible of absorbing such flavors, several packages of cigarettes were wrapped and sealed in the film. All the cigarette packages were placed in a controlled environment which exposed them to an aromatic hydrocarbon that provides a typical or potential odorant that can be readily identified chemically and measured quantitatively. In this case the aromatic hydrocarbon was toluene. Individual cigarette packs were withdrawn from the controlled environment in a time sequence. A small air space sample was then taken from within the package with a hypodermic syringe. This sample was analyzed chromatographically. The chromatographic peak stayed relatively low as time progressed and raised only slowly at longer times. The test was carried out over a time period of from 0-200 hours. This showed that polymerized d-limonene is an excellent odor barrier when mixed with polypropylene.

EXAMPLE 2

The technique of Example 1 was repeated except that polymerized beta-pinene was employed as the material blended with the polypropylene. Film samples were made in the same manner as in Example 1. Several packages of cigarettes were wrapped and sealed as indicated above and subjected to the same time exposure to toluene. A dramatic increase in the amount of toluene transported through the film wrapper was noted after approximately 100 h of exposure. The level was about three to four times higher than observed when polymerized beta-pinene was employed as the effective barrier agent blended with the polypropylene. This indicates that the polymerized alpha-pinene is an ineffective odor barrier material.

A synthetic combination of polymerized d-limonene and polymerized beta-pinene obtainable from Hercules as PS676 is also an effective odor and flavor barrier and can be used in the same manner as the polymerized d-limonene and beta-pinene.

Over 60% of the natural and synthetic polyterpenes tested in blends with polypropylene had little or no effect on aroma barrier.

Claims

1. Use of an oriented film which comprises a blend of:
   (i) one or more polymers of an acyclic α-monolefin; and
   (ii) one or more polymers of a natural or synthetic d-limonene and/or β-pinene
   as a barrier for reducing the migration to a product of aromatic oils which provide unwanted odors and flavors.

2. Use according to claim 1 wherein (i) comprises polypropylene.

3. Use according to claim 1 or 2 wherein (ii) constitutes from 1 to 20% by weight of the blend.

4. Use according to any preceding claim wherein the film includes a heat sealable skin layer comprising a polyolefin of comparatively low stereoregularity on at least one surface thereof.

5. Use according to claim 4 wherein the polyolefin is a terpolymer of ethylene, propylene and butylene.

6. Use according to any preceding claim to furnish the product in a sealed package.

Patentsprüche

1. Verwendung eines orientierten Films, der ein Gemisch aus
   (i) einem oder mehreren Polymeren eines acyclischen α-Monolefins und
(ii) einem oder mehreren Polymeren eines natürlichen oder synthetischen d-Limonens und/oder β-Pinens enthält, als Sperre zum Reduzieren des Wanderns aromatischer Öle, die einen unerwünschten Geruch und Geschmack hervorrufen, zu einem Produkt.

2. Verwendung nach Anspruch 1, worin (i) Polypropylen enthält.

3. Verwendung nach Anspruch 1 oder 2, worin (ii) 1 bis 20 Gew% des Gemisches ausmacht.

4. Verwendung nach einem der vorstehenden Ansprüche, worin der Film an mindestens einer Oberfläche eine heißsiegelbare Hautschicht aufweist, die ein Polyolefin mit einer vergleichsweise niedrigen Stereotheiligkeit enthält.

5. Verwendung nach Anspruch 4, worin das Polyolefin ein Terpolymer aus Ethylen, Propylen und Butylen ist.


Revidendations

1. Utilisation d'un film orienté qui comprend un mélange de :

   (i) un ou plusieurs polymères d'une α-monocyclique acyclique ; et
   (ii) un ou plusieurs polymères de d-limonène et/ou β-pinène naturels ou synthétiques

   pour diminuer la migration dans un produit d'huiles aromatiques et qui constitue une protection vis-à-vis des odeurs et saveurs indésirables.

2. Utilisation selon la revendication 1, dans laquelle (i) comprend du polypropylène.

3. Utilisation selon la revendication 1 ou 2, dans laquelle (ii) constitue de 1 à 20 % en poids du mélange.

4. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le film comprend une couche de peau thermosoudable comprenant une polyoléfine d'une stéréorégularité relativement basse sur au moins l'une de ses faces.

5. Utilisation selon la revendication 4, dans laquelle la polyoléfine est un terpolymer d'éthylène, de pro-

pylène et de butylène.

6. Utilisation selon l'une quelconque des revendications précédentes, pour fournir le produit sous un emballage scellé.