

[54] **PROCESS FOR PREPARING ARTICLES
FABRICATED FROM
POLYOLEFIN/POLYAMIDE BLENDS
HAVING LOW PERMEABILITY TO GASES**

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[58] Field of Search 264/234-235,
264/345-346; 260/857 L

[56] **References Cited**

UNITED STATES PATENTS

3,293,341 12/1966 Boeke et al. 264/235

3,317,642 5/1967 Bailey 264/235
3,383,375 5/1968 van der Vegt et al. 264/235
3,415,925 12/1968 Marans 264/331
3,544,673 12/1970 Inskeep et al. 264/235
3,595,952 7/1971 Boyer et al. 264/346

OTHER PUBLICATIONS

Polythene, 1st ed., Renfrew & Morgan, Interscience
Publishers Inc. N.Y. TP 986 P56 R 4 c4 1960 pp.
109-111, 113, 250 & 255.

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[57] **ABSTRACT**

The gas permeability of shaped articles fabricated
from polyolefin/linear polyamide blends is decreased
by heating the article at a temperature of 140°-250°F
for 0.1 to 30 minutes.

6 Claims, No Drawings

PROCESS FOR PREPARING ARTICLES FABRICATED FROM POLYOLEFIN/POLYAMIDE BLENDS HAVING LOW PERMEABILITY TO GASES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to shaped articles fabricated from a blend of a polyolefin and a synthetic linear polyamide and more particularly to articles fabricated from polyolefin/linear polyamide blends having decreased permeability to gases.

2. The Prior Art

U.S. Pat. No. 3,467,283 Discloses a product dispensing container which includes a product containing compartment and a propellant compartment. The compartments are generally separated by a common wall of the product containing compartment. The common wall of such a dispensing container is defined by a collapsible bag positioned internally of the container body and secured to a top closure of the latter. The top closure generally includes a manually operable valve-actuated dispensing mechanism for dispensing a product packaged within the bag under the influence of a pressurized propellant housed in the propellant chamber between the bag and the container body.

Containers of the type disclosed in U.S. Pat. No. 3,457,283 are used for the packaging of a variety of products where it is desired that the product to be dispensed be maintained in the container separate from the propellant as the propellant such as isobutane when contacted with or absorbed into the product has a deleterious effect on the product such as offtaste, product consistency and the like.

It has been proposed to fabricate the collapsible bag of U.S. Pat. No. 3,467,283 from a polymeric mixture of substantially equal weight proportions of a polyolefin such as polyethylene and a synthetic linear polyamide such as nylon which polymeric mixtures are disclosed in U.S. Pat. Nos. 3,093,255, 3,373,223 and 3,373,224.

Although plastic bags fabricated from polyethylene/nylon mixtures exhibit exceptional impermeability to a variety of organic liquid products such as medicinal and cosmetic preparations, deodorants, oils and the like, the plastic bags have only marginal impermeability properties with regard to gaseous propellants such as isobutane and this marginal impermeability to such propellants has inhibited the use of this polymeric mixture in packaging applications where propellant permeability is a critical factor such as in containers of the type disclosed in U.S. Pat. No. 3,467,283.

The conventional manner to improve the gas permeability characteristics of polymeric base materials has been to laminate to the polymeric substrate a thin second coating of a material which is impermeable to the gas. These lamination processes are costly, time-consuming and unless such coatings which are applied remain completely continuous without being broken or damaged in any spot or location, articles fabricated therefrom will not have adequate resistance to penetration by the propellant gas. Therefore there is a definite need in the art for improving, that is decreasing, the gas permeability of the polyethylene/nylon mixture from which the plastic bags are fabricated.

It is known to the art, namely U.S. Pat. No. 3,415,925, that heating shaped articles fabricated from blends of polyethylene with minor amounts (2-8%) of

wax at 60°-110°C (140°-230°F) increases the gas permeability of the article. U.S. Pat. No. 3,323,206 teaches that temperatures up to 250°F have no effect on the permeability of nylon and that to prevent permeation of gases such as propane and butane it is necessary to laminate the nylon with aluminum foil or other suitable barrier film.

SUMMARY OF THE INVENTION

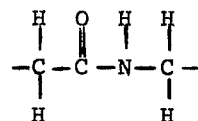
It has been unexpectedly discovered that the permeability of articles fabricated from a blend of a polyolefin and a synthetic linear polyamide can be substantially decreased by heating the article at a temperature between about 140°F and 250°F for a period between about 0.1 minute and about 30 minutes.

The present invention provides a simple, rapid heat treatment process which is highly effective in decreasing the gas permeability of articles fabricated from polyolefin/linear polyamide blends. As will hereinafter be more fully described the heat treatment process of the present invention effects a decrease in the gas permeability of articles fabricated from polyolefin/polyamide blends from marginal permeability to a permeability acceptable in commercial applications where permeation of gaseous propellants is presently a problem.

PREFERRED EMBODIMENTS

To decrease the permeability of articles formed from the polyolefin/polyamide blends to propellant gases such as propane and isobutane, an article fabricated therefrom such as a hollow container or a collapsible bag is heated in any suitable medium, which may be a gas such as air, nitrogen, steam or a liquid inert to the polymer blend such as glycerine or mineral oil at a temperature between about 140°F and about 250°F for a period, varying inversely as the temperature, in the range from about 0.1 minute to about 30 minutes. It has not been found necessary in any instance to employ periods of heat treatment longer than about 30 minutes and in general, little if any advantage occurs by heating for periods extending beyond 30 minutes, even when operating at temperatures such as 140°F near the lower end of the herein-claimed range. When the heat treatment is effected, for example, at 212°F using steam, which is near the upper end of the claimed temperature range, it is preferred not to heat beyond 5 minutes and little advantage has been found to accrue to a heat treatment at temperature prolonged beyond 2 minutes. Noticeable decreases in gas permeability are obtained through the use of the present heat treatment, even for periods less than 1 minute. Preferred heat treatment conditions are steam at 175°F for 15 minutes or 212°F for 1 minute.

The term "synthetic linear polyamide" as used in the present specification and claims means a long-chain synthetic polymeric amide which has recurring amide groups as an integral part of the main polymer chain having the structure:



separated by alkylene groups containing at least 2 carbon atoms and having an intrinsic viscosity of at least

0.1. Intrinsic viscosity is defined in U.S. Pat. No. 2,130,948.

Among the polyamides which are useful in preparing polymeric blends of the present invention are polypentamethylene sebacamide, polyhexamethylene adipamide (Nylon 66), polyhexamethylene nonanamide (Nylon 69), polyhexamethylene sebacamide (Nylon 610), polydecamethylene adipamide, polydecamethylene sebacamide, poly-m-phenylene sebacamide, polycaproatide (Nylon 6), poly-7-heptanoamide (Nylon 7), poly-11-undecanoamide (Nylon 11), polylauryl lactam (Nylon 12), as well as other polyamides and interpolymers of the types mentioned in U.S. Pat. Nos. 2,071,253, 2,130,523 and 2,130,948 issued to W. H. Carothers, and U.S. Pat. No. 2,285,009 issued to M. M. Braubaker et al.

The commercially available polyamides of the nylon type melt at temperatures of the order of about 180° to about 260°C.

Nylon 6 and Nylon 66 are the preferred polyamide resin components of the polymer blends treated in accordance with the present invention.

The linear polyamide component of the polymer blend is present in an amount ranging from about 10 to about 60 percent by weight of the total polymer blend, and preferably about 40 to about 55 percent by weight of the total polymer blend.

The term "polyolefin" as used in the present specification and claims refers to homopolymers of monoolefines containing from 2 to 4 carbon atoms, such as ethylene, propylene, and butylenes, such as isobutylene, butene-1, and butene-2, and styrene, as well as copolymers of said monoolefines.

The polyolefin component is present in the polymer blend in an amount ranging from about 40 to about 90 percent by weight of the total blended polymer mixture and preferably 45 to 60 percent by weight of the total polymer mixture. While polyethylene and polypropylene or poly (propylene:ethylene) copolymers are the preferred polyolefin resins, other members of this group of similar molecular weight distributions are useable. When low density (approximately 0.92-0.93) polyethylene is employed, it has been found preferable to maintain the presence of such component in the polymer blend within from about 45 to about 75 percent by weight. When employing polyethylene of approximately 0.95 density, the preferred range is from 75 to 90 percent by weight. When employing polypropylene type resins, a preferred range is from 70 to 90 percent by weight of the total blended polymer system.

Suitable polyolefins are: regular branched, low density (0.92-0.93) polyethylene available from the Union Carbide Company under the "Bakelite DYNK-1", high density (0.95 or above) polyethylene available from the Phillips Chemical Co. under the "Marlex 5012" tradename, and an isotactic-type polypropylene resin containing a minor amount of copolymerized ethylene having a density of 0.91 and a melt index of 0.55 at 230°C. A suitable polypropylene is marketed as TC-6-12 by the Shell Chemical Co.

The polyolefin/polyamide blends treated in accordance with the present invention may contain from about 1 to about 20 percent by weight of an ionic hydrocarbon copolymer of an alpha olefin and a 3 to 5

carbons, alpha, beta-ethylenically unsaturated carboxylic acid, the acid groups of which may optionally be neutralized with a metal ion in accordance with the teachings of U.S. Pat. No. 3,437,718, the disclosure of which patent is incorporated herein by reference.

The ionic copolymer improves the dispersion and capatibility of the polyolefin and polyamide resin mixture and also stabilizes the dispersion against agglomeration in the molten state.

The ionic hydrocarbon copolymer employed as a component of the blends of this invention is a copolymer of an alpha olefin having the formula $R-CH=CH_2$ wherein R is a radical selected from the class of hydrogen and alkyl radicals containing 1-3 carbon atoms, and an alpha, beta-ethylenically unsaturated carboxylic acid containing 3-5 carbon atoms. The alpha-olefin content of the copolymer is at least 70 mole percent, based on the ionic copolymer.

The carboxylic acid groups are randomly distributed over the copolymer molecules and can be 0-100% neutralized by metal cations distributed over the carboxylic acid groups of the copolymer. The metal cations can be derived from metals selected from the class consisting of Groups I, II, and IV of the Periodic Table of elements published by the Fisher Scientific Company.

Illustrative of alpha, beta-ethylenically unsaturated carboxylic acids useful in the preparation of the ionic hydrocarbon copolymer are acrylic acid, methacrylic acid, ethacrylic acid, itaconic acid, maleic acid, fumaric acid, and monoesters of itaconic acid, maleic acid, and fumaric acid. Other monomers can, of course be terpolymerized in the copolymer.

Preferably the ionic hydrocarbon copolymer is an ethylene/acrylic or methacrylic acid copolymer comprising 80-99 mole percent ethylene and 1 to 10 mole percent acrylic or methacrylic acid. The carboxylic acid groups of the ethylene/acrylic or methacrylic acid copolymer may be unneutralized or neutralized up to 100% by a cation derived from a metal of Group I, II, or IV. Preferably, the carboxylic acid groups of the ethylene/acrylic or methacrylic acid copolymer are neutralized to the extent of 30-60%. The preferred cations used in the neutralization of said carboxylic acid groups are Na^+ , K^+ , Ca^{++} , Zn^{++} and Pb^{++} .

A preferred embodiment of a polymeric blend treated in accordance with the present invention is comprised of 40-90 percent by weight of the polyolefin resin, 10 to 60 percent by weight of the synthetic linear polyamide and 1 to 10 percent by weight of the ionic hydrocarbon copolymer.

The blends of the present invention are obtained by dispersing the polyamide into the polyolefin resin along with the ionic hydrocarbon copolymer at temperatures ranging from about 300° to 500°F, preferably 388° to 450°F and at pressures ranging from 10 to 5000 pounds per square inch and preferably about 400 to 2000 pounds per square inch.

In addition to the ionic hydrocarbon copolymer, it is obvious that other well-known ingredients may be used and included in the polymer blend. These may include, for example, pigments, dyestuffs, inorganic fillers or the like.

The following example will serve to further illustrate the invention.

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EXAMPLE

Collapsible bags having an open end essentially like the bags illustrated in U.S. Pat. No. 3,467,283 were blow molded from a homogenous blend of 50 parts nylon 6, 45 parts of a low density (0.92) polyethylene and 5 parts of ethylene/methacrylic acid copolymer comprised of 96 molar percent ethylene and 4 molar percent methacrylic acid, the methacrylic acid being neutralized about 38% by sodium ions.

A test series was conducted wherein the bags were subjected to a treatment with steam ranging at temperatures from 155°F to 212°F for 0.25 minutes to 15 minutes.

The permeability of the heat treated bags were determined in accordance with the following test procedure:

A 200 cc collapsible bag open at one end was filled with 200 cc water. The edge portions adjacent the open end of the bag were crimped into sealing engagement about the edge portions of the open end of a dome closure by the curled edges of a valve cup supporting a dispensing valve. The rim of the dome closure was placed in sealing engagement with the open end of a standard 6 ounce hollow cylindrical aerosol container, the collapsible bag being positioned in the interior of the container before sealing as shown in U.S. Pat. No. 3,467,283. The interior of the container was then charged to 50 psi with isobutane propellant through a grommet seated in the bottom closure plate of the container. The water in the bag was then displaced with 200 cc nitrogen at 50 psi. The aerosol containers were stored at room temperature for 4 and 6 week periods. After the storage period expired the gas permeability of the bag contained in the aerosol container was determined by analyzing the nitrogen gas contained in the bag for isobutane content. The concentration of isobutane in nitrogen was determined chromatographically using a 6 foot Poropak QS column maintained at 135°C.

The results of these tests (run numbers 1 through 6) are summarized in the Table below. For purposes of comparison permeability tests were conducted on identical bags used in the test series of the example with the exception that the bags were not heat treated before sealing in the isobutane filled aerosol container. The results of these control tests (run numbers C₁-C₂) are also summarized in the Table.

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TABLE

Run No.	Steam Treatment Temp. °F	Time (Mins.)	Storage Period In Isobutane After Treatment (Weeks)	Isobutane Permeation (ppm)	% Decrease in Permeation
C ₁	Control	—	4	43,900	—
1.	212°	0.25	4	39,600	10
2.	212°	0.75	4	37,100	15
C ₂	Control	—	6	84,500	—
3.	175°	5.0	6	73,800	13
4.	175°	15.0	6	68,500	19
5.	155°	5.0	6	73,900	12
6.	155°	15.0	6	70,400	17

By reference to the above table, it is immediately apparent that heat treatment of bags fabricated from polyethylene/nylon blends has a material effect in reducing the gas permeability of the bag.

What is claimed is:

1. A method of decreasing the gas permeability of shaped articles fabricated from blends of polyolefins and synthetic linear polyamides which comprises

- fabricating a shaped article from a mixture comprised of about 40 to about 90 percent by weight of a polyolefin and about 10 to about 60 percent by weight of a synthetic linear polyamide and then
- heating the fabricated article at about 140° to about 250°F for a time sufficient to effect a decrease in the gas permeability of the article.

2. The method of claim 1 wherein the article is heated for a period of about 0.1 to 30 minutes.

3. The method of claim 1 wherein the polyolefin is polyethylene.

4. The method of claim 1 wherein the polyamide is polycaproamide.

5. The method of claim 1 wherein the article is heated with steam in the range of 155° to 212°F for 0.1 to 15 minutes.

6. The method of claim 1 wherein a copolymer of an alpha olefin having the formula



wherein R is a radical selected from the group consisting of hydrogen and alkyl radicals containing 1 to 3 carbon atoms and an alpha, beta-ethylenically unsaturated carboxylic acid containing 3 to 5 carbon atoms, is incorporated in the polymer mixture at a concentration ranging from about 1 to about 20 percent by weight.

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