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(54) VINYL CHLORIDE POLYMER BARRIER PACKAGING COMPOSITIONS

(71) We, UNION CARBIDE CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to vinyl chloride polymer-ethylene/vinyl alcohol copolymer barrier packaging compositions and in particular to those compositions having enhanced resistance to gas permeability and moisture vapor transmission.

Polyvinyl alcohol and its copolymers containing large numbers of hydroxyl groups are known to possess very low gas permeabilities. However, the use of these materials in packaging applications is severely restricted by moisture sensitivity imparted by the hydroxyl function. The gas permeabilities of polyvinyl alcohol homopolymer increase exponentially as a function of relative humidity. Copolymers of vinyl alcohol although somewhat less sensitive are still prone to this defect for packaging materials. Commercial standards for acceptable packaging materials require that the films used have a low gas permeability particularly to oxygen and in addition have a low moisture vapor transmission rate. One solution to this problem has been proposed in United States Patent Specification No. 3,585,177 in which a lower alpha olefin/vinyl alcohol copolymer is prepared having a residual ester content below 3.0% and an olefin content between 5.0 and 40% by weight and wherein the differential thermal analysis curve for the copolymer is a single narrow endotherm having a melting range of less than 30°C.

A more economical solution to the problem of providing suitable packaging materials having good barrier properties resides in blending cheaper resins with a balance of properties. This approach however is limited because of the problem of incompatibility which exists between many available resins.

It has now been found that a composition suitable for barrier packaging materials having enhanced resistance to gas permeability and moisture vapor transmission is provided by a mixture of a vinyl chloride polymer having no carboxyl groups and from 10 to 30% by weight based on the weight of vinyl chloride polymer of an ethylene/vinyl alcohol copolymer containing greater than 61 weight percent or 50 mole percent, and preferably at least 74 weight present, of vinyl alcohol in the said copolymer.

Ethylene/vinyl alcohol copolymers suitable for use in this invention are commercially available. These can be used as purchased or ethylene/vinyl acetate copolymers also commercially available can be converted by hydrolysis to suitable ethylene/vinyl alcohol copolymers. The ethylene/vinyl alcohol copolymers described herein are essentially fully hydrolyzed ethylene/vinyl acetate copolymers although copolymers containing up to 3% by weight of residual vinyl acetate may also be used. It is worthy of note that ethylene/vinyl alcohol copolymers containing greater than 50 mole percent vinyl alcohol copolymerized therein can be converted into films which have outstanding resistance to oxygen but are unsatisfactory because of their poor sensitivity to moisture. This deficiency is remedied by blending these ethylene/vinyl alcohol copolymers with vinyl chloride polymers including both homopolymers and copolymers of vinyl chloride with copolymerizable ethylenically unsaturated monomers which contain no carboxyl groups.

The vinyl chloride polymer must not contain carboxyl groups as would be

present where vinyl chloride is copolymerized with acrylic acid, methacrylic acid, or maleic acid since the carboxyl functionality which results in cross-linking with pendant OH groups in the ethylene-vinyl alcohol copolymers results in gelation and loss of compatibility of the two resins.

5 A particularly preferred vinyl chloride polymer is one containing at least 98.1 percent by weight of vinyl chloride and from 0.3 to 1.9 percent by weight of ethylene. The preparation of this copolymer is described in United States Patent Specification No. 3,843,616. Other exemplary monomers which can be
10 copolymerized with vinyl chloride to provide one of the components of this invention include vinyl esters, such as, vinyl acetate, vinyl propionate, vinyl laurate, and vinyl stearate; other lower alpha-olefins, such as propylene and butylene; acrylonitrile; and alkyl acrylates or methacrylates having up to 18 carbon atoms in the alkyl moiety such as methyl acrylate, butyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate, ethyl methacrylate, decyl methacrylate, and
15 hexadecyl methacrylate. The vinyl chloride/vinyl ester copolymers may contain from 5 to 20 weight percent of vinyl acetate copolymerized therein with a range of from 8 to 15 percent by weight of vinyl acetate being particularly preferred. The preferred inherent viscosity of these vinyl chloride/vinyl acetate copolymers, which are known in the art, lies in the range of from 0.50 to 0.54, although inherent viscosities of from 0.47 to 1.0 can also be used if desired. Vinyl chloride
20 homopolymers, also known in the art, may be used in the practice of this invention preferably at inherent viscosities in the range of from 0.5 to 1.0 although those having values from 0.40 to 1.4 can also be used if desired (ASTM 1243, Method A).

A preferred commercial grade of vinyl chloride polymer is one known in the art as moulding resins. These contain additives, as for example, impact modifiers, such as, methyl methacrylate-butadiene-styrene terpolymers; extrusion aids, such as, methyl methacrylate polymers; heat stabilizers, such as, dioctyl tin mercaptide and maleates; antioxidants, such as, epoxidized soybean oil; lubricants, such as, hydrocarbon waxes; ultraviolet stabilizers, and colourants. Even when these
25 additives are present at levels as high as from 20 to 25% by weight of the vinyl chloride polymer, surprisingly they do not interfere with the resistance of the combination of vinyl chloride polymers and ethylene/vinyl alcohol polymers to oxygen permeability and moisture vapor transmission.

It was unexpected that a combination of a vinyl chloride polymer and an ethylene/vinyl alcohol copolymer would be compatible particularly after films
35 fabricated from these compositions had been biaxially oriented.

Another desirable feature of these films is that they are transparent which is particularly desirable in a food packaging film. When the vinyl chloride polymers in the compositions described above were replaced by several readily available and
40 commercially used thermoplastic resins, including, polyethylene, poly(acrylonitrile-butadiene-styrene), polystyrene, and styrene-acrylonitrile copolymer, films made from these blends exhibited gross incompatibility, opacity, and a pronounced tendency to delaminate making them unacceptable for use as barrier packaging materials.

45 As will be seen in the working examples following, the amounts of vinyl chloride polymers and ethylene/vinyl alcohol copolymers in these compositions is critical in order to obtain a balance of low oxygen permeability coupled with low moisture vapor transmission. The fortuitous combination of these two polymers affords an opportunity to take advantage of one property of each without seriously
50 detracting from the desired physical properties of each. In addition the blends of vinyl chloride polymers and ethylene/vinyl copolymers provide films with desirable mechanical properties. The criticality of the vinyl alcohol content of the ethylene/vinyl alcohol copolymers is demonstrated in the Figure which delineates the permeability of films from hydrolyzed ethylene/vinyl acetate copolymers to
55 both moisture vapor transmission and oxygen transmission. This graph shows that while the oxygen transmission of hydrolyzed ethylene/vinyl acetate is markedly decreased in the range from 50 mole percent vinyl alcohol content upwards, the moisture vapor transmission is markedly increased thus negating the advantages derived from ethylene/vinyl alcohol copolymer used alone for a barrier packaging
60 material.

The film or sheets fabricated from the compositions of the present invention preferably have a maximum oxygen permeability of 1.1 cc./mil/100 in.²/24 hrs. atm. and a maximum moisture vapor transmission of 1.7 g./100 in.²/24 hrs. mil at 38°C. and 90% relative humidity. Most preferably the biaxially oriented film or sheets
65 have an oxygen permeability of less than 0.5 cc./mil./100 in.²/24 hrs. atm.

EXAMPLE 1

A compounding extruder was used to blend twenty parts by weight of an ethylene/vinyl alcohol copolymer containing 26 percent of ethylene and 74 percent of vinyl alcohol having a reduced viscosity of 0.88 (in dimethyl formamide at 25°C. as 0.2% solution) and a Tg of 65°C. with 80 parts by weight of Bakelite® QMDA-4488 (a vinyl chloride molding resin consisting of about 79 percent of a vinyl chloride resin containing 1.2 percent ethylene copolymerized therein, 13.5 percent of a methyl methacrylate-butadiene-styrene terpolymer impact modifier, 2.5 percent of a polymethylacrylate extrusion aid and the remainder conventional heat and light stabilizers, colorants, antioxidants, lubricants and the like, commonly used in the vinyl chloride polymer field). The two resins were then converted into films in a heated press. Some of these films obtained thereby were biaxially oriented (3:1 stretch ratio). The oxygen permeability of non-oriented and biaxially oriented films were recorded in Table 1 as well as the moisture vapor transmission of non-oriented film. For comparison films made from 100 percent vinyl chloride resin and 100 percent ethylene/vinyl alcohol copolymer were also prepared and examined together with combinations of 90/100 by weight of vinyl chloride polymer/ethylene-vinyl alcohol copolymer and 70/30 vinyl chloride polymer/ethylene-vinyl alcohol copolymers.

As can be seen from the data in Table 1 below the poor oxygen permeability of vinyl chloride resin is greatly altered by combining this resin with the ethylene-vinyl alcohol copolymer without loss of the desirable low oxygen permeability values of the latter copolymer. In addition the resistance to moisture vapor transmission of the ethylene/vinyl alcohol copolymer is enhanced.

TABLE 1
Effect of Orientation and EVOH Content on Film
Permeability and Moisture Vapor Transmission

Polymer Blend PVC ^(a) /EVOH ^(b)	Oxygen Permeability ^(c) Non-oriented	Biaxially Oriented	Moisture Vapor Transmission ^(d) Non-oriented
100/0	15.0	ca. 15	3
90/10	8.2	4.5	—
80/20	2.8	0.5	2.3
70/30	1.1	0.5	1.7
0/100	0.5	0.5	5

(a) Vinyl chloride molding resin described in Example 1.

(b) Ethylene/vinyl alcohol polymer described in Example 1.

(c) cc/mil/100 in.²/24 hrs. atm.

(d) g./mil/100 in.²/24 hrs. at 100°F. (38°C.) and 90% relative humidity (R.H.).

Table 2 contains a comparison of non-oriented and biaxially oriented films prepared from an 80/20 mixture of vinyl chloride polymer/ethylene-vinyl alcohol copolymer (PVC/EVOH) in mechanical properties.

TABLE 2
Effect of Orientation on Mechanical Properties of
PVC/EVOH Blends (80/20 wt. %)

Property	Non-oriented	Oriented
Tensile Modulus ⁽¹⁾ , psi	300,000	280,000
Tensile Strength ⁽¹⁾ , psi	5,900	4,800
Elongation at break ⁽¹⁾ , %	3	86
Pendulum Impact ⁽²⁾ ft. lbs./in ³	5	25
Glass Transition Temperature ⁽³⁾ , °c.	70	70

(1) ASTM D-63860

(2) ASTM D-256-56

(3) Determined by the method described in "Mechanical Properties of Polymers", L. E. Nielsen, Reinhold Publishers, NYC, (1962).

EXAMPLE 2

Eighty parts of a vinyl chloride/ethylene molding resin containing 1.2 percent of ethylene copolymerized therein having an inherent viscosity of about 0.96 (ASTM D-1243, Method A) was blended in a 2-roll mill with twenty parts of the ethylene/vinyl alcohol copolymer described in Example 1. The vinyl chloride resin contained a small amount (0.5% based on the vinyl chloride resin) of a petroleum wax lubricant.

Bioriented films of the blend were obtained having an oxygen permeability of 0.41 and 0.54 cc./mil/100 in.²/24 hrs. atm. Samples of non-oriented film of this blend showed an oxygen permeability of 4.2 cc./mil/100 in.²/24 hrs. atm.

EXAMPLE 3

A vinyl chloride homopolymer (80 parts) having an inherent viscosity (ASTM D-1243 Method A) of 0.78 was blended on a two-roll mill with 20 parts of the ethylene/vinyl alcohol copolymer described in Example 1. The vinyl chloride homopolymer contained about 1% of dioctyl tin mercaptide and 0.5% of dioctyl tin maleate as heat stabilizers based on the weight of vinyl chloride homopolymer.

A plaque was made of the compatible blend as well as biaxially oriented films. The mechanical properties of these are shown in Table 3.

TABLE 3

Property	Molded Plaque	Biaxially Oriented Film
Tensile Modulus ⁽¹⁾ , psi	313,000	400,000
Tensile Strength ⁽¹⁾ , psi	4,370	17,800
Elongation at break ⁽¹⁾ , psi	1.6	57
Pendulum impact ⁽²⁾ , ft. lbs./in. ³	5	590
(1) ASTM D-638-60		
(2) ASTM D-256-56		

EXAMPLE 4

When Example 1 is repeated with the exception that normally solid vinyl chloride homopolymer is substituted for the vinyl chloride/ethylene copolymer, biaxially oriented films having comparable oxygen permeability and moisture vapor transmission are obtained.

EXAMPLE 5

When Example 1 is repeated with the exception that normally solid vinyl chloride/vinyl acetate copolymer is substituted for the vinyl chloride/ethylene copolymer, biaxially oriented films having comparable oxygen permeability and moisture vapor transmission are obtained.

EXAMPLE 6

Forty parts of a normally solid vinyl chloride/acrylonitrile copolymer containing 20 percent by weight of acrylonitrile copolymerized therein having an inherent viscosity of 0.6 (ASTM 1243, Method A) was stabilized with 5 percent of dioctyl tin maleate based on the weight of copolymer and mixed in a Brabender mixer at 200°C. for ten minutes with the ethylene/vinyl alcohol copolymer described in Example 1. The resultant blend was compatible and had a melt index at 180°C. (10 P and 10 minutes — ASTM D-1238-625) of 3.38 dg./min. A bioriented film of this blend showed an oxygen permeability of 0.51 cc./mil/100 in.²/24 hrs. atm. Mechanical properties of a plaque of the blend include a Tg of 75°C., a tensile modulus of 379,000 psi, a tensile strength of 7390 psi, an elongation at break of 2.2% and a pendulum impact strength of 3 ft. lbs./in.³.

The oxygen permeability of a bioriented film of the vinyl chloride/acrylonitrile copolymer alone was 3.3 cc./mil/100 in.²/24 hrs.

Controls A, B and C

Attempts to obtain a compatible blend of the ethylene/vinyl alcohol copolymer described in Example 1 with low density polyethylene, high density polyethylene and styrene/acrylonitrile copolymer at weight ratios of 1:1 to 1:3 with a mixing extruder at 190°C. were unsuccessful. Films obtained from such blends were physically unacceptable and delaminated.

WHAT WE CLAIM IS:—

1. A composition suitable for the fabrication of barrier packaging materials comprising a mixture of:
- 5 (A) a vinyl chloride polymer having no carboxyl groups, and
(B) from 10 to 30 percent by weight, based on the weight of vinyl chloride polymer, of an ethylene/vinyl alcohol copolymer containing greater than 61 weight percent or 50 mole percent of vinyl alcohol in the copolymer. 5
2. A composition as claimed in Claim 1, wherein the vinyl chloride polymer is a homopolymer. 10
3. A composition as claimed in Claim 1, wherein the vinyl chloride polymer is a copolymer of a C₁ to C₄ alpha-olefin and vinyl chloride. 10
4. A composition as claimed in Claim 3, wherein the alpha-olefin is ethylene.
5. A composition as claimed in Claim 3, wherein the alpha-olefin is propylene.
- 15 6. A composition as claimed in Claim 1, wherein the vinyl chloride polymer is a copolymer of acrylonitrile and vinyl chloride. 15
7. A composition as claimed in any one of the preceding claims, wherein the ethylene/vinyl alcohol copolymer contains at least 74 weight percent of vinyl alcohol copolymerized therein.
- 20 8. A composition as claimed in any one of the preceding claims including an impact modifier, an extrusion aid, a heat stabilizer, an antioxidant, a lubricant, an ultraviolet stabilizer or a colourant. 20
9. A composition as claimed in Claim 1 substantially as hereinbefore described.
- 25 10. A composition as claimed in Claim 1 substantially as hereinbefore described in any one of the Examples. 25
11. A packaging film or sheet when fabricated from a composition as claimed in any one of the preceding claims.
- 30 12. A film or sheet as claimed in Claim 11 having a maximum oxygen permeability of 1.1 cc./mil/100 in.²/24 hrs. atm. and a maximum moisture vapor transmission of 1.7 g./100 in.²/24 hrs. mil at 38°C and 90% relative humidity. 30
13. A film or sheet as claimed in Claim 11 or Claim 12 when biaxially oriented.
14. A film or sheet as claimed in Claim 13 having an oxygen permeability of less than 0.5 cc./mil/100 in.²/24 hrs. atm.
- 35 15. A sheet or film as claimed in Claim 11 substantially as hereinbefore described in any one of the Examples. 35

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