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(54) MULTILAYER, SYNTHETIC-RESIN LAMINATES
AND A PROCESS FOR THE PRODUCTION THEREOF

(71) We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a company organised and existing under the Laws of Japan, of 8, Nihonbashi Horidome-cho, 1-chome, Chuo-ku, Tokyo-To, Japan, 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: 5

This invention relates generally to multilayer synthetic-resin laminates and to a process for producing them. More particularly, the invention relates to a process for producing a multilayer laminate article from an olefin-containing polymer and a nitrile-containing polymer in which process a polymer mixture formed by blending an olefin-containing polymer and a nitrile-containing polymer is interposed between an olefin-containing polymer layer and a nitrile-containing polymer layer for the purpose of imparting high adhesive strength between the two polymer layers. 10

Heretofore, olefin-containing polymers have been widely used as packaging materials such as blow-moulded bottles, sheets, films and tubes. Olefin-containing polymers, however, have the characteristic of a high permeability with respect to inorganic gases such as oxygen and carbon dioxide gases and to organic gases such as hydrocarbon gases, and, for this reason, these materials have not yet been used in applications requiring a gas-barrier characteristic in the fields of packaging of products such as foodstuffs pharmaceutical products and cosmetics. 15

Nitrile-containing polymers, in general, have a very low gas permeability with respect to inorganic gases and organic gases, but their gas-barrier characteristic with respect to water vapour cannot be said to be satisfactory in comparison with that of olefin-containing polymers. Furthermore, olefin-containing polymers, in general, possess excellent pliability and also a high impact strength and a good resistance to low temperatures. On the other hand, nitrile containing polymers in general, have a high rigidity and poor pliability in products with a thick wall, and their impact strengths are not sufficient. Accordingly, with the aim of making the most of the desirable characteristics of the two kinds of polymers, a method wherein the two kinds of polymers are rendered into a composite structure by superimposing them in layered or laminated form has been used. By this method, materials possessing excellent properties are afforded. 20

In general, resins of various kinds are rendered into a composite material of layered form by mutual adhesion using a method which comprises prefabricating beforehand the materials in layered form, and then applying heat and pressure thereto, thereby causing adhesion by heat fusion or by a melt adhesion method which comprises cocurrent melt extrusion (coextrusion) by which the individual resins are caused in molten state to adhere to each other within or outside of the extrusion die. Still another method is the so-called lamination method wherein pre-formed layers are bonded together by an adhesive. 25

In the production of a composite formed product by bonding together a nitrile-containing polymer and an olefin-containing polymer, however, these resins cannot be sufficiently bonded together by any of these methods, or, even if bonding thereof is possible, various restrictions are imposed on the materials or the fabrication process, whereby disadvantages in production or economy cannot be avoided. More specifically, in the formation of a composite structure by the lamination method, various restrictions relating to properties and performance are imposed on the adhesive, and only a limited number of kinds thereof can be used. Furthermore, the adhesive itself is expensive, and, moreover, the application 30 35 40 45

of the adhesive is complicated, so that this technique is disadvantageous both in production and in cost.

The method of bonding the resins in the molten state, in general, is simple and convenient and is also economically advantageous. However, when an attempt is made, to bond by this heat fusion method a nitrile-containing polymer (I) and an olefin-containing polymer (III), sufficient adhesion between the two polymers cannot be obtained, and a melt adhering method such as coextrusion cannot be used.

This invention provides, in the melt adhesion of a nitrile-containing polymer (I) and an olefin-containing polymer (III), a polymer mixture (II) interposed in layer form between the two resin layers so as to make possible the melt adhesion of the two resin layers.

The invention also provides a process for producing laminates of high barrier characteristic with respect to gases such as inorganic and organic gases and water vapour.

The invention further provides laminates having an excellent mechanical strength and a process for producing them.

According to this invention, in one aspect thereof, there is provided a synthetic-resin laminate comprising: a first layer of a nitrile-containing polymer (I) comprising (I)(i) a resin formed by copolymerisation of a monomer mixture of 40 to 90 mol percent of a component (a) consisting of acrylonitrile and/or methacrylonitrile, and 60 to 10 mol percent of a component (b) consisting of at least one monomer copolymerisable with acrylonitrile and/or methacrylonitrile: or (I)(ii) a graft copolymer produced by polymerisation of the components (a) and (b) in the presence of an elastomer; a second layer of a polymer mixture II comprising, in blended state 50 to 80 parts by weight of a nitrile-containing polymer (A) and 50 to 20 parts by weight of an olefin-containing polymer (B), the nitrile-containing polymer (A) being a copolymer of 20 to 90 mol percent of (c) acrylonitrile and/or methacrylonitrile and 80 to 10 mole percent of a component (d) consisting of a vinyl and/or vinylidene monomer- and

a third layer of an olefin-containing polymer (III) comprising a homo-polymer of an α -olefin or a copolymer of an α -olefin and another monomer copolymerisable therewith; wherein the first, second and third layers are bonded together in a laminated state with the second layer interposed between the first and third layers.

According to this invention in another aspect there is provided a process for producing a synthetic-resin laminate as just defined which comprises bonding together in a laminated state the first layer (I), the second layer (II) and the third layer (III), the second layer (II) being interposed between the first (I) and third (III) layers.

Reference is now made to the accompanying drawings in which:

Figure 1(A) and *1(B)* are enlarged, fragmentary perspective views, respectively showing synthetic-resin laminated sheets of three and five layers according to this invention;

Figure 2 is a fragmentary perspective view, with wall thickness enlarged for the sake of clarity, of a tubular structure according to the invention; and

Figure 3 is an elevation, with a part cut away, showing a bottle representative of a hollow structure according to the invention.

The resin compositions of the various layers constituting the multilayer composite products of the invention will first be described.

This nitrile-containing polymer (I) is a thermoplastic resin formed by copolymerization of a monomer mixture comprising:

a) 40 to 90 percent preferably 60 to 85 mol percent of acrylonitrile and/or methacrylonitrile, and

b) 60 to 10 percent preferably 40 to 15 mol percent of at least one monomer copolymerizable with acrylonitrile and/or methacrylonitrile.

This nitrile-containing resin has a low permeability for gases such as oxygen and carbon dioxide, and is receiving attention as a basic material for packaging products such as foodstuffs, pharmaceutical products, and cosmetics.

The gas-barrier characteristic of this resin is related to the quantity of the monomer containing a nitrile group polymerised therein, the gas-barrier characteristic improving with an increase in the content of the nitrile group.

When the content of a nitrile-containing monomer in this copolymer exceeds 90 mol percent, the thermoplasticity of the copolymer is lowered, and the forming and working thereof is difficult. For this reason, a composition in the range set forth above is desirable.

The typical monomer (comonomer) copolymerizable with the nitrile-containing monomer in this case is:

(1) an α -olefin such as isobutylene;

(2) an aromatic olefin represented by the formula $\text{CH}_2 = \text{CR} - \text{Ar}$ (where R is hydrogen or a methyl group, and Ar is an aromatic residue which may be nuclear-substituted), examples being styrene, α -methylstyrene, *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, and 2,5-dimethylstyrene, of which styrene and α -methylstyrene are

particularly preferred:

(3) acrylic acid or an acrylic ester represented by the formula $\text{CH}_2 = \text{CR}_1\text{COOR}_2$ (where R_1 is hydrogen, a methyl group, or an ethyl group, and R_2 is hydrogen, an alkyl group having 1 to 8 carbon atoms, or a halogen atom), examples being acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, methyl methacrylate, ethyl methacrylate, and methyl ethacrylate;

(4) a vinyl ester represented by the formula $\text{CH}_2 = \text{CHCOOR}$ (where R is an alkyl group having 1 to 18 carbon atoms), examples being vinyl acetate, vinyl laurate, and vinyl stearate;

(5) a vinyl ether represented by the formula $\text{CH}_2 = \text{CHOR}$ (where R is an alkyl group having 1 to 4 carbon atoms), examples being methyl vinyl ether, ethyl vinyl ether, and butyl vinyl ether- or

(6) a vinyl halide or a vinylidene halide represented by the formula $\text{CH}_2 = \text{CX}_1\text{X}_2$ (where X_1 is hydrogen or a chlorine or bromine atom, and X_2 is a chlorine or bromine atom), examples being vinyl chloride, vinyl bromide, and vinylidene chloride.

Furthermore, this nitrile-containing polymer (I) (i) may be so-called graft copolymer resulting from the polymerization of the aforementioned monomer a) and monomer b) in the presence of an elastomer such as a diene rubber, an ethylene-propylene copolymer, or an acrylate polymer. For this nitrile-containing polymer (I) (i), moreover, a mixed resin resulting from the admixture of another resin with the nitrile-containing polymer as defined above may be used. Furthermore, this polymer (I) (i) may be a resin as defined above to which an additive such as a plasticizer, a processing aiding agent such as a lubricant, a stabilizer, or a filler has been added.

There are no particular limitations relating to the method of polymerization for obtaining the nitrile-containing polymer, which can be prepared by a known method in the presence of a polymerization initiator. More specifically, the polymerization method may be a bulk polymerization, a solution polymerization, a suspension polymerization or an emulsion polymerization.

The olefin-containing polymer (III) is a homopolymer of an α -olefin or a copolymer of an α -olefin and another monomer copolymerizable therewith. Examples of the α -olefin are ethylene, propylene, and butene. Examples of the comonomer are the same vinyl ester as that defined hereinbefore and represented by the formula $\text{CH}_2 = \text{CHCOOR}$ (where R is an alkyl group having 1 to 18 carbon atoms) and acrylic acid or an acrylate ester represented by the formula $\text{CH}_2 = \text{CHCOOR}$ (where R is hydrogen or an alkyl group having 1 to 4 carbon atoms), examples being acrylic acid, methyl acrylate, ethyl acrylate, and butyl acrylates.

When the comonomer is a vinyl ester, a copolymer in which part or all of the vinyl ester of the copolymer has been hydrolysed such as, for example, an ethylene/vinyl alcohol copolymer, is also included. When the comonomer is acrylic acid or an acrylate ester, an ionomeric which has been formed by reacting the polymer with a metal ion of a metal such as an alkali metal or an alkaline earth metal is also included.

The method of preparing the olefin-containing polymer (III) is not subject to any particular restrictions and can be any suitable known method.

The polymer mixture (II) is a polymer mixture comprising in a blended state:

50 to 80, preferably 50 to 70, parts by weight of a nitrile-containing polymer (A); and

50 to 20, preferably 50 to 30, parts by weight of an olefin-containing polymer (B).

The nitrile-containing polymer (A) is a copolymer of

c) 20 to 90, preferably 50 to 70, mol percent of acrylonitrile or methacrylonitrile; and

d) 10 to 80, preferably 30 to 50 mol percent of at least one comonomer consisting of a vinyl or vinylidene monomer.

Examples of the vinyl and vinylidene monomers are the same as those of comonomers in the nitrile-containing polymer (I).

A comonomer with which especially good results are obtained is, in general, a comonomer of the same kind as that in the nitrile-containing polymer (I). Thus for example, when the nitrile-containing polymer (I) is a copolymer prepared by copolymerizing acrylonitrile and an alkyl acrylate, ethyl, butyl, and octyl acrylates, produce particularly good results as a comonomer of the nitrile-containing polymer (A). It is to be understood, however, that these are general trends and are not restrictive. For example, with a nitrile-containing polymer (I) of the monomer constitution described hereinbefore, very good results are obtained even when the comonomer in the nitrile-containing polymer (A) is a monomer of a different kind such as vinyl acetate.

Furthermore, the nitrile-containing polymer (A) may be a so-called graft polymer prepared by polymerizing a mixture of the monomers of c) and d) above in the presence of an elastomer such as a diene, an olefin, or an acrylic elastomer. Moreover, it may be a resin mixture of a nitrile-containing polymer (A) and another resin.

A suitable content of the acrylonitrile or methacrylonitrile of the nitrile-containing

polymer (A) is in the range of 20 to 90 mol percent as set forth above. We have found that, when the content of this monomer is outside this range, the polymer mixture (II) does not exhibit sufficient adhesiveness with respect to the nitrile-containing polymer (I) and the olefin-containing polymer (III). Preferably, the range is 50 to 70 mol percent.

5 While the olefin polymer (B) may be a polymer as defined for the olefin-containing polymer (III), and may be the same copolymer as the olefin containing polymer (III), it is not so limited. Most preferably, this olefin-containing polymer (B) is one having a melt index of from 0.3 to 5. 5

10 The blending proportions of the polymer mixture (II) are 50 to 20 parts by weight of the olefin-containing polymer (B) and 50 to 80 parts by weight of the nitrile-containing polymer (A). We have found that, when the proportion of the nitrile-containing polymer (A) is less than 50 parts by weight, the adhesiveness with respect to the nitrile-containing polymer (I) is insufficient, while, when it is greater than 80 parts by weight, the adhesiveness with respect to the olefin-containing polymer (III) is insufficient. In either case, a satisfactory composite structure cannot be obtained. Preferably, the proportion of the olefin-containing polymer (B) in the mixture (II) is 30 to 50 parts by weight. 15

20 The method of polymerization for obtaining the nitrile containing polymer (A) is not subject to any particular restrictions, and this polymerization can be carried out by a known method in the presence of a polymerization initiator. Furthermore, the method of preparing the olefin-containing polymer (B) is also not subject to any restrictions, it being possible to carry out this preparation by a known method. 20

25 The nitrile-containing polymer (A) and the olefin containing polymer (B) may be mixed by any of the generally known methods such as a melt mixing method in which a roll kneader, a Banbury kneader or a screw extruder is used or a method wherein the polymers are mixed in the form of an emulsion or a solution. In the case where multilayer articles are formed by the coextrusion method, however, the two resins (A) and (B) are subjected as in powder or pellet form to dry blending and are then fed into an extruder, in which the resins are thoroughly kneaded by a screw. 25

30 By the method of this invention, adhesion of the nitrile-containing polymer and the olefin-containing polymer is easily achieved, and multilayer formed articles such as sheets, bottles and films can be produced by a method such as compression moulding, multilayer blow moulding, multilayer inflation forming, or a multilayer extrusion method such as multilayer T-die extrusion or coextrusion. 30

35 We have found that these articles produced in accordance with the invention exhibit good gas-barrier and fragrance-retaining characteristics and a high practical strength when they are used as packaging materials particularly for products such as foodstuffs, pharmaceutical products and cosmetic products, and that these articles can be formed to possess properties in a wide range from hard formed articles resembling glass articles to flexible formed or moulded articles suitable for applications requiring squeezable vessels such as those for ketchup, mayonnaise or toothpaste. 40

45 The number of layers in a laminate according to this invention is not limited to three, that is, one each of the nitrile-containing polymer (I), the polymer mixture (II) and the olefin-containing polymer (III), it is possible to use any number of layers provided that a layer of the polymer mixture (II) is interposed between layers of the polymers (I) and (III), respectively, which must not be mutually and adjacently bonded together. 45

50 Furthermore, there is no limit, theoretically, to the total wall thickness of a laminate of the essential three layers of the invention. Moreover this total thickness will depend on the structure of the laminate and its use. However, in almost all practical cases, this total thickness will probably be of the order of 0.02 to 5 mm., particularly 0.2 to 1.5 mm. 50

The laminate is produced by cocurrent melt-extrusion of the three layers to be bonded together or by pressing a stack of the three layers at 120-240°C and at 10-1,000 kg/cm² for 0.1 to 30 minutes. 50

55 Typical examples of synthetic-resin laminates according to this invention are illustrated in the accompanying drawing, in which layers of the nitrile-containing polymer (I), the polymer mixture (II) and the olefin-containing polymer (III) are respectively indicated by the reference numerals 1, 2, and 3. 55

60 Figure 1(A) shows a three-ply sheet structure. Figure 1(B) shows a five-ply sheet with layers 3 of the olefin-containing polymer (III) at the opposed outer surfaces and a layer of the nitrile-containing polymer (I) in the core position. Figure 2 illustrates an example of a tubular structure according to this invention. According to a particular embodiment of the invention, the laminate is in the form of a hollow structure which can be closed to seal the hollow interior thereof from the outside. For example, Figure 3 shows an example of a bottle, which is representative of a hollow structure according to the invention. 60

65 In order to indicate still more fully the various features of this invention, the following specific examples of practice constituting preferred embodiments of the invention and a 65

comparison example are set forth, it being understood that these examples are illustrative only and are not intended to limit the scope of the invention.

Example I

Preparation of acrylonitrile-containing polymer (I)
(hereinafter referred to as "polymer (I)")

The following ingredients in their respectively indicated quantities were charged into an autoclave and agitated for 20 hours with the temperature within the autoclave regulated to 40°C:

	Parts by weight	
	75	
acrylonitrile	25	
methyl acrylate	1.8	15
<i>n</i> -dodecylmercaptan	0.04	
K ₂ S ₂ O ₈	0.01	
Na H SO ₃	1.0	
sodium dodecylbenzenesulphonate	200	
water		20

Upon completion of the polymerization, the resulting latex was taken out and added to 450 parts of an aqueous solution of aluminium sulphate with a concentration of approximately 0.4 percent so as to subject the latex to salting out and to convert it to a slurry.

The slurry was heated to 65°C, filtered, washed with water, and dried, whereupon an acrylonitrile/methyl acrylate copolymer of white colour was obtained in a yield of 97 percent. The reduced viscosity η_{SP}/C in a dimethylformamide solution at 30°C of this copolymer was 0.0881 litre/g. ($C = 4$ grams/litre)

The acrylonitrile/methyl acrylate copolymer obtained by the above-described polymerization process was press-formed for 3 minutes at 200°C and 200 kg./cm². to form a sheet with a thickness of 0.35 mm.

For the olefin-containing polymer (III) (hereinafter referred to as "polymer (III)"), an ethylene/vinyl acetate copolymer (trademark "EVATATE" D2021, with a melt index of 1.5 and a vinyl acetate content of 10 percent by weight) was used. This copolymer was press-formed for 3 minutes at 150°C and 200 kg/cm². to form a sheet of 0.7 mm in thickness.

Preparation of acrylonitrile-containing polymer (A) (hereinafter referred to as "polymer (A)")

A monomer mixture of the following composition was prepared:

	Parts by weight	
	60	
acrylonitrile	40	
methyl acrylate	1.0	40
<i>n</i> -dodecylmercaptan		

This monomer mixture was polymerised by the process specified above for the polymer (I). The product thus obtained was filtered, washed with water, and dried, whereupon an acrylonitrile/methyl acrylate copolymer of white colour was obtained in a yield of 96 percent.

For the olefin-containing polymer (B) (hereinafter referred to as "polymer (B)"), an ethylene/vinyl acetate copolymer (trademark "EVATATE" D2021, with a melt index of 1.5 and a vinyl acetate content of 10 per cent by weight) was used.

60 parts of the above-specified polymer (A) and 40 parts of the above-identified polymer (B) were roll-blended for 3 minutes at 120°C to produce a polymer mixture (II) in the form of a sheet of 0.2-mm. in thickness.

The sheets of the polymer (I), the polymer mixture (II), and the polymer (III), respectively were disposed in a laminar arrangement in the order just given and the resulting stack was press-formed for 5 minutes at 200°C and 200 kg./cm². to form a multilayer sheet of 0.87-mm. thickness, which was used as a test specimen. In this test specimen, the thickness of the polymer (I) layer was 0.32 mm.; that of the polymer mixture (II) layer was 0.32 mm.; that of the polymer mixture (II) layer was 0.15 mm.; and that of the polymer (III) layer was 0.40 mm.

This test specimen was subjected to a 180° peel strength test, an oxygen transmission test, and a water vapour (Wt. Vap.) transmission test, whereupon the following results were obtained:

180°C Peel strength	800 g/cm
Wt. Vap. transmission	2.2 g/m ² .24 hr
Oxygen transmission	0.8 cc/m ² .24 hr.atm

5 In this Example 1 and the following Examples, these tests were carried out according to the following standard specifications:

180° Peel strength test - -

ASTM D903-49, Peel or Stripping Strength of Adhesion Bonds, Test for.

Water vapour transmission test - -

10 ASTM E 96-66, Water Vapour Transmission of Materials in Sheet form, Test for. 1

Oxygen transmission test - -

ASTM D 1434-66, Gas Transmission Rate of Plastic Film and Sheeting, Test for.

Comparison Example 1

15 A two-layer sheet of the polymer (I) and the polymer (III) was formed by the procedure set forth in Example 1 except that the polymer mixture (II) was not used. In this sheet, which was used as a test specimen, the thickness of the polymer (I) was 0.33 mm., and the thickness of the polymer (III) was 0.42mm. 1

20 This test specimen was subjected to the same three tests as those specified in Example 1, whereupon the following results were obtained. 2

180° Peel strength	2 g/cm
Wat. Vap. transmission	2.7 g/cm ² .24 hr
Oxygen transmission	0.8 cc/m ² .24 hr.atm

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Examples 2 to 4

The procedure set forth in Example 1 was repeated except for a change of the blend ratio of the polymer (A) and the polymer (B) to those shown in Table 1 set forth hereinafter, thereby to fabricate five multilayer sheets each with a thickness of 0.87 mm., and each comprising respective layers of the polymer (I), the polymer mixture (II), and the polymer (III). 30

The results of the 180° peel strength test, the water vapour transmission test, and the oxygen transmission test carried out on these test specimens were as set forth in Table 1.

35

Examples 5 and 6

The procedure specified in Example 1 was repeated except for a change in the composition of the polymer (A) to those shown in Table 2 set forth hereinafter so as to fabricate four multilayer sheets each with a thickness of 0.87 mm and each comprising respective layers of the polymer (I), the polymer mixture (II), and the polymer (III). 40

These test specimens were subjected to the same three tests specified in the preceding Examples, whereupon the results set forth in Table 2 were obtained. 40

Examples 7, 8 and 9

45 The procedure set forth in Example 5 was repeated substituting a low-density polyethylene (trade mark "Sumikathene" G 701 with a melt index of 7), an ethylene/vinyl acetate polymer (trade mark "EVATATE" VA 1717 with a melt index of 2 and a vinyl acetate content of 5 per cent by weight), and an ethylene/ethyl acrylate ester copolymer (trade mark "NUC EEA copolymer" DPDJ 8026 with a melt index of 13 and an ethyl acrylate ester content of 8 per cent by weight) for the polymer (III), thereby to fabricate respectively three multilayer sheets each comprising respective layers of the polymer (I), the polymer mixture (II), and the polymer (III) with layer thicknesses as shown in Table 3 set forth hereinafter. 50

These test specimens were subjected to the same three tests as those specified in the preceding Examples, whereupon the results shown in Table 3 were obtained. 55

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Example 10

For the polymer (A), the following composition was used.

60

	Parts by weight	
acrylonitrile	50	60
methyl acrylate	50	
<i>n</i> -dodecylmercaptan	1.0	

65 This monomer composition was polymerised by the procedure specified in Example 1, 65

and the acrylonitrile/methyl acrylate copolymer thus obtained was used. Furthermore, for the copolymer (B), an ethylene/vinyl acetate polymer (trade mark "EVATATE" K2010 with a melt index of 3 and a vinyl acetate content of 25 percent by weight) was used.

70 parts of the above specified polymer (A) and 30 parts of the polymer (B) were roll-blended for 3 minutes at 120°C., and thus converted to a polymer mixture (II) in the form of a sheet of 0.2-mm. in thickness. 5

The procedure set forth in Example 1 was carried out with this sheet used for the polymer mixture (II), so as to fabricate a test specimen in the form of a multilayer sheet comprising respective layers of the polymer (I), the polymer mixture (II), and the polymer (III).

10 This test specimen was subjected to the same three tests as in the preceding Examples, whereupon the results shown in Table 3 were obtained. 10

Example 11
Preparation of the polymer (A)

15 The following ingredients in their respectively indicated quantities were charged into an autoclave provided with an agitator. 15

		<i>Parts by weight</i>	
20	acrylonitrile	70	20
	ethyl acrylate	30	
	"Gosenol" (trade mark) GH-20*	0.2	
	(*suspension agent produced by Nippon Gossei (Co.))		
	azo-bis-isobutyronitrile	0.2	
25	<i>n</i> -dodecylmercaptan	1.8	25
	Na ₄ P ₂ O ₇ ·10H ₂ O	0.2	
	water	200	

30 The autoclave was purged with nitrogen, and then polymerization was carried out with agitation at 200 rpm. and at 60°C for 24 hours, whereupon a copolymer in the form of white particles was obtained in a yield of 97 per cent. 30

With the exception of the use of this polymer (A), the procedure specified in Example 1 was carried out to fabricate a test specimen in the form of a multilayer sheet comprising respective layers of the polymer (I), the polymer mixture (II), and the polymer (III). In this test specimen, the thickness of the layer of the polymer (I) was 0.30 mm.; that of the polymer mixture (II) was 0.15 mm.; and that of the polymer (III) was 0.40 mm. 35

This test specimen was subjected to the three tests set forth in the preceding Examples, whereupon the following results were obtained:

40	180° Peel strength	50 g/cm	40
	Wat. Vap. transmission	2.2 g/m ² .24 hr	
	Oxygen transmission	0.85 cc/m ² .24 hr.atm	

Example 12

45 *Preparation of the polymer (I)* 45
A monomer mixture of the following composition was prepared.

		<i>Parts by weight</i>	
50	acrylonitrile	80	50
	ethyl acrylate	20	
	<i>n</i> -dodecylmercaptan	1.0	

55 The monomer composition was polymerised by the process set forth for the polymer (A) in Example 11, whereupon a copolymer in the form of white particles was obtained in a yield of 95 percent. 55

Except for the use of the polymer (I) obtained in the above-described manner, the procedure set forth in Example 1 was carried out to fabricate a multilayer sheet comprising respective layers of the polymer (I), the polymer mixture (II), and the polymer (III). 60
In this sheet, the thickness of the polymer (I) layer was 0.35 mm.; that of the polymer mixture (II) layer was 0.13 mm.; and that of the polymer (III) was 0.40 mm. 60

This sheet was used as a test specimen and subjected to the same three tests as in the preceding Examples, whereupon the following results were obtained.

180° Peel strength
 Wat. Vap. transmission
 Oxygen transmission

510 g/cm
 3.5 g/m² 24 hr
 2.0cc/m².24 hr. atm.

5

Table 1

Example:	2	1	3	4	
10 Blend ratio (by weight)-- Polymer (A) Polymer (B)	50 50	60 40	70 30	80 20	11
15 180° Peel strength (g/cm) Wat.Vap. transmission (g/m.24hr) Oxygen transmission(cc/m ² .24hr.atm)	250 2.2 0.8	300 2.2 0.8	120 2.2 0.8	50 2.2 0.8	12

Table 2

Example:	5	1	6	
20 polymer (A) Composition (ratio by weight)	50 50 1.0	60 40 1.0	75 25 1.8	21
25 180° Peel strength (g/cm) Wat.Vap.transmission (g/m2.24 hr) Oxygen transmission (cc/m ² .24hr.atm)	260 2.2 0.8	300 2.2 0.8	120 2.2 0.8	22
35 * AN : acrylonitrile ** MA : methyl acrylate *** NDM : <i>n</i> -dodecylmercaptan				23

Table 3

Example	7	8	9	10	
40 Thickness (mm.) of -- Polymer (I) layer Polymer mix.(II) layer Polymer (III) layer	0.30 0.13 *LDPE	0.30 0.12 **EVA5	0.30 0.13 ***EEA8	0.30 0.13 ***EVA10	40
45 Peel strength at 180° (g/cm) Wat. Vap. transmission (g/m2.24.hr) Oxygen transmission (cc/m ² .24hr.atm)	0.42 205 0.85 0.85	0.42 230 1.4 0.85	0.28 340 1.4 0.85	0.40 200 2.2 0.85	45
55 *LDPE Low-density polyethylene **EVA 5 Ethylene/vinyl acetate copolymer (vinyl acetate content 5% by wt.) ***EEA 8 Ethylene/ethyl acrylate copolymer (ethyl acrylate content 8% by wt.) ****EVA10 Ethylene/vinyl acetate copolymer (vinyl acetate content 10% by wt.)					55

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Examples 13 to 15

The same composition as that used in Example 1 was used for the polymer (I), and a low-density polyethylene (trade mark "Sumikathene" G201 with a melt index of 2.0) was used for the polymer (III). For the polymer mixture (II), the same polymer (A) as that used in Example 5 and an ethylene/vinyl acetate copolymer (trade mark "EVATATE" H 1011

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with a melt index of 0.6 and a vinyl acetate content of 15 per cent by weight) were blended in the ratios shown in Table 4 set forth hereinafter. Sheets respectively of the polymer (I), the polymer mixture (II), and the polymer (III) were stacked in the order just given and pressed for 5 minutes at 200°C and 200 kg/cm². to make a test specimen in the form of a laminated sheet of 0.60-mm. thickness for each of the above mentioned blend ratios. 5

In each of the six test specimens thus fabricated, the thickness of the polymer (I) layer was 0.10 mm.; that of the polymer mixture (II) layer was 0.10 mm.; and that of the polymer (III) layer was 0.40 mm.

10 These six test specimens were subjected to the same three tests as in the preceding Examples, whereupon the results set forth in Table 4 were obtained. 10

Examples 16 to 18

15 For the polymer (B) an ethylene/vinyl acetate copolymer (trade mark "Ultrathene" 631 with a melt index of 1.5 and a vinyl acetate content of 20 per cent by weight) was used, and the polymers (A) and (B) were blended in the ratios shown in Table 5 set forth hereinafter. In all other details, the procedure specified in Example 13 was followed to fabricate six test specimens each in the form of a laminated sheet of 0.60-mm. thickness comprising 20

20 These six test pieces were subjected to the same three tests as in the preceding Examples, whereupon the results indicated in Table 5 were obtained. 20

Examples 19 and 20

25 For the polymer (B), an ethylene/vinyl acetate copolymer (trade mark "EVATATE" K2010 with a melt index of 3.0 and a vinyl acetate content of 25 per cent by weight) was used, and the polymers (A) and (B) were blended in the ratios shown in Table 6 set forth hereinafter. In all other details, the procedure specified in Example 13 was followed to fabricate 4 test specimens each in the form of a laminated sheet of 0.60-mm. in thickness comprising respective layers of the polymer (I), the polymer mixture (II), and the polymer (III). 25

30 These four test pieces were subjected to the same three tests as in the preceding Examples, whereupon the results set forth in Table 6 were obtained. 30

Examples 21 to 24

Preparation of polymer (I)

35 The following monomers and additives were charged in their respectively indicated quantities into an autoclave. 35

	<i>Parts by weight</i>	
acrylonitrile	65	
methyl acrylate	85	40
<i>n</i> -dodecylmercaptan	1.0	
K ₂ S ₂ O ₈	0.04	
NaHSO ₃	0.01	
Sodium dodecylbenzenesulphonate	1.0	
45 Water	200	45

These monomers were then polymerised by the procedure for the preparation of the polymer (I) in Example 1, whereupon a copolymer in the form of a white powder was obtained in a yield of 94.5 percent.

50 This copolymer was used for the polymer (I) and the polymer (A), and six mixtures were prepared with blend ratios of polymers (A) and (B) as shown in Table 7 set forth hereinafter. In all other details, the procedure specified in Example 3 was followed to fabricate six test specimens each in the form of multilayer laminated sheet with a thickness of 0.60 mm. comprising respective layers of polymer (I), the polymer mixture (II), and the polymer (III). 55

55 These test specimens were subjected to the same three tests as in the preceding Examples, whereupon the results set forth in Table 7 were obtained.

Example 25

60 The polymer (I) specified in Example 13 was melted in an extruder and supplied at 120°C to the dies of a blow-moulding machine. Pellets of the polymer mixture (II) specified in Example 13, which had been pelletized, beforehand in a pelletizer at 180°C, were melted in another extruder and supplied at 200°C to the same dies. The polymer (III) specified in Example 13 was melted in a third extruder and supplied at 180°C to the dies.

65 The dies were provided therewithin with concentric and separate passages for the three 65

resins. The polymer (I), the polymer mixture (II), and the polymer (III) were extruded respectively through the outer, intermediate, and inner passages. A parison was extruded in this manner and was blow-molded into a bottle of 500-cc. inner capacity.

At the body part of this bottle, the bottle side wall had a total thickness of 0.33 mm. and was made up of an outer layer of 0.1-mm. thickness, an intermediate layer of 0.03-mm. thickness, and an inner layer of 0.2-mm. thickness. The total outer surface area of this bottle was approximately 450 cm².

The 180° peel strength, the water vapour transmission rate and the oxygen transmission rate of this bottle were measured and found to be as follows.

180° Peel strength	210 g/cm
Wat. Vap. transmission	0.022 g/24 hr. package
Oxygen transmission	0.025 cc/24 hr. atm. package

Example 26

The polymer (I) as specified in Example 13 was melted in an extruder and fed at 210°C to the dies of a blow-moulding machine. Pellets previously prepared by pelletizing the polymer (A) specified in Example 13 in a pelletizer at 180°C were mixed in the pellet state with the polymer (B) specified in Example 13. The resulting pellet mixture was melted and kneaded in another extruder and supplied at 200°C to the dies. In addition, the polymer (III) specified in Example 13 was melted in a third extruder and supplied at 180°C to the dies.

The dies were provided therewithin with concentric and separate passages for the resins. The resins were passed through these dies to form five concentric layers, namely from the inner side outward in sequence, layers of the polymer (III), the polymer mixture (III), the polymer (I), the polymer mixture (II), and the polymer (III). A parison was thus extruded through the dies and was blow-moulded into a bottle of 500-cc. inner capacity.

At the body part of this bottle, the thicknesses of the concentric layers were respectively, from the inner side outward, 0.1 mm., 0.015 mm., 0.02 mm., 0.02 mm., and 0.015. The total outer surface area of this bottle was approximately 450 cm².

The 180° peel strength, the water vapour transmission rate, and the oxygen transmission rate of this bottle were measured and found to be as follows.

180° Peel strength	210 g/cm
wat. Vap. transmission	0.018 g/24 hr. package
Oxygen transmission	0.13 cc/24 Hr. atm. package

Table 4

Example:	13	14	15
Blend ratio (by weight)	--	--	--
polymer (A)	50	60	70
Polymer (B)	50	40	30
180° Peel strength	(Unit) g/cm		
Wat. Vap. transmission	350	80	30
	1.1	1.1	1.1
Oxygen transmission	cc/m ² .24 hr. atm	2.5	2.5
		2.5	2.5

Table 5

	Example:	16	17	18	5
5	Blend by ratio (by weight)	--			
	Polymer (A)	50	60	70	
	Polymer (B)	50	60	30	10
10		(Unit)			
	180° Peel strength	g/cm	340	120	30
	Wat. Vap. transmission	g/m ² .24 hr	1.1	1.1	1.1
	Oxygen transmission	cc/m ² .24 hr. atm	2.5	2.5	2.5
15					15

Table 6

	Example:	19	20	20
20	Blend ratio (by weight) --			
	Polymer (A)	50	60	
	Polymer (B)	50	40	25
25		(Unit)		
	180° Peel strength	g/cm	320	100
	Wat. Vap. transmission	g/m ² .24 hr	1.1	1.1
	Oxygen transmission	cc/m ² .24 hr.atm	2.5	2.5
30				30

Table 7

	Example:	21	22	23	24	35
35	Blend ratio (by weight)	--				
	Polymer (A)	50	60	70	80	
	Polymer (B)	50	40	30	20	
40		(Unit)				40
	180° Peel strength	g/cm	400	230	230	120
	Wat. Vap. transmission	g/m ² .24 hr	1.2	1.2	1.2	1.2
	Oxygen transmission	cc/m ² .24 hr.atm	5.1	5.1	5.1	5.1
45						45

Examples 27 to 29

The same polymer (I) as that specified in Example I was used. For the polymer (III), a transparent polypropylene for cold resistance and impact resistance (trade mark "Mitsui Noblene" GEB-G with a melt index of 0.4 to 0.7) was used. The same polymer (A) as in Example 5 was used. For the polymer (B), a polypropylene for nylon adhesion (trade mark "ADMER" QF 300 of a melt index 9.0) was used. The polymers (A) and (B) were mixed in the blend ratios set forth in Table 8 to prepare five polymer mixtures (II).

Five test specimens, each in the form of a multilayer sheet of 0.5-mm. thickness, were made by stacking, in each case, the polymer (I), one of the polymer mixture (II), and the polymer (III) in the order named and pressing the stack at 200°C and 200 kg/cm². for 5 minutes.

In each of these test specimens, the thickness of the polymer (I) layer was 0.10 mm.; that of the polymer mixture (II) layer was 0.10 mm.; and that of the polymer (III) layer was 0.30 mm.

These test specimens were subjected to the same three tests as in the preceding Examples, whereupon results as shown in Table 8 were obtained.

In addition, a 5-ply bottle was made through the use of the same resin composition as in Example 27 by the same procedure as in Example 26 except for a melting temperature of the polymer (III) of 210°C. At the body part of this bottle, the thicknesses of the successive layers in sequence from the inner side outward were 0.2 mm., 0.01 mm., 0.04 mm., 0.01

mm., and 0.2 mm. The total outer surface area was approximately 450 cm².

This bottle was found to have sufficient peel strength for practical use and to have the following transmissions:

- 5 Water vapour transmission 0.004 g./24 hr., package
Oxygen transmission 0.07 cc./24 hr., package.

Table 8

10	Examples:	27	28	29	1
	Blend ratio (by weight)	--			
	Polymer (A)	50	60	70	
15	Polymer (B)	50	40	30	1
	(Unit)				
	180° Peel strength	g/cm	580	180	30
	Wat. Vap. transmission	g/m ² .24 hr	0.9	0.9	0.9
20	Oxygen transmission	cc/m ² .24hr.atm	2.5	2.5	2.5

WHAT WE CLAIM IS:

1. A synthetic-resin laminate comprising:
 - 25 a first layer of a nitrile-containing polymer (I) comprising
 - (I)(i) a resin formed by copolymerisation of a monomer mixture of 40 to 90 mol percent of a component (a) consisting of acrylonitrile and/or methacrylonitrile, and 60 to 10 mole percent of a component (b) consisting of at least one monomer copolymerisable with acrylonitrile and/or methacrylonitrile; or (I) (ii) a graft copolymer produced by polymerisation of the components (a) and (b) in the presence of an elastomer;
 - 30 a second layer of a polymer mixture (II) comprising, in blended state, 50 to 80 parts by weight of a nitrile-containing polymer (A) and 50 to 20 parts by weight of an olefin-containing polymer (B), the nitrile-containing polymer (A) being a copolymer of 20 to 90 mol percent of (c) acrylonitrile and/or methacrylonitrile and 80 to 10 mol percent of a component (d) consisting of a vinyl and/or vinylidene monomer; and
 - 35 a third layer of an olefin-containing polymer (III) comprising a homo-polymer of an α -olefin or a copolymer of an α -olefin and another monomer copolymerisable therewith; wherein the first, second and third layers are bonded together in laminated state with the second layer interposed between the first and third layers.
 - 40 2. A synthetic-resin laminate according to claim 1, in which the olefin-containing polymer (B) has a melt index of from 0.3 to 5.
 3. A synthetic-resin laminate as claimed in claim 1 or 2, which is in the form of a sheet.
 4. A synthetic-resin laminate as claimed in claim 1 or 2, which is in the form of a tubular structure.
 - 45 5. A synthetic-resin laminate as claimed in claim 1 or 2, which is in the form of a hollow structure which can be closed to seal the hollow interior thereof from the outside.
 6. A synthetic-resin laminate as claimed in any of claims 1 to 5 which has a total thickness of from 0.02 to 5 mm.
 7. A synthetic-resin laminate as claimed in claim 6, in which the total thickness is from
 - 50 0.2 to 1.5 mm.
 8. A process for producing a synthetic-resin laminate as claimed in claim 1, which comprises bonding together in laminated state the first layer, the second layer and the third layer, said second layer being interposed between said first layer and third layer.
 9. A process for producing a synthetic-resin laminate as claimed in claim 8 in which the olefin-containing polymer (B) has a melt index of from 0.3 to 5.
 - 55 10. A process for producing a synthetic-resin laminate as claimed in claim 8 or 9, in which said laminate is in the form of a sheet.
 11. A process for producing a synthetic-resin laminate as claimed in claims 8 or 9 in which said laminate is in the form of a tubular structure.
 - 60 12. A process for producing a synthetic-resin laminate as claimed in claim 8 or 9, in which said laminate is in the form of a hollow structure which can be closed to seal the hollow interior thereof from the outside.
 13. A process for producing a synthetic-resin laminate as claimed in claims 8 or 9, in which said laminate has a total thickness of from 0.02 to 5 mm.
 - 65 14. A process as claimed in claim 13 in which the thickness is from 0.2 to 1.5 mm.

15. A process for producing a synthetic-resin laminate as claimed in any of claims 9 to 14 in which said first, second, and third layers are bonded together in laminated state by coextrusion.

5 16. A process for producing a synthetic-resin laminate as claimed in any of claims 8 to 14 in which said first, second and third layers are stacked in laminar arrangement and then bonded together by press forming at a temperature of from 120 to 240°C, at a pressing pressure of from 10 to 1,000 kg./cm², and for a period of from 0.1 to 30 minutes. 5

10 17. A process for producing a synthetic-resin laminate as claimed in claim 12 in which said first, second and third layers are bonded together to form a parison by co-extrusion through an extrusion having concentric passages respectively for the polymer (I), the polymer mixture (II), and the polymer (III) and the parison is then blow-moulded into said hollow structure. 10

18. A synthetic-resin laminate as claimed in claim 1, substantially as hereinbefore described with reference to any one of the specific Examples.

15 19. A process for producing a synthetic-resin laminate as claimed in claim 8 substantially as hereinbefore described with reference to any one of the specific Examples. 15

20 20. A synthetic-resin laminate whenever produced by a process as claimed in any one of claims 8 to 17 and 19.

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FIG. 1(A)

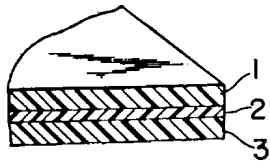


FIG. 1(B)

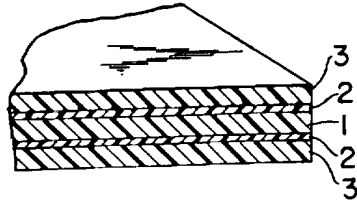


FIG. 2

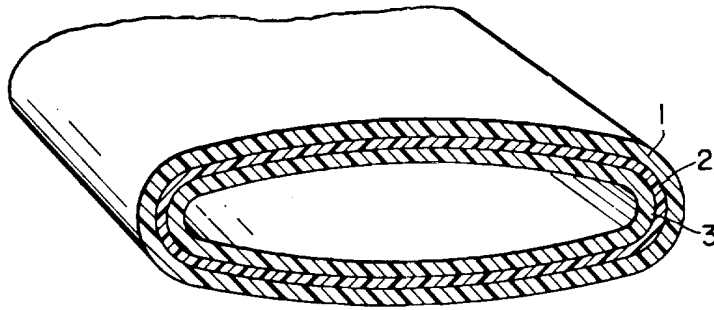


FIG. 3

