

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
9 February 2006 (09.02.2006)

PCT

(10) International Publication Number
WO 2006/013766 A1

(51) International Patent Classification : ⁷ C08K 3/30,
3/00, 3/16, 3/28, C08L 29/04

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(21) International Application Number:
PCT/JP2005/013787

(22) International Filing Date: 21 July 2005 (21.07.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2004-225246 2 August 2004 (02.08.2004) JP

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG,
KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM,
PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM,
SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN,
YU, ZA, ZM, ZW.

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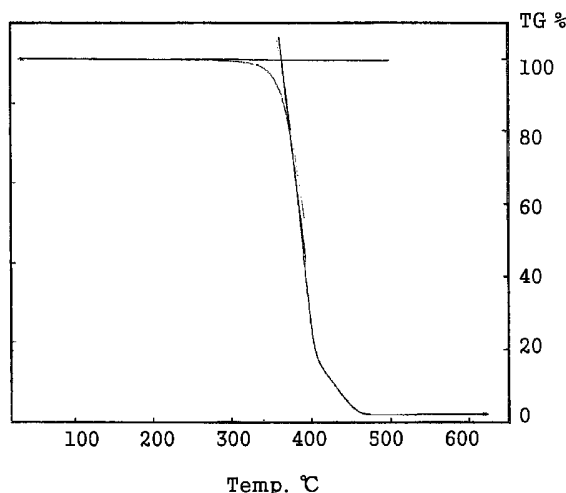
(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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[Continued on next page]

(54) Title: RESIN COMPOSITION



(57) Abstract: A resin composition comprising (1) a saponification product of an ethylene-vinyl acetate copolymer, and (2) 10 to 5,000 ppm of a salt formed from an acid having a dissociation constant, pKa, and a base having a dissociation constant, pKb, both satisfying the following formula, $pK_a \leq pK_b - 1$, wherein ppm is based upon an amount of said saponification product; a process for producing a resin composition comprising the step of melt-kneading at least (1) the above-mentioned saponification product, and (2) 10 to 5,000 ppm of the above-mentioned salt, wherein ppm is based on an amount of said saponification product; and a method for improving heat stability of the above-mentioned saponification product, which comprises the step of melt-kneading at least (1) the above-mentioned saponification product, and (2) 10 to 5,000 ppm of the above-mentioned salt, wherein ppm is based on an amount of said saponification product.

WO 2006/013766 A1



Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

DESCRIPTION

RESIN COMPOSITION

5 Technical Field

The present invention relates to a resin composition comprising a saponification product of an ethylene-vinyl acetate copolymer; a process for producing said resin composition; and a method for improving heat stability of said saponification product.

Background Art

In connection with a saponification product of an ethylene-vinyl acetate copolymer, which product has an ability to restrain a poor appearance (for example, coloring, a fish eye and a shark skin) possibly caused when producing a molded material such as a film, a sheet and a container according to a melt process from said saponification product, there are known the following production processes (1) and (2):

20 (1) a process comprising the step of removing an impurity contained in a chip of said saponification product by washing said chip in a washing tower (US 6,609,528 B2); and

(2) a process comprising the step of saponifying an ethylene-vinyl acetate copolymer, in the presence of an alkali catalyst, in an alcohol solvent containing water in an amount of 100 to 15,000 ppm based on an amount of said ethylene-vinyl

acetate copolymer (US 2002-032267 A1).

However, a molded material of a copolymer produced according to the above-mentioned process (1) or (2) may not be restrained in its poor appearance because of its deterioration
5 caused by (i) a too long molding cycle of said copolymer, which cycle puts said copolymer under a melt condition for a long time, (ii) a too long residence of said copolymer in a molding machine (for example, in a dead space thereof), or (iii) a too long exposure of said copolymer under a high temperature at the time
10 a molding machine is started or stopped.

Disclosure of Invention

In view of the above-mentioned problem in the conventional art, an object of the present invention is to
15 provide (1) a resin composition comprising a saponification product of an ethylene-vinyl acetate copolymer, which composition has excellent heat stability, and therefore, can give a molded material having excellent appearance; (2) a process for producing said resin composition; and (3) a method
20 for improving heat stability of said saponification product.

The present inventors have studied extensively to accomplish the above-mentioned object of the present invention. As a result, it has been found that said saponification product can be improved remarkably in its heat stability by a specific
25 salt, and thereby, the present invention has been obtained.

The present invention is a resin composition

comprising:

(1) a saponification product of an ethylene-vinyl acetate copolymer; and

5 (2) 10 to 5,000 ppm of a salt formed from an acid having a dissociation constant, pK_a , and a base having a dissociation constant, pK_b , both satisfying the following formula [1],

$$pK_a < pK_b - 1 \quad [1]$$

10 wherein ppm is based upon an amount of said saponification product.

Also, the present invention is a process for producing a resin composition comprising the step of melt-kneading at least:

15 (1) a saponification product of an ethylene-vinyl acetate copolymer; and

(2) 10 to 5,000 ppm of the above-mentioned salt; wherein ppm is based on an amount of said saponification product.

20 Further, the present invention is a method for improving heat stability of a saponification product of an ethylene-vinyl acetate copolymer, which comprises the step of melt-kneading at least:

(1) a saponification product of an ethylene-vinyl acetate copolymer; and

25 (2) 10 to 5,000 ppm of the above-mentioned salt;

wherein ppm is based on an amount of said saponification product.

Brief Description of Drawings

5 Each of Figs. 1 to 4 represents a TG curve (thermogravimetry curve) showing loss in weight (vertical axis) upon heating (horizontal axis) each of the kneaded products obtained in Example 1 and Comparative Examples 1 to 3, wherein the intersection of two straight lines drawn along
10 the curve corresponds to a temperature showing remarkable loss in weight.

Best Mode for Carrying Out the Invention

15 An ethylene-vinyl acetate copolymer in the present invention may be produced according to a process known in the art. Examples of said process are (1) a process comprising the step of copolymerizing ethylene and vinyl acetate in an alcohol solvent, and (2) a process comprising the step of copolymerizing ethylene and vinyl acetate according to a
20 high-pressure ionic polymerization method.

Examples of the above-mentioned alcohol solvent are an alcohol having 1 to 4 carbon atoms such as methanol, ethanol, n-butanol, and tert-butanol; and a combination of two or more thereof. Among them, preferred is methanol.

25 Said alcohol solvent may be combined with other component such as dimethyl sulfoxide. An amount of the alcohol

solvent contained in the combination is generally 60% by weight or larger, and preferably 70% by weight or larger, wherein an amount of said combination is 100% by weight.

An example of a polymerization catalyst used for
5 copolymerizing ethylene and vinyl acetate is a radical
initiator such as azonitrile compounds and organic peroxides.
Said azonitrile compound is preferably
2,2'-azobisisobutyronitrile,
2,2'-azobis-(2,4-dimethylvaleronitrile),
10 2,2'-azobis-(4-methyl-2,4-dimethylvaleronitrile),
2,2'-azobis-(4-methoxy-2,4-dimethylvaleronitrile), or
2,2'-azobis-(2-cyclopropylpropionitrile).

The above-mentioned organic peroxide is preferably
isobutyryl peroxide, cumyl peroxyneodecanoate, diisopropyl
15 peroxy carbonate, di-n-propyl peroxydicarbonate, tert-butyl
peroxyneodecanoate, lauroyl peroxide, benzoyl peroxide, or
tert-butyl hydroperoxide.

An ethylene-vinyl acetate copolymer in the present
invention means a copolymer containing at least an ethylene
20 unit and a vinyl acetate unit. Therefore, said ethylene-vinyl
acetate copolymer may contain other monomer unit than the
ethylene unit and the vinyl acetate unit, wherein said other
monomer can be copolymerized with ethylene and vinyl acetate.
The term "unit" contained in the above-mentioned "monomer
25 unit" such as the ethylene unit, the vinyl acetate unit and other
monomer unit means a unit of a polymerized monomer.

Examples of the above-mentioned other monomer are an α -olefin such as propylene, isobutylene, α -octene, and α -dodecene; an unsaturated acid such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, and itaconic acid; salts, anhydrides, monoalkyl esters, and dialkyl esters of said unsaturated acids; a nitrile such as acrylonitrile and methacrylonitrile; an amide such as acrylamide and methacrylamide; an olefin sulfonic acid such as ethylene sulfonic acid, allyl sulfonic acid, and metallyl sulfonic acid; salts of said olefin sulfonic acids; an alkyl vinyl ether; a vinyl ketone; N-vinylpyrrolidone; vinyl chloride; and vinylidene chloride.

A typical example of the ethylene-vinyl acetate copolymer in the present invention is a copolymer containing only an ethylene unit and a vinyl acetate unit.

An amount of an ethylene unit contained in the ethylene-vinyl acetate copolymer is preferably 20 to 70% by mol, and more preferably 25 to 60% by mol, in order to improve a moisture resistance or a gas barrier property of (i) the resin composition of the present invention, (ii) a resin composition produced according to the process of the present invention, or (iii) a heat stability-improved saponification product obtained by the method of the present invention, wherein a total amount of the ethylene unit and the vinyl acetate unit contained in the ethylene-vinyl acetate copolymer is 100% by mol. However, when each of the above-mentioned resin

compositions (i) and (ii), or the above-mentioned heat stability-improved saponification product (iii) is used for coating a surface of other material, the amount of the ethylene unit contained in the ethylene-vinyl acetate copolymer may be smaller than 20% by mol.

A polymerization temperature of the ethylene-vinyl acetate copolymer is preferably 50 to 80°C; an ethylene-gas pressure in a gas phase of a polymerization reactor is preferably 2 to 8 MPa; a polymerization time in a batchwise polymerization is preferably 3 to 24 hours; an average residence time in a continuous polymerization is also preferably 3 to 24 hours; and conversion of vinyl acetate is preferably 30 to 80%.

A "saponification product" of an ethylene-vinyl acetate copolymer in the present invention means a copolymer containing a vinyl alcohol unit formed by saponifying a vinyl acetate unit contained in the ethylene-vinyl acetate copolymer. A process for producing said saponification product is not particularly limited, and may be a process known in the art. An example thereof is a process comprising the step of saponifying an ethylene-vinyl acetate copolymer with an alkali catalyst. An industrially preferable process comprises the step of saponifying continuously an ethylene-vinyl acetate copolymer in a tower-type saponification reactor. Said tower-type saponification reactor produces a saponification product having high conversion of saponification.

An example of a general saponification process is a process comprising the steps of (i) adding a methanol solution of an alkali catalyst such as sodium hydroxide to a methanol solution of an ethylene-vinyl acetate copolymer, and then (ii) blowing a methanol vapor into said methanol solution in order to remove methyl acetate as a by-product out of a reactor, wherein the methanol solution of an alkali catalyst, the methanol solution of an ethylene-vinyl acetate copolymer, or the methanol vapor may be combined with water, respectively. Among them, preferred is a combination of water with the methanol solution of an alkali catalyst, or with the methanol solution of an ethylene-vinyl acetate copolymer, because an accurate amount of water can be added thereto. An amount of water combined with the methanol solution of an alkali catalyst, or with the methanol solution of an ethylene-vinyl acetate copolymer is suitably determined based on an amount of an ethylene unit contained in the ethylene-vinyl acetate copolymer, and saponification conditions, and said amount is usually 0.1 to 10% by weight, wherein a total amount of the methanol solution of an alkali catalyst and water combined therewith, or a total amount of the methanol solution of an ethylene-vinyl acetate copolymer and water combined therewith is 100% by weight.

Since solubility of a saponification product of an ethylene-vinyl acetate copolymer in a solvent depends upon an amount of an ethylene unit contained in the saponification product, the saponification product may not be dissolved

easily in methanol (solvent) under an atmospheric pressure, and as a result, the saponification product may adhere easily to an inner wall of a saponification reactor. Therefore, a pressure in the saponification reactor is preferably 0.1 to 1.0 MPa from a viewpoint of a continuous operation of the saponification reactor for a long time. From a viewpoint similar thereto, and also from a viewpoint of enhancing a saponification reaction rate, a temperature in the saponification reactor is preferably 60 to 150°C.

When the above-mentioned tower-type saponification reactor is used, it is particularly desirable to control a concentration of a methanol solution of an ethylene-vinyl acetate copolymer supplied to the reactor so as not to make a viscosity of said solution too high. Said concentration is preferably 30 to 60% by weight.

An amount of the above-mentioned alkali catalyst is determined according to an item such as an amount of a vinyl acetate unit contained in an ethylene-vinyl acetate copolymer, and predetermined conversion of saponification. When the predetermined conversion of saponification is 90% by mol or higher, the amount of the alkali catalyst is preferably 0.5 to 20% by mol, wherein an amount of a vinyl acetate unit contained in the ethylene-vinyl acetate copolymer is 100% by mol.

The above-mentioned methanol vapor blown into the methanol solution is required preferably in such an amount that methyl acetate as a by-product is substantially completely

removed out of a saponification reactor. Said amount is preferably 1 to 10 parts by weight per one part by weight of an ethylene-vinyl acetate copolymer. A temperature of said vapor is set at, for example, a boiling point of methanol under
5 a pressure in the saponification reactor.

A partial saponification product of an ethylene-vinyl acetate copolymer can be produced by a method of regulating an amount of water combined with a methanol solution of an alkali catalyst, a methanol solution of an ethylene-vinyl acetate
10 copolymer, or a methanol vapor. Said partial saponification product has an advantage that a distribution of a degree of saponification thereof is narrower than that of a partial saponification product produced by other production method.

The above-mentioned partial saponification product of
15 an ethylene-vinyl acetate copolymer is so adhesive that it can be used as an intermediate layer of a laminated product, and also, can be combined with a complete saponification product of an ethylene-vinyl acetate copolymer in order to give an adhesive property to said complete saponification product.

20 The above-mentioned partial saponification product may further be saponified. An example of a process for producing said further saponification product is a process comprising the step of saponifying the partial saponification product with an aqueous solution of an alkali catalyst in an alcohol
25 solvent.

While a vinyl acetate unit contained in the

ethylene-vinyl acetate copolymer is changed to a vinyl alcohol unit by saponifying said copolymer, the above-mentioned "partial saponification product" contains an ethylene unit, a vinyl acetate unit (not saponified), and a vinyl alcohol unit; and the above-mentioned "complete saponification product" contains an ethylene unit and a vinyl alcohol unit, and contains no vinyl acetate unit.

A melt index of a saponification product in the present invention is preferably 0.1 to 200 g/10 minutes measured at 190°C under a load of 2,160 g. However, a melt index of a saponification product having a melting point in the vicinity of, or higher than 190°C is obtained by a method comprising the steps of (i) measuring two or more melting indexes thereof under a load of 2,160 g at two or more temperatures higher than said melting point, respectively, (ii) making a graph showing a relation between a temperature and a melt index by plotting said two or more melting indexes on a vertical axis in a logarithmic scale, and plotting reciprocal numbers of absolute temperatures corresponding said two or more temperatures on a horizontal axis in a normal scale, and (iii) extrapolating a melt index (vertical axis) at the temperature of 190°C (horizontal axis), which is regarded as a melt index of the saponification product having a melting point in the vicinity of, or higher than 190°C.

Generally, a saponification product produced by saponifying an ethylene-vinyl acetate copolymer is extruded

into a coagulation bath containing water or a mixture of methanol therewith, and then, is cut into pellets. Said pellets are washed with a liquid, and then, are separated from the liquid, and are further treated, if necessary, with a compound such as
5 a boron compound, a carboxylic acid and a phosphoric acid, in order to improve physical properties such as mechanical characteristics and heat stability.

An acid in the present invention is an organic or inorganic acid. An example of said acid is a strong acid such
10 as sulfuric acid having pKa of -3.0 (first stage) and pKa of 2.0 (second stage); nitric acid having pKa of -1.3; hydrochloric acid; trifluoroacetic acid having pKa of -0.25; trichloroacetic acid; iodic acid; oxalic acid; dichloroacetic acid; phosphorous acid; sulfurous acid; hypophosphorous acid;
15 and phosphoric acid, all of which are industrially available.

An example of the base in the present invention is a weak base such as ammonia having pKb of 4.76; methylamine; dimethylamine; ethylamine; and trimethylamine.

A salt in the present invention is formed preferably
20 from an acid having an acid dissociation constant, pKa, and a base having a base dissociation constant, pKb, which satisfy the following formula [2],

$$pK_a < pK_b - 2 \quad [2];$$

25

and more preferably form an acid having pKa of 2 or smaller,

and a base having pK_b of 4 to 5. Examples of the salt are ammonium sulfate and ammonium chloride.

An amount of a salt, which is contained in the resin composition of the present invention, which is used in the process thereof, and which is used in the method thereof, is
5 10 to 5,000 ppm, preferably 100 to 5,000 ppm, and more preferably 150 to 1,500 ppm, based on an amount of a saponification product of an ethylene-vinyl acetate copolymer. When said amount is smaller than 10 ppm, heat stability of the resin composition
10 of the present invention, that of a resin composition produced according to the process of the present invention, and that in the method of the present invention may not be sufficiently improved, respectively.

Examples of a process for producing the resin
15 composition of the present invention, examples of a specific embodiment in the process thereof, and examples of a specific embodiment in the method thereof are (1) a process (or method) comprising the step of melt-kneading a salt with a saponification product of an ethylene-vinyl acetate copolymer,
20 and (2) a process (or method) comprising the step of adding a solution of a salt to a saponification product thereof. Among them, preferred is the process (or method) (1) from a viewpoint of an economical advantage.

Specific examples of the above-mentioned process (or
25 method) (1) are (1-1) a process (or method) comprising the step of melt-kneading a salt with a saponification product of an

ethylene-vinyl acetate copolymer with a uniaxial, biaxial or multi-axial continuous kneading machine, and (1-2) a process (or method) comprising the step of melt-kneading a salt with a saponification product of an ethylene-vinyl acetate copolymer with a batch-type kneading machine. Among them, preferred is a process (or method) comprising the step of melt-kneading a salt with a saponification product of an ethylene-vinyl acetate copolymer with a biaxial continuous kneading machine, from a viewpoint of an economical advantage.

A kneading temperature in the above-mentioned step of melt-kneading, which means a temperature of a saponification product, is preferably 150 to 280°C, and a cylinder temperature of the above-mentioned kneading machine is set generally at 150 to 260°C, in consideration of quantity of heat absorbed by the saponification product to be melted, and quantity of heat generated by the saponification product to be sheared in a kneading machine.

The resin composition of the present invention, a resin composition produced according to the process thereof, or a heat stability-improved saponification product obtained according to the method thereof is melt-molded to an article such as a film, a sheet, a container, a pipe, and a fiber.

Examples of said melt-molding are an extrusion molding, an inflation molding, a blow molding, an injection molding, and a melt spinning. A melt-molding temperature is preferably 150 to 270°C.

It is permitted to melt-mold a blend containing two or more kinds of saponification products, which are different from one another in their properties such as a degree of polymerization, an amount of an ethylene unit contained therein, and a degree of saponification.

A saponification product in the resin composition of the present invention, that in the process of the present invention, or that in the method of the present invention may be combined with other component.

Examples of said other component are a thermoplastic resin; and an agent such as a plasticizer, a stabilizer, a surfactant, a cross-linking agent, a metal salt, a filler, and a reinforcement (for example, fiber).

Examples of the above-mentioned thermoplastic resin are:

- (1) a polyolefin such as polyethylene, polypropylene, poly-1-butene, poly-4-methyl-1-pentene, an ethylene-propylene copolymer, and a copolymer of ethylene with an α -olefin having 4 or more carbon atoms;
- (2) a copolymer of an olefin with maleic anhydride;
- (3) a copolymer of ethylene with vinyl acetate;
- (4) a copolymer of ethylene with an acrylic ester;
- (5) a modified polymer produced by graft-modifying each of the above-mentioned (co)polymers (1) to (4) with an unsaturated carboxylic acid or its derivative;
- (6) a nylon such as nylon-6, nylon-66, an olefin-nylon-6/66 copolymer; and

(7) a polymer such as polyvinyl chloride, polyvinylidene chloride, a polyester, polystyrene, polyacrylonitrile, a polyurethane, polyacetal, and a modified polyvinyl alcohol resin.

5

The present invention is explained with reference to the following Example, which does not limit the scope of the present invention.

10 Example 1

An aqueous solution of ammonium sulfate was added to a saponification product of an ethylene-vinyl acetate copolymer in an amount of 200 ppm based on an amount of said saponification product, EVAL F101A, manufactured by Kuraray Co., Ltd., which
15 contains an ethylene unit in an amount of 32% by mol, and has a melt index of 1.5 g/10 minutes measured at 190°C under a load of 2,160 g, a melt index of 4.3 g/10 minutes measured at 190°C under a load of 5,000 g, a density of 1.19 g/cm³ measured at 20°C, a melting point of 183°C, and a glass transition
20 temperature of 69°C. Then, 96 g thereof was melt-kneaded with a kneading machine, LABOPLASTOMIL, manufacture by Toyo Seiki Co., Ltd. at 200°C for 5 minutes at its screw-rotation speed of 80 rpm.

The kneaded product was taken out of the kneading
25 machine, and then, was cooled, thereby obtaining a solidified product (resin composition). Heat stability of said resin

composition was measured in an air atmosphere with an instrument, TG/DTA-200, manufactured by Seiko Instruments Inc., at a heating speed of 5°C/minute, thereby obtaining a TG curve shown in Fig. 1, wherein "DTA" is an abbreviation of
5 "differential thermal analysis".

There was obtained a result from Fig. 1 that (1) a weight decrease-initiating temperature of the resin composition was almost the same (359.5°C) as a remarkably weight-decreasing temperature thereof, (2) an amount of the resin composition
10 decreased at the weight decrease-initiating temperature was about 0.5 to 5% by weight, and an amount of the resin composition decreased at the remarkably weight-decreasing temperature was 15 to 20% by weight, wherein a total amount of the resin composition used for the measurement was 100% by weight, and
15 (3) a color of the resin composition was not changed by heating.

Comparative Example 1

Example 1 was repeated except that the aqueous solution of ammonium sulfate was not added, thereby obtaining a TG curve
20 shown in Fig. 2.

There was obtained a result from Fig. 2 that a weight decrease-initiating temperature of the obtained resin composition was 276.0°C, and a remarkably weight-decreasing temperature thereof was 352.7°C.

25

Comparative Example 2

Example 1 was repeated except that the aqueous solution of ammonium sulfate was changed to an aqueous solution of tetramethylammonium hydroxide in an amount of 10,000 ppm, thereby obtaining a TG curve shown in Fig. 3.

5 There was obtained a result from Fig. 3 that a weight decrease-initiating temperature of the obtained resin composition was 286.9°C, and a remarkably weight-decreasing temperature thereof was 350.8°C.

10 Comparative Example 3

Example 1 was repeated except that the aqueous solution of ammonium sulfate was changed to an aqueous solution of p-toluenesulfonic acid in an amount of 400 ppm, thereby obtaining a TG curve shown in Fig. 4.

15 There was obtained a result from Fig. 4 that the obtained resin composition had a remarkably black-colored part, although a weight decrease-initiating temperature of the resin composition was almost the same (357.6°C) as a remarkably weight-decreasing temperature thereof.

20

Comparing Example 1 with Comparative Examples 1 to 3, it is recognized that the resin composition obtained in Example 1 has (1) a high temperature, at which said resin composition shows remarkable loss in weight upon heating, and (2) no change
25 in color upon heating, and therefore, said resin composition gives a molded material having excellent heat stability and

excellent appearance.

Industrial Applicability

The resin composition of the present invention, a resin
5 composition produced according to the process thereof, or a
heat stability-improved saponification product obtained
according to the method thereof can be coextruded with the
above-mentioned thermoplastic resin, respectively, to
produce a laminated product.

10 Also, a layer of the resin composition of the present
invention, that of a resin composition produced according to
the process thereof, or that of a heat stability-improved
saponification product obtained according to the method
thereof can be laminated with a layer of a substrate such as
15 paper, a plastic film and a metal foil, to produce a laminated
product.

Further, the resin composition of the present invention,
a resin composition produced according to the process thereof,
or a heat stability-improved saponification product obtained
20 according to the method thereof can be coated on the
above-mentioned substrate layer by a coextrusion method or a
solution-coating method, to produce a laminated product.

CLAIMS

1. A resin composition comprising:

(1) a saponification product of an ethylene-vinyl
5 acetate copolymer; and

(2) 10 to 5,000 ppm of a salt formed from an acid having
a dissociation constant, pK_a , and a base having a dissociation
constant, pK_b , both satisfying the following formula [1],

10
$$pK_a < pK_b - 1 \quad [1]$$

wherein ppm is based upon an amount of said saponification
product.

15 2. The resin composition according to claim 1, wherein
the base is ammonia or an amine.

3. The resin composition according to claim 1, wherein
the salt is ammonium sulfate or ammonium chloride.

20

4. The resin composition according to claim 1, wherein
the salt is contained in amount of 100 to 5,000 ppm.

25 5. The resin composition according to claim 1, wherein
the salt is contained in amount of 150 to 1,500 ppm.

6. A process for producing a resin composition comprising the step of melt-kneading at least:

(1) a saponification product of an ethylene-vinyl acetate copolymer; and

5 (2) 10 to 5,000 ppm of a salt formed from an acid having a dissociation constant, pK_a , and a base having a dissociation constant, pK_b , both satisfying the following formula [1],

$$pK_a < pK_b - 1 \quad [1]$$

10

wherein ppm is based upon an amount of said saponification product.

7. The process for producing a resin composition according to claim 6, wherein the base is ammonia or an amine.

15

8. The process for producing a resin composition according to claim 6, wherein the salt is ammonium sulfate or ammonium chloride.

20

9. The process for producing a resin composition according to claim 6, wherein an amount of the salt is 100 to 5,000 ppm.

25

10. The process for producing a resin composition according to claim 6, wherein an amount of the salt is 150 to

1,500 ppm.

11. A method for improving heat stability of a saponification product of an ethylene-vinyl acetate copolymer, which comprises the step of melt-kneading at least:

(1) a saponification product of an ethylene-vinyl acetate copolymer; and

(2) 10 to 5,000 ppm of a salt formed from an acid having a dissociation constant, pK_a , and a base having a dissociation constant, pK_b , both satisfying the following formula [1],

$$pK_a < pK_b - 1 \quad [1]$$

wherein ppm is based upon an amount of said saponification product.

12. The method for improving heat stability of a saponification product of an ethylene-vinyl acetate copolymer according to claim 11, wherein an amount of the salt is 100 to 5,000 ppm.

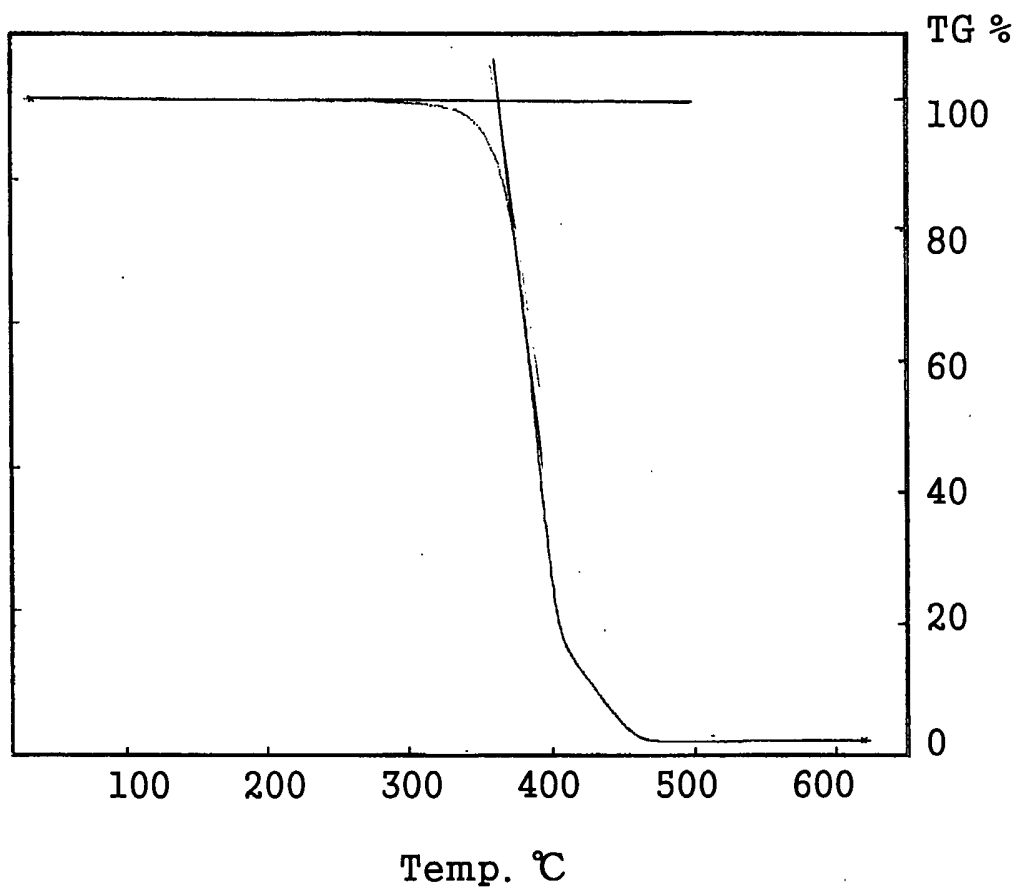


Fig. 1

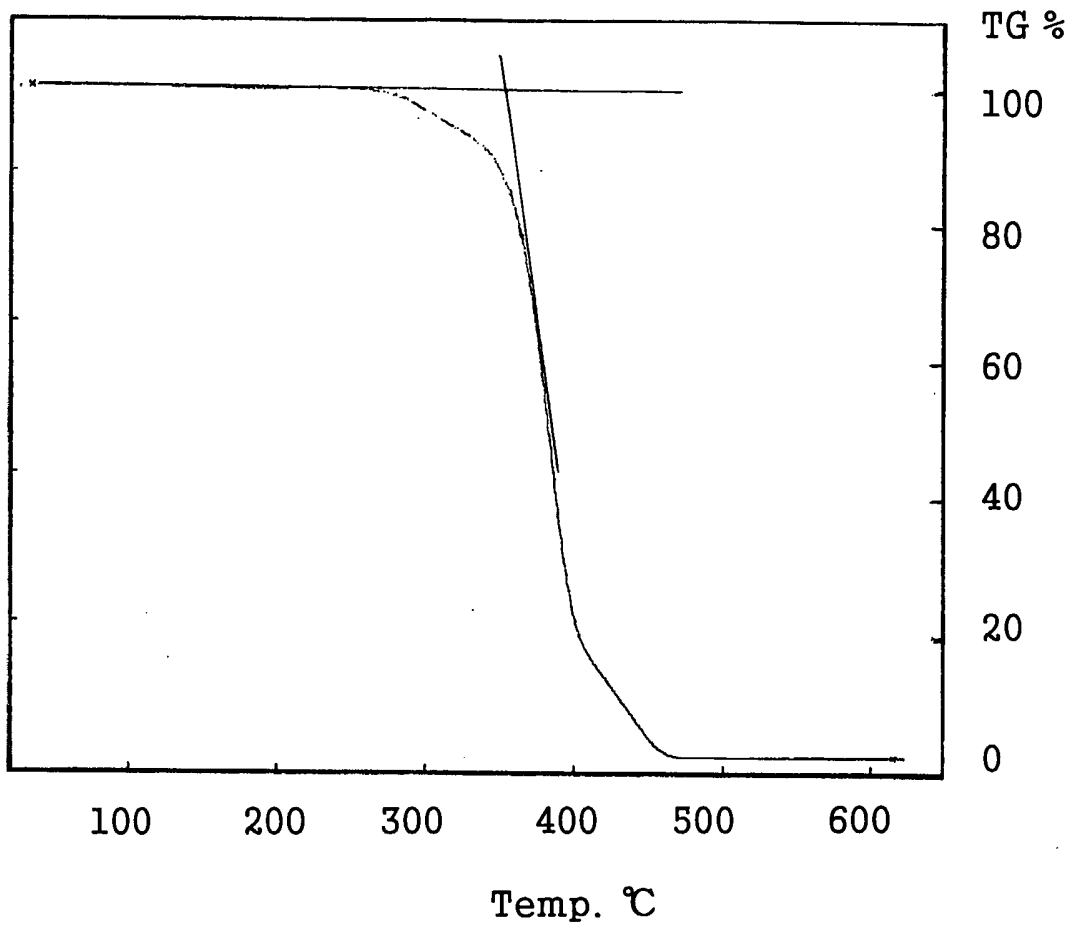


Fig. 2

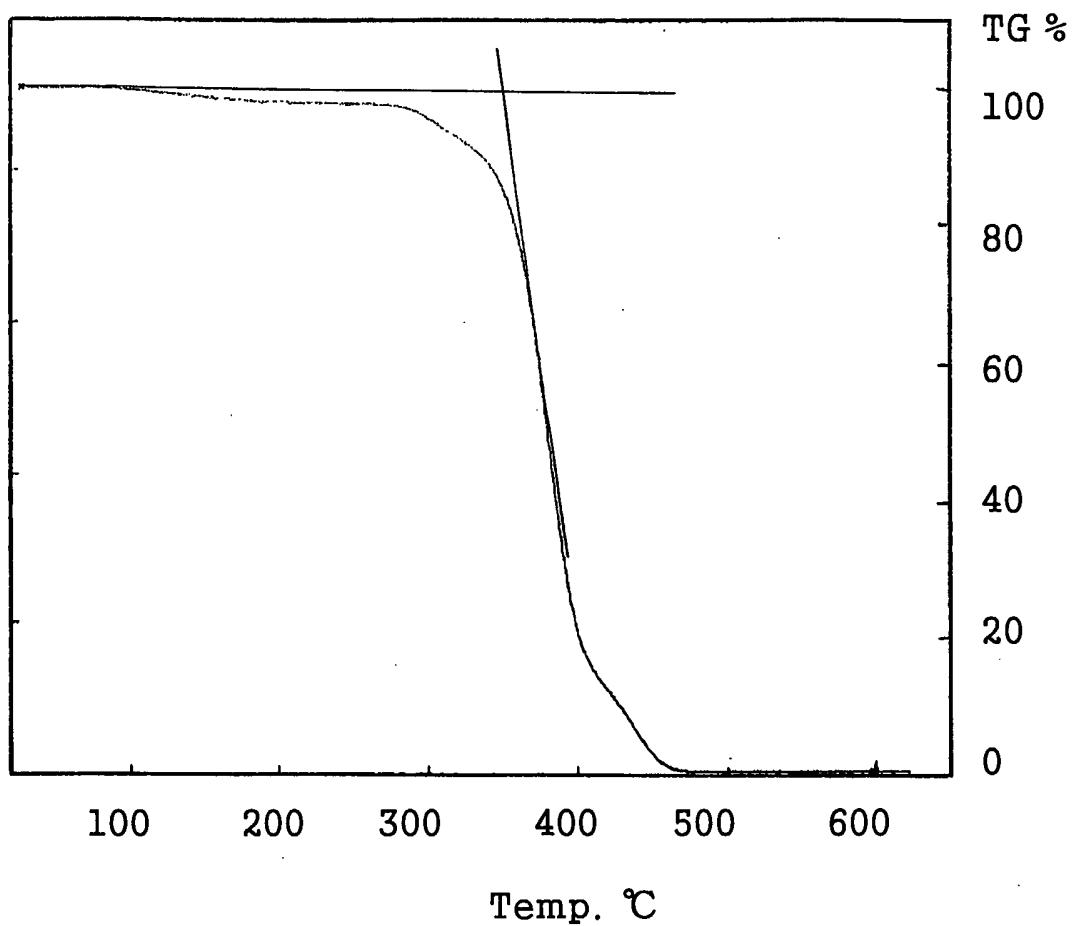


Fig. 3

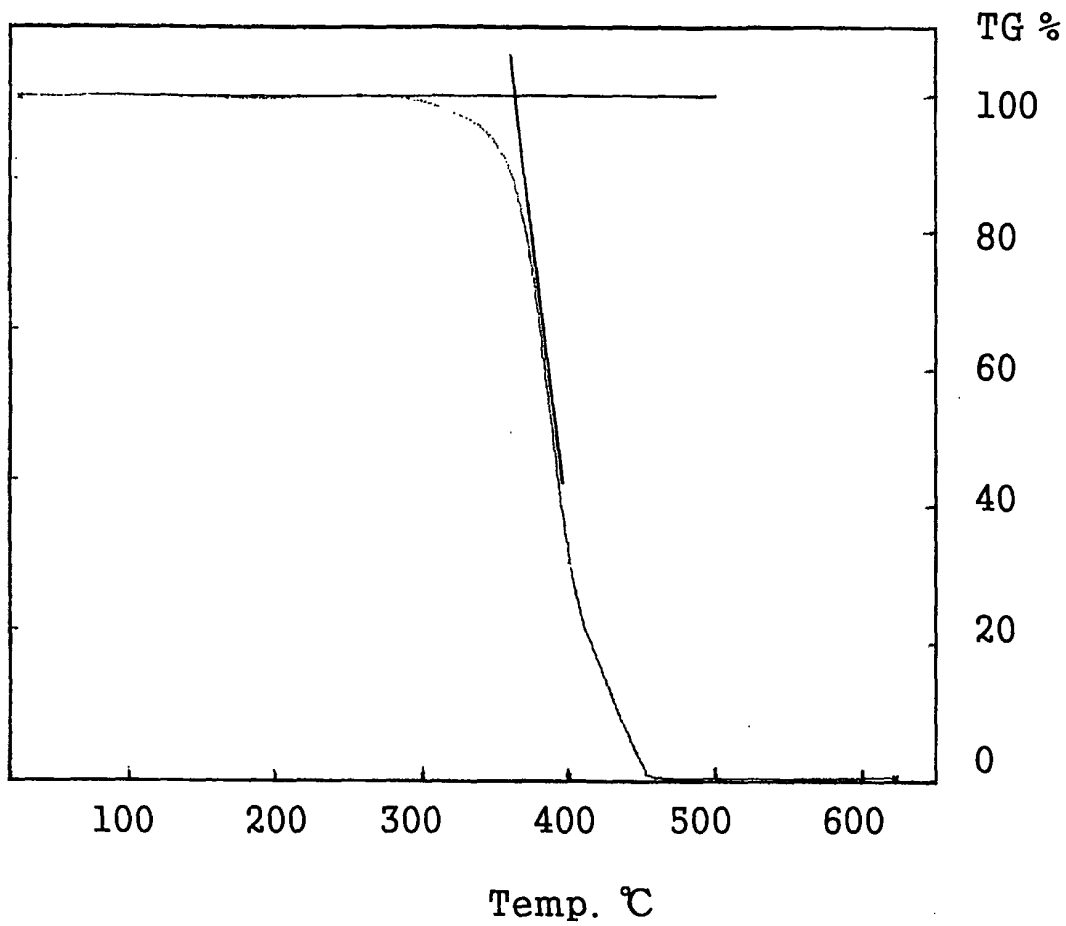


Fig. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2005/013787

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K3/30 C08K3/00 C08K3/16 C08K3/28 C08L29/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 769 426 A (IWASAKI ET AL) 6 September 1988 (1988-09-06) abstract; claims 1-4	1-12
Y	EP 1 022 305 A (NIPPON GOHSEI KAGAKU KOGYO) 26 July 2000 (2000-07-26) abstract; claims 1-8 page 2, lines 5-34	1-12
X	US 4 464 443 A (FARRELL ET AL) 7 August 1984 (1984-08-07) abstract; claims 1-7	1-12

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

8 September 2005

Date of mailing of the international search report

15/09/2005

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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