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(54) Titre : ARTICLE COMPORTANT UNE PROPRIETE BARRIERE
(54) Title: ARTICLE HAVING BARRIER PROPERTY

(57) **Abrégé/Abstract:**

An article having barrier properties is provided. The article includes a nanocomposite having barrier properties dispersed in a polyolefin resin to have superior mechanical strength and form a strong barrier to oxygen, organic solvent, and moisture.



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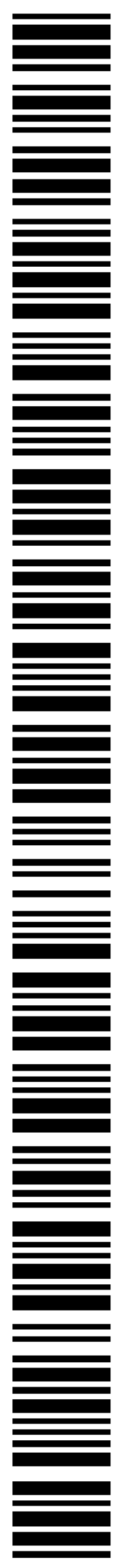
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(54) Title: ARTICLE HAVING BARRIER PROPERTY

(57) Abstract: An article having barrier properties is provided. The article includes a nanocomposite having barrier properties dispersed in a polyolefin resin to have superior mechanical strength and form a strong barrier to oxygen, organic solvent, and moisture.



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Description

ARTICLE HAVING BARRIER PROPERTY

Technical Field

- [1] The present invention relates to an article having barrier properties, in which a nanocomposite of an intercalated clay and a resin having barrier properties is dispersed in a polyolefin resin matrix in a specific form.

Background Art

- [2] General-purpose resins, such as polyethylene and polypropylene, are used in many fields due to their superior moldability, mechanical properties, and moisture barrier properties. However, these resins are limited in their use in packaging or containers for agrochemicals and foods, which require superior chemical and oxygen barrier properties. Therefore, general-purpose resins are used for packaging or containers for such materials with other resins as multiple layers by co-extrusion, lamination, coating, etc.
- [3] An ethylene-vinyl alcohol (EVOH) copolymer and polyamide resins are used for multi-layered plastic products due to their transparency and good gas barrier properties. However, because an ethylene-vinyl alcohol copolymer and polyamide resins are more expensive than general-purpose resins, a resin composition having good barrier properties even when small amounts of these resins are used is required.
- [4] Meanwhile, when a nano-sized intercalated clay is mixed with a polymer compound to form a fully exfoliated, partially exfoliated, intercalated, or partially intercalated nanocomposite, it has improved barrier properties due to its morphology. Thus, an article having barrier properties using such a nanocomposite is emerging.
- [5] It is important for the nanocomposite to maintain its fully exfoliated, partially exfoliated, intercalated, or partially intercalated morphology even after being molded and fully exfoliated morphology is advantageous in the improvement of barrier properties. In particular, when a molded article is prepared from a composition of the nanocomposite and a matrix polymer, the morphology of the nanocomposite dispersed in the matrix polymer is also important to improve barrier properties.

Disclosure of Invention

Technical Problem

- [6] The present invention provides an article having superior mechanical strength and superior oxygen, organic solvent, and moisture barrier properties, in which a nanocomposite maintains exfoliated morphology even after being molded and is dispersed in a matrix polymer in a specific form.

Technical Solution

- [7] According to an aspect of the present invention, there is provided an article having barrier properties prepared from a dry-blended composition including: 40 to 98 parts by weight of a polyolefin resin; 0.5 to 60 parts by weight of a nanocomposite having barrier properties, including an intercalated clay and at least one resin having barrier properties, selected from the group consisting of an ethylene-vinyl alcohol (EVOH) copolymer, an ionomer and a polyvinyl alcohol (PVA); and 1 to 30 parts by weight of a compatibilizer, wherein the nanocomposite is dispersed in the polyolefin resin in a disc form.
- [8] According to another aspect of the present invention, there is provided an article having barrier properties prepared from a dry-blended composition including: 40 to 98 parts by weight of a polyolefin resin; 0.5 to 60 parts by weight of a nanocomposite having barrier properties, including a polyamide and an intercalated clay; and 1 to 30 parts by weight of a compatibilizer, wherein the nanocomposite is dispersed in the polyolefin resin in a multiple lamella form.
- [9] In an embodiment of the present invention, the article having barrier properties may be a pipe, a container, a sheet, a film, etc. and may be prepared in a single layer or multi layer form.
- [10] In another embodiment of the present invention, the polyolefin resin may be at least one compound selected from the group consisting of a high density polyethylene (HDPE), a low density polyethylene (LDPE), a linear low density polyethylene (LLDPE), an ethylene-propylene copolymer, metallocene polyethylene, and polypropylene. The polypropylene may be at least one compound selected from the group consisting of a homopolymer of propylene, a copolymer of propylene, metallocene polypropylene and a composite resin having improved physical properties by adding talc, flame retardant, etc. to a homopolymer or copolymer of propylene.
- [11] In another embodiment of the present invention, the nanocomposite having barrier properties may be prepared by mixing an intercalated clay with a polyamide or at least one resin selected from the group consisting of an ethylene-vinyl alcohol (EVOH) copolymer, an ionomer and a polyvinyl alcohol (PVA). The prepared nanocomposite has fully exfoliated, partially exfoliated, intercalated, or partially intercalated morphology.
- [12] In another embodiment of the present invention, the intercalated clay may be at least one material selected from the group consisting of montmorillonite, bentonite, kaolinite, mica, hectorite, fluorohectorite, saponite, beidelite, nontronite, stevensite, vermiculite, hallosite, volkonskoite, suconite, magadite, and kenyalite.
- [13] In another embodiment of the present invention, the polyamide may be nylon 4.6, nylon 6, nylon 6.6, nylon 6.10, nylon 7, nylon 8, nylon 9, nylon 11, nylon 12, nylon 46, MXD6, amorphous polyamide, a copolymerized polyamide containing at least two

of these, or a mixture of at least two of these.

[14] In another embodiment of the present invention, the ionomer may have a melt index of 0.1 to 10 g/10 min (190 °C , 2,160 g).

[15] In another embodiment of the present invention, the compatibilizer may be at least one compound selected from an ethylene-ethylene anhydride-acrylic acid copolymer, an ethylene-ethyl acrylate copolymer, an ethylene-alkyl acrylate-acrylic acid copolymer, a maleic anhydride modified (graft) high-density polyethylene, a maleic anhydride modified (graft) linear low-density polyethylene, an ethylene-alkyl (meth)acrylate-(meth)acrylic acid copolymer, an ethylene-butyl acrylate copolymer, an ethylene-vinyl acetate copolymer, a maleic anhydride modified (graft) ethylene-vinyl acetate copolymer.

[16] The present invention will now be explained in more detail.

[17] An article having barrier properties according to an embodiment of the present invention is prepared from a dry-blended composition including: 40 to 98 parts by weight of a polyolefin resin; 0.5 to 60 parts by weight of a nanocomposite having barrier properties, including intercalated clay and at least one resin having barrier properties, selected from the group consisting of an ethylene-vinyl alcohol (EVOH) copolymer, an ionomer and a polyvinyl alcohol (PVA); and 1 to 30 parts by weight of a compatibilizer, wherein the nanocomposite is dispersed in the polyolefin resin in a disc form.

[18] An article having barrier properties according to another embodiment of the present invention is prepared from a dry-blended composition including: 40 to 98 parts by weight of a polyolefin resin; 0.5 to 60 parts by weight of a nanocomposite having barrier properties, including a polyamide and an intercalated clay; and 1 to 30 parts by weight of a compatibilizer, wherein the nanocomposite is dispersed in the polyolefin resin in a multiple lamella form.

[19] The polyolefin resin may include at least one compound selected from the group consisting of a high density polyethylene (HDPE), a low density polyethylene (LDPE), a linear low density polyethylene (LLDPE), an ethylene-propylene copolymer, metallocene polyethylene, and polypropylene. The polypropylene may be at least one compound selected from the group consisting of a homopolymer of propylene, a copolymer of propylene, metallocene polypropylene and a composite resin having improved physical properties by adding talc, flame retardant, etc. to a homopolymer or copolymer of propylene.

[20] The content of the polyolefin resin is preferably 40 to 98 parts by weight, and more preferably 70 to 96 parts by weight. If the content of the polyolefin resin is less than 40 parts by weight, molding is difficult. If the content of the polyolefin resin is greater than 98 parts by weight, the barrier property is poor.

- [21] The nanocomposite having barrier properties may be prepared by mixing an intercalated clay with a polyamide or at least one resin selected from the group consisting of an ethylene-vinyl alcohol (EVOH) copolymer, an ionomer and a polyvinyl alcohol (PVA).
- [22] The weight ratio of the resin having barrier properties to the intercalated clay in the nanocomposite is 58.0:42.0 to 99.9:0.1, and preferably 85.0:15.0 to 99.0:1.0. If the weight ratio of the resin having barrier properties to the intercalated clay is less than 58.0:42.0, the intercalated clay agglomerates and dispersing is difficult. If the weight ratio of the resin having barrier properties to the intercalated clay is greater than 99.9:0.1, the improvement in the barrier properties is negligible.
- [23] The intercalated clay is preferably organic intercalated clay. The content of an organic material in the intercalated clay is preferably 1 to 45 wt %. When the content of the organic material is less than 1 wt%, the compatibility of the intercalated clay and the resin having barrier properties is poor. When the content of the organic material is greater than 45 wt%, the intercalation of the resin having barrier properties is difficult.
- [24] The intercalated clay includes at least one material selected from montmorillonite, bentonite, kaolinite, mica, hectorite, fluorohectorite, saponite, beidelite, nontronite, stevensite, vermiculite, hallosite, volkonskoite, suconite, magadite, and kenyalite; and the organic material preferably has a functional group selected from primary ammonium to quaternary ammonium, phosphonium, maleate, succinate, acrylate, benzylic hydrogen, oxazoline, and dimethyldistearylammonium.
- [25] If an ethylene-vinyl alcohol copolymer is included in the nanocomposite, the content of ethylene in the ethylene-vinyl alcohol copolymer is preferably 10 to 50 mol %. If the content of ethylene is less than 10 mol %, melt molding becomes difficult due to poor processability. If the content of ethylene exceeds 50 mol %, oxygen and liquid barrier properties are insufficient.
- [26] If polyamide is included in the nanocomposite, the polyamide may be nylon 4.6, nylon 6, nylon 6.6, nylon 6.10, nylon 7, nylon 8, nylon 9, nylon 11, nylon 12, nylon 46, MXD6, amorphous polyamide, a copolymerized polyamide containing at least two of these, or a mixture of at least two of these.
- [27] The amorphous polyamide refers to a polyamide having insufficient crystallinity, that is, not having an endothermic crystalline melting peak when measured by a differential scanning calorimetry (DSC) (ASTM D-3417, 10 °C /min).
- [28] In general, the polyamide can be prepared using diamine and dicarboxylic acid. Examples of the diamine include hexamethylenediamine, 2-methylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, bis(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)isopropylidene, 1,4-diaminocyclohexane,

1,3-diaminocyclohexane, meta-xylenediamine, 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane, 2-ethyldiaminobutane, 1,4-diaminomethylcyclohexane, methane-xylenediamine, alkyl-substituted or unsubstituted m-phenylenediamine and p-phenylenediamine, etc. Examples of the dicarboxylic acid include alkyl-substituted or unsubstituted isophthalic acid, terephthalic acid, adipic acid, sebacic acid, butanedicarboxylic acid, etc.

[29] Polyamide prepared using aliphatic diamine and aliphatic dicarboxylic acid is general semicrystalline polyamide (also referred to as crystalline nylon) and is not amorphous polyamide. Polyamide prepared using aromatic diamine and aromatic dicarboxylic acid is not easily treated using a general melting process.

[30] Thus, amorphous polyamide is preferably prepared, when one of diamine and dicarboxylic acid used is aromatic and the other is aliphatic. Aliphatic groups of the amorphous polyamide are preferably C_1-C_{15} aliphatic or C_4-C_8 alicyclic alkyls. Aromatic groups of the amorphous polyamide are preferably substituted C_1-C_6 mono- or bicyclic aromatic groups. However, all the above amorphous polyamide is not preferable in the present invention. For example, metaxylenediamine adipamide is easily crystallized when heated during a thermal molding process or when oriented, therefore, it is not preferable.

[31] Examples of preferable amorphous polyamides include hexamethylenediamine isophthalamide, hexamethylene diamine isophthalamide/terephthalamide terpolymer having a ratio of isophthalic acid/terephthalic acid of 99/1 to 60/40, a mixture of 2,2,4- and 2,4,4-trimethylhexamethylenediamine terephthalamide, a copolymer of hexamethylenediamine or 2-methylpentamethylenediamine and an isophthalic acid, terephthalic acid or mixtures thereof. While polyamide based on hexamethylenediamine isophthalamide/terephthalamide, which has a high terephthalic acid content, is useful, it should be mixed with another diamine such as 2-methyldiaminopentane in order to produce an amorphous polyamide that can be processed.

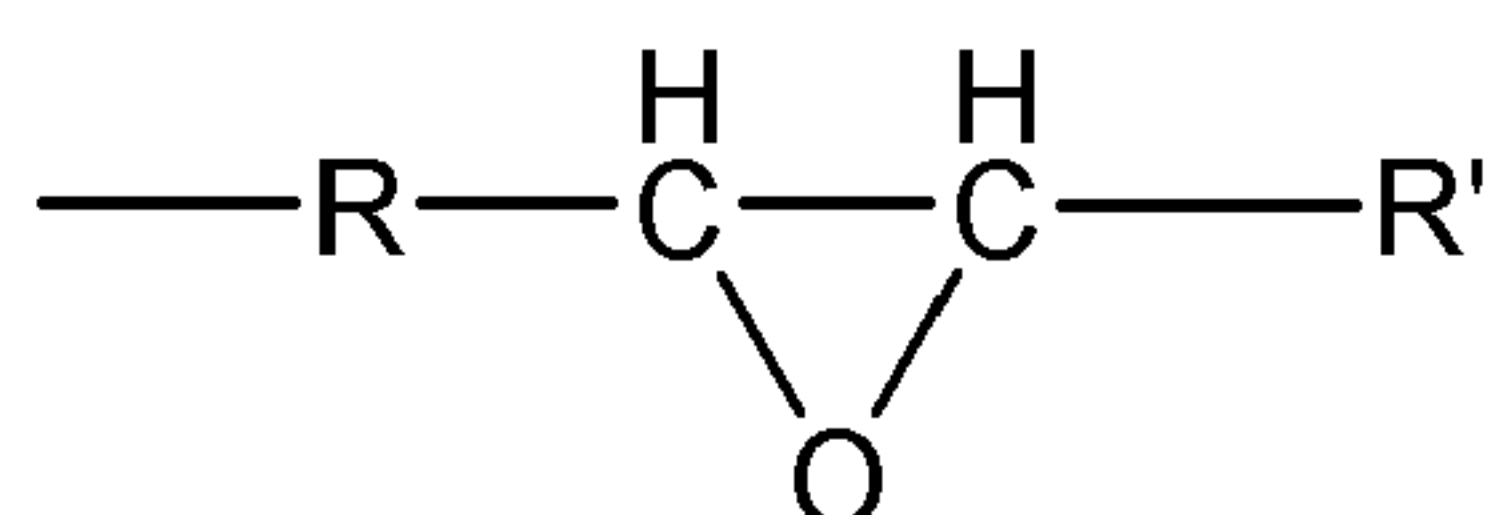
[32] The above amorphous polyamide comprising only the above monomers may contain a small amount of lactam, such as caprolactam or lauryl lactam, as a comonomer. It is important that the polyamide be amorphous. Therefore, any comonomer that does not crystallize polyamide can be used. About 10 wt% or less of a liquid or solid plasticizer, such as glycerole, sorbitol, or toluenesulfoneamide (Santicizer 8 monsanto) can also be included in the amorphous polyamide. For most applications, a glass transition temperature T_g (measured in a dried state, i.e., with a water content of about 0.12 wt% or less) of amorphous polyamide is about 70-170 °C, and preferably about 80-160 °C. The amorphous polyamide, which is not blended, has a T_g of approximately 125 °C in a dried state. The lower limit of T_g is not clear, but 70

°C is an approximate lower limit. The upper limit of T_g is not clear, too. However, when polyamide with a T_g of about 170 °C or greater is used, thermal molding is difficult. Therefore, polyamide having both an acid and an amine having aromatic groups cannot be thermally molded due to too high T_g, and thus, is not suitable for the purposes of the present invention.

- [33] The polyamide may also be a semicrystalline polyamide. The semicrystalline polyamide is generally prepared using lactam, such as nylon 6 or nylon 11, or an amino acid, or is prepared by condensing diamine, such as hexamethylenediamine, with dibasic acid, such as succinic acid, adipic acid, or sebacic acid. The polyamide may be a copolymer or a terpolymer such as a copolymer of hexamethylenediamine/adipic acid and caprolactame (nylon 6, 66). A mixture of two or more crystalline polyamides can also be used. The semicrystalline and amorphous polyamides are prepared by condensation polymerization well-known in the art.
- [34] If an ionomer is included in the nanocomposite, the ionomer is preferably a copolymer of acrylic acid and ethylene, with a melt index of 0.1 to 10 g/10 min (190 °C, 2,160 g).
- [35] The nanocomposite may include additives such as a thermal stabilizer or a plasticizer in addition to the intercalated clay and the resin having barrier properties.
- [36] The content of the nanocomposite is preferably 0.5 to 60 parts by weight, and more preferably 4 to 30 parts by weight. If the content of the nanocomposite is less than 0.5 part by weight, an improvement of barrier properties is negligible. If the content of the nanocomposite is greater than 60 parts by weight, processing is difficult.
- [37] The finer the intercalated clay is exfoliated in the resin having barrier property in the nanocomposite, the better the barrier properties that can be obtained. This is because the exfoliated intercalated clay forms a barrier film and thereby improves barrier properties and mechanical properties of the resin itself, and ultimately improves barrier properties and mechanical properties of a molded article prepared from the composition. Accordingly, the ability to form a barrier to gas and liquid is maximized by compounding the resin having barrier properties and the intercalated clay, and dispersing the nano-sized intercalated clay in the resin, thereby maximizing the contact area of the polymer chain and the intercalated clay.
- [38] The compatibilizer reduces brittleness of the polyolefin resin and improves the compatibility of the polyolefin resin in the nanocomposite to form a molded article with a stable structure.
- [39] The compatibilizer may be a hydrocarbon polymer having polar groups. When a hydrocarbon polymer having polar groups is used, the hydrocarbon polymer portion increases the affinity of the compatibilizer to the polyolefin resin and to the nanocomposite having barrier properties, thereby obtaining a molded article with a

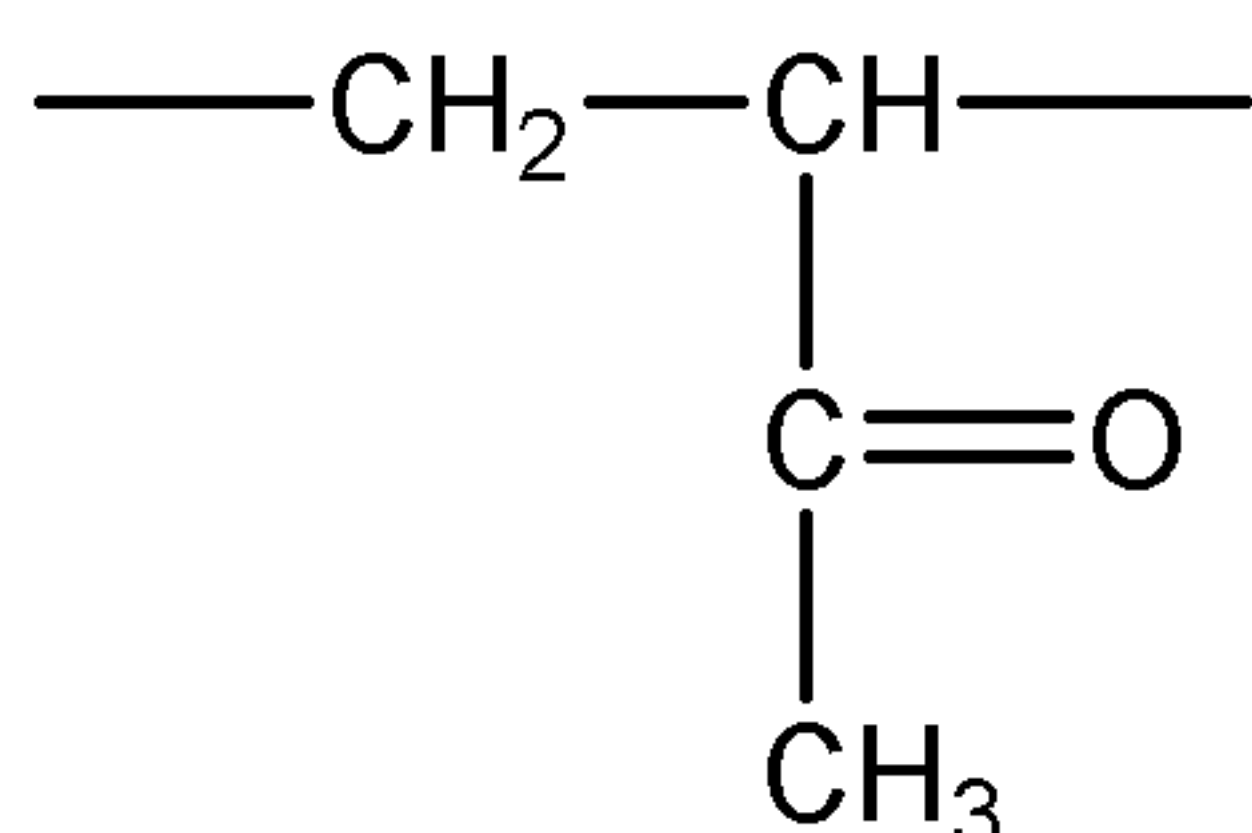
stable structure.

- [40] The compatibilizer can include a compound selected from an epoxy-modified polystyrene copolymer, an ethylene-ethylene anhydride-acrylic acid copolymer, an ethylene-ethyl acrylate copolymer, an ethylene-alkyl acrylate-acrylic acid copolymer, a maleic anhydride modified (graft) high-density polyethylene, a maleic anhydride modified (graft) polypropylene, a maleic anhydride modified (graft) linear low-density polyethylene, an ethylene-alkyl (meth)acrylate-(meth)acrylic acid copolymer, an ethylene-butyl acrylate copolymer, an ethylene-vinyl acetate copolymer, a maleic anhydride modified (graft) ethylene-vinyl acetate copolymer, and a modification thereof.
- [41] The content of the compatibilizer is preferably 1 to 30 parts by weight, and more preferably 2 to 15 parts by weight. If the content of the compatibilizer is less than 1 part by weight, the mechanical properties of a molded article from the composition are poor. If the content of the compatibilizer is greater than 30 parts by weight, the molding of the composition is difficult.
- [42] When an epoxy-modified polystyrene copolymer is used as the compatibilizer, a copolymer comprising a main chain which comprises 70 to 99 parts by weight of styrene and 1 to 30 part by weight of an epoxy compound represented by Formula 1, and branches which comprise 1 to 80 parts by weight of acrylic monomers represented by Formula 2, is preferable.



(1)

- [43] where each of R and R' is independently a C₁-C₂₀ aliphatic residue or a C₅-C₂₀ aromatic residue having double bonds at its termini



(2).

- [44] Each of the maleic anhydride modified (graft) high-density polyethylene, maleic anhydride modified (graft) polypropylene, maleic anhydride modified (graft) linear low-density polyethylene, and maleic anhydride modified (graft) ethylene-vinyl acetate copolymer preferably comprises branches having 0.1 to 10 parts by weight of maleic anhydride based on 100 parts by weight of the main chain. When the content of the maleic anhydride is less than 0.1 part by weight, it does not function as the com-

patibilizer. When the content of the maleic anhydride is greater than 10 parts by weight, it is not preferable due to an unpleasant odor.

- [45] The composition of the present invention is prepared by dry-blending the nanocomposite having barrier properties in a pellet form, the compatibilizer and the polyolefin resin at a constant compositional ratio in a pellet mixer.
- [46] An article having barrier properties according to the present invention is obtained by molten-blending and molding the dry-blended pelleted composition. In the article having barrier properties, the form of the nanocomposite dispersed in the polyolefin resin matrix is particularly important in the improvement of barrier properties. When a polyamide is used as the resin having barrier properties, the nanocomposite is dispersed in a multiple lamella form and when at least one resin selected from the group consisting of an EVOH copolymer, an ionomer and a polyvinylalcohol is used, the nanocomposite is dispersed in a disc form. Due to such a dispersion form, the passage route of gases and organic solvents is extended, and thus the passage speed is decreased, thereby obtaining superior barrier properties.
- [47] The structure of the article having barrier properties according to the present invention is schematically illustrated in FIGS. 1 and 2. FIG. 1 schematically illustrates cross-sections of an extrusion molded article having barrier properties when the resin having barrier properties is a polyamide, wherein a polyamide nanocomposite 2 forms a multiple lamella structure in a continuous polyolefin 1. FIG. 1A is a machine direction (MD) cross-sectional view and FIG. 1B is a transverse direction (TD) cross-sectional view. FIG. 2 schematically illustrates cross-sections of a blow-molded article having barrier properties when the resin having barrier properties is at least one resin selected from the group consisting of an EVOH copolymer, an ionomer and a polyvinylalcohol, wherein a nanocomposite 3 forms a disc structure in a continuous polyolefin 1. FIG. 2A is a MD cross-sectional view and FIG. 1B is a TD cross-sectional view.
- [48] When a polyamide is used as the resin having barrier properties, the nanocomposite is dispersed in the polyolefin resin in a multiple lamella form in which 2 to 300 lamellas are included in the unit length of 1 mm, the thickness of the lamella is in the range of 0.001-200 μ m, and an average aspect ratio, ϕn , is 10 to 1,000. The average aspect ratio, ϕn , is obtained by the equation of $\phi n = \sum N_i \phi_i / \sum N_i$, where N_i is the number of lamella in the unit length (1 mm) and ϕ_i is an aspect ratio of each lamella.
- [49] When a polyvinylalcohol, an ionomer or an EVOH copolymer is used as the resin having barrier properties, the nanocomposite is dispersed in the polyolefin resin in a disc form in which 10^2 to 10^5 discs are included in unit area of 1 mm², the thickness of the disc is in the range of 0.001-200 μ m, the length of the major axis of the disc is 5 to 1000 μ m and an average aspect ratio, ϕn , is 2 to 1,000. The average aspect ratio, ϕn , is

obtained by the equation of $\phi_n = \sum N_i \phi_i / \sum N_i$, where N_i is the number of disc in the unit area (1 mm^2) and ϕ_i is an aspect ratio of each disc.

[50] In the preparation of the article having barrier properties according to the present invention, the nanocomposite is prepared through plasticization and blending processes at the melting point or higher using a single screw extruder, a co-rotation twin screw extruder, a counter-rotation twin screw extruder, a continuous compounder, a planetary gear extruder, a batch compounder etc. The article having barrier properties can be prepared by general molding methods including blow molding, extrusion molding, pressure molding, and injection molding. The molded article having barrier properties may be a pipe, a container, a sheet, a film, and the like. The article having barrier properties can also be a single-layered product composed of only the nanocomposite composition or a multi-layered product having the nanocomposite composition layer and another resin layer.

[51] Since the intercalated clay in the nanocomposite is arranged during the molding process to form a multi-layered barrier, the article having barrier properties of the present invention has further improved barrier properties.

[52] Hereinafter, the present invention is described in more detail through examples. The following examples are meant only to increase understanding of the present invention, and are not meant to limit the scope of the invention.

Advantageous Effects

[53] The article having barrier properties of the present invention has superior mechanical strength and forms a strong barrier to oxygen, organic solvent, and moisture. Also, the nanocomposite composition has superior chemical barrier properties and moldability.

Description of Drawings

[54] The above and other features and advantages of the present invention will become more apparent by describing in detail exemplary embodiments thereof with reference to the attached drawings in which:

[55] FIGS. 1A and 1B schematically illustrate machine direction (MD) and transverse direction (TD) cross sections of an article having barrier properties, prepared according to an embodiment of the present invention;

[56] FIGS. 2A and 2B schematically illustrate MD and TD cross-sections of an article having barrier properties, prepared according to another embodiment of the present invention;

[57] FIGS. 3A and 3B are electron microscopic photographs of MD and TD cross-sections of an article having barrier properties, blow-molded according to Example 1; and

- [58] FIGS. 4A and 4B are electron microscopic photographs of MD and TD cross-sections of an article having barrier properties, blow-molded according to Example 2.

Mode for Invention

- [59] Examples

- [60] The materials used in the following examples are as follows:

- [61] EVOH: E105B (Kuraray, Japan)

- [62] Nylon 6: EN 300 (KP Chemicals)

- [63] SURLYN™ 8527 Ionomer (SURLYN is a trade-mark of Dupont)

- [64] HDPE-g-MAH: Compatibilizer, PB3009 (CRAMPTON)

- [65] Polyolefin resin: High-density polyethylene (BDO 390, LG CHEM, melt index: 0.3 g/10 min, density: 0.949 g/cm³)

- [66] Clay: Closite 20A (SCP)

- [67] Thermal stabilizer: IR 1098 (Songwon Inc.)

- [68] Preparation Example 1

- [69] (Preparation of EVOH/Intercalated Clay Nanocomposite)

- [70] 97 wt % of an ethylene-vinyl alcohol copolymer (EVOH; E-105B (ethylene content: 44 mol %); Kuraray, Japan; melt index: 5.5 g/10 min; density: 1.14 g/cm³) was put in the main hopper of a twin screw extruder (SM Platek co-rotation twin screw extruder; ϕ 40). Then, 3 wt% of organic montmorillonite (Southern Intercalated Clay Products, USA; Closite 20A) as an intercalated clay and 0.1 part by weight of IR 1098 as a thermal stabilizer based on total 100 parts by weight of the EVOH copolymer and the organic montmorillonite was separately put in the side feeder of the twin screw extruder to prepare an EVOH/intercalated clay nanocomposite in a pellet form. The extrusion temperature condition was 180-190-200-200-200-200-200 °C, the screws were rotated at 300 rpm, and the discharge condition was 30 kg/hr.

- [71] Preparation Example 2

- [72] (Preparation of Nylon 6/Intercalated Clay Nanocomposite)

- [73] 97 wt % of a polyamide (nylon 6, EN300) was put in the main hopper of a twin screw extruder (SM Platek co-rotation twin screw extruder; ϕ 40). Then, 3 wt% of organic montmorillonite as an intercalated clay and 0.1 part by weight of IR 1098 as a thermal stabilizer based on total 100 parts by weight of the polyamide and the organic montmorillonite was separately put in the side feeder of the twin screw extruder to prepare a polyamide/intercalated clay nanocomposite in a pellet form. The extrusion temperature condition was 220-225-245-245-245-245-245 °C, the screws were rotated at 300 rpm, and the discharge condition was 40 kg/hr.

- [74] Preparation Example 3

- [75] (Preparation of Ionomer/Intercalated Clay Nanocomposite)

- [76] 97 wt % of an ionomer was put in the main hopper of a twin screw extruder (SM

Platek co-rotation twin screw extruder; ϕ 40). Then, 3 wt% of organic montmorillonite as an intercalated clay and 0.1 part by weight of IR 1098 as a thermal stabilizer based on total 100 parts by weight of the ionomer and the organic montmorillonite was separately put in the side feeder of the twin screw extruder to prepare an ionomer/intercalated clay nanocomposite in a pellet form. The extrusion temperature condition was 220-225-245-245-245-245 °C, the screws were rotated at 300 rpm, and the discharge condition was 40 kg/hr.

[77] Example 1

[78] 25 parts by weight of the EVOH/intercalated clay nanocomposite obtained in the Preparation Example 1, 5 parts by weight of a compatibilizer, and 70 parts by weight of high-density polyethylene were dry-blended in a double cone mixer (MYDCM-100) for 30 minutes and put in the main hopper of a blow-molder (SMC- ϕ 60 blow-molder). Under the extrusion temperature condition of 185-195-195-195 °C, the blow-molding process was performed to manufacture a 1000 mL container having barrier properties.

[79] Example 2

[80] 25 parts by weight of the nylon 6/intercalated clay nanocomposite obtained in the Preparation Example 2, 5 parts by weight of a compatibilizer, and 70 parts by weight of high-density polyethylene were dry-blended in a double cone mixer (MYDCM-100) for 30 minutes and put in the main hopper of a blow-molder (SMC- ϕ 60 blow-molder). Under the extrusion temperature condition of 195-210-220-220 °C, the blow-molding process was performed to manufacture a 1000 mL container having barrier properties.

[81] Example 3

[82] 25 parts by weight of the nylon 6/intercalated clay nanocomposite obtained in the Preparation Example 2, 5 parts by weight of a compatibilizer, and 70 parts by weight of HDPE were dry-blended and simultaneously put in the main hopper of a blow molder (SMC- ϕ 60 blow-molder) through belt-type feeders (K-TRON Nos. 1, 2 and 3), respectively. Under the extrusion temperature condition of 195-210-220-220 °C, the blow-molding process was performed to manufacture a 1000 mL container having barrier properties.

[83] Example 4

[84] 5 parts by weight of the nylon 6/intercalated clay nanocomposite obtained in the Preparation Example 2, 2 parts by weight of a compatibilizer, and 93 parts by weight of high-density polyethylene were dry-blended in a double cone mixer (MYDCM-100) for 30 minutes and put in the main hopper of a blow-molder (SMC- ϕ 60 blow-molder). Under the extrusion temperature condition of 195-210-220-220 °C, the blow-molding process was performed to manufacture a 1000 mL container having barrier

properties.

[85] Example 5

[86] 40 parts by weight of the nylon 6/intercalated clay nanocomposite obtained in the Preparation Example 2, 20 parts by weight of a compatibilizer, and 40 parts by weight of high-density polyethylene were dry-blended in a double cone mixer (MYDCM-100) for 30 minutes and put in the main hopper of a blow-molder (SMC- φ 60 blow-molder). Under the extrusion temperature condition of 195-210-220-220 °C , the blow-molding process was performed to manufacture a 1000 mL container having barrier properties.

[87] Example 6

[88] 25 parts by weight of the ionomer/intercalated clay nanocomposite obtained in the Preparation Example 3, 5 parts by weight of a compatibilizer, and 70 parts by weight of high-density polyethylene were dry-blended and put in the main hopper of a blow-molder (SMC- φ 60 blow-molder). Under the extrusion temperature condition of 240-265-265-265 °C , the blow-molding process was performed to manufacture a 1000 mL container having barrier properties.

[89] Comparative Example 1

[90] A container having barrier properties was manufactured in the same manner as in Example 1, except that the organic montmorillonite as an intercalated clay was not used.

[91] Comparative Example 2

[92] A container having barrier properties was manufactured in the same manner as in Example 2, except that the organic montmorillonite as an intercalated clay was not used.

[93] Comparative Example 3

[94] A container having barrier properties was manufactured in the same manner as in Example 3, except that the organic montmorillonite as an intercalated clay was not used.

[95] Experimental Example

[96] a) Liquid barrier properties

[97] Toluene, Desys herbicide (1% of deltametrine+emulsifier, stabilizer, and solvent; Kyung Nong), Batsa insecticide (50% of BPMC+50% of emulsifier and solvent), and water were put in the containers manufactured in Examples 1 to 6 and Comparative Examples 1 to 3. Then, the weight change was determined after 30 days under a condition of forced exhaust at 50 °C . For toluene, the weight change was further determined at room temperature.

[98] b) Gas barrier properties ($\text{cc/m}^2 \cdot \text{day} \cdot \text{atm}$)

[99] The containers manufactured in Examples 1 to 6 and Comparative Examples 1 to 3

were left alone under a temperature of 23 °C and a relative humidity of 50% for 1 day. Then, the gas penetration rate was determined (Mocon OX-TRAN 2/20, U.S.A).

[100] TABLE 1
[101] Gas Barrier Properties

	Oxygen penetration (cm ² /m ² · 24 hrs · atm)	Moisture penetration (g/m ² · 24 hrs)
Example 1	10.5	1.24
Example 2	5.9	1.11
Example 3	6.3	1.18
Example 4	24.9	1.04
Example 5	2.3	1.27
Example 6	19.6	1.32
Comparative Example 1	79.4	1.59
Comparative Example 2	86.8	1.52
Comparative Example 3	98.1	2.11

[102] TABLE 2
[103] Liquid Barrier Properties

Classification	Liquid barrier properties (%)				
	Weight change at 25 °C	Weight change at 50 °C			
	Toluene	Toluene	Desys	Batsa	Water
Example 1	0.037	0.421	0.153	0.031	0.0014
Example 2	0.012	0.118	0.084	0.013	0.0017
Example 3	0.015	0.143	0.095	0.018	0.0016
Example 4	0.048	0.814	0.195	0.031	0.0014
Example 5	0.009	0.049	0.052	0.008	0.0018
Example 6	0.044	0.685	0.119	0.099	0.0019
Comparative Example 1	0.430	5.993	1.274	0.474	0.0020
Comparative Example 2	0.623	6.319	1.532	0.651	0.0031

Comparative Example 3	1.125	8.304	1.849	0.847	0.0033
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[104] As shown in Tables 1 and 2, containers of Examples 1 to 6 have superior barrier properties to liquid and gas compared to those of Comparative Examples 1 to 3.

[105] Electron microscopic photographs of the cross sections of the blow-molded containers manufactured in Examples 1 and 2 are shown in FIGS. 3 and 4.

[106] FIGS. 3A and 3B show MD and TD cross sections of the blow-molded container of Example 1. In FIGS. 3A and 3B, 10 to 400 discs are included in the unit area of 1 mm^2 , the thickness of disc is in the range of 3 to $200 \text{ \AA}$, the length of the major axis is in the range of 5 to $1000 \text{ \AA}$, and an average aspect ratio is 32.

[107] FIGS. 4A and 4B show MD and TD cross sections of the blow-molded container of Example 2. In FIGS. 4A and 4B, 10 to 300 lamellas are included in the unit length of 1 mm, the thickness of lamella is in the range of 3 to $200 \text{ \AA}$, and an average aspect ratio is 523.

[108] As can be seen from the figures, the article having barrier properties according to the present invention includes the nanocomposite dispersed in the continuous resin in the form of a multiple lamella or disc to have good barrier properties.

[109] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

Claims

- [1] An article having barrier properties prepared from a dry-blended composition comprising:
40 to 98 parts by weight of a polyolefin resin;
0.5 to 60 parts by weight of a nanocomposite having barrier properties, comprising an intercalated clay and at least one resin having barrier properties selected from the group consisting of an ethylene-vinyl alcohol (EVOH) copolymer, an ionomer and a polyvinyl alcohol (PVA); and
1 to 30 parts by weight of a compatibilizer,
wherein the nanocomposite is dispersed in the polyolefin resin in a disc form.
- [2] An article having barrier properties prepared from a dry-blended composition comprising:
40 to 98 parts by weight of a polyolefin resin;
0.5 to 60 parts by weight of a nanocomposite having barrier properties, comprising a polyamide and an intercalated clay; and
1 to 30 parts by weight of a compatibilizer,
wherein the nanocomposite is dispersed in the polyolefin resin in a multiple lamella form.
- [3] The article having barrier properties of claim 1, wherein the nanocomposite having barrier properties is prepared by mixing the intercalated clay with at least one resin having barrier properties selected from the group consisting of the ethylene-vinyl alcohol (EVOH) copolymer, the ionomer and the polyvinyl alcohol (PVA).
- [4] The article having barrier properties of claim 1 or 2, wherein the polyolefin resin is at least one compound selected from the group consisting of a high density polyethylene (HDPE), a low density polyethylene (LDPE), a linear low density polyethylene (LLDPE), an ethylene-propylene copolymer, metallocene polyethylene, and polypropylene.
- [5] The article having barrier properties of claim 4, wherein the polypropylene is at least one compound selected from the group consisting of a homopolymer or copolymer of propylene, metallocene polypropylene, and a composite resin prepared by adding talc or flame retardant to homopolymer or copolymer of propylene.
- [6] The article having barrier properties of claim 1 or 2, wherein the intercalated clay is at least one compound selected from the group consisting of montmorillonite, bentonite, kaolinite, mica, hectorite, fluorohectorite, saponite, beidelite, nontronite, stevensite, vermiculite, hallosite, volkonskoite, suconite, magadite,

and kenyalite.

- [7] The article having barrier properties of claim 1 or 2, wherein the weight ratio of the resin having barrier properties to the intercalated clay in the nanocomposite is 58.0:42.0 to 99.9:0.1.
- [8] The article having barrier properties of claim 1 or 2, wherein the intercalated clay comprises 1 to 45 wt % of an organic material.
- [9] The article having barrier properties of claim 8, wherein the organic material has at least one functional group selected from the group consisting of primary ammonium to quaternary ammonium, phosphonium, maleate, succinate, acrylate, benzylic hydrogen, oxazoline, and dimethyldistearylammonium.
- [10] The article having barrier properties of claim 1, wherein the ethylene-vinyl alcohol copolymer contains 10 to 50 mol % of ethylene.
- [11] The article having barrier properties of claim 2, wherein the polyamide is nylon 4.6, nylon 6, nylon 6.6, nylon 6.10, nylon 7, nylon 8, nylon 9, nylon 11, nylon 12, nylon 46, MXD6, amorphous polyamide, a copolymerized polyamide containing at least two of these, or a mixture of at least two of these.
- [12] The article having barrier properties of claim 1, wherein the ionomer has a melt index of 0.1 to 10 g/10 min (190 °C , 2,160 g).
- [13] The article having barrier properties of claim 1 or 2, wherein the compatibilizer is one or more compounds selected from the group consisting of an ethylene-ethylene anhydride-acrylic acid copolymer, an ethylene-ethyl acrylate copolymer, an ethylene-alkyl acrylate-acrylic acid copolymer, a maleic anhydride modified (graft) high-density polyethylene, a maleic anhydride modified (graft) polypropylene, a maleic anhydride modified (graft) linear low-density polyethylene, an ethylene-alkyl (meth)acrylate-(meth)acrylic acid copolymer, an ethylene-butyl acrylate copolymer, an ethylene-vinyl acetate copolymer, and a maleic anhydride modified (graft) ethylene-vinyl acetate copolymer.
- [14] The article having barrier properties of claim 1 or 2, wherein the nanocomposite maintains its fully exfoliated, partially exfoliated, intercalated, or partially intercalated morphology even when being molded.
- [15] The article having barrier properties of claim 1 or 2, wherein the nanocomposite is prepared through plasticizing and blending processes at the melting point or higher using a single screw extruder, a co-rotation twin screw extruder, a counter-rotation twin screw extruder, a continuous compounder, a planetary gear extruder or a batch compounder.
- [16] The article having barrier properties of claim 1 or 2, prepared through blow molding, extrusion molding, pressure molding, or injection molding.

- [17] The article having barrier properties of claim 1 or 2, having a single layer form or a multiple layer form.
- [18] The article having barrier properties of claim 1, wherein the nanocomposite is dispersed in the polyolefin resin in a disc form in which 10^2 to 10^5 discs are included in unit area of 1 mm^2 , the thickness of disc is in the range of 0.001 to $200 \mu\text{m}$, the length of the major axis of disc is 5 to $1000 \mu\text{m}$ and an average aspect ratio, ϕ_n , is 2 to 1,000.
- [19] The article having barrier properties of claim 2, wherein the nanocomposite is dispersed in the polyolefin resin in a multiple lamella form in which 2 to 300 lamellas are included in unit length of 1 mm, the thickness of the lamella is in the range of 0.001- $200 \mu\text{m}$, and an average aspect ratio, ϕ_n , is 10 to 1,000.
- [20] The article having barrier properties of claim 11, wherein the glass transition temperature of the amorphous polyamide is about 70-170 °C.
- [21] The article having barrier properties of claim 11, wherein the amorphous polyamide is selected from the group consisting of hexamethylenediamine isophthalamide, hexamethylene diamine isophthalamide/terephthalamide terpolymer having a ratio of isophthalic acid/terephthalic acid of 99/1 to 60/40, a mixture of 2,2,4- and 2,4,4-trimethylhexamethylenediamine terephthalamide, and a copolymer of hexamethylenediamine or 2-methylpentamethylenediamine and isophthalic acid, terephthalic acid, or a mixture thereof.
- [22] The article having barrier properties of claim 21, wherein the amorphous polyamide is hexamethylene diamine isophthalamide/terephthalamide terpolymer having a ratio of isophthalic acid to terephthalic acid of 70:30.
- [23] The article having barrier properties of claim 13, wherein the maleic anhydride modified (graft) high-density polyethylene, maleic anhydride modified (graft) linear low-density polyethylene, maleic anhydride modified (graft) polypropylene, or maleic anhydride modified (graft) ethylene-vinyl acetate copolymer comprises branches having 0.1 to 10 parts by weight of maleic anhydride based on 100 parts by weight of the main chain.

FIG. 1A

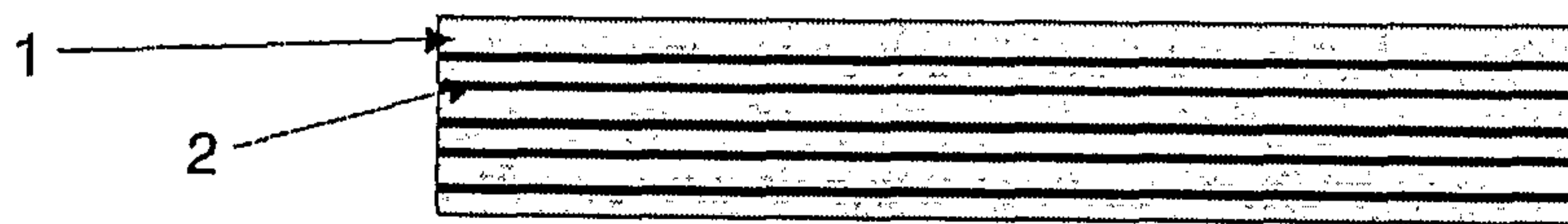


FIG. 1B

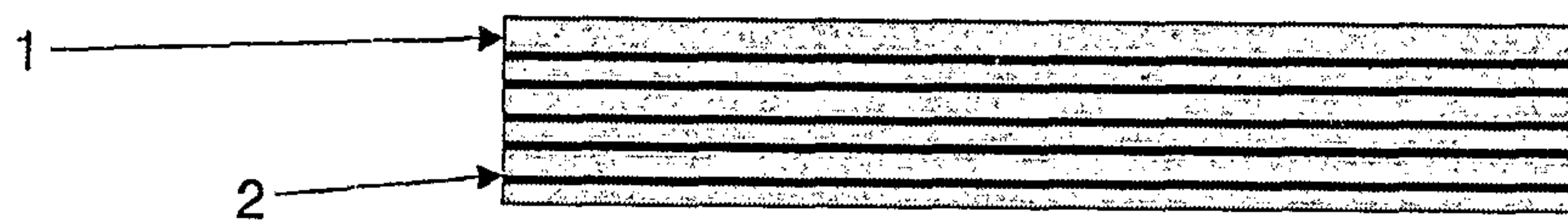


FIG. 2A

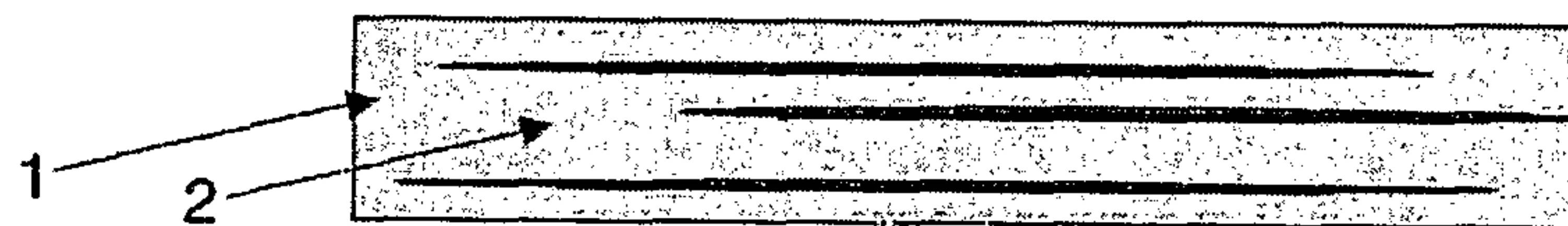


FIG. 2B

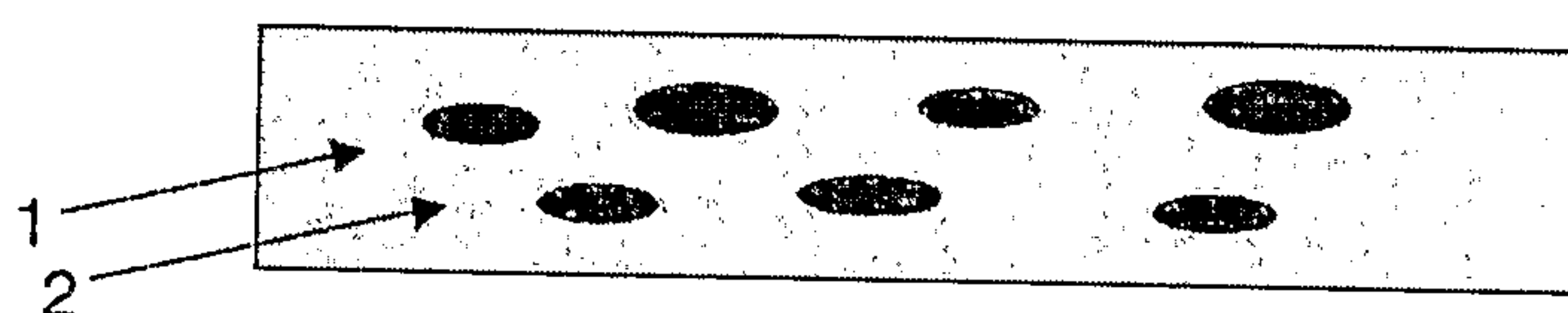


FIG. 3A



FIG. 3B

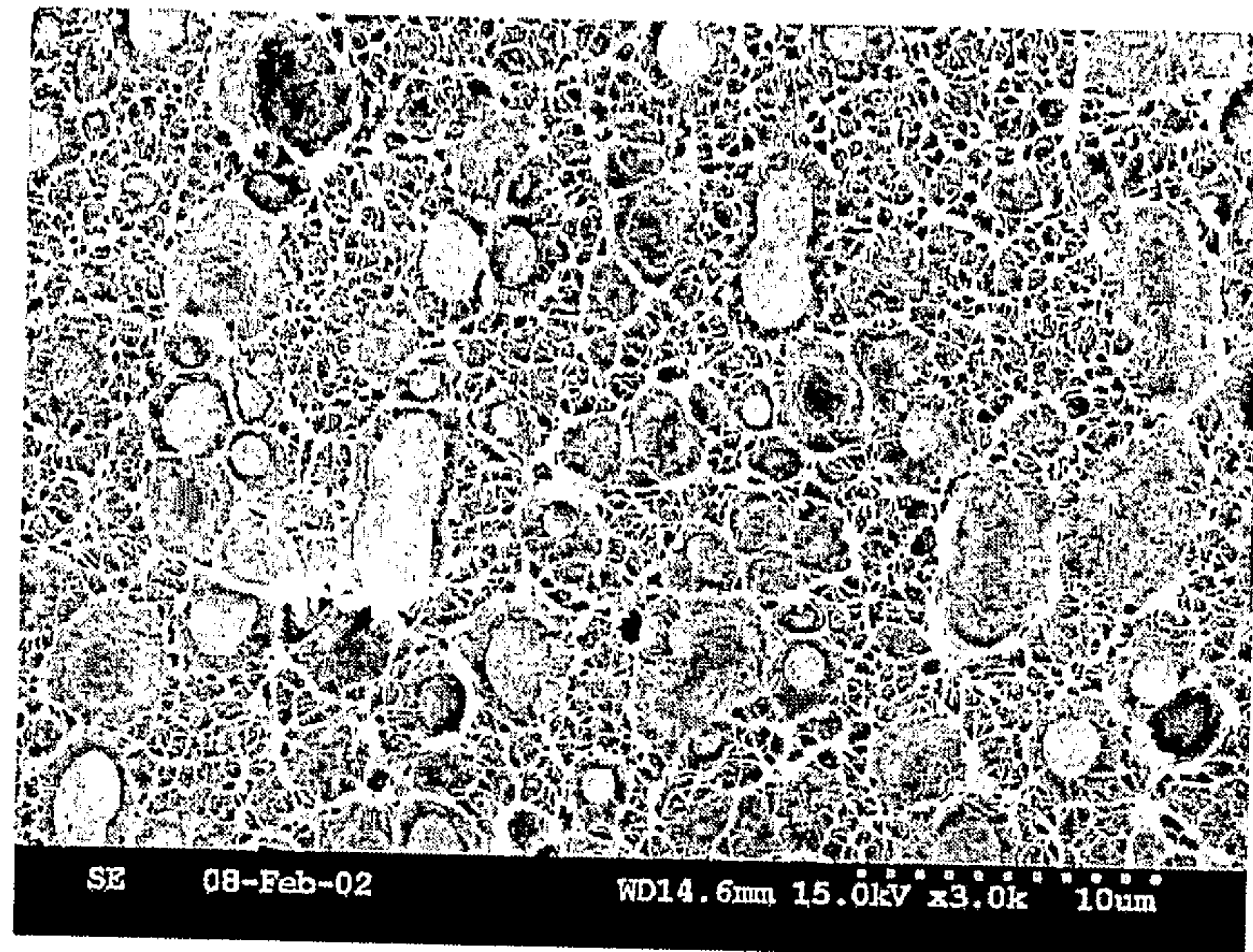


FIG. 4A

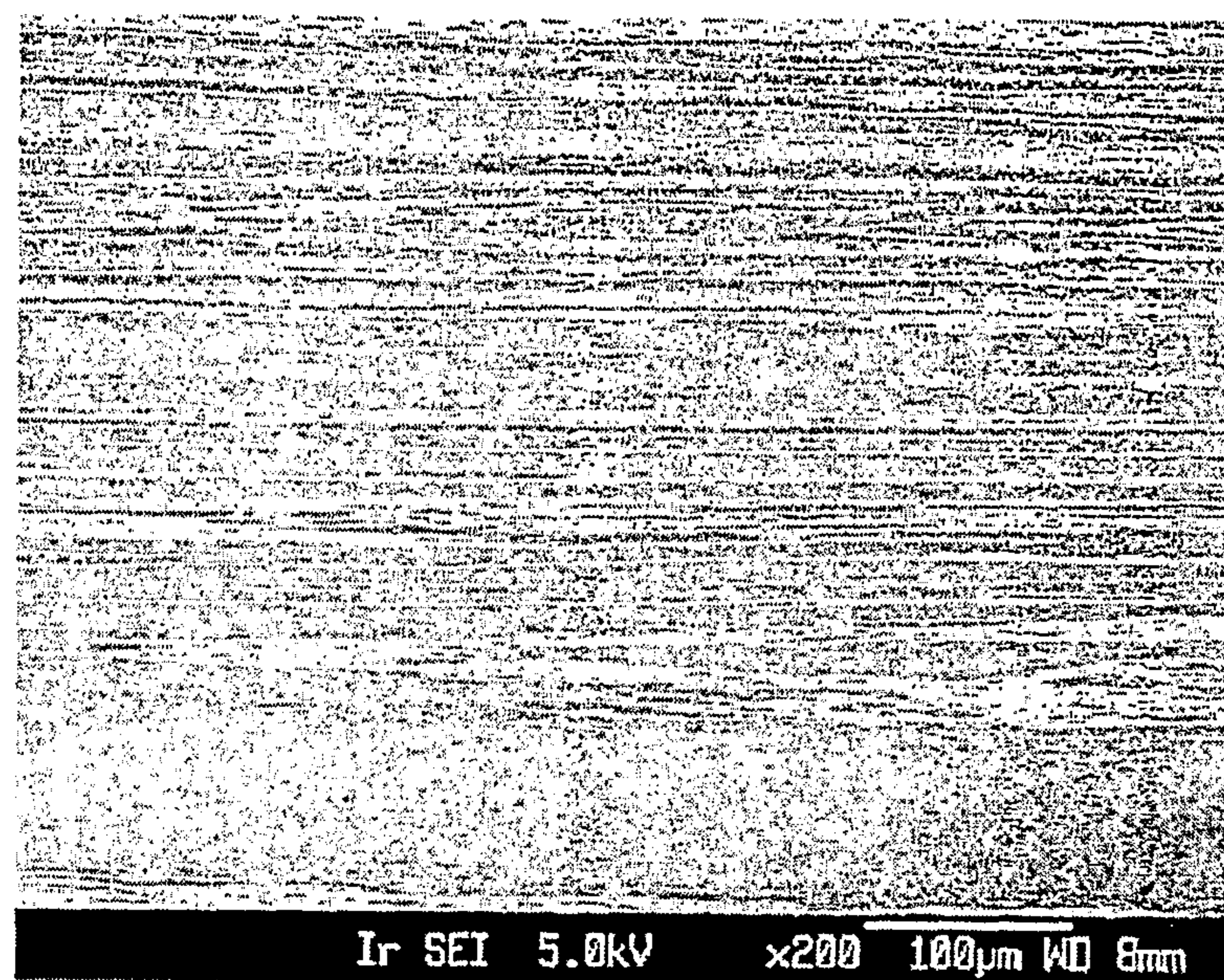


FIG. 4B

