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(54) Title: OXYGEN BARRIER COATING COMPOSITION

(57) Abstract: Good bond strength and shelf life in a composition for preparing a gas barrier coating comprising an aqueous dispersion of a clay and a polyvinyl alcohol and/or an ethylene vinyl alcohol copolymer are achieved by including in the composition a poly (ethyleneimine).



WO 2009/098463 A1

OXYGEN BARRIER COATING COMPOSITION

The present invention relates to gas barrier coatings, particularly having the
5 ability to block the passage of oxygen, and which may be used to coat and impart gas
barrier properties to a variety of materials, notably packaging for foods and
pharmaceuticals, where exposure to oxygen needs to be eliminated or restricted.

Synthetic plastics materials have long been used for the packaging of foods and
other materials which need protection from handling and from moisture. However, in
10 recent years, it has become appreciated that, in addition, many foods and other sensitive
materials benefit from being protected from atmospheric oxygen. A wide variety of
multilayer laminate structures has been developed to provide barrier properties and
other performance characteristics suited to a pack's purpose. These laminates may be
any combination of plastic, metal or cellulosic substrates, and may include one or more
15 coating or adhesive layers. Laminates which include polymeric films having metals or
inorganic compounds, such as silicon oxides, deposited thereon have been found to give
good general barrier properties and are widely used. However, they may lose their
ability to prevent the ingress of oxygen altogether at high temperatures, for example
when the packaged material is retorted in order to sterilise and/or cook it. Moreover,
20 the inorganic layer of these types of laminate is rather brittle and may crack or break
when the laminate is flexed, resulting in a loss of the gas barrier properties.

More recently, gas barrier coatings comprising dispersed clay, especially
nanoparticles, and a hydrophilic polymer, such as polyvinyl alcohol (PVA) or ethylene-
vinyl alcohol copolymer (EVOH), have been used, as described, for example, in US
25 6 599 622 or EP 0 590 263. Where these are used as a surface coating, as is described
in this prior art, there are no problems. However, we have found that, for many
purposes, it is desirable that the coating should have a covering as well as a substrate,
and, if the gas barrier coating is to be sandwiched between two films of a laminate in
this way, then the bond strength between the films and the coating becomes an issue.

We have surprisingly found that, if a mixture of the clay and the polymer used for the gas barrier coating is prepared and left for a period of time, which can be as low as 24 hours, and if it is then used sandwiched between two or more films forming part of an adhesively formed laminate, the bond strength will have deteriorated alarmingly
5 as compared with the same assembly in which the gas barrier coating mixture has been freshly prepared. There is no obvious explanation for this behaviour and we have no explanation for it, but it is a significant finding with significant commercial consequences.

Coating compositions of this type are commonly prepared by a manufacturer in
10 an appropriate liquid solvent or dispersant and sold as such to the user, who will then coat the appropriate packaging material as required. It is evident that, in the normal course of events, such a pre-prepared coating composition will have been kept for considerably more than 24 hours before it is used. Accordingly, for any applications where any degree of bond strength is important, the resulting coating material will be
15 useless.

Subsequently, as disclosed in UK Patent Application No. 0716580.6, filed 24 August 2007, we found that, in order to maintain adequate bond strength of a composite in which a gas barrier coating is positioned between two flexible plastics films using an adhesive, it is necessary that the clay dispersion and the polymer solution or dispersion
20 should be kept separate until shortly before they are to be applied, and we have described a two pack composition, one pack comprising a solution or dispersion of a PVA and/or EVOH, and the other comprising an aqueous dispersion of a clay.

These coatings, although delivering excellent oxygen barrier, required that the PVA/EVOH solution and the clay dispersion be blended shortly before application in
25 instances where the coated films would subsequently be formed into adhesively formed laminates. The reason for this was that the bond strengths decreased as the blended coating was allowed to stand. This was an important finding in its own right as it demonstrated an innate problem with this type of coating in terms of practical handling. Clearly, for ease of use, a 1-pack formulation would be preferable. Furthermore, the 2-
30 pack compositions did not adhere well to a wide range of substrates, particularly

poly(propylene) and poly(ethylene) films. This has necessitated the use of a primer applied to such films prior to coating the 2-pack composition and subsequent lamination.

It is well known that primers can be applied to plastic films prior to depositing an oxygen barrier coating based on PVA/EVOH. Examples of these include
5 US6106950 (H.B. Fuller) and EP 254468 (DuPont), where polyurethane primers are described. The use of PEI (poly(ethyleneimine)) as a primer coating for oxygen barrier coatings has also been described, for example in EP 461772 A3 (Mobil Oil Co.). WO
98/34982 (Mobil Oil) also describes a primer based on PVA and PEI; this provided the
10 required adhesion and a degree of oxygen barrier. However, to achieve high oxygen barrier, coatings based solely on PVA/EVOH are insufficient.

EP 761739 A1 discloses a gas barrier resin composition which is a combination of resin and an aggregated inorganic layer compound which may be a clay mineral. The average particle size of the inorganic layer compound after being aggregated (i.e., after
15 having its size increased) is greater than 1 μm or else the gas barrier properties of the composition is unsatisfactory. Aggregation to increase the average particle size up to 5 times can be effected by use of a coagulant which is soluble in a dispersion medium the resin composition may contain and can be a water-soluble high molecular weight substance or an electrolyte. Water soluble polyamides and polysaccharides are
20 preferred but PEI can also be used.

We have now surprisingly found that the incorporation of a poly(ethyleneimine) into the coating composition allows the disadvantages of our two-part coating method to be overcome.

Thus, the present invention consists in a composition for preparing a gas barrier
25 coating, said composition comprising an aqueous dispersion of a clay, a PVA and/or EVOH and a poly(ethyleneimine).

In a further aspect, the invention provides a gas barrier film comprising a flexible polymer film coated with a coating comprising a clay, a PVA and/or EVOH and a poly(ethyleneimine).

5 In a still further aspect, the present invention provides a gas barrier film comprising: a first flexible polymer film having a gas barrier coating comprising a clay, a PVA and/or EVOH and a poly(ethyleneimine); and a second flexible polymer film adhered to the first flexible polymer film, such that the coating is between the first and the second polymer films.

10 In yet a further aspect, the present invention consists in a process for preparing a gas barrier film, comprising:

1. coating a first flexible polymer film with an aqueous dispersion of a clay, a PVA and/or EVOH and a poly(ethyleneimine);
2. allowing the coating to dry;
3. applying an adhesive coating to either or both of the coated side of the first film or to
15 a second flexible polymer film; and
4. adhering the first and second films together.

The bond strength between the two films is preferably at least 1.0N/15mm, more preferably at least 1.5N/15mm, after full cure of the adhesive has been achieved.

20 The time taken for the adhesive to cure fully will vary depending on the nature of the adhesive and will be well known to those skilled in the field. For example, it can take up to 10 days at room temperature with conventional isocyanate-based adhesives, and up to 10 days at 50°C with aliphatic isocyanate 2-pack types.

25 Where the adhesive is applied to the second film only, steps 1 and 3 may be carried out in any order. Step 2 is, in any event, carried out after Step 1, and Step 4 is carried out after steps 1, 2 and 3.

There is no particular restriction on the nature of the PVA or EVOH used in the present invention, provided that it can form a solution or dispersion in an aqueous medium. Such polymers have a high proportion of free hydroxy groups which can form hydrogen bonds with salt groups in the metal silicate and thus serve as a dispersing agent for the silicate. Examples of such polymers are described in, for example, 5 US 6 599 622 or EP00590263B1, the disclosure of which is incorporated herein by reference.

The clay used is preferably nanoparticulate, that is having an average particle size less than 1 μm , although somewhat larger particles of up to 10 μm can also be 10 employed. Also preferably a portion of the clay mineral has been intercalated or exfoliated during the dispersion process. The clay is not an aggregated material, and in fact when intercalated and/or exfoliated, the particle size is reduced relative to that of the neat clay. There is no restriction on the type of clay used in this invention provided that it is sufficiently dispersible in an aqueous medium and that it is capable of being 15 intercalated or exfoliated during dispersion. In an exfoliated form the aspect ratio of the clay (i.e. the ratio between the length and thickness of a single clay 'sheet') will have an impact on the level of oxygen barrier achieved. The greater the aspect ratio, the more the rate of oxygen diffusion through the dry coating and laminate will be reduced. Clay minerals with aspect ratios between 20 and 10,000 are preferably used. Particularly 20 preferred are those minerals having an aspect ratio greater than 100. Examples of suitable clays include kaolinite, montmorillonite, atapulgite, illite, bentonite, halloysite, kaolin, mica, diatomaceous earth and fuller's earth, calcined aluminium silicate, hydrated aluminium silicate, magnesium aluminium silicate, sodium silicate and magnesium silicate. Commercial examples of suitable materials are Cloisite Na+ 25 (available from Southern Clay), Bentone ND (available from Elementis). Of these, the clays are preferred, nanoparticulate clays being most preferred.

The coating composition is applied in the form of a solution or dispersion of the clay, the polymer and the poly(ethyleneimine) in a suitable solvent. The solvent is preferably aqueous, and is more preferably water, optionally containing a small quantity 30 of a miscible co-solvent, such as an alcohol (for example ethanol, n-propanol or

isopropanol) or a ketone (such as acetone). Where a co-solvent is present, this can be up to 75% (w/w) of the total composition. However, it is preferred that the content of the co-solvent is less than 50%, more preferably less than 50% of the entire composition. The preferred co-solvent is an alcohol, preferably ethanol or isopropanol.

5 If desired, in addition to the PVA and/or EVOH, other polymers or resins may be included in the coating composition, provided that these co-resins are themselves compatible in the final composition. Examples of such polymers and resins include solution acrylics, acrylic emulsions, polyesters, alkyds, sulphopolyesters, polyurethanes, vinyl acetate emulsions, poly(vinyl butyral), poly(vinyl pyrrolidone), poly(ethylene
10 imine), polyamides, polysaccharides, proteins, epoxies, etc. It is also possible to include sol-gel precursors in these compositions, e.g. a hydrolysate of tetraethyl orthosilicate.

 Also, additives, such as biocides, fungicides, surfactants, wetting aids, and others well known to those versed in the art, may be included, provided that they do not
15 adversely affect the oxygen barrier, adhesion and laminate bond strength properties of the coating, or adversely affect these properties to an unacceptable extent.

 The amount of polymer (total of PVA, EVOH and optional polymers and resins) in the coating composition is preferably from 40 to 95% of the total solids comprising polymer and clay, and more preferably from 50 to 90%. In other words, the ratio of
20 clay to polymer is preferably from 1.5:1 to 1:19, more preferably from 1:1 to 1:9. The concentration of clay and polymer in the solution will depend on their solubility/dispersability and the way in which the coating will be applied (gravure, flexo, curtain coating, roll coating, dip coating, spray, etc.), the amount of solvent employed preferably being the minimum needed to achieve sufficient flowability to coat
25 the substrate adequately. In general, the clay will be employed in the form of a 1.0-15% by weight solution/dispersion in water or water+co-solvent (prior to its addition to the PVA/EVOH containing component), and this will dictate the contents of the remaining components.

In accordance with the present invention, the composition includes poly(ethyleneimine). In general, it is preferred that there should be sufficient poly(ethyleneimine) present to ensure that the composition has a printable viscosity, although the viscosity of the composition is also affected by the other components, as is well known in the art. The amount of poly(ethyleneimine) in the composition is not sufficient to cause aggregation of the clay and thereby cause the average particle size to increase. It is preferably from 0.05 to 5.0% (w/w) (of the total coating composition), more preferably from 0.2 to 2.5% and most preferably from 0.25 to 1.0%. We also prefer that the ratio of poly(ethyleneimine) to clay should be in the range from 0.1 to 2.0 (on a weight-for-weight basis), more preferably from 0.2 to 1.5, most preferably from 0.25 to 1.0. Poly(ethyleneimine)s are available commercially from a large number of suppliers, for example, BASF, under the trade names Lupasol WF, Lutensol and Polymin, Epomin (Nippon Shokubai), Dow PEI-18 (Dow Chemical Co.).

The overall solids content of the coating is preferably from 0.5 to 15%; more preferably from 2 to 8% (w/w), which is relatively low, in order to delay or prevent the premature onset of gelation of the coating, which results from the build up of structure held in place by weak electrostatic charges.. The overall solids content of the coating will be determined by the viscosity requirement and also the content of the nanoclay, which can increase viscosity due to the electrostatic interparticle interactions. The coatings may be applied by known methods; for example gravure, flexographic coating, roll coating, dip coating, etc.

The coating composition of the present invention comprising the clay, the polymer, the poly(ethyleneimine) and a solvent or dispersant therefor may be applied to a substrate by any conventional means. The solvent or dispersant may then be removed, e.g. by heating, leaving a film comprising the clay dispersed through the polymer on the substrate. The resulting gas barrier film is then preferably adhered to a further flexible plastics sheet.

The thickness of the coating of the present invention will depend in part on the ability of the clay to form a continuous, coherent coating layer. However, in general,

we prefer that the coating should be from 50 nm to 3000 nm thick, more preferably from 200 to 2000 nm thick.

There is no particular restriction on the nature of the flexible substrate, although it is preferably a plastics film, and any material suitable for the intended use may be employed. However, where the matter being packaged with the coating film of the present invention is a foodstuff or pharmaceutical, it will normally be preferred that the plastics film or other substrate should be food grade. Examples of suitable materials include: polyolefins, such as polyethylene or polypropylene; polyesters, such as polyethylene terephthalate, polybutylene terephthalate or polyethylene naphthenate; polyamides, such as nylon-6 or nylon-66; and other polymers, such as polyvinyl chloride, polyimides, acrylic polymers, polystyrenes, celluloses, or polyvinylidene chloride,. It is also possible to use copolymers of any compatible two or more of the monomers used to produce these polymers. Furthermore, compositions of the present invention may be included in adhesively formed laminates comprising paper substrates (such as polyester and polyolefin coated paperboards commonly encountered in food packaging).

The two flexible polymer films may be the same as each other or they may be different from each other.

There is no particular restriction on the nature of the adhesive used, and any adhesive commonly used for the adhesion of two or more plastics films may be employed in the present invention. Examples of suitable adhesives include solvent-based (polyurethane) types such as those from Henkel (Liofol UR3969/UR 6055, Liofol UR3640/UR6800, Liofol UR3894/UR6055), Rohm&Haas (Adcote 811/9L10) and Coim (CA2525/2526), Solvent-free polyurethane adhesives such as Liofol 7780/UR6082, UR7750/UR6071 from Henkel, and Mor-Free ELM-415A/Mor-Free CR140 from Rohm&Haas, can also be used. As well as polyurethane adhesives, epoxy-based types such as Lamal 408-40A/C5083 may be used. Waterborne adhesives, such as Aqualam 300A/300D, an epoxy type from Rohm&Haas may also be used.

The adhesive may be applied directly to one of the films and then adhered to the gas barrier coating on the other film, or it may be applied to the gas barrier coating on one film and then adhered to the other film. In any case, the order of layers will be: a plastics film; the gas barrier coating; an adhesive; and another plastics film. If desired, 5 layers of other materials may be interposed between any two of these layers, or on either side of the 2 flexible plastic substrates having the barrier coating between them.

The invention still further provides a packaged foodstuff, pharmaceutical or other material sensitive to oxygen, wherein the packaging comprises a gas barrier material of the present invention.

10 The invention is further illustrated by the following non-limiting Examples.

EXAMPLES

The oxygen transmission rates of the coated samples in the following Examples were determined on a Mocon Oxtran 2/21 gas permeability tester at 23°C and 50% relative humidity. The substrates, which were corona discharge treated prior to 15 application of the coatings, were 25µm OPP (oriented polypropylene - MB400), 12µm PET (polyethylene terephthalate - Mylar 800), 25µm PLA (polylactic acid - Treofan PLA121), 23µm cellulose acetate (Natureflex) and a 20µm starch-based film (Mater-Bi.). The coatings were applied with a No.2 K-bar and were dried in a warm flow of air (laboratory prints were dried with a hair dryer).

20 The coatings were prepared by blending an 8% aqueous solution of PVA (a 80/20 blend of Exceval AQ-4104 and Mowiol 3-96) containing 10% (w/w) of isopropanol, a 3% aqueous dispersion of montmorillonite clay (Cloisite Na) which contained 30% (w/w) of isopropanol, and a 10% solution of PEI [poly(ethyleneimine) - Lupasol WF] in IPA (isopropanol), according to Table 1. As well as the compositional 25 data, Table 1 also records the viscosities of these coatings. A Zahn-2 flow cup was used for these measurements and the viscosity is noted as the time required for the coating to flow out of the cup. For a gravure applied coating, a viscosity of 18-23seconds is normal.

Adhesion was assessed by the well known tape test; whereby adhesive tape is applied to the coated surface and removed rapidly. The quality of adhesion is determined by the amount of coating remaining, 100% being full adhesion and 0% no adhesion. The adhesion results, as well as the oxygen transmission rates on various substrates are provided in Table 2.

Laminates were prepared by applying an adhesive over the top of the dried coating and then laminating this to a further plastic film. The adhesive used in these experiments was Morchem 614A/614C, a 2-pack polyurethane type, made according to the manufacturer's instructions. The laminates were allowed to cure fully before the laminate bond strengths were determined. The bond strengths are reported as the force required to separate the webs (in N/15mm). Where the bonds were sufficiently strong to cause film tear the results were then reported as FT (Film Tear) with the maximum bond strength recorded before rupture. Table 3 reports the laminate structures and the bond strengths. It should be noted that any suitable laminating adhesive could be used, including biodegradable types derived from sustainable sources such as those supplied by Sustainable Adhesive Products company.

Table 1: Description of Examples and Coating Viscosities

Example	IPA (g)	Deionised Water (g)	PVA Solution (g)	Clay Dispersion (g)	PEI Solution (g)	Viscosity (s)
Comparative Example 1	3.0	14.5	20.7	-	1.85	18
Comparative Example 2	3.0	14.5	20.7	-	2.7	18
Comparative Example 3	2.0	6.75	15.0	15.0	-	21
Example 1	2.0	6.75	15.0	15.0	0.75	>60 (unprintable)
Example 2	2.0	6.75	15.0	15.0	1.0	>60 (unprintable)
Example 3	2.0	6.75	15.0	15.0	1.25	28
Example 4	2.0	6.75	15.0	15.0	1.60	23
Example 5	2.0	6.75	15.0	15.0	1.90	20
Example 6	2.0	6.75	15.0	15.0	2.3	19
Example 7	2.0	6.75	15.0	15.0	2.7	19
Example 8	2.0	6.75	15.0	15.0	3.8	19
Example 9	2.0	11	15.0	8.0g Microlite 963	3.0	19

Note: Microlite 963 is an aqueous dispersion of vermiculite, supplied by W.R.Grace

Table 2: Adhesion and Oxygen Transmission Rates

Example	Film	Adhesion (%)	Oxygen Transmission Rate (cm³/m²/day)
Comparative Example 1	cdt MB400 (OPP)	100	8.28
Comparative Example 2	cdt MB400 (OPP)	100	61.8
Comparative Example 3	cdt MB400 (OPP)	0	1.45
Example 3	cdt MB400 (OPP)	100	1.93
Example 4	cdt MB400 (OPP)	100	3.63
Example 5	cdt MB400 (OPP)	100	1.17
Example 5	cdt Mylar 800	100	0.33
Example 5	cdt PLA	100	0.19
Example 5	cdt Natureflex	100	0.45
Example 5	cdt Materbi	100	4.61
Example 6	cdt MB400 (OPP)	100	0.81
Example 7	cdt MB400 (OPP)	100	1.64
Example 8	cdt MB400 (OPP)	100	6.00
Example 9	cdt MB400 (OPP)	100	0.14
No Coating	cdt MB400 (OPP)	-	>1000
No Coating	cdt Mylar 800	-	100-110
No Coating	cdt PLA	-	500-550
No Coating	cdt Natureflex	-	12.54
No Coating	cdt Materbi	-	>1000

Table 3: Laminate Structures and Bond Strengths

Base Film	Coating	Laminating Film	Bond Strength (N/15mm)
cdt MB400 (OPP)	Comparative Example 1	20µm cast poly(propylene); 'CPP'	FT; M=2.9
cdt MB400 (OPP)	Comparative Example 3	CPP	<0.2
cdt MB400 (OPP)	Example 3	CPP	1.7
cdt MB400 (OPP)	Example 4	CPP	2.8
cdt MB400 (OPP)	Example 5	CPP	FT; M=3.7
cdt MB400 (OPP)	Example 6	CPP	FT; M=3.3
cdt MB400 (OPP)	Example 7	CPP	FT; M=3.8
cdt MB400 (OPP)	Example 8	CPP	FT; M=3.4
cdt MB400 (OPP)	Example 9	CPP	1.1
cdt MB400 (OPP)	Examples 9+5	CPP	1.2
cdt Mylar 800	Example 7	20µm PE	FT; M=3.4
cdt Natureflex	Example 7	PE	2.8
cdt Materbi	Example 7	Natureflex	1.3

Note: Where the bond strength was sufficient to cause film tear of the film this is recorded as 'FT' along with the maximum bond strength prior to film tear.

5

EXAMPLE 10

A coating prepared according to Example 3 was allowed to stand for 2 months before being applied to a primed OPP film (the primer being based on a solution of

PVA and PEI), before being laminated to the CPP film. An oxygen transmission rate of 0.34 was recorded for this laminate and the MB400 tore during the bond strength test.

COMPARATIVE EXAMPLE 4

The coating described in Comparative Example 3 was applied to the primed
5 MB400 film as described in example 10, and then laminated. With no ageing of the coating the MB400 web tore during the bond strength test. However, after allowing the coating to stand for 1 week the resulting bond strength of the laminate had fallen to 0.5N/15mm.

CLAIMS:

1. A composition for preparing a gas barrier coating, said composition comprising an aqueous dispersion of a clay, polymer which is a polyvinyl alcohol and/or an ethylene vinyl alcohol copolymer, and a poly(ethyleneimine).
2. A composition according to Claim 1, in which some or all of the clay has been intercalated or exfoliated during dispersion.
3. A composition according to Claim 1 or Claim 2, in which the clay has an aspect ratio from 20 to 10,000.
4. A composition according to any one of the preceding Claims, in which the amount of polymer is from 40 to 95% of the total solids comprising polymer and clay.
5. A composition according to any one of the preceding Claims, in which the amount of polymer is from 50 to 90% of the total solids comprising polymer and clay.
6. A composition according to any one of the preceding Claims, in which the amount of poly(ethyleneimine) in the composition is from 0.05 to 5.0% w/w of the total coating composition.
7. A composition according to Claim 6, in which the amount of poly(ethyleneimine) in the composition is from 0.2 to 2.5%.
8. A composition according to Claim 7, in which the amount of poly(ethyleneimine) in the composition is from 0.25 to 1.0%.
9. A composition according to any one of the preceding Claims, in which the ratio of poly(ethyleneimine) to clay is from 0.1:1 to 2.0:1 on a weight-for-weight basis.
10. A composition according to Claim 9, in which the ratio of poly(ethyleneimine) to clay is from 0.2:1 to 1.5:1, preferably from 0.25:1 to 1.0:1.
11. A composition according to any one of the preceding Claims, in which the clay has an average particle size of less than 1 μm .

12. A gas barrier film comprising a flexible polymer film coated with a coating comprising a clay, a polyvinyl alcohol and/or an ethylene vinyl alcohol copolymer and a poly(ethyleneimine).

13. A gas barrier film comprising: a first flexible polymer film having a gas barrier coating comprising a clay, polymer which is a polyvinyl alcohol and/or an ethylene vinyl alcohol copolymer, and a poly(ethyleneimine); and a second flexible polymer film adhered to the first flexible polymer film, such that the gas barrier coating is between the first and the second polymer films.

14. A film according to Claim 12 or Claim 13, in which some or all of the clay has been intercalated or exfoliated during dispersion.

15. A film according to any one of Claims 12 to 14, in which the clay has an aspect ratio from 20 to 10,000.

16. A film according to any one of Claims 12 to 15, in which the amount of polymer is from 40 to 95% of the total solids comprising polymer and clay.

17. A film according to any one of Claims 12 to 16, in which the amount of polymer is from 50 to 90% of the total solids comprising polymer and clay.

18. A film according to any one of Claims 12 to 17, in which the amount of poly(ethyleneimine) is from 0.05 to 5.0% w/w of the total gas barrier coating.

19. A film according to Claim 18, in which the amount of poly(ethyleneimine) in the gas barrier coating is from 0.2 to 2.5%.

20. A film according to Claim 19, in which the amount of poly(ethyleneimine) in the gas barrier coating is from 0.25 to 1.0%.

21. A film according to any one of Claims 12 to 20, in which the ratio of poly(ethyleneimine) to clay is from 0.1:1 to 2.0:1 on a weight-for-weight basis.

22. A film according to Claim 21, in which the ratio of poly(ethyleneimine) to clay is from 0.2:1 to 1.5:1, preferably from 0.25:1 to 1.0:1.

23. A film according to any one of Claims 12 to 22, in which the thickness of the coating is from 50 nm to 3000 nm.

24. A film according to Claim 23, in which the thickness of the coating is from 200 to 2000 nm.

25. A film according to any one of Claims 13 to 24, further comprising an adhesive.

26. A process for preparing a gas barrier film, comprising:

a. coating a first flexible polymer film with an aqueous dispersion of a clay, polymer which is a polyvinyl alcohol and/or an ethylene vinyl alcohol copolymer, and a poly(ethyleneimine);

b. allowing the coating to dry;

c. applying an adhesive coating to either or both of the coated side of the first film or to a second flexible polymer film; and

d. adhering the first and second films together.

27. A process according to Claim 26, in which some or all of the clay has been intercalated or exfoliated during dispersion.

28. A process according to Claim 26 or Claim 26, in which the clay has an aspect ratio from 20 to 10,000.

29. A process according to any one of Claims 26 to 28, in which the amount of polymer is from 40 to 95% of the total solids comprising polymer and clay.

30. A process according to any one of Claims 26 to 29, in which the amount of polymer is from 50 to 90% of the total solids comprising polymer and clay.

31. A process according to any one of Claims 26 to 30, in which the amount of poly(ethyleneimine) is from 0.05 to 5.0% w/w of the dispersion.

32. A process according to Claim 31, in which the amount of poly(ethyleneimine) in the dispersion is from 0.2 to 2.5%.
33. A process according to Claim 32, in which the amount of poly(ethyleneimine) in the dispersion is from 0.25 to 1.0%.
34. A process according to any one of Claims 26 to 33, in which the ratio of poly(ethyleneimine) to clay is from 0.1:1 to 2.0:1 on a weight-for-weight basis.
35. A process according to Claim 34, in which the ratio of poly(ethyleneimine) to clay is from 0.2:1 to 1.5:1, preferably from 0.25:1 to 1.0:1.
36. A process according to any one of Claims 26 to 35, in which the thickness of the coating is from 50 nm to 3000 nm.
37. A process according to Claim 36, in which the thickness of the coating is from 200 to 2000 nm.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2009/000325

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08L27/04 C08J5/18 C08J7/04 C08L29/04 C09D129/04
 ADD. C08K3/34 C08L79/02

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)

C09D C08L C08J C09J

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, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BE 699 763 A (UNION CHEMIQUE-CHEMISCHE BEDRIJVEN S.A.) 12 December 1967 (1967-12-12) claims; examples	1-37
X	----- DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LIU, JIANLIN: "Process for producing modified poly(vinyl alcohol) coating solution" XP002525786 retrieved from STN Database accession no. 145:439974 abstract -& CN 1 847 334 A (PEOP. REP. CHINA) 18 October 2006 (2006-10-18) ----- -/--	1-37

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 April 2009	12/05/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Enrique de Los Arcos

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2009/000325

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 03/062321 A (SECR DEFENCE [GB]; BREWER STUART ANSON [GB]; STONE CORINNE AMY [GB]; W) 31 July 2003 (2003-07-31) claims; examples -----	1-37

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2009/000325

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CN 1847334	A	18-10-2006	NONE	
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WO 03062321	A	31-07-2003	AT 410482 T BR 0306936 A CA 2473035 A1 CN 1643062 A EP 1465953 A1 ES 2311687 T3 JP 2005515288 T MX PA04006817 A NZ 534161 A US 2004166350 A1	15-10-2008 09-11-2004 31-07-2003 20-07-2005 13-10-2004 16-02-2009 26-05-2005 19-04-2005 31-03-2006 26-08-2004