

A Coating

References to Related Applications

- 5 This application claims priority to Singapore application number 10202102155P filed with the Intellectual Property Office of Singapore on 3 March 2021, the disclosure of which is hereby incorporated by reference.

Technical Field

- 10 The present invention generally relates to a coating. The present invention also relates to a composite coating emulsion and a method of preparing the same. The present invention further relates to a coated article comprising the coating as described herein and a method of preparing the same.

Background Art

- 15 Food requires a packaging with barrier properties (for example, against oxygen and/or moisture) to extend its shelf life. Plastics are heavily used in food packaging owing to their favorable features of processability, light weight, printability and high transparency. However, the increasing use of plastic packaging leads to plastic pollution since around 40% of all plastic produced is used for packaging. This drives the development of safer and more sustainable packaging solutions. Replacing plastic packaging with recyclable and compostable paper packaging may provide a solution to plastic pollution. However, paper has poor barrier properties, especially against moisture.

- 20 Conventionally, the barrier properties of paper are improved by applying a layer (or more commonly multiple layers wherein each layer performs different functions) of plastics and/or foils onto the paper substrate using lamination or extrusion techniques. Nevertheless, it is difficult (and often impossible) to recycle laminated paper packaging materials. In addition, the barrier properties of paper against moisture is still poor without a significant increase in the paper's thickness.

- 30 Polyvinylidene chloride and its copolymers, often referred to as PVDC, are conventionally used in food packaging for their excellent barrier properties against water vapor, gases (notably oxygen) and aroma. The low permeability of the material arises from a high degree of crystallinity and a high packing density of the PVDC chains. Crystalline domains are considered as physical obstacles to diffusive molecules; a good packing of polymer chains, due to the high symmetric nature of vinylidene chloride units, creates very low free volumes in the amorphous domains also making the material less permeable to diffusive molecules. However, PVDC generally has an oxygen transmission rate of about 5 cc/(m².day) and a water vapor transmission rate of about 5 g/(m².day). Such barrier properties cannot satisfy the

crucial need for packing foods, especially those that are highly sensitive to water vapor or oxygen.

5 A conventional method for preparing food packaging with high barrier properties requires making polymer composites comprising a polymer matrix with inorganic fillers dispersed inside, which have better mechanical, thermal and barrier properties than a polymer composite without the inorganic fillers. Inorganic fillers (such as silicate platelets) are incorporated because of their high specific surface area, availability, low cost, significant reinforcing effects and simple processability. A conventional method of preparing such food packaging requires physically blending
10 silicate with melted PVDC. However, this method rarely exfoliates the plate-like silicate fillers properly in the polymer matrix and is not suitable for barrier enhancement.

Another conventional method for preparing such food packaging requires a waterborne process for better dispersion of silicate in PVDC, either by blending the
15 silicate with preformed PVDC latexes or by performing in-situ aqueous suspension or emulsion polymerization in the presence of silicate. However, the moisture barrier performance of the silicate/PVDC is still unsatisfactory due to the hydrophilic nature of the silicate filler.

Further, conventional silicate/PVDC composites have only been applied onto
20 plastics. It remains challenging as to how to develop a PVDC composite coating that is applicable to a paper substrate while achieving satisfactory barrier properties for food packaging. It is also known that the coating should not interfere with paper recycling, but it remains challenging as to how to reduce the amount of coating needed (with respect to the paper substrate) to achieve satisfactory barrier properties.

25 Accordingly, there is a need for a method of making a coating that ameliorates one or more disadvantages mentioned above.

Summary

In one aspect, there is provided a coating comprising an acidified, silane modified silicate material bound to a polymer matrix having at least one acidic group and at least one
30 halogen group.

Advantageously, the coating may be applied on recyclable materials to address the issue of plastic pollution. This is due to the silicate group being acidified to replace Na⁺ cations with proton, leading to a decrease in its moisture sensitivity and an increase in its hydrophobicity. The hydrophobicity of the coating may result in higher
35 water resistance and higher performance as a moisture barrier at low thickness. The silane may further enhance the bound structure of the modified silicate and the polymer matrix. The bound structure of the modified silicate and the polymer matrix may further result in higher performance as a gas barrier or a moisture barrier at lower thickness.

Further advantageously, the coating may exhibit higher stability against dehydrohalogenation. This is due to the silicate material being acidified to replace Na⁺ cations with proton, leading to a decrease in its pH. The silicate material with decreased pH has higher compatibility with the polymer matrix having at least one acidic group and at least one halogen group.

Still further advantageously, the coating may exhibit higher stability in prolonged use. This is due to the silicate material being surface modified with a silane. Where the silane is a combination of an amino-silane and a halogen-containing silane, the silane modified silicate material may comprise amino groups and halogen groups. The amino groups on a surface of the silicate material may bind to acidic groups in the polymer matrix by amine-acid coupling. The halogen groups on the surface of the silicate material may be compatible to the halogen groups in the polymer matrix for high miscibility between the modified silicate material and the polymer matrix.

In another aspect, there is provided a composite coating emulsion comprising an acidified, silane modified silicate material and a polymer matrix having at least one acidic group and at least one halogen group dispersed in a solvent.

Advantageously, the composite coating emulsion may be used for coating a desired substrate to impart high barrier performances to the substrate. This is due to the hydrophobicity and stability of the materials in the composite coating emulsion.

In another aspect, there is provided a coated article comprising the coating as defined herein, an optional primer coating and a substrate.

Advantageously, the coated article may have higher barrier properties against transmission of moisture and oxygen. This is due to the high hydrophobicity of the modified silicate and the bound structure between the modified silicate and the polymer matrix.

Further advantageously, the coated article may be highly recyclable in use for packaging. This is due to the lower thickness and weight percentage of the coating needed to have high barrier properties against moisture and oxygen transmission.

In another aspect, there is provided a method of preparing a composite coating emulsion comprising the step of mixing an acidified, silane modified silicate material, and a polymer matrix having at least one acidic group and at least one halogen group in a solvent.

Advantageously, the acidified, silane modified silicate material may have a high interfacial bonding and compatibility with the polymer matrix having at least one acidic group and at least one halogen group. When this is formed as a coating, the coating may be used as an effective barrier to ambient oxygen and moisture.

In another aspect, there is provided a method of preparing a coated article comprising the step of applying the composite coating as defined herein on a substrate.

Definitions

The following words and terms used herein shall have the meaning indicated:

5 The term “polyvinylidene chloride” or “PVDC” as used herein refers to a polymer matrix comprising a copolymer of vinylidene chloride repeating units and acid-containing repeating units. Therefore, the copolymer may have a portion of vinylidene chloride repeating units. The acid-containing repeating units may comprise acidic groups such as carboxylic acid, sulfonate, phosphate, and the like. The term “polyvinylidene chloride latex” or “PVDC latex” then refers to a composition of the copolymer of vinylidene chloride repeating units and acid-containing repeating units as defined above in an aqueous medium or solvent, where the copolymer of vinylidene chloride repeating units and acid-containing repeating units may be a product of emulsion polymerization. Additionally, the copolymer may be in the form of micelles.

15 The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

20 Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

The term "about" as used herein typically means +/- 5 % of the stated value, more typically +/- 4 % of the stated value, more typically +/- 3 % of the stated value, more typically, +/- 2 % of the stated value, even more typically +/- 1 % of the stated value, and even more typically +/- 0.5 % of the stated value.

25 Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

35 Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from

the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a coating will now be disclosed.

- 5 The coating may comprise an acidified, silane modified silicate material bound to a polymer matrix having at least one acidic group and at least one halogen group.

The acidified, silane modified silicate material may be silane modified by an amino-silane, a halogen-containing silane or a combination thereof. Where the silicate material is silane modified by a combination of an amino-silane and a halogen-
10 containing silane, the silane modified silicate material may then comprise amino groups and halogen groups. The amino groups on a surface of the silicate material may bind to acidic groups in the polymer matrix by amine-acid coupling. The halogen groups on the surface of the silicate material may be compatible to the halogen groups in the polymer matrix for high miscibility between the modified silicate material and
15 the polymer matrix.

The silicate material may have more Si-OH groups as a result of being acidified. The Si-OH groups may react with the silane when being silane modified. The silicate material may thus have an enhanced bonding with the polymer matrix as a result of being silane modified. When the coating is applied to a substrate, the enhanced
20 bonding may lead to an alignment of the silicate material along the substrate. The enhanced bonding may also generate highly efficient tortuous paths against oxygen molecules and moisture when the coating is applied as an oxygen or moisture barrier.

The acidified silicate material may be uniformly conjugated to amino groups (where present) and halogen groups (where present) when being silane modified.

- 25 Therefore, the acidified, silane modified silicate material may have a uniform distribution of Si-OH groups, amino groups (where present) and halogen groups (where present) as a result of being acidified and silane modified.

The silicate material may be a mineral selected from serpentine, clay, mica. Non-limiting examples of the silicate material include antigorite, chrysotile, lizardite,
30 halloysite, kaolinite, illite, montmorillonite, vermiculite, talc, sepiolite, palygorskite, pyrophyllite, biotite, fuchsite, muscovite, phlogopite, lepidolite, margarite, glauconite, bentonite or combinations thereof. The silicate material may be a clay.

The polymer matrix may comprise a copolymer of halogen-containing repeating units, acidic-containing repeating units, and optionally hydrocarbon repeating units.

- 35 The halogen-containing repeating units may be formed by polymerisation of halogen-containing monomers. Non-limiting examples of the halogen-containing monomers include vinyl fluoride, vinylidene fluoride, vinyl chloride, vinylidene chloride, vinyl

bromide, vinylidene bromide, vinyl iodide, vinylidene iodide or combinations thereof.

- The acid-containing repeating units may be formed by polymerisation of acid-containing monomers. Non-limiting examples of the acid-containing monomers
- 5 include acrylic acid, methacrylic acid, maleic acid, vinylphosphonic acid, vinyl phosphoric acid, styrenesulfonic acid or combinations thereof.

The optionally hydrocarbon repeating units may be formed by polymerisation of hydrocarbon monomers. Non-limiting examples of the hydrocarbon monomers include ethylene, propylene, isoprene, neoprene, styrene or combinations thereof.

- 10 The polymer matrix may be a copolymer of vinylidene chloride repeating units and acid-containing repeating units.

- The weight percentage of the acidified, silane modified silicate material may be in the range of about 0.1 weight% to about 50 weight%, about 5 weight% to about 50 weight%, about 10 weight% to about 50 weight%, about 15 weight% to about 50 weight%, about 20 weight% to about 50 weight%, about 25 weight% to about 50 weight%, about 30 weight% to about 50 weight%, about 35 weight% to about 50 weight%, about 40 weight% to about 50 weight%, about 45 weight% to about 50 weight%, about 0.1 weight% to about 45 weight%, about 0.1 weight% to about 40 weight%, about 0.1 weight% to about 35 weight%, about 0.1 weight% to about 30 weight%, about 0.1 weight% to about 25 weight%, about 0.1 weight% to about 20 weight%, about 0.1 weight% to about 15 weight%, about 0.1 weight% to about 10 weight% or about 0.1 weight% to about 5 weight%, based on the weight of the polymer matrix.
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- The acidified, silane modified silicate material may be in the form of particles having
- 25 an average dimension in the range of about 20 nm to about 10000 nm, about 100 nm to about 10000 nm, about 300 nm to about 10000 nm, about 500 nm to about 10000 nm, about 1000 nm to about 10000 nm, about 20 nm to about 1000 nm, about 20 nm to about 500 nm, about 20 nm to about 300 nm, about 20 nm to about 100 nm, about 100 nm to about 1000 nm or about 300 nm to about 500 nm.

- 30 The thickness of the coating may be in the range of about 0.2 μm to about 10 μm , about 1 μm to about 10 μm , about 2 μm to about 10 μm , about 3 μm to about 10 μm , about 4 μm to about 10 μm , about 5 μm to about 10 μm , about 6 μm to about 10 μm , about 7 μm to about 10 μm , about 8 μm to about 10 μm , about 9 μm to about 10 μm , about 0.2 μm to about 9 μm , about 0.2 μm to about 8 μm , about 0.2 μm to about 7 μm , about 0.2 μm to about 6 μm , about 0.2 μm to about 5 μm , about 0.2 μm to about 4 μm , about 0.2 μm to about 3 μm , about 0.2 μm to about 2 μm or about 0.2 μm to about 1 μm .
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Exemplary, non-limiting embodiments of a composite coating emulsion will now be disclosed.

The composite coating emulsion may comprise an acidified, silane modified silicate material and a polymer matrix having at least one acidic group and at least one halogen group dispersed in a solvent.

5 The silicate material may be a mineral selected from serpentine, clay, mica. Non-limiting examples of the silicate material include antigorite, chrysotile, lizardite, halloysite, kaolinite, illite, montmorillonite, vermiculite, talc, sepiolite, palygorskite, pyrophyllite, biotite, fuchsite, muscovite, phlogopite, lepidolite, margarite, glauconite, bentonite or combinations thereof. The silicate material may be a clay.

10 The acidified, silane modified silicate material may be in the form of particles having an average dimension in the range of about 20 nm to about 10000 nm, about 100 nm to about 10000 nm, about 300 nm to about 10000 nm, about 500 nm to about 10000 nm, about 1000 nm to about 10000 nm, about 20 nm to about 1000 nm, about 20 nm to about 500 nm, about 20 nm to about 300 nm, about 20 nm to about 100 nm, about 100 nm to about 1000 nm or about 300 nm to about 500 nm.

15 The polymer matrix may comprise a copolymer of halogen-containing repeating units, acidic-containing repeating units, and optionally hydrocarbon repeating units.

The halogen-containing repeating units may be formed by polymerisation of halogen-containing monomers. Non-limiting examples of the halogen-containing monomers include vinyl fluoride, vinylidene fluoride, vinyl chloride, vinylidene chloride, vinyl
20 bromide, vinylidene bromide, vinyl iodide, vinylidene iodide or combinations thereof.

The acid-containing repeating units may be formed by polymerisation of acid-containing monomers. Non-limiting examples of the acid-containing monomers include acrylic acid, methacrylic acid, maleic acid, vinylphosphonic acid, vinyl
25 phosphoric acid, styrenesulfonic acid or combinations thereof.

The optionally hydrocarbon repeating units may be formed by polymerisation of hydrocarbon monomers. Non-limiting examples of the hydrocarbon monomers include ethylene, propylene, isoprene, neoprene, styrene or combinations thereof.

30 The polymer matrix may be a copolymer of vinylidene chloride repeating units and acid-containing repeating units.

The solvent in the composite coating emulsion may be a polar solvent that can dissolve silicate and the polymer matrix described herein. Non-limiting examples of the solvent include water, lower alcohols or combinations thereof. Non-limiting examples of the lower alcohols may be methanol, ethanol, propan-1-ol, 2-methylpropan-1-ol, propan-2-ol, butan-2-ol, pent-3-ol, 2-methylpropan-2-ol, 2-methylbutan-2-ol, butan-1-ol or combinations thereof.

The weight percentage of the acidified, silane modified silicate material may be in the range of about 0.1 weight% to about 50 weight%, about 5 weight% to about 50

weight%, about 10 weight% to about 50 weight%, about 15 weight% to about 50 weight%, about 20 weight% to about 50 weight%, about 25 weight% to about 50 weight%, about 30 weight% to about 50 weight%, about 35 weight% to about 50 weight%, about 40 weight% to about 50 weight%, about 45 weight% to about 50 weight%, about 0.1 weight% to about 45 weight%, about 0.1 weight% to about 40 weight%, about 0.1 weight% to about 35 weight%, about 0.1 weight% to about 30 weight%, about 0.1 weight% to about 25 weight%, about 0.1 weight% to about 20 weight%, about 0.1 weight% to about 15 weight%, about 0.1 weight% to about 10 weight% or about 0.1 weight% to about 5 weight%, based on the weight of the polymer matrix.

The composite coating emulsion may have a weight percentage of solid content in the range of about 2 weight% to about 45 weight%, about 10 weight% to about 45 weight%, about 15 weight% to about 45 weight%, about 20 weight% to about 45 weight%, about 25 weight% to about 45 weight%, about 30 weight% to about 45 weight%, about 35 weight% to about 45 weight%, about 40 weight% to about 45 weight%, about 2 weight% to about 40 weight%, about 2 weight% to about 35 weight%, about 2 weight% to about 30 weight%, about 2 weight% to about 25 weight%, about 2 weight% to about 20 weight%, about 2 weight% to about 15 weight% or about 2 weight% to about 10 weight%, based on the total weight of the composite coating emulsion.

Exemplary, non-limiting embodiments of a coated article will now be disclosed.

The coated article may comprise the coating as described herein, an optional primer coating and a substrate.

The coating may have a weight percentage in the range of about 0.5 weight% to about 5 weight%, about 1 weight% to about 5 weight%, about 3 weight% to about 5 weight%, about 0.5 weight% to about 3 weight%, about 0.5 wt % to about 1 wt % or about 1 weight% to about 3.2 weight% based on the total weight of the coated article.

The optional primer coating may be a film-forming solvent-borne dispersion of a primer material that resides on the surface of substrate. Non-limiting examples of the primer material include polyacrylate, polyurethane, ethylene propylene diene monomer, polyvinyl chloride, synthetic rubber or combinations thereof.

The substrate may be a non-hydrolysable thin film. Non-limiting examples of the substrate material include paper, plastic or combinations thereof.

Where the substrate is paper, the substrate may be selected from the group consisting of plain paper, metallised paper, sandpaper, wax paper, leather paper, kraft paper and combinations thereof.

Where the substrate is plastic, the substrate may be selected from the group consisting of polyethylene, polypropylene, polyester, cellulose acetate, cellophane, nylon, metalized plastic and combinations thereof.

The oxygen transmission rate of the coated article may be in the range of about 0.1 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 1 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 2 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 3 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 4 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 5 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 6 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 7 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 8 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 9 cc m⁻² day⁻¹ to about 10 cc m⁻² day⁻¹, about 0.1 cc m⁻² day⁻¹ to about 9 cc m⁻² day⁻¹, about 0.1 cc m⁻² day⁻¹ to about 8 cc m⁻² day⁻¹, about 0.1 cc m⁻² day⁻¹ to about 7 cc m⁻² day⁻¹, about 0.1 cc m⁻² day⁻¹ to about 6 cc m⁻² day⁻¹, about 0.1 cc m⁻² day⁻¹ to about 5 cc m⁻² day⁻¹, about 0.1 cc m⁻² day⁻¹ to about 4 cc m⁻² day⁻¹, about 0.1 cc m⁻² day⁻¹ to about 3 cc m⁻² day⁻¹, about 0.1 cc m⁻² day⁻¹ to about 2 cc m⁻² day⁻¹ or about cc m⁻² day⁻¹ to about 1 cc m⁻² day⁻¹ as measured according to the standard of ASTM D3985.

The water vapour transmission rate of the coated article may be in the range of about 0.1 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 1 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 2 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 3 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 4 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 5 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 6 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 7 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 8 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 9 g m⁻² day⁻¹ to about 10 g m⁻² day⁻¹, about 0.1 g m⁻² day⁻¹ to about 9 g m⁻² day⁻¹, about 0.1 g m⁻² day⁻¹ to about 8 g m⁻² day⁻¹, about 0.1 g m⁻² day⁻¹ to about 7 g m⁻² day⁻¹, about 0.1 g m⁻² day⁻¹ to about 6 g m⁻² day⁻¹, about 0.1 g m⁻² day⁻¹ to about 5 g m⁻² day⁻¹, about 0.1 g m⁻² day⁻¹ to about 4 g m⁻² day⁻¹, about 0.1 g m⁻² day⁻¹ to about 3 g m⁻² day⁻¹, about 0.1 g m⁻² day⁻¹ to about 2 g m⁻² day⁻¹ or about 0.1 g m⁻² day⁻¹ to about 1 g m⁻² day⁻¹ as measured according to the standard of ASTM F1249.

Exemplary, non-limiting embodiments of a method of preparing a composite coating emulsion will now be disclosed.

The method may comprise the step of mixing an acidified, silane modified silicate material, and a polymer matrix having at least one acidic group and at least one halogen group in a solvent.

The method may further comprise, before the mixing step, the steps of:

(a) acidifying a silicate material to form an acidified silicate material; and

(b) subjecting the acidified silicate material to a silane treatment to form an acidified, silane modified silicate material. Therefore, the method may comprise the step of forming the acidified, silane modified silicate material, where the forming step

comprises steps (a) and (b).

The acidifying step may comprise stirring an acid resin into the silicate material. As an example, the stirring may be carried out at about 65 °C for about 5 hours. The acidifying step may further comprise a step of centrifuging the acidified silicate material. As an example, the centrifuging step can be undertaken at 10,000 rpm for

about 3 to 4 hours. The acidifying step may still further comprise a washing step by rinsing the centrifuged silicate material with deionised water and re-dispersing the rinsed silicate mixture in deionised water.

- 5 The acid resin used in the acidifying step is not particularly limited and may be any acid resin that is capable of cation exchange. An exemplary acid resin may be Lewatit MonoPlus S 108 H.

- 10 The silane treatment may comprise adding an amino-silane and a halogen-containing silane to the acidified silicate material sequentially at a certain homogenization rate. As an example only, the amino-silane and halogen-containing silane may be added sequentially at a rate of 0.05 mL min^{-1} under a high speed of homogenizing process at 15,000 rpm. The silane treatment may further comprise stirring of the acidified, silane modified silicate material to complete the silane treatment. As an example, the stirring step may be carried out at about 65°C for about 6 hours.

- 15 The amino-silane and halogen-containing silane may have a weight percentage in the range of about 0.5 weight% to about 20 weight%, about 0.5 weight% to about 10 weight% or about 10 weight% to about 20 weight%, based on the total weight of the silicate material.

The amino-silane and halogen-containing silane may have a weight ratio in the range of about 1:9 to about 9:1, about 1:9 to about 1:1 or about 1:1 to about 9:1.

- 20 The amino-silane may comprise amino groups. The amino-silane may additionally comprise alkoxy groups such as methoxy groups, ethoxy groups or a combination thereof. The amino-silane may be (3-aminopropyl)trimethoxysilane.

- 25 The halogen-containing silane may comprise halogen groups. The halogen-containing silane may additionally comprise alkoxy groups such as methoxy groups, ethoxy groups or a combination thereof. The halogen-containing silane may be (3-chloropropyl)trimethoxysilane (CP-TMS), (3-chloropropyl)dimethoxy(methyl)silane (CP-DMMS) or combinations thereof.

The method may further comprise, before the acidifying step, a step of (a1) dispersing the silicate material in the solvent and stirring the silicate material.

- 30 The stirring of the silicate material may be undertaken for a duration in the range of about 6 hours to about 8 hours. The stirring may be undertaken overnight.

- 35 The solvent may be a polar solvent that can disperse the silicate minerals. Non-limiting examples of the solvent include water, lower alcohols or combinations thereof. Non-limiting examples of the lower alcohols may be methanol, ethanol, propan-1-ol, 2-methylpropan-1-ol, propan-2-ol, butan-2-ol, pent-3-ol, 2-methylpropan-2-ol, 2-methylbutan-2-ol, butan-1-ol or combinations thereof.

The polymer matrix having at least one acidic group and at least one halogen group in the solvent may be in the form of a latex.

- The weight percentage of the silicate material may be in the range of about 1 weight% to about 5 weight%, about 2.5 weight% to about 5 weight%, about 3 weight% to about 5 weight%, about 3.5 weight% to about 5 weight%, about 4 weight% to about 5 weight%, about 4.5 weight% to about 5 weight%, about 1 weight% to about 4.5 weight%, about 1 weight% to about 4 weight%, about 1 weight% to about 3.5 weight%, about 1 weight% to about 3 weight% or about 1 weight% to about 2.5 weight%, based on the total weight of the silicate material and the solvent.
- 10 In the step of mixing the acidified, silane modified silicate material, and the polymer matrix having at least one acidic group and at least one halogen group in a solvent, the mixing may comprise stirring of the mixture at about 200 to 1000 rpm for a duration in the range of about 0.5 to about 4 hours, about 1 to about 4 hours, about 1.5 to about 4 hours, about 2 to about 4 hours, about 2.5 to about 4 hours, about 3 to about 4 hours, about 3.5 to about 4 hours, about 0.5 to about 3.5 hours, about 0.5 to about 3 hours, about 0.5 to about 2.5 hours, about 0.5 to about 2 hours, about 0.5 to about 1.5 hours or about 0.5 to about 1 hour.

- The method may further comprise, before stirring of the mixture, a step of adding the acidified, modified silicate material to the polymer matrix at a rate in the range of about 0.5 mL min⁻¹ to about 3 mL min⁻¹, about 1 mL min⁻¹ to about 3 mL min⁻¹, about 1.5 mL min⁻¹ to about 3 mL min⁻¹, about 2 mL min⁻¹ to about 3 mL min⁻¹, about 2.5 mL min⁻¹ to about 3 mL min⁻¹, about 0.5 mL min⁻¹ to about 2.5 mL min⁻¹, about 0.5 mL min⁻¹ to about 2 mL min⁻¹, about 0.5 mL min⁻¹ to about 1.5 mL min⁻¹ or about 0.5 mL min⁻¹ to about 1 mL min⁻¹.

- 25 The method may further comprise, before adding the acidified, silane modified silicate material to the polymer matrix, a step of treating the acidified, silane modified silicate material by stirring a dispersion of the acidified, silane modified silicate material in the solvent for a suitable period of time. The stirring may be undertaken for about 1 hour, or as required for the acidified, silane modified silicate material to be dispersed in the solvent.

Exemplary, non-limiting embodiments of a method of preparing a coated article will now be disclosed.

The method may comprise the step of adding the composite coating emulsion as described herein on a substrate.

- 35 The adding of the composite coating emulsion may be undertaken by thin film coating techniques. Non-limiting examples of the thin film coating techniques include blade coating, bar coating, slot-die coating, gravure coating or combinations thereof.

The method may further comprise, before the adding step, a step of applying a primer coating on the substrate.

The primer coating may be selected from the group consisting of polyacrylate, polyurethane, ethylene propylene diene monomer, polyvinyl chloride, synthetic rubber and combinations thereof.

The applying step may be undertaken by thin film coating techniques. Non-limiting examples of the thin film coating techniques include blade coating, bar coating, slot-die coating, gravure coating or combinations thereof.

The applying step may further comprise, after applying the primer coating, a step of drying the primer coating at an elevated temperature for a duration.

The elevated temperature may be in the range of about 20°C to about 150°C, about 30°C to about 150°C, about 40°C to about 150°C, about 50°C to about 150°C, about 60°C to about 150°C, about 70°C to about 150°C, about 80°C to about 150°C, about 90°C to about 150°C, about 100°C to about 150°C, about 110°C to about 150°C, about 20°C to about 110°C, about 20°C to about 100°C, about 20°C to about 90°C, about 20°C to about 80°C, about 20°C to about 70°C, about 20°C to about 60°C, about 20°C to about 50°C, about 20°C to about 40°C or about 20°C to about 30°C.

The duration of drying may be in the range of about 0.1 minutes to about 10 minutes, about 1 minutes to about 10 minutes, about 2 minutes to about 10 minutes, about 3 minutes to about 10 minutes, about 4 minutes to about 10 minutes, about 5 minutes to about 10 minutes, about 6 minutes to about 10 minutes, about 7 minutes to about 10 minutes, about 8 minutes to about 10 minutes, about 9 minutes to about 10 minutes, about 0.1 minutes to about 9 minutes, about 0.1 minutes to about 8 minutes, about 0.1 minutes to about 7 minutes, about 0.1 minutes to about 6 minutes, about 0.1 minutes to about 5 minutes, about 0.1 minutes to about 4 minutes, about 0.1 minutes to about 3 minutes, about 0.1 minutes to about 2 minutes or about 0.1 minutes to about 1 minute.

The method may further comprise, after the adding step, a step of curing of the composite coating emulsion. The curing step may be undertaken at a suitable curing temperature for a certain period of time, such as at about 45°C for about 48 hours.

With reference to Fig. 1, it is appreciated that the method may comprise the steps of:

- (a) acidifying a silicate material **102** to form an acidified silicate material;
- (b) subjecting the acidified silicate material to a silane treatment to form an acidified, silane modified silicate material **104**;
- (c) mixing the acidified, silane modified silicate material **104**, and a polymer matrix having at least one acidic group and at least one halogen group in a solvent to form a composite coating emulsion **106**; and
- (d) adding the composite coating emulsion **106** and optionally a primer coating on a substrate to form the coated article **108**.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1

[Fig. 1] is a schematic diagram of a general procedure for preparing a coated article as described herein.

Fig. 2

[Fig. 2] shows the change in pH value and conductivity of the silicate material as described herein after being acidified for varying durations.

Fig. 3

[Fig. 3] shows scanning electron microscope (SEM) micrographs of an exemplary coated article comprising a paper substrate, a primer coating and a silicate/PVDC coating, where Fig. 3(a) is a cross-sectional view of the coated article with a scale bar of 10 μm ($\times 1000$ magnification); and Fig. 3(b) is a magnified view of the area represented by the in square in Fig. 3(a), where Fig. 3(b) has a scale bar of 1 μm ($\times 2000$ magnification).

Fig. 4

[Fig. 4] shows SEM micrographs of an exemplary coated article comprising a polyethylene terephthalate substrate, a polyurethane primer coating and a silicate/PVDC coating, where Fig. 4(a) is a top view of the coated article with a scale bar of 10 μm ($\times 350$ magnification); Fig. 4(b) is another top view of the coated article with a scale bar of 1 μm ($\times 5000$ magnification); Fig. 4(c) is a cross-sectional view of the coated article with a scale bar of 1 μm ($\times 2000$ magnification); and Fig. 4(d) has the area in square in Fig. 4(c) further magnified with a scale bar of 1 μm ($\times 10000$ magnification).

Detailed Description of Figures

With reference to Fig. 1, a schematic diagram of a general procedure for preparing a coated article as described herein is shown. Here, the following steps are carried out:

(a) acidifying a silicate material **102** to form an acidified silicate material;

(b) subjecting the acidified silicate material to a silane treatment to form an acidified, silane modified silicate material **104**, where acidic groups, silane groups and amino groups are present;

- (c) mixing the acidified, silane modified silicate material **104**, and a polymer matrix having at least one acidic group and at least one halogen group in a solvent to form a composite coating emulsion **106**. In Fig. 1, the polymer matrix is exemplified by a polyvinylidene chloride latex (which comprises a composition of the copolymer of vinylidene chloride repeating units and acid-containing repeating units in a solvent) as shown in micellar spheres; and
- (d) adding the composite coating emulsion **106** and a primer coating on a substrate to form the coated article **108**. The coated article **108** comprises a substrate, the coating made from the composite coating emulsion **106** and the primer coating sandwiched between the substrate and the coating made from the composite coating emulsion **106**. While Fig. 1 show that the primer coating is used, it is to be appreciated that the primer coating is an optional layer and therefore, may or may not be present in the final coated article.

Examples

- Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1 – Preparation of an Acidified Silicate Material

- An aqueous dispersion of silicate material (3.75 wt%) was prepared by dispersing a silicate material (3.75 g, PGN, MMT type, purchased from Nanocor Inc., USA) in deionised water (96.25 g) and stirred overnight. Acid-exchange resins (1 g, Lewatit MonoPlus S 108 H, purchased from LANXESS Pte. Ltd) were equally loaded into 4 tea bags. The resin bags were soaked in deionised water (100 g) and rinsed twice with deionised water. The rinsed resin bags were then transferred to the aqueous dispersion of the silicate material. As shown in Fig. 2, the silicate material had a decreasing pH value and an increasing conductivity with an increasing duration of exposure to the resin bags. The aqueous dispersion was then subjected to a heat treatment by stirring at 65 °C for 5 hours. After the heat treatment, the resin bags were removed from the dispersion. The treated silicate material was then collected by centrifugation at 10,000 rpm for 3 to 4 hours, rinsed by deionised water, and re-dispersed in deionised water for storage and further use.

Example 2 – Preparation of an Acidified, Silane Modified Silicate Material

- (3-aminopropyl)trimethoxysilane (APTMS, 78 µL, 4 weight% based on the weight of acidified silicate material, purchased from Sigma-Aldrich, Singapore) and (3-chloropropyl)dimethoxy(methyl)silane (CP-DMMS, 118 µL, 6 weight% based on the weight of acidified silicate material, purchased from TCI, Tokyo, Japan) were slowly injected (0.05 mL/min) into the acidified silicate material (100 g, 2 weight%

in aqueous dispersion, obtained in Example 1) sequentially under high speed of homogenizing process at 15,000 rpm (via IKA T18 Basic Ultra Turrax homogenizer). Afterwards, the mixture was further stirred at 65 °C for 6 hours for completing the silane modification.

- 5 A series of acidified, silane modified silicate material were prepared by varying the amount of the silane mixture in the range of 0 to 18 weight% based on the weight of silicate, and the ratio of APTMS to CP-DMMS from 0/10 to 6/4 (by weight, see Table 1).

10 **Table 1.** The silane modification, composition and physicochemical properties of the coating emulsions.

Entry	Sample description	Acidified PGN	Silane modification		Composite coating emulsion			
			APTMS (wt% of silicate)	CP-DMMS (wt% of silicate)	Solid content (wt%)	Silicate/PVDC	Viscosity (Zahn cup, second)*	pH
1	Silicate/PVDC emulsion [1]	R7	-	-	40	1/100	12	0.96
2	Silicate/PVDC emulsion [2]	R7	0	10	40	1/100	11.5	0.83
3	Silicate/PVDC emulsion [3]	R7	2	8	40	1/100	NA	NA
4	Silicate/PVDC emulsion [4]	R7	4	6	40	1/100	12	1.10
5	Silicate/PVDC emulsion [5]	R7	6	4	36	1/100	NA	NA
6	Silicate/PVDC emulsion [6]	R7	6	12	41.5	0.6/100	12	1.10
7	Silicate/PVDC emulsion [7]	R7	6	12	35.1	1.2/100	NA	NA
8	Silicate/PVDC emulsion [8]	R7	6	12	24	2.4/100	NA	NA
9	Silicate/PVDC emulsion [9]	R7	6	12	14	3.6/100	NA	NA
10	Silicate/PVDC emulsion [10]	R7	6	12	10	5/100	NA	NA
11	Silicate/PVDC emulsion [11]	R7	6	12	5	10/100	NA	NA

*Viscosity of the coating emulsion was measured by using Zahn cup 3 (Rigosha, Japan). The cup was dipped into the coating emulsion and completely filled with the

coating emulsion. The duration of the emulsion streaming out of the cup through the hole at its bottom is recorded.

Example 3 – Preparation of a Composite Coating Emulsion

5 The acidified, silane modified silicate material obtained in Example 2 (39.6 g) was mixed with deionised water (2.1 g) and stirred for 1 hour. The mixture was then added dropwise to a PVDC latex (158.3 g, 50% solids by weight, QL-701G PVDC latex, purchased from Zhejiang Juhua Co., Ltd. Electric-Chemical Plant, China) under stirring at 200 to 300 rpm and then further stirred for another 1 to 3 hours. The resultant composite coating emulsion had a solid content of 40 weight% with a
10 silicate/PVDC ratio of 1/100 by weight.

A series of composite coating emulsions were prepared by varying the solid content from 5 to 45 weight% based on the total weight of the coating emulsion, and the silicate/PVDC ratio from 0.6/100 to 50/100 (by weight, see Table 1).

15 Example 4 – Preparation of a Coated Article on a Metallized Paper Substrate

Laboratory equipment was used to prepare the coated article. First, a primer coating (55% solids by weight, P2300, purchased from Michelman Inc., USA) was applied onto a metallized paper substrate (with basis weight of 60 g/m², purchased from Yantai Boyuan Technology Materials Co., Ltd, China) using a wire wound rod with
20 a wet coating thickness of 4 µm. The coating was dried at 105 °C for 1 minute. A composite coating emulsion obtained in Example 3 was coated on top of the primer coating using a wire wound rod. The coating thickness was varied by the selected wet coating thickness of the wire wound rod, typically from 0.5 to 3 µm. The coating was cured at 45 °C for 48 hours.

25 *Scanning electron microscopy*

Scanning electron microscope (SEM, JEOL JSM-6700F) was used to measure the morphology and thickness of the coating on the coated article. The coated article was cut with a sharp blade and embedded into epoxy to cure overnight. The specimen was then polished to achieve a flat cross section by using microtoming.

30 As shown in Fig. 3, a primer coating was evenly applied onto a metallized paper. This primer coating was used to improve the wettability and adhesion of the subsequent coating. The silicate/PVDC coating showed a densely packed structure and good adhesion to the primer coating.

Water vapor transmission rate

35 Water vapor permeability of the coated article was measured by using Mocon water vapor permeability PERMATRAN-W Model 3/33 according to the standard of ASTM F1249. Each film was placed on a stainless steel mask with an open testing

area of 50 cm². Water vapor permeability measurements were conducted at 37.8 °C (1 atm) and 90% RH.

Oxygen transmission rate

Oxygen permeability of the coated article was measured by using Mocon oxygen permeability OX-TRAN Model 2/21 according to the standard of ASTM D3985. Each coated article was placed on a stainless steel mask with an open testing area of 50 cm². Oxygen permeability measurements were conducted at 23 °C (1 atm) and 0% RH.

As shown in Table 2, PVDC coating could reduce the WVTR of metallized paper, but without effect on its OTR. Incorporation of acidified silicate materials into PVDC coating could reduce both the WVTR and OTR of the PVDC coated metallized paper. The reduction of WVTR and OTR of acidified and silane modified silicate/PVDC coated paper was higher than that of acidified silicate/PVDC coated paper.

Table 2. Transmission rates of water vapor for the coated article on the metallized paper substrate.

Entry	Sample description	Coating emulsion	Barrier properties	
			WVTR [g/(m ² ·day)]	OTR [cc/(m ² ·day)]
1	Metallized Paper	-	6.68	Beyond test limit, >200
2	Metallized Paper/Primer/PVDC	PVDC	5.66	Beyond test limit, >200
3	Metallized Paper/Primer/PVDC-silicate (acidified)	Silicate/PVDC emulsion [1]	4.20	37.78
4	Metallized Paper/Primer/PVDC-silicate (acidified, silane modified)	Silicate/PVDC emulsion [2]	3.83	35.27

[1]: silicate treated by acid-exchange resin (Lewatit MonoPlus S 108 H); [2]: silicate treated by acid-exchange resin, followed by silane modification with a mixture of APTMS and CP-DMMS at 4 wt% and 6 wt% of silicate, respectively.

Example 5 – Preparation of a Coated Article on a Polyethylene Terephthalate (PET) Substrate

First, an adhesive was prepared by mixing urethane coating agents of A310 (purchased from Takeda Seiyaku Co., Japan), A3 (purchased from Takeda Seiyaku

Co., Japan) in ethyl acetate at a mass ratio of 5:1:20 and stirring the mixture for 1 hour. The mixture was then applied as a primer coating onto a PET film (12 μm thick) using a bar applicator. The primer coating thickness was varied by adjusting the bar applicator's wet coating thickness, typically from 0.5 to 2.5 μm . The primer coating
5 was then dried in air for 5 minutes. A composite coating emulsion obtained in Example 3 was subsequently coated on top of the primer coating using a bar applicator. The coating thickness was varied by adjusting the bar applicator's wet coating thickness, typically from 0.5 to 10 μm . The coating was cured at 45 °C for 48 hours.

10 *Scanning electron microscopy*

SEM as described above in Example 4 was used to observe the morphology and measure the thickness of the coating on the coated article. As shown in Fig. 4, a densely packed silicate/PVDC coating with even distribution on the primer precoat was prepared.

15 *Oxygen transmission rate and water vapor transmission rate*

Oxygen transmission rate and water vapor transmission rate of the coated article were measured according to the protocols described in Example 4.

As shown in Table 3, both the OTR and WVTR of PET film decreased after coating with PVDC emulsion and incorporation of modified silicate into PVDC emulsion
20 could further reduce the OTR and WVTR of the coated PET film. The reduction of OTR and WVTR of the acidified and silane modified silicate/PVDC coated PET film was higher than those of acidified silicate/PVDC or silane modified silicate/PVDC coated PET film, respectively.

Table 3. Transmission rates of water vapor and oxygen for the coated article on the PET substrate.

Entry	Sample description	Coating emulsion					Barrier properties		
		Solid content (weight%)	Silicate/PVDC	Viscosity (Zahn cup, second)	pH	WVTR [g/(m ² ·day)]	OTR [cc/(m ² ·day)]		
1	PET	-	-	-	-	46.49	130.65		
2	PET/Primer/PVDC	50	-	12	0.57	9.23	11.13		
3	PET/Primer/PVDC-silicate[1]	40	1/100	12	0.96	2.80	1.31		
4	PET/Primer/PVDC-silicate[2]	35	1/100	12	0.70	8.89	9.41		
5	PET/Primer/PVDC-silicate[3]	40	1/100	12	1.10	2.37	0.63		

[1]: an acidified silicate material was used; [2] a silane modified silicate material was used; [3] an acidified, silane modified silicate material was used.

Industrial Applicability

The coating of the disclosure may be used to prepare packaging with high barrier properties and high recyclability.

- 5 The packaging may be used for oxygen-sensitive and/or moisture-sensitive food, electronics or pharmaceuticals.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A coating comprising an acidified, silane modified silicate material bound to a polymer matrix having at least one acidic group and at least one halogen group.
- 5 2. The coating of claim 1, wherein the silicate material is selected from the group consisting of serpentine, clay, mica and combinations thereof.
3. The coating of claim 1 or 2, wherein the polymer matrix comprises a copolymer of halogen-containing repeating units, acidic-containing repeating units, and optionally hydrocarbon repeating units.
- 10 4. The coating of any one of claims 1 to 3, wherein the polymer matrix is a copolymer of vinylidene chloride repeating units and acid-containing repeating units.
- 15 5. A composite coating emulsion comprising an acidified, silane modified silicate material and a polymer matrix having at least one acidic group and at least one halogen group dispersed in a solvent.
- 20 6. The composite coating emulsion of claim 5, wherein the silicate material is selected from the group consisting of serpentine, clay, mica and combinations thereof.
7. The composite coating emulsion of claim 5 or 6, wherein the polymer matrix comprises a copolymer of halogen-containing repeating units, acidic-containing repeating units, and optionally hydrocarbon repeating units.
- 25 8. The composite coating emulsion of any one of claims 5 to 7, wherein the polymer matrix is a copolymer of vinylidene chloride repeating units and acid-containing repeating units.
- 30 9. The composite coating emulsion of any one of claims 5 to 8, wherein the solvent is water, an alcohol or combinations thereof.
10. A coated article comprising the coating of any one of claims 1 to 4, an optional primer coating and a substrate.
- 35 11. The coated article of claim 10, wherein the coating has a weight percentage in the range of 0.5 weight% to 5 weight% based on the weight of the article.
- 40 12. A method of preparing a composite coating emulsion comprising the step of mixing an acidified, silane modified silicate material, and a polymer matrix having at least one acidic group and at least one halogen group in a solvent.
13. The method of claim 12, further comprising, before said mixing step, the steps of:
(a) acidifying a silicate material to form an acidified silicate material; and
45 (b) subjecting the acidified silicate material to a silane treatment to form an acidified, silane modified silicate material.

14. The method of claim 13, further comprising, before said acidifying step (a), the step of (a1) dispersing silicate minerals in the solvent and stirring overnight to form a silicate dispersion.
- 5 15. The method of any one of claims 12 to 14, wherein the silicate material is selected from the group consisting of serpentine, clay, mica and combinations thereof.
- 10 16. The method of any one of claims 12 to 15, wherein the polymer matrix comprises a copolymer of halogen-containing repeating units, acidic-containing repeating units, and optionally hydrocarbon repeating units.
17. The method of any one of claims 12 to 16, wherein the polymer matrix is a copolymer of vinylidene chloride repeating units and acid-containing repeating units.
- 15 18. The method of any one of claims 12 to 17, wherein the solvent is water, an alcohol or combinations thereof.
19. A method of preparing a coated article comprising the step of applying the composite coating emulsion of any one of claims 5 to 9 on a substrate.
- 20 20. The method of claim 19, further comprising a step of applying a primer coating on the substrate before the step of applying the composite coating emulsion on the substrate.