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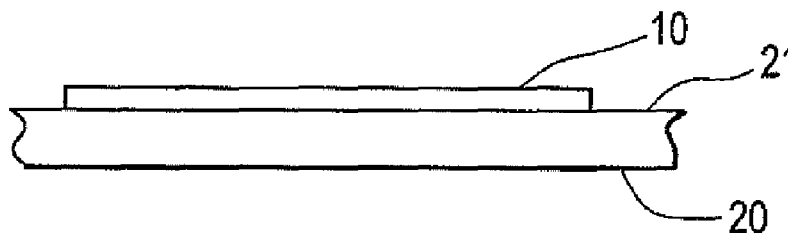
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FIG. 1



(57) Abstract: Coating compositions containing a reaction product of polyvinyl alcohol, one or more metal alkoxides and an organic acid are disclosed. Cured coatings formed from the coating compositions are also disclosed. Methods of making and using coating compositions containing a reaction product of polyvinyl alcohol, one or more metal alkoxides and an organic acid are further disclosed.



COATING COMPOSITIONS, CURED COATINGS AND METHODS OF MAKING AND USING THE SAME

TECHNICAL FIELD

[0001] The present invention relates to coating compositions, in particular to coating compositions containing a reaction product of polyvinyl alcohol (PVOH), one or more metal alkoxides and an organic acid, as well as cured coatings formed from the coating compositions, and methods of making and using the same.

BACKGROUND

[0002] Food and beverage packaging materials are known. Such food and beverage packaging materials typically provide a desired amount of gas barrier performance so as to protect the food packaged therein. Traditionally, thermoplastic resins such as polypropylene have been used to provide a gas barrier.

[0003] Polyvinyl alcohol (PVOH) is known to provide high gas barrier performance among thermoplastic resins. However, PVOH has poor gas barrier performance in high humidity environments due to the presence of hydroxyl groups, which attract water. A number of attempts have been made to try to improve the performance of PVOH. See, for example, methods of making PVOH-ethylene copolymer in Japanese Patent Application 2006-219518, and U.S. Patent No. 7,435,446; methods of using sol-gel reactions with silicon alkoxides and polyvinyl alcohol in Japanese Patent Application 2010-89321, U.S. Patent No. 7,341,782, and U.S. Patent No. 7,763,335; and methods of using esterification reactions between PVOH and acrylic acid in Japanese Patent Application 2008-36914, and U.S. Patent No. 7,524,900.

[0004] Although efforts have been made to improve the performance of PVOH as a gas barrier, known approaches suffer from one of more shortcomings including, but not limited to, the resulting coating composition fails to provide a coating having both water resistance and gas barrier properties; the process utilized to form the coating composition requires the use of unstable reactants; the process utilized to form the coating composition requires the use of one or more inorganic acids (e.g., HCl); and/or a film resulting from the coating composition is too cloudy for use as a food packing material component.

[0005] Efforts continue in the development of coating compositions containing a reaction product of PVOH, wherein the coating composition provides both water resistance and exceptional gas barrier properties, even in relatively high humidity conditions.

SUMMARY

[0006] The present invention continues the effort to develop coating compositions containing a reaction product of PVOH, wherein the coating composition provides both water resistance and exceptional gas (e.g., oxygen) barrier properties. In particular, the present invention is directed to a coating composition comprising a reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid.

[0007] In one exemplary embodiment of the present invention, the coating composition comprises a reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid, wherein the coating composition optionally further comprises one or more optional additives such as a colorant. In some desired embodiments, the polyvinyl alcohol comprises hydrolyzed polyvinyl alcohol, the one or more metal alkoxides comprise methyltrimethoxysilane, tetraethoxysilane, or a combination thereof, and the organic acid comprises a low molecular weight organic acid comprising at least one carboxylic acid group.

[0008] The present invention is further directed to cured coatings comprising the disclosed coating compositions, wherein the coating composition is heated to a curing temperature for a period of time to remove all or substantially all of any solvent used to form the coating composition. The cured coatings of the present invention provide exceptional water resistance as measured by a Water Rub Test (discussed below), as well as exceptional oxygen transmission rates (OTR). In some exemplary embodiments, the cured coating of the present invention has (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 20, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 50 cc/m²/day. In other exemplary embodiments, the cured coating of the present invention has (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at about 80% relative humidity of less than 50 cc/m²/day.

[0009] Another embodiment of the present invention relates to a coating comprising a reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid, wherein the coating possesses a contact angle of at least 35 degrees. In other embodiments of the present invention, the coating possesses a contact angle of at least 40 degrees, or a contact angle of at least 45 degrees.

[0010] A further embodiment of the present invention relates to a gas and moisture barrier coating that includes a reaction product of polyvinyl alcohol, and one or more metal

alkoxides, wherein the coating possesses a contact angle of at least 35 degrees. In other embodiments of the present invention, the coating possesses a contact angle of at least 40 degrees, or a contact angle of at least 45 degrees.

[0011] Another embodiment of the present invention relates to an article where a substrate includes and a moisture and gas barrier coating thereon, the coating including a reaction product of polyvinyl alcohol, and one or more metal alkoxides, wherein the coating after being cured includes one or more of the following properties (i) a contact angle of at least 35 degrees; (ii) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 20; or (iii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 50 cc/m²/day. In a further embodiment, the coated substrate comprises a film, a foil or a sheet. In an even further embodiment of the present invention, the coated substrate further comprises an oxygen scavenging film.

[0012] The present invention is even further directed to methods of making the disclosed coating compositions and cured coatings. In one exemplary embodiment, the method of making a coating composition of the present invention comprises forming a mixture comprising polyvinyl alcohol in a solvent; adding the organic acid to the mixture; and adding one or more metal alkoxides to the mixture. The method of making the coating composition (or a cured coating therefrom) may further comprise curing the coating composition to remove solvent. In desired embodiments, the method comprises using an amount of the organic acid in the mixture so as to (1) catalyze a reaction between (i) the hydroxyl groups on the polyvinyl alcohol and (ii) the one or more metal alkoxides, and (2) enable an esterification reaction between (i) any remaining hydroxyl groups on the polyvinyl alcohol (i.e., hydroxyl groups not reacted with the one or more metal alkoxides) and (ii) the organic acid.

[0013] The present invention is also directed to methods of using the disclosed coating compositions and cured coatings. In one exemplary embodiment, the method of using a coating composition of the present invention comprises applying the coating composition onto a substrate, and curing the coating composition. In some exemplary embodiments, the method of using a coating composition of the present invention comprises applying the coating composition onto a substrate such as a film so as to form a multi-layer article, which may include an oxygen scavenging layer.

[0014] In other exemplary embodiments, the method of using a cured coating of the present invention comprises at least partially encompassing an item of food with the cured

coating. In some exemplary embodiments, the method of using a coating composition or a cured coating of the present invention comprises shielding a food item from environmental exposure to oxygen so as to preserve the food item for an extended period of time.

[0015] These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The present invention is further described with reference to the appended figures, wherein:

[0017] FIG. 1 depicts an exemplary coating composition of the present invention coated onto a substrate; and

[0018] FIG. 2 depicts a cross-sectional view of an exemplary article comprising one or more food items packaged within food packaging materials, wherein an exemplary cured coating of the present invention comprises one component of the food packaging materials.

DETAILED DESCRIPTION

[0019] To promote an understanding of the principles of the present invention, a description of specific embodiments of the invention follow and specific language is used to describe the specific embodiments. It will nevertheless be understood that no limitation of the scope of the invention is intended by the use of specific language. Alterations, further modifications, and such further applications of the principles of the present invention discussed are contemplated as would normally occur to one ordinarily skilled in the art to which the invention pertains.

[0020] In addition, with regard to figures used to describe the invention, it should be noted that some embodiments of the invention contain one or more of the features depicted in the figures. In some embodiments, the invention may actually contain one or more of the features depicted in the figures, as well as other features not specifically shown in the figures. In yet other embodiments, the invention may actually contain one or more of the features depicted in the figures, and no other features. Consequently, in some embodiments of the invention, features not specifically shown in the figures are specifically excluded from the invention (i.e., if the feature is not shown in the figures, the feature is expressly excluded from the invention in some embodiments).

[0021] It must be noted that as used herein and in the appended claims, the singular forms "a", "and", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "an oxide" includes a plurality of such oxides and reference to "oxide" includes reference to one or more oxides and equivalents thereof known to those skilled in the art, and so forth.

[0022] "About" modifying, for example, the quantity of an ingredient in a composition, concentrations, volumes, process temperatures, process times, recoveries or yields, flow rates, and like values, and ranges thereof, employed in describing the embodiments of the disclosure, refers to variation in the numerical quantity that may occur, for example, through typical measuring and handling procedures; through inadvertent error in these procedures; through differences in the ingredients used to carry out the methods; and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial concentration or mixture. Whether modified by the term "about" the claims appended hereto include equivalents to these quantities.

[0023] The term "polyvinyl alcohol" as used herein refers to a polymer that has a degree of polymerization ranging from about 300 to about 5000. It is manufactured by the polymerization of vinyl acetate followed by partial hydrolysis. The process of hydrolysis is based on the partial replacement of ester group in vinyl acetate with the hydroxyl group, and is completed in the presence of aqueous sodium hydroxide. Following gradual addition of the aqueous saponification agent, the polyvinyl alcohol is precipitated, washed and dried. The degree of hydrolysis is determined by the time point at which the saponification reaction is stopped. The acetate groups are hydrolyzed by ester interchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide. The physical characteristics and its specific functional uses depend on the degree of polymerization and the degree of hydrolysis.

[0024] As used herein the term "metal alkoxides" is defined as chemical compounds of mineral alkoxide precursor (in most cases an alkoxide of formula $M(OR)_n$ wherein M denotes silicon or a metal such as Al, Ti or Zr; n denotes the valence of the element M; and the n groups -OR are identical or different organic groups, for example alkoxy groups). Such compounds may include silicon and alcohol of general formula $Si(OR)_4$ where R is one or more different alkyl groups.

[0025] As used herein, "organic acid" is defined as an organic compound (e.g., contains carbon) with acidic properties. The most common organic acids are the carboxylic

acids, whose acidity is associated with their carboxyl group -COOH (e.g., formic, acetic, lactic, citric, propionic, valeric, oxalic, mellitic, etc.). Sulfonic acids, containing the group $\text{-SO}_2\text{OH}$, are relatively stronger acids. Alcohols, with -OH , can act as acids but they are usually very weak. The relative stability of the conjugate base of the acid determines its acidity. Other groups can also confer acidity, usually weakly: the thiol group -SH , the enol group, and the phenol group. In biological systems, organic compounds containing these groups are generally referred to as organic acids.

[0026] The present invention is directed to coating compositions comprising a reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid. The present invention is further directed to cured coatings (e.g., films) comprising the reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid. The present invention is even further directed to methods of making and using the disclosed coating compositions and cured coatings.

[0027] In one exemplary embodiment, the coating compositions of the present invention comprise (i) a reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid, and optionally (ii) one or more optional additives. Suitable optional additives include, but are not limited to, a colorant, inorganic nano-particle filler, crosslinker, antioxidants, adhesion promoters, oxygen scavenger, or a combination thereof. When present, each additive may be present in an any amount, but typically is present in an amount of up to about 5.0 weight percent (wt%) (or from greater than 0 wt% to about 3.0 wt%; or from greater than 0 wt% to about 1.0 wt%) based on a total weight of solids in the coating composition (or based on a total weight of a cured coating formed from the coating composition).

[0028] The coating compositions of the present invention typically further comprise a solvent system at least during formation of the coating composition. Suitable solvents for a given coating composition of the present invention may include, but are not limited to, water (e.g., deionized water), methanol, ethanol, ethylene glycol, 2-propanol or a combination thereof. In one exemplary embodiment, the coating composition comprises a solvent comprising deionized and ethanol in a 1:1 weight ratio.

[0029] In desired embodiments of the present invention, the polyvinyl alcohol used to form the reaction product in the coating compositions of the present invention comprises hydrolyzed polyvinyl alcohol. As used herein, the term "hydrolyzed" polyvinyl alcohol is used to describe polyvinyl alcohol, wherein at least about 90% of acetate groups on the raw material polyvinyl acetate that is used to form the polyvinyl alcohol are hydrolyzed.

Typically, the hydrolyzed polyvinyl alcohol used in the present invention comprises polyvinyl alcohol, wherein at least about 90% (or about 91%, or about 92%, or about 93%, or about 94%, or about 95%, or about 96%, or about 97% or about 98% or about 99% or 100%) of acetate groups on raw material polyvinyl acetate that is used to form the polyvinyl alcohol are hydrolyzed. This enables the polyvinyl alcohol to be soluble in the reaction medium.

[0030] Further, the polyvinyl alcohol used to form the reaction product in the coating compositions of the present invention typically comprises polyvinyl alcohol having a degree of polymerization ranging from about 300 to about 5000. In desired embodiments, the polyvinyl alcohol used to form the reaction product in the coating compositions of the present invention comprises polyvinyl alcohol having a degree of polymerization ranging from about 400 to about 4000 (or from about 450 to about 2000; or from about 470 to about 1800; or any degree of polymerization between about 300 and about 5000).

[0031] In one desired embodiment of the present invention, the polyvinyl alcohol used to form the reaction product in the coating composition comprises hydrolyzed polyvinyl alcohol (e.g., above 95%) having a degree of polymerization ranging from about 470 to about 1800.

[0032] A number of commercially available polyvinyl alcohols may be used to form the reaction product in the coating compositions of the present invention. Suitable commercially available polyvinyl alcohols include, but are not limited to, OKS-1081, a hydrolyzed (hydrolysis mol.% from 98-99%) PVOH commercially available from Nihon Synthetic Chemical (City, State, Country) and having a degree of polymerization of 1800; OKS-8049, a hydrolyzed (hydrolysis mol.% from 99.0-99.6%) PVOH commercially available from Nihon Synthetic Chemical (City, State, Country) and having a degree of polymerization of 470; PVA105, a hydrolyzed (hydrolysis mol.% from 98-99%) PVOH commercially available from Kuraray America, Inc. (Houston, TX) and having a degree of polymerization of 500;; and EXCEVAL™ HR-3010, a hydrolyzed (hydrolysis mol.% from 99.0-99.6%) PVOH-ethylene copolymer commercially available from Kuraray America, Inc. (Houston, TX).

[0033] The one or more metal alkoxides used to form the reaction product in the coating compositions of the present invention may comprise any metal alkoxide. In one embodiment of the present invention, the metal alkoxide includes silicon alkoxide. Suitable silicon alkoxides for use in the present invention include, but are not limited to, methyltrimethoxysilane, tetraethoxysilane, vinyltrimethoxysilane, glycidoxypropyltrimethoxysilane, or any combination thereof. In one exemplary embodiment, the one or more

silicon alkoxides used to form the reaction product in the coating compositions of the present invention comprise methyltrimethoxysilane or tetraethoxysilane or a combination thereof. In another exemplary embodiment, the one or more silicon alkoxides used to form the reaction product in the coating compositions of the present invention comprises tetraethoxysilane.

[0034] A number of commercially available silicon alkoxides may be used to form the reaction product in the coating compositions of the present invention. Suitable commercially available silicon alkoxides include, but are not limited to, a methyltrimethoxysilane commercially available under the trade designation KBM-13 from Shin-Etsu Chemical Company, Ltd. (Tokyo, Japan); a tetraethoxysilane (TEOS) from any number of suppliers including Shin-Etsu Chemical Company, Ltd. under the trade designation KBE-04; a vinyltrimethoxysilane commercially available under the trade designation KBM-1003 from Shin-Etsu Chemical Company, Ltd.; and a glycidoxypropyltrimethoxysilane commercially available under the trade designation KBM-403 from Shin-Etsu Chemical Company, Ltd.

[0035] The coating compositions of the present invention comprise the above-described polyvinyl alcohol (PVOH) and metal alkoxide(s) (MA(s)) at a PVOH/MA ratio (i.e., "MA" representing the total amount of the one or more metal alkoxide(s) present in the coating composition) that may vary depending on a number of factors including, but not limited to, the PVOH used, the one or more metal alkoxides used, and the final properties desired in the cured coating formed from the coating composition. Typically, the coating compositions of the present invention comprise the above-described polyvinyl alcohol (PVOH) and metal alkoxide(s) (MA(s)) at a PVOH/MA ratio from about 9/1 (i.e., 9 parts by weight of PVOH to 1 part by weight of one or more metal alkoxides) to about 5/5. In some exemplary embodiments, the polyvinyl alcohol (PVOH) and one or more metal alkoxides (MA) are present at a PVOH/MA ratio of from about 8/2 to about 7/3.

[0036] The organic acid used to form the reaction product in the coating compositions of the present invention may comprise any organic acid. Suitable organic acids for use in the present invention include, but are not limited to, low molecular weight organic acids. As used herein, the term "low molecular weight organic acids" is used to refer to an organic acid having a molecular weight of less than 120 grams per mole of organic acid. In some embodiments, the organic acid used to form the reaction product in the coating compositions of the present invention comprises a carboxylic acid. In some desired embodiments, the organic acid used to form the reaction product in the coating compositions of the present invention comprises a carboxylic acid selected from formic acid, acetic acid, propionic acid, or a combination thereof.

[0037] The present invention is further directed to methods of making coating compositions. In one exemplary embodiment, the method of making a coating composition of the present invention comprises forming a mixture comprising polyvinyl alcohol in a solvent; adding an organic acid to the mixture; and subsequently adding one or more metal alkoxides to the mixture. As discussed above, in desired embodiments, the method comprises using an amount of the organic acid in the mixture so as to (1) catalyze a reaction between (i) hydroxyl groups on the polyvinyl alcohol and (ii) the one or more metal alkoxides, and (2) enable an esterification reaction between (i) any remaining hydroxyl groups (e.g., any percentage of the remaining hydroxyl groups, desirably, a large percentage (>50%, or >60%, or >70%, or >80%, or >90%, or >95%) of the remaining hydroxyl groups, or all of the remaining hydroxyl groups) on the polyvinyl alcohol (i.e., hydroxyl groups not reacted with the one or more metal alkoxides) and (ii) the organic acid.

[0038] Although the amounts of each reactant and the solvent may vary in the coating compositions of the present invention, typically, the polyvinyl alcohol is present in a given coating composition in an amount ranging from about 5% to about 20% parts by weight (pbw) of the coating composition; the one or more metal alkoxides are present in an amount ranging from about 1% to about 20% pbw of the coating composition; the organic acid is present in an amount ranging from about 1% to about 20% pbw of the coating composition; and the solvent is present in an amount ranging from about 60% to about 95% pbw of the coating composition, wherein all parts by weight are based on a total weight of the coating composition.

[0039] In some embodiments, the polyvinyl alcohol is present in an amount ranging from about 5% to about 20% pbw of the coating composition; the one or more metal alkoxides are present in an amount ranging from about 1% to about 20% pbw of the coating composition; the organic acid is present in an amount ranging from about 1% to about 10% pbw of the coating composition; and the solvent is present in an amount ranging from about 60% to about 95% pbw of the coating composition, wherein all parts by weight are based on a total weight of the coating composition. Regardless of the amount of each component, as discussed above, in desired embodiments, the coating composition has a PVOH/SA ratio of from about 9/1 to about 6/4 or 5/5, more desirably, a PVOH/SA ratio of from about 8/2 to about 7/3.

[0040] The methods of making coating compositions of the present invention may further comprise applying the coating composition onto a substrate, including any substrate that is suitable for the food packaging industry. The coating composition may be applied

onto a given substrate using any known coating method. Further, the coating composition may be applied onto any given substrate. In one exemplary embodiment, the coating composition is applied onto a substrate comprising a film. Such an exemplary embodiment is shown in FIG. 1.

[0041] As shown in FIG. 1, exemplary coating composition 10 of the present invention is coated onto an outer surface 21 of substrate 20. In this embodiment, substrate 20 comprises a film. However, it should be understood that exemplary coating composition 10 may also be applied to any number of various types of substrates including, but not limited to, a polymer substrate, a paper substrate, a metal foil substrate, a fabric, a hard surface (e.g., glass, wood, stone, etc.), or any other substrate.

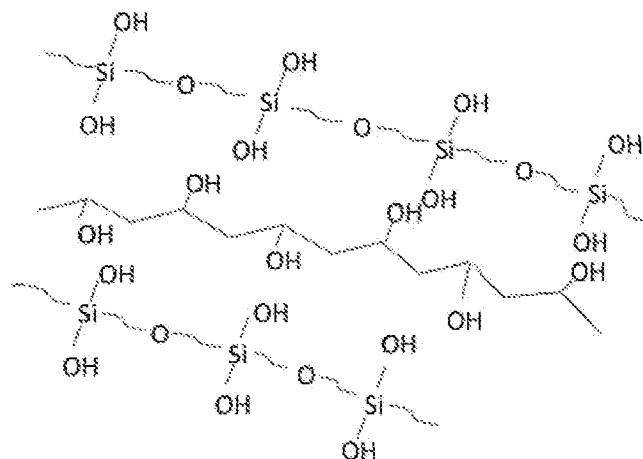
[0042] It should be understood that, in some embodiments, the coating composition may comprise (1) polyvinyl alcohol, (2) one or more metal alkoxides, (3) an organic acid, (4) a solvent system, and (5) one or more optional additives as discussed above. In other embodiments, the coating composition may consist essentially of (1) polyvinyl alcohol, (2) one or more metal alkoxides, (3) an organic acid, (4) a solvent system, and (5) one or more optional additives as discussed above. As used herein, the term “consists essentially of” is used to describe a coating composition that might unintentionally contain some residual component such as one or more impurities. In other embodiments, the coating composition consists of (1) polyvinyl alcohol, (2) one or more metal alkoxides, (3) an organic acid, (4) a solvent system, and (5) one or more optional additives as discussed above.

[0043] In addition, the methods of making coating compositions of the present invention may further comprise curing the coating composition to remove solvent (e.g., water, ethanol, or a combination thereof) so as to result in a cured coating of the present invention. Although the curing step may comprise a variety of parameters (e.g., temperature and period of time), typically, the curing step comprises heating the mixture or coating composition or coated composition (i.e., already coated onto a substrate) to a temperature of at least 50°C for a period of time of at least about 30 minutes. In other embodiments, the curing step comprises heating the mixture or coating composition or coated composition (i.e., already coated onto a substrate) to a temperature of from about 50 °C to about 140 °C for a period of time ranging from about 5 minutes to about 30 minutes (or from about 100°C to about 140 °C for a period of time ranging from about 2 minutes to about 10 minutes).

[0044] The resulting cured coating typically comprises up to 100 wt% of the reaction product formed from the polyvinyl alcohol, the one or more metal alkoxides, and the organic acid. As discussed above, the cured coating may comprise one or more optional additives.

Typically, the cured coating comprises from about 70 to 100 wt% of the reaction product formed from the polyvinyl alcohol, the one or more metal alkoxides, and the organic acid, and from about 30 wt% to 0 wt% of one or more additives, more typically, from about 85 to 100 wt% of the reaction product formed from the polyvinyl alcohol, the one or more metal alkoxides, and the organic acid, and from about 15 wt% to 0 wt% of one or more additives.

[0045] It is believed that the reaction product resulting from (i) a first reaction between the hydroxyl groups on the polyvinyl alcohol and the one or more metal alkoxides, and (ii) a second esterification reaction between remaining hydroxyl groups on the polyvinyl alcohol and the organic acid has a molecular structure that mimics the molecular structure of the PVOH polymer. In other words, the resulting reaction product has very little, if any, inorganic polymeric chains formed from the one or more metal alkoxides.



[0046] It should be understood that, in some embodiments, the cured coating may comprise (1) the reaction product of (i) polyvinyl alcohol, (ii) one or more metal alkoxides, and (iii) an organic acid, and (2) one or more optional additives as discussed above. In other embodiments, the cured coating may consist essentially of (1) the reaction product of (i) polyvinyl alcohol, (ii) one or more metal alkoxides, and (iii) an organic acid, and (2) one or more optional additives as discussed above. As used herein, the term "consists essentially of" is used to describe a cured coating that might unintentionally contain some residual component such as one or more impurities, one or more solvent components (e.g., trapped within the coating thickness), one or more unreacted reactants, or any combination thereof. In other embodiments, the cured coating consists of (1) the reaction product of (i) polyvinyl alcohol, (ii) one or more metal alkoxides, and (iii) an organic acid, and (2) one or more optional additives as discussed above. Ethanol may be added to the reaction mixture, which

controls the size of any particles formed during the reaction. This results in a stable coating composition (i.e., stable viscosity and extended shelf life). Add to the claims.

[0047] The cured coating desirably comprises a combination of properties that enable the cured coating to be used, for example, as a food packaging material. Two properties used to evaluate the cured coatings of the present invention are (1) the Water Rub Test, and (2) an Oxygen Transmission Rate test (i.e., the OTR test), both of which are described in the example section below. Desirably, the cured coatings of the present invention have a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 20. More desirably, the cured coatings of the present invention have a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 30 (or at least about 40, or at least about 50, or at least about 60, or at least about 70, or at least about 80, or at least about 90, or at least about 100). Desirably, the cured coatings of the present invention also pass the Water Rub Test using heated water (e.g., at from about 60 to 70°C, preferably, from about 70 to 80°C).

[0048] In addition, desirably, the cured coatings of the present invention have an oxygen transmission rate as measured using the OTR test at 23°C and at less than about 50% relative humidity of less than 50 cc/m²/day. More desirably, the cured coatings of the present invention have an oxygen transmission rate as measured using the OTR test at 23°C and at less than about 50% relative humidity of less than 45 cc/m²/day (or less than about 40 cc/m²/day, or less than about 30 cc/m²/day, or less than about 25 cc/m²/day, or less than about 20 cc/m²/day, or less than about 15 cc/m²/day, or less than about 10 cc/m²/day).

[0049] In some exemplary embodiments of the present invention, the cured coating has (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 20, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 50 cc/m²/day. In other exemplary embodiments of the present invention, the cured coating has (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 25 cc/m²/day. In yet other exemplary embodiments of the present invention, the cured coating has (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 10 cc/m²/day.

[0050] Desirably, the cured coatings of the present invention provide a desired degree of water resistance and oxygen transmission rate in higher relative humidity conditions. In

some exemplary embodiments of the present invention, the cured coating has (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at about 65% relative humidity of less than 10 cc/m²/day. In other exemplary embodiments of the present invention, the cured coating has (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at about 80% relative humidity of less than 50 cc/m²/day.

[0051] Desirably, the cured coatings of the present invention possess the above properties even while having a relative thin coating thickness. For example, in some exemplary embodiments of the present invention, the cured coating has the above-mentioned water resistance values and oxygen transmission rates when the cured coating has a coating thickness of less than 10 microns (μm). In other exemplary embodiments of the present invention, the cured coating has the above-mentioned water resistance values and oxygen transmission rates when the cured coating has a coating thickness of less than about 5 μm. In yet other exemplary embodiments of the present invention, the cured coating has the above-mentioned water resistance values and oxygen transmission rates when the cured coating has a coating thickness of less than about 1.0 μm.

[0052] The present invention is further directed to methods of using the disclosed coating compositions and cured coatings. In one exemplary embodiment, the method of using a coating composition of the present invention comprises applying the coating composition onto a substrate, and curing the coating composition. As discussed above, in some exemplary embodiments, the method of using a coating composition of the present invention comprises applying the coating composition onto a substrate, such as a film, so as to form a multi-layer article.

[0053] In other exemplary embodiments, the method of using a cured coating of the present invention comprises at least partially encompassing an item of food with the cured coating. In some exemplary embodiments, the method of using a coating composition or a cured coating of the present invention comprises shielding a food item from environmental exposure to oxygen so as to preserve the food item for an extended period of time. Such a use is depicted in FIG. 2.

[0054] As shown in FIG. 2, exemplary article 100 comprising one or more food items 40 packaged within one or more food packaging materials 10 and 30, wherein at least a portion of the one or more food packaging materials 10 and 30 comprises an exemplary cured coating 10 of the present invention. As shown in FIG. 2, exemplary cured coating 10

comprises an inner surface **11** and an outer surface **12**, while base container **30** comprises an inner surface **31**, an outer surface **32**, and an upper edge **33**. Food items **40** are supported by base container **30** (i.e., on inner surface **31**), which may comprise, for example, a paper product, a STYROFOAMTM product, or a molded polymeric product (e.g., a molded polypropylene product). Exemplary cured coating **10** forms a gas barrier between food items **40** and the environment along outer surface **12**.

[0055] The present invention is described above and further illustrated below by way of examples, which are not to be construed in any way as imposing limitations upon the scope of the invention. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

EXAMPLES

Materials Used:

[0056] The following materials as shown in Table 1 were used in the examples below. Even though the metal alkoxide utilized in the Examples is silicon alkoxide, any metal alkoxide may be used.

Table 1. Materials

Material	Product Description	Source
<i>PVOH Polymer or Co-Polymer</i>		
OKS-1081	a hydrolyzed PVOH (hydrolysis mol.% from 98-99%) having a degree of polymerization of 1800	Nihon Synthetic Chemical (Osaka, Japan)
OKS-8049	a hydrolyzed PVOH (hydrolysis mol.% from 99.0-99.6%) having a degree of polymerization of 470	
PVA105	a hydrolyzed PVOH (hydrolysis mol.% from 98-99%) having a degree of polymerization of 500	Kuraray America, Inc. (Houston, TX)
PVA217	a partially hydrolyzed PVOH (hydrolysis mol.% from 87-89%) having a degree of polymerization of 1700	
PVA235	a partially hydrolyzed PVOH (hydrolysis mol.% from 87-89%) having a degree of polymerization of 3500	
EXCEVAL TM HR-3010	a hydrolyzed PVOH-ethylene copolymer (hydrolysis mol.% from 99.0-99.6%)	

Silicon Alkoxides		
KBM-13	a methyltrimethoxysilane	Shin-Etsu Chemical Company, Ltd. (Tokyo, Japan)
KBE-04	a tetraethoxysilane (TEOS)	
KBM-1003	a vinyltrimethoxysilane	
KBM-403	a glycidoxypropyltrimethoxysilane	
Acids		
acetic acid	organic acid	Sigma-Aldrich Corporation (St. Louis, MO)
hydrochloric acid	inorganic acid	
lactic acid	organic acid	
citric acid	organic acid	
formic acid	organic acid	
propionic acid	organic acid	
valeric acid	organic acid	
nitric acid	inorganic acid	
Solvent Components		
deionized water	deionized water	Sigma-Aldrich Corporation (St. Louis, MO)
ethanol	ethanol	
Inorganic nano-particle fillers		
LUDOX SM	Colloidal silica	W. R. Grace Columbia, MD, USA
LUDOX SM-AS	Colloidal silica	
LUDOX AS30	Colloidal silica	
LUDOX AS40	Colloidal silica	
LUDOX HS30	Colloidal silica	

Sample Preparation Method:

The gas and moisture barrier coating formulation is prepared by the following:

[0057] A solution of PVOH is prepared by mixing 10g of PVOH in 900g of deionized water using a mechanical disperser at room temperature. After 20 minutes of mixing, the PVOH dispersion is heated at 95°C for 4 hrs, whereby the PVOH is dissolved and a solution containing 10% by weight of PVOH is obtained. 27g of the PVOH solution is diluted to 5% by adding 13.5g DI water, and then 1.157g of the silicon alkoxide (100%), 1.12g of the acid catalyst, and 13.5 g of the alcohol (95%) is added while stirring for 10 minutes at room temperature. This reaction mixture is stirred for about one hour at room temperature until the reaction is complete. A stable coating formulation is obtained.

The cured gas and moisture barrier film is prepared by the following:

[0058] 10 g/ml of the coating formulation is applied onto a substrate (polypropylene or PET sheet obtained from Teijin Limited) using a pipette. The coating

formulation is spread out on the substrate to form a film having a wet thickness of 20-80 microns using an application bar available from KBY. The coated film is then cured for 3~10 minutes at 100°C~140°C to form a cured coating/film having a thickness of 1-4 microns.

Test Methods:

[0059] The following test methods were used in the Examples.

Water Resistance Tests

[0060] For a given cured coating sample, the sample was subjected to various tests to evaluate water or moisture resistance of the cured coating samples. These tests are described as follows:

1) Water Rub Test (ASTM D4752)

[0061] A cured coated film as prepared above in the Sample Preparation Method is locked onto a glass plate which is placed on a stable table. Using a spinal clip, a 5cm x 5cm of white cotton fabric is attached to the finger of the crock meter. The fabric on finger of the crock meter is lowered onto the coated film. The hand crank is turned at the rate of one turn per second for 50 cycles. The white cotton fabric rubbing test cloth is visually examined for any deposition of coating thereon, and coated film is examined to determine there is any change in appearance and transparency. If the appearance of the cured film changes, the hand crank is stopped, and the number of cycles is recorded.

2) Boiling Water Test

[0062] A cured coated film as prepared above in the Sample Preparation Method is dipped into 100°C boiling water for 20 seconds. The film is then removed from the water and the cured coating surface is visually observed for defects and tackiness. The film surface is then allowed to dry at 100 centigrade for 2 minutes. The film is again visually examined for defects, tackiness and transparency. If the film has no defects, is not tacky, and is transparent, it is characterized as having good water resistance.

Oxygen Transmission Rate Test

[0063] For a given cured coating sample as prepared above in the Sample Preparation Method, the gas barrier properties of the sample were evaluated to measure oxygen transmission rate by using the MOCON method (JIS K7126-2/ASTM D3985). This method is a steady-state, isostatic technique that uses a coulometric sensor. A Mocon Oxtran 2/20 commercially available from Mocon, Inc. (Minneapolis, MN USA) was utilized in the test. This test is described as follows:

[0064] The coated film sample as prepared above in the Sample Preparation Method is cut to form a 10cm×10cm sample and placed in the instrument. The temperature is set to 23°C and the instrument is set to convergence mode. Air passes on one side of the sample and nitrogen passes on the other side. The amount of oxygen that permeates through the sample to the nitrogen stream is measured by the sensor. The test is performed over a period of 24 hours.

Contact Angle Test

[0065] For a given cured coating sample as prepared above in the Sample Preparation Method, the surface properties of the sample are evaluated to measure hydrophobicity of the coating by the half-angle measuring method (ASTM D7334-08) described in U.S. Pat. No.5,268,733 using a Tantec CAM-Plus contact angle meter available from ChemInstruments International (Mentor, OH USA). The lower the contact angle, the more hydrophilic is the film. The contact angle is defined as the angle between the film surface and the tangent line at the point of contact of the liquid droplet with the film. The value of the contact angle of the liquid droplet will depend upon the surface energy of the film and the surface tension of the liquid. If complete wetting takes place between the liquid and the film surface, the droplet will spread out over the film and the contact angle will approach zero, whereas if wetting is only partial, the resulting contact angle will lie in the range of 0 to 180 degrees.

Example 1 - Effect of Acid Catalyst on Coating Properties

[0066] Samples 1-7 were prepared by mixing OKS-1081 into a solvent system comprising a 1:1 weight ratio of deionized water and ethanol so as to provide a solid content of 5 wt% (i.e., 27 g OKS-1081 was added to 60.55 g of DI/ethanol). A given acid and silicon alkoxide were then added to the mixture. Each mixture was stirred for an hour at room temperature (23°C). The parts by weight of each component are provided in Table 2 below.

Table 2. Sample Compositions

Sample No.	PVOH	Silicon Alkoxides			Acid Catalyst			
	OKS-1081	KBM 13	TEOS	KBM 1003	Acetic acid	Hydro-chloric acid	Lactic acid	Citric acid
1	7	3			2.8			
2	7	3				2.8		
3	7	3					2.8	
4	7	3						2.8
5	7		3		2.8			
6	7			3	2.8			
7	7			3		2.8		

[0067] Each sample was formed into a cured coating by coating a given sample onto a polypropylene film so as to produce a 2.0 μm cured coating thickness, and curing each coating at 100°C for 7 minutes. Each cured coating was subsequently tested for water resistance and oxygen transmission rate using the Water Rub Test and the Oxygen Transmission Rate (OTR) Test described above. Samples 1, 5 and 6 are Samples of the subject invention and Samples 2-4 and 7 are comparative. The results are shown in Table 3 below.

Table 3. Sample Test Results

Sample No.	Water Resistance Test (Water Rub Test) (cycles at room temperature)	OTR (cc/m^2 day atm) 23°C 65% RH
1	>50	8.3
2	30	285.57
3	<10	NM
4	<10	NM
5	>50	1.2
6	>50	27.52
7	>50	259.10

NM=not measured

Example 2 - Effect of PVOH Polymer/Co-Polymer on Coating Properties

[0068] Samples 8-19 were prepared by mixing a given PVOH into a solvent system comprising a 1:1 weight ratio of deionized water and ethanol so as to provide a solid content of 5 wt% (i.e., 27 g PVOH was added to 60.55 g of DI/ethanol). A given acid and silicon alkoxide were then added to the mixture. Each mixture was stirred for an hour at room temperature (23°C). Samples 9-16 are Samples of the subject invention and Samples 8 and 17-19 are comparative. The parts by weight of each component are provided in Table 4 below.

Table 4. Sample Compositions

Sample No.	PVOH						Silicon Alkoxides				Acid Catalyst
	OKS 1081	OKS 8049	PVA 105	PVA 217	PVA 235	HR 3010	KBM 13	TEOS	KBM 1003	KBM 403	Acetic acid
8	9						1				3.6
9	8						2				3.2
10	7						3				2.8
11	7							3			2.8
12	7								3		2.8

13	7								3	2.8
14		7					3			2.8
15			7				3			2.8
16			7					3		2.8
17				7			3			2.8
18					7		3			2.8
19						7	3			2.8

[0069] Each sample was formed into a cured coating by coating a given sample onto a polypropylene film so as to produce a 2.0 μm cured coating thickness, and curing each coating at 100°C for 7 minutes. Each cured coating was subsequently tested for water resistance and oxygen transmission rate using the Water Rubbing Test and the Oxygen Transmission Rate (OTR) Test described above. The results are shown in Table 5 below.

Table 5. Sample Test Results

Sample No.	Coating thickness (μ)	Water Resistance (Water Rub Test) (cycles at room temperature)	OTR (cc/m^2 day atm)		
			23°C <50% RH	23°C 65% RH	23°C 80% RH
8	1	20	NM	>800	>800
9	1	50	4.53	NM	NM
10	1	>50	5.07	24	300
	4	>50	NM	8.3	139
	7	>50	NM	5.5	NM
11	1	>50	0.15	NM	NM
	4	>50	NM	1.1	49
	10	>50	NM	1.5	10
12	1	>50	27.52	NM	NM
13	1	>50	15.93	NM	NM
14	1	>50	9.82	NM	NM
15	1	>50	4.51	42	400
	4	>50	NM	13	117
	7	>50	NM	8.3	NM
16	4	>50	NM	1.3	61
17	1	>50	288.82	NM	NM
18	1	>50	187.44	NM	NM
19	1	>50	10.39	NM	NM

NM= not measured

Example 3 – Contact Angle and Hot Water Resistance of Cured Coatings Using Various Acid Catalysts

[0070] Samples 20-26 and a control sample were prepared by mixing OKS-1081 into a solvent system comprising a 1:1 weight ratio of deionized water and ethanol so as to

provide a solid content of 5 wt% (i.e., 27 g OKS-1081 was added to 60.55 g of DI/ethanol). A given acid and TEOS were then added to the mixtures of samples 20-26. Each mixture was stirred for an hour at room temperature (23°C). The parts by weight of each component are provided in Table 6 below.

Table 6. Sample Compositions

Sample No.	Composition							
	PVOH OKS 1081	Silicon alkoxide TEOS	Acid Catalyst					
			carboxylic acid				inorganic acid	
			formic acid	acetic acid	propionic acid	valeric acid	nitric acid	HCL
Control	7							
20	7	3	2.8					
21	7	3		2.8				
22	7	3			2.8			
23	7	3				2.8		
24	7	3					0.04	
25	7	3					0.33	
26	7	3						0.33

[0071] Each sample was formed into a cured coating by coating a given sample onto a polypropylene film so as to produce a 2.0 μm cured coating thickness, and curing each coating at 100°C for 7 minutes. Each cured coating was subsequently tested for Contact Angle and water resistance using the Water Rub Test and Boiling Water Test described above. Samples 20-23 are Samples of the subject invention and Samples 24-26 are comparative. The results are shown in Table 7 below.

Table 7. Sample Test Results

Sample No.	pH	contact angle	Water resistance		
			Water Rub Test (cycles at room temperature)	Boiling Water Test (30 sec)	
				60-70°C	70-80°C
Control	5	24.4			
20	2.58	49.2	50<	Pass	Pass
21	3.54	55.4	50<	Pass	Pass
22	3.89	48.4	50<	Pass	Pass

23	4.31	41.6	50<	Pass	Pass
24	3.4	NM	1	Fail	NM
25	1.86	29	50<	Pass	Failure
26	1.62	32.8	50<	Pass	Failure

NM = Not Measured

[0072] As shown in Table 7, Samples 25-26 give a slightly higher contact angle after sol-gel reaction when compared to the control. Consequently, the water resistance of the cured coatings of Samples 25-26 shows improvement; however, water resistance is poor.

[0073] In comparison, Samples 20-23, which use relatively low molecular weight carboxyl acids, give high contact angles indicating stronger hydrophobicity. Further, cured coatings of Samples 20-23 also provide better water resistance possibly due to less steric hindrance during esterification.

[0074] While the specification has been described in detail with respect to specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Further, as discussed above, it should be understood that the coating compositions, coatings or films made therefrom, and methods of making and using the same of the present invention may comprise, consist essentially of, or consist of any one or combination of the herein-described components/steps/features of the disclosed compositions, coatings or films made therefrom, and methods of making and using the same. For example, the coating compositions, coatings or films made therefrom, and methods of making and using the same of the present invention may comprise, consist essentially of, or consist of one or more of the above-described components. In addition, the coating compositions, coatings or films made therefrom, and methods of making and using the same of the present invention may comprise, consist essentially of, or consist of one or more of the above-described components along with other components not specifically discussed herein. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto. All parts and percentages in the examples, as well as in the remainder of the specification, are by weight unless otherwise specified. Further, any range of numbers recited in the specification or claims, such as that representing a particular set of properties, units of measure, conditions, physical states or percentages, is intended to literally incorporate expressly herein by reference or otherwise, any number falling within

such range, including any subset of numbers within any range so recited. For example, whenever a numerical range with a lower limit, R_L , and an upper limit R_U , is disclosed, any number R falling within the range is specifically disclosed. In particular, the following numbers R within the range are specifically disclosed: $R = R_L + k(R_U - R_L)$, where k is a variable ranging from 1% to 100% with a 1% increment, e.g., k is 1%, 2%, 3%, 4%, 5%. ... 50%, 51%, 52%. ... 95%, 96%, 97%, 98%, 99%, or 100%. Moreover, any numerical range represented by any two values of R , as calculated above is also specifically disclosed. Any modifications of the invention, in addition to those shown and described herein, will become apparent to those skilled in the art from the foregoing description and accompanying drawings. Such modifications are intended to fall within the scope of the appended claims. All publications cited herein are incorporated by reference in their entirety.

WHAT IS CLAIMED IS:

1. A coating composition comprising a reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid.
2. The coating composition of claim 1, further comprising a solvent, said solvent comprising water, methanol, ethanol, or a combination thereof.
3. The coating composition of claim 1 or 2, further comprising one or more optional additives, said one or more optional additives comprising a colorant, inorganic nano-particle filler, crosslinker, antioxidants, adhesion promoters, oxygen scavenger, or a combination thereof.
4. The coating composition of any one of claims 1 to 3, wherein said polyvinyl alcohol is solubilized hydrolyzed and has a degree of polymerization ranging from about 300 to about 5000.
5. The coating composition of any one of claims 1 to 4, wherein said polyvinyl alcohol is fully hydrolyzed and has a degree of polymerization ranging from about 500 to about 3500.1000
6. The coating composition of any one of claims 1 to 5, wherein said polyvinyl alcohol (PVOH) and said one or more metal alkoxides (MA) are present at a PVOH/MA ratio of from about 9/1 to about 5/5.
7. The coating composition of any one of claims 1 to 6, wherein said polyvinyl alcohol (PVOH) and said one or more metal alkoxides (MA) are present at a PVOH/MA ratio of from about 8/2 to about 7/3.
8. The coating composition of any one of claims 1 to 7, wherein said one or more metal alkoxides comprise one or more silicon alkoxides.

9. The coating composition of any one of claims 1 to 8, wherein said one or more silicon alkoxides comprise tetraethoxysilane, methyltrimethoxysilane, vinyltrimethoxysilane, glycidoxypropyltrimethoxysilane, or any combination thereof.

10. The coating composition of any one of claims 1 to 9, wherein said organic acid comprises a carboxylic acid.

11. The coating composition of any one of claims 1 to 10, wherein said organic acid comprises a carboxylic acid selected from formic acid, acetic acid, propionic acid, or a combination thereof.

12. The coating composition of any one of claims 1 to 11, wherein said organic acid comprises acetic acid.

13. The coating composition of any one of claims 1 to 12, wherein said polyvinyl alcohol is present in an amount ranging from about 5% to about 20% parts by weight (pbw) of said coating composition, said one or more metal alkoxides are present in an amount ranging from about 1% to about 20% pbw of said coating composition, said organic acid is present in an amount ranging from about 1% to about 10% pbw of said coating composition, and a solvent is present in an amount ranging from about 65% to about 90% pbw of said coating composition, wherein all parts by weight are based on a total weight of said coating composition.

14. The coating composition of any one of claims 1 to 13, wherein said polyvinyl alcohol is present in an amount ranging from about 5% to about 20% pbw of said coating composition, said one or more metal alkoxides are present in an amount ranging from about 1% to about 20% pbw of said coating composition, said organic acid is present in an amount ranging from about 1% to about 10% pbw of said coating composition, and a solvent is present in an amount ranging from about 65% to about 90% pbw of said coating composition, wherein all parts by weight are based on a total weight of said coating composition.

15. The coating composition of any one of claims 1 to 14, wherein said reaction product has a molecular structure formed via (i) a first reaction between some hydroxyl groups of said

polyvinyl alcohol and said one or more metal alkoxides, and (ii) a second esterification reaction between remaining hydroxyl groups on said polyvinyl alcohol and said organic acid.

16. The coating composition of any one of claims 1 to 15, wherein said coating composition consists essentially of (i) said reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid, and (ii) one or more optional additives selected from the group consisting of a colorant, inorganic nano-particle filler, crosslinker, antioxidants, adhesion promoters, oxygen scavenger, or a combination thereof.

17. The coating composition of any one of claims 1 to 15, wherein said coating composition consists of (i) said reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid, and (ii) one or more optional additives selected from the group consisting of a colorant, inorganic nano-particle filler, crosslinker, antioxidants, adhesion promoters, oxygen scavenger, or a combination thereof.

18. The coating composition of any one of claims 1 to 17 coated onto a substrate.

19. The coating composition of any one of claims 1 to 17 coated onto a substrate, wherein the substrate comprises a film.

20. A cured coating comprising the coating composition of any one of claims 1 to 17.

21. The cured coating of claim 20, wherein said cured coating having (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 20, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 50 cc/m²/day.

22. The cured coating of claim 20 or 21, wherein said cured coating having (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 25 cc/m²/day.

23. The cured coating of any one of claims 20 to 22, wherein said cured coating having (i) a water resistance as measured using the Water Rub Test, using water at room temperature,

of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 10 cc/m²/day.

24. The cured coating of any one of claims 20 to 23, wherein said cured coating having (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at about 65% relative humidity of less than 10 cc/m²/day.

25. The cured coating of any one of claims 20 to 24, wherein said cured coating having (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at about 80% relative humidity of less than 50 cc/m²/day.

26. The cured coating of any one of claims 20 to 25, wherein said cured coating has a coating thickness of less than 10 microns (μm).

27. The cured coating of any one of claims 20 to 26, wherein said cured coating has a coating thickness of less than about 5 μm.

28. The cured coating of any one of claims 20 to 27, wherein said cured coating has a coating thickness of up to about 1.0 μm.

29. The cured coating of any one of claims 20 to 28, wherein said cured coating possesses a contact angle of at least 40 degrees.

30. The cured coating of any one of claims 20 to 29, wherein said coating possesses a contact angle of at least 45 degrees.

31. A coated substrate comprising a substrate and a coating thereon, said coating comprising the cured coating of any one of claims 20 to 30.

32. The coated substrate of claim 31, wherein the substrate comprises a film.

33. The coated substrate of claim 31, wherein the substrate further comprises an oxygen scavenging film.

34. An article comprising one or more food items packaged within one or more food packaging materials, wherein at least a portion of said one or more food packaging materials comprises the cured coating of any one of claims 20 to 33.

35. A method of making the coating composition of any one of claims 1 to 17, said method comprising:

forming a mixture comprising the polyvinyl alcohol in a solvent;

adding the organic acid to the mixture; and

adding the one or more metal alkoxides to the mixture;

wherein an amount of the organic acid is added to the mixture so as to (1) catalyze a reaction between (i) hydroxyl groups on the polyvinyl alcohol and (ii) the one or more metal alkoxides, and (2) enable an esterification reaction between (i) remaining hydroxyl groups on the polyvinyl alcohol and (ii) the organic acid.

36. The method of claim 35, further comprising:

applying the coating composition onto a substrate.

37. The method of claim 36, wherein the substrate comprises a film.

38. The method of any one of claims 35 to 37, further comprising curing the coating composition to remove solvent.

39. The method of any one of claims 35 to 37, wherein the solvent comprises water, alcohols, glycols, or a combination thereof.

40. The method of claim 38, wherein said curing step comprises heating the mixture to a temperature of at least 100°C for a period of time of at least about 5 minutes.

41. A coating comprising a reaction product of polyvinyl alcohol and one or more metal alkoxides;

wherein the coating possesses (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 20, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 50 cc/m²/day.

42. The coating of claim 41, wherein said coating possesses (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 25 cc/m²/day.

43. The coating of claim 41, wherein said coating possesses (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at less than about 50% relative humidity of less than 10 cc/m²/day.

44. The coating of claim 41, wherein said coating possesses (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at about 65% relative humidity of less than 10 cc/m²/day.

45. The coating of claim 41, wherein said coating possesses (i) a water resistance as measured using the Water Rub Test, using water at room temperature, of at least about 50, and (ii) an oxygen transmission rate as measured at 23°C and at about 80% relative humidity of less than 50 cc/m²/day.

46. The coating of claim 41, wherein said coating has a coating thickness of less than 10 microns (μm).

47. The coating of claim 41, wherein said coating has a coating thickness of less than about 5 μm.

48. The coating of claim 41, wherein said coating has a coating thickness of up to about 1.0 μm.

49. A coating comprising a reaction product of polyvinyl alcohol, one or more metal alkoxides, and an organic acid;

wherein the coating possesses a contact angle of at least 35 degrees.

50. The coating of claim 49, wherein said coating possesses a contact angle of at least 40 degrees.

51. The coating of claim 49, wherein said coating possesses a contact angle of at least 45 degrees.

52. A gas and moisture barrier coating comprising a reaction product of polyvinyl alcohol, and one or more metal alkoxides;

wherein the coating possesses a contact angle of at least 35 degrees.

53. The coating of claim 52, wherein said coating possesses a contact angle of at least 40 degrees.

54. The coating of claim 52, wherein said coating possesses a contact angle of at least 45 degrees.

FIG. 1

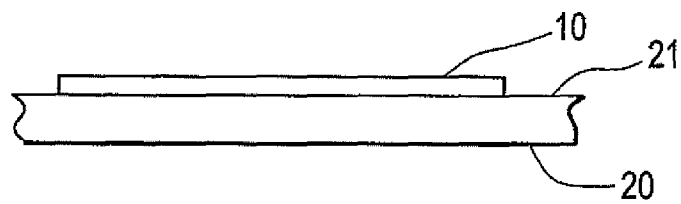


FIG. 2

