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(54) Title: ANTIMICROBIAL AGENT FOR POWDER COATING COMPOSITIONS

(57) Abstract: A microbe-resistant powder coating composition including an antimicrobial agent is described. The antimicrobial agent is an inorganic bismuth-containing compound, and may be used in conjunction with other bismuth-containing compounds or other biocidal agents or methods.



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ANTIMICROBIAL AGENT FOR POWDER COATING COMPOSITIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to U.S. Provisional Patent Application No. 62/164,870 filed May 21, 2015, the disclosure of which is herein incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

[002] Coatings are typically applied to substrates to provide protective or decorative qualities, and can be applied to a wide variety of substrates. Coatings, particularly powder coatings, have a broad range of residential and commercial uses, including uses where many people come in contact with the same surface and surface contamination is common. Due to the broad range of applications, there is a longstanding need in the industry for a powder coating composition that can resist or even prevent microbial growth, including bacterial and fungal growth on coated surfaces. Microbial contamination constitutes a health problem, especially indoors, and can also have significant impact on the aesthetic appearance of a coating.

[003] Antimicrobial coatings are generally recognized in the powder coating industry. However, many such coatings include antimicrobial additives that are potentially toxic and create significant health hazards. Conventional antimicrobials include, for example, inorganic nano-compounds (silver or copper), ligating species, organic compounds capable of absorption by microbes, and known pesticides or biocides. Additionally, some antimicrobial additives may be difficult to combine with standard powder coating compositions. Other conventional antimicrobial components can be rendered ineffective over time due to abrasion and general wear of the coating. Additionally, several antimicrobials may not be economically feasible.

SUMMARY

[004] The present description discloses a microbe-resistant powder coating composition that preferably includes at least a polymeric binder, pigment and an antimicrobial agent. In certain embodiments, the present description includes a powder coating composition having an antimicrobial agent, a method of creating a coated article from the powder

coating composition possessing an antimicrobial agent, and a coated article having an antimicrobial coating present in the coating.

[005] In one embodiment, the powder coating composition preferably includes an effective amount of at least one antimicrobial agent including at least one inorganic bismuth-containing compound. The inorganic bismuth-containing compound may be a multivalent bismuth salt of various anions. In another embodiment, the inorganic bismuth-containing compound is bismuth aluminate. The antimicrobial agent of this disclosure when incorporated into a powder coating composition and subsequently applied onto an article offers antimicrobial activity without incorporating toxic or harmful compounds, poisons, heavy metals or volatile compounds generally recognized with conventional antimicrobial agents.

[006] In another embodiment, the present description includes a method of forming a powder coating composition containing an effective amount of at least one antimicrobial agent including at least an inorganic bismuth-containing compound. The antimicrobial agent may be premixed with a polymeric binder, one or pigments and other optional additives to form a suitable powder coating composition through conventional melt processing practices and equipment.

[007] In yet another embodiment, this disclosure describes a method of forming a coated article with the powder coating composition having an effective amount of at least one antimicrobial agent having at least one inorganic bismuth-containing compound. The powder coating composition may be deposited onto at least a portion of an article. The composition may be subsequently formed into a film to create a coated article.

[008] The above summary of the present invention is not intended to describe each disclosed embodiment or every implementation of the present invention. The description that follows more particularly exemplifies illustrative embodiments. In several places throughout the application, guidance is provided through lists of examples, which can be used in various combinations. In each instance, the recited list serves only as a representative group and should not be interpreted as an exclusive list.

[009] The details of one or more embodiments of the invention are set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description, and from the claims.

SELECTED DEFINITIONS

[010] Unless otherwise specified, the following terms as used herein have the meanings provided below.

[011] The term “antimicrobial agent” refers to a compound or component that kills microorganisms or inhibits their growth. A microorganism in this context can be any microbe or microscopic organism, including for example, a bacterium, a fungus, or a virus. As used herein, the term “antimicrobial” includes compounds or components regarded as being “antibacterial” or “antifungal.”

[012] As used herein, the term “microbe-resistant,” when applied to a coating composition, means a coating composition that includes an effective amount of an antimicrobial agent to produce a biostatic effect (e.g. significantly reduce microbial contamination) or even a biocidal effect (e.g. eliminate microbial contamination).

[013] The term “bismuth aluminate” refers to either the hydrated or anhydrous form of the compound.

[014] The term “component” refers to any compound that includes a particular feature or structure. Examples of components include compounds, monomers, oligomers, polymers, and organic groups contained therein.

[015] The term “effective amount” when used in conjunction with an antimicrobial agent refers to an amount sufficient to at least measurably impede the growth of microbes.

[016] The term “on”, when used in the context of a coating applied on a surface or substrate, includes both coatings applied directly or indirectly to the surface or substrate. Thus, for example, a coating applied to a primer layer overlying a substrate constitutes a coating applied on the substrate.

[017] The term “powder coating” as used herein, refers to a process that generally deposits a powder composition onto an article. In certain embodiments, the powder may be electrostatically charged to assist in the deposition of the coating composition onto the article. A film is subsequently formed from the powder coating composition by heating, for example, to create a coated article.

[018] As used herein, the term “powder coating system” refers to the powder coating composition, the substrate to be coated, and any and all associated equipment required to carry out a powder coating operation.

[019] Unless otherwise indicated, the term “polymer” includes both homopolymers and copolymers (i.e., polymers of two or more different monomers).

[020] The term “comprises” and variations thereof do not have a limiting meaning where these terms appear in the description and claims.

[021] The terms “preferred” and “preferably” refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

[022] As used herein, “a,” “an,” “the,” “at least one,” and “one or more” are used interchangeably. Thus, for example, a coating composition that comprises “an” additive can be interpreted to mean that the coating composition includes “one or more” additives.

[023] Also herein, the recitations of numerical ranges by endpoints include all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.). Furthermore, disclosure of a range includes disclosure of all subranges included within the broader range (e.g., 1 to 5 discloses 1 to 4, 1.5 to 4.5, 1 to 2, etc.).

DETAILED DESCRIPTION

[024] The present description provides a microbe-resistant powder coating composition that includes an antimicrobial agent. Certain embodiments of the powder coating compositions may include, for example, at least a polymeric binder, and the antimicrobial agent of this disclosure, and optional components including, for example: one or more pigments, crosslinking agents, dispersing agents, additives, fillers or combinations thereof. In an aspect, the coating composition preferably resists microbial growth. Preferred embodiments incorporate at least one or more pigments in the powder coating composition. However, clear powder coating compositions without pigments may benefit from the incorporation of the disclosed inorganic bismuth-containing compound as an antimicrobial agent.

[025] The powder composition may be any type of organic, inorganic, or hybrid coating, or combinations thereof that preferably incorporate the disclosed antimicrobial agent. Preferred powder coating composition may include a polymeric binder or film forming

polymer, one or more pigments, and optionally, a curing or crosslinking agent for the polymer, along with one or more optional additives.

[026] In some embodiments, the individual components of the powder coating compositions are generally premixed and processed, typically at elevated temperatures near or exceeding the melting point or softening point of the polymeric binder or binders, by means of a conventional polymer processing techniques, such as extrusion. The resulting melt-blended mixture typically is solidified and subsequently comminuted into a desired particulate size or size distribution. Depending on the desired coating end use, the comminuting conditions may be adjusted to preferably achieve a median particle size of about 25-150 microns.

[027] The polymeric binder may be selected from any polymer or combination of polymers that are capable of providing the desired film properties. Embodiments of this disclosure contemplate the use of thermoset polymers, thermoplastic polymers, or a combination thereof to form the powder coating composition. Non-limiting examples of suitable polymeric binders include an epoxy, a polyamide, a polyepoxide, acrylic, polyurethane, polyester, polyvinyl chloride, fluoropolymer, silicone or combinations thereof. Acrylics, epoxies, polyurethanes and polyesters are particularly preferred. The polymeric binder may represent at least 40 wt%, preferably at least 60 wt%, more preferably at least 80 wt% and even more preferably at least 90 wt % of the total powder coating composition. In other embodiments, the polymeric binder comprises less than 99.5 wt%, preferably less than 95 wt%, more preferably less than 85 wt% and even more preferably less than 80 wt % based on the total weight of the powder coating composition.

[028] In certain embodiments, a crosslinking agent may be utilized. Those of ordinary skill in the art are capable of selecting a crosslinking agent to match a polymeric binder employed in a powder coating composition. Non-limiting examples of preferred polymeric binders with crosslinking agents include the following: carboxyl-functional polyester resins cured with epoxide-functional compounds such as triglycidylisocyanurate (TGIC), carboxyl-functional polyester resins cured with polymeric epoxy resins, carboxyl-functional polyester resins cured with hydroxyalkyl amides (PRIMID), hydroxyl-functional polyester resins cured with blocked isocyanates or uretdiones, epoxy resins cured with amines such as dicyandiamide, epoxy resins cured with phenolic-functional resins, epoxy resins cured with carboxyl-functional curatives, carboxyl-functional acrylic

resins cured with polymeric epoxy resins, hydroxyl-functional acrylic resins cured with blocked isocyanates or uretdiones, unsaturated resins curing through free radical reactions, and silicone resins used either as the sole binder or in combination with organic resins. Crosslinking agents may be included in the powder coating compositions at levels of 0.5 wt% or greater, preferably 1 wt% or greater, more preferably 2 wt% or greater and most preferably 5 wt% or greater. The crosslinking agent may be included at levels up to about 50 wt%, preferably up to about 35 wt%, more preferably up to about 25 wt% and most preferably up to about 10 wt%.

[029] In an aspect, the powder coating composition may include one or more pigment components, including pigments used to tone or opacify the film formed from the coating composition. Suitable examples of pigments include, without limitation, titanium dioxide white, carbon black, lamp black, black iron oxide, red iron oxide, yellow iron oxide, brown iron oxide (a blend of yellow and red oxide with black oxide), phthalocyanine green, phthalocyanine blue, organic reds (such as naphthol red, quinacridone red and toluidine red), quinacridone magenta, quinacridone violet, DNA orange, and/or organic yellows (such as Hansa yellow), for example. In some embodiments, a stable colorant dispersion may be employed. A stable colorant dispersion may include dyes, one or more pigments or a combination thereof. In another aspect, one or more pigments may include a core particle and at least a partial shell about the core particle. In certain embodiments, the one or more pigments may comprise about 50 wt% or less, preferably 30 wt% or less, more preferably 15 wt% or less and even more preferably 5 wt% or less. In other embodiments, a pigment may not be included in the powder coating composition.

[030] Accordingly, in one embodiment, the present description may include an inorganic bismuth-containing compound as antimicrobial agent to prevent, reduce or at least partially eliminate microbial contamination or growth on a coated article. A variety of such antimicrobial agents may be employed. Specific bismuth-containing antimicrobial agents may be selected based upon, for example, the microorganism(s) to be treated; the physical and chemical compatibility of the antimicrobial agent with the system to be treated; the stability of the antimicrobial agent under storage conditions; and toxicity, along with other environmental, and economical factors. The antimicrobial agent desirably is non-allergenic material with low human toxicity. Mixtures of antimicrobial agents, which may or may not have synergistic activity, may also be used.

[031] Accordingly, in an aspect, the antimicrobial agent includes at least a bismuth-containing compound, preferably an inorganic bismuth compound, more preferably multivalent bismuth salts of various anions, and most preferably an inorganic bismuth salt of a metal oxyanion. These compounds include their anhydrous forms as well as various hydrates, including hemihydrate, pentahydrate, and other hydrated forms, along with mixtures and combinations thereof, and the like.

[032] Suitable examples of such bismuth salts of various anions include, without limitation, bismuth silicate, bismuth magnesium aluminosilicate, bismuth aluminate, bismuth borate, bismuth manganate, bismuth phosphate, and the like. In a preferred aspect, the inorganic bismuth-containing compound is a bismuth salt of a metal oxyanion, such as, for example, bismuth aluminate, bismuth manganate, and mixtures or combinations thereof, and the like.

[033] In some embodiments, the inorganic bismuth compound may measurably impede the growth of microbes as indicated by the presence of Colony Forming Units. For example, the presence of an inorganic bismuth-containing compound may reduce the growth of microbes by at least 10%, at least 15% or preferably at least 20% over powder coating compositions without an inorganic bismuth-containing compound or any antimicrobial agent. In other embodiments, the presence of an inorganic bismuth-containing compound may reduce microbial colonies introduced to a coated article by at least 5%, preferably by at least 10%, more preferably by a 1-log reduction and even more preferably by a 2-log reduction.

[034] In some embodiments, the inorganic bismuth-containing compound may be used with one or more organic bismuth-containing compounds, including, for example, bismuth subcarbonate, bismuth subcitrate, bismuth citrate, bismuth titrate, bismuth gallate, bismuth subgallate, bismuth salicylate, bismuth subsalicylate, and the like, for example. The inorganic bismuth-containing compound may be used with one or more other inorganic bismuth-containing compounds, e.g. bismuth compounds that are not metal oxyanions of bismuth. Suitable examples of such compounds include, without limitation, bismuth hydroxide, bismuth trioxide, bismuth nitrate, bismuth subnitrate, and the like, and mixtures or combinations thereof.

[035] Many inorganic compounds are considered difficult to use as antibacterial agents and many have serious drawbacks including environmental toxicity and cost. Surprisingly,

an inorganic bismuth-containing compound, such as bismuth aluminate, demonstrates effective antimicrobial activity when used in a powder coating composition, are relatively inexpensive, and are not toxic to the environment.

[036] Moreover, many conventional biocide or biosurfactant systems currently used with coating compositions are used primarily to reduce or inhibit biofilm formation, e.g. sessile microorganism contamination where the microorganisms become attached to parts or substrates to which the coating composition is applied. In contrast, the antimicrobial agent may be used to treat both sessile microorganism contamination as well as contamination caused by freely moving microorganisms, i.e. motile microorganism contamination.

[037] In an aspect, the inorganic bismuth-containing compound may be present in an amount of at least 0.1 wt%, preferably at least 0.2 wt%, more preferably at least 0.5 wt% or even more preferably at least 1 wt%. In preferred embodiments, the powder coating composition includes less than 30 wt%, preferably less than 10 wt%, more preferably less than 5 wt% and even more preferably less than 2 wt %. If the inorganic bismuth-containing compound is used in conjunction with an organic bismuth-containing compound or other catalyst, the inorganic bismuth-containing compound may be present in an amount of about 0.025 wt %, 0.05 wt%, 0.075 wt % to about 0.5 wt %, 1 wt%, 2 wt % or about 5 wt%, based on the total weight of resin solids in the composition. In an alternative embodiment, the antimicrobial agent may provide not only a biocidal function but also serve as a filler in the coating composition.

[038] Alternatively, the inorganic bismuth-containing compound may also be combined with other antimicrobial agents conventionally recognized by those of ordinary skill in the art. Non-limiting examples of antimicrobials include inorganic nano-compounds, ligating species, organic compounds capable of absorption by microbes, and known pesticides or biocides. The amounts of the inorganic bismuth-containing compound may vary depending upon a selected combination.

[039] In addition to at least one polymeric binder, the at least one inorganic bismuth-containing antimicrobial agent, and optionally at least one or more pigments, the powder coating composition may include one or more additives. Additives generally employed in typical powder coating compositions may be used in conjunction with the disclosed inorganic bismuth-containing compound. Suitable additives may include, without limitation, fillers, thixotropes, rheological modifiers, matting agents, antioxidants, color

stabilizers, slip and mar additives, UV absorbers, hindered amine light stabilizers, photoinitiators, conductivity additives, tribocharging additives, anti-corrosion additives, extenders, inert pigments, texture agents, degassing additives, flow control agents, dyes, dispersants, degassing agents, anti-outgassing agents, processing aids, flow aids, anti-fouling compounds, scents and the like. Desirable performance characteristics of a powder coating composition as include, for example, chemical resistance, corrosion resistance, microbe resistance, abrasion resistance, tack resistance, hardness, gloss, reflectivity, extended shelf life, appearance and/or a combination of such properties and similar other properties. Preferred performance enhancing additives include lacquers, waxes, flattening agents, antimicrobial agents, additives to prevent mar, abrasion, and the like. Those of ordinary skill in the art will recognize that selected additives, or combinations of additives, may be included in the powder coating composition at varying levels. Preferably, the additives are included at about 10% or less, and more preferably 5 wt% or less. In some embodiments, fillers, such as for example magnesium sulfide or calcium carbonate, may be used for economic purposes to reduce the overall polymeric binder content in the powder coating composition. In such circumstances, fillers may be included in amounts up to 50 wt% or less, preferably 35 wt% or less and even more preferably 25 wt% or less.

[040] The formation of the powder coating composition containing an inorganic-bismuth-containing compound may involve conventional mixing and melt processing practices. In various embodiments, the components of the powder coating composition may be pre-mixed prior to melt processing or they may be directly fed into the melt processing equipment, such as an extruder, wherein certain elements of the internal conveying equipment may be used to address mixing. The melt mixed composition may be solidified, typically by cooling. The solidified composition may be in the form of pellets, strands, sheets or any form that renders them suitable for subsequent processing or use. In another embodiment, the inorganic bismuth-containing compound may be added after extrusion of the polymeric binder and other optional components.

[041] In certain embodiments, the solidified composition resulting from melt processing practices is preferably modified into a preferred particle size or size range suitable for powder coating applications. The solidified compositions may be comminuted to match a desired sizing specification. Those of ordinary skill in the art are capable of selecting a

grinder, powder mill or other comminuting equipment to achieve a desired sizing parameter.

[042] The resulting powder coating composition is preferably at a particle size that can effectively be used in the application process. The particle size (D50) of the powder coating composition may vary from at least about 10 microns, 25 microns, 50 microns, or 100 microns up to about 200 microns, 250 microns, 300 microns, or about 400 microns. For smooth finishes, particles up to 150 microns in size, with a median particle size of 45 microns are most preferred. For textured finishes, particles up to 300 microns in size, with a median particle size of 60 microns may be preferred. The median particle size may vary and is preferably 25 microns, 50 microns or 75 microns up to about 80 microns, 90 microns or 100 microns.

[043] The completed powder coating composition may then be applied onto at least a portion of an article using any conventional method, including spraying, electrostatic spraying, fluidized beds and the like. Following application of the powder coating composition, the article is heated to a temperature sufficient to cause the powder particles to melt and flow and form a film. Various heating sources may be used, including convection heating, infrared heating, induction heating, or a combination thereof. Optionally, the powder may be applied to a preheated substrate.

[044] The methods and practices used for final formation and hardening of the film on the article may vary depending upon the polymeric binder used in the powder coating composition. For example, when thermoset polymeric binders are employed in the coating composition, the film is optionally cured, and such curing may occur via thermal radiation in the form of continued heating, subsequent heating, or residual heat in the substrate. In another embodiment, if a radiation curable polymeric binder is selected, a film may be formed by a relatively short or low temperature heating cycle, and then may be exposed to actinic radiation to initiate the curing process. One example of this embodiment is a UV-curable powder. Other examples of radiation curing include using UV, Visible light, near-IR, IR and E-beam radiation. When thermoplastic polymeric binders are employed in the coating composition, the film, after the application of thermal radiation, is allowed to cool and harden to form a coated article.

[045] Preferably, the coated substrate is desirably colored and possesses the physical and mechanical properties necessary to meet end use demands. The thickness of the film may

depend upon the desired application of the substrate and the additives selected. Typically, the final film on the coated article may have a thickness of at least 10 microns, preferably at least 25 microns, more preferably at least 75 microns and most preferably at least 100 microns. The coating thickness may be up to 500 microns or less, preferably 350 microns or less, even more preferably 250 microns or less and most preferably 200 microns or less.

[046] Preferably, the inorganic bismuth containing compound functioning as an antimicrobial agent is dispersed throughout the film. In certain embodiments, the film may be relatively thick and the inorganic bismuth containing compound may be present at various levels and locations throughout the film. Such an embodiment may offer advantages to coatings that are susceptible to wear. The inorganic bismuth-containing compound, when dispersed through the film, may offer continued functionality as portion of the coating are worn off of coated article and other inorganic bismuth-containing compounds become exposed or offer microbe-resistance.

[047] In certain embodiments, a coated article having an inorganic bismuth-containing compound incorporated into the coating may exhibit microbe-resistant characteristics. In some aspects, the concentration of the inorganic bismuth-containing compound in the coated article is sufficient to reduce or inhibit microbial contamination. However, the effectiveness of the inorganic bismuth-containing antimicrobial agent may vary depending on factors such as the loading level in the coating, the severity of the contamination, among other factors.

[048] The microbe-resistant powder coating composition possessing an effective amount of at least one antimicrobial agent may be used coat a wide range of articles with various materials of construction. Non-limiting examples include furniture, tables, chairs, benches, hospital equipment and fixtures, public transit equipment and fixtures, fitness equipment, laboratory equipment, manufacturing equipment, hand rails, restroom equipment and accessories, appliances, shower enclosures and cabinets, storage containers, shelves, tanks, vessels, kitchen equipment, recreational equipment, office equipment, automotive interiors and parts, and hotel equipment and fixtures.

EXAMPLES

[049] The invention is illustrated by the following examples. It is to be understood that the particular examples, materials, amounts, and procedures are to be interpreted broadly

in accordance with inventions as set forth herein. Unless otherwise indicated, all parts and percentages are by weight and all molecular weights are weight average molecular weight. Unless otherwise specified, all chemicals used are commercially available from, for example, Sigma-Aldrich, St. Louis, Missouri.

[050] Unless indicated otherwise, the following test methods were utilized in the Examples that follow.

[051] JIS Z 2801: Test for Antibacterial Activity: the test is used to test for antibacterial activity and efficacy to bacteria on the surface of antibacterial powder coating compositions. To test the applied and cured powder coating's ability to kill bacteria, Japanese Industrial Standard JIS Z 2801 was used with the following parameters and modifications: The *E. coli* (Bacterial Strain ATCC8739) was used for Examples 1-7 and methicillin resistant staphylococcus (Bacterial Strain *s.aureus*) was used for Examples 8-11.

[052] Preparation of Inoculum. Prepare bacterial cultures 24 hours before test is scheduled to start by selecting one colony from a plate with a 10 μ L inoculating loop, adding it to 10mL of sterile TSB and placing it on a shaking incubator. Once cultures are in their log growth phase (16-24 hours after inoculation) they may be used for testing. Combine 1mL of the organism into a pool in a conical tube. Take 1mL of the created pool and add it to 9mL of sterile TSB in a conical tube to get an inoculum concentration of $\sim 10^8$ CFU/mL.

[053] Preparation of the Coating Sample. Streak the coating samples to a TSA/SDA agar bi-plate to check for sterility to make sure sample was not previously contaminated upon receipt. Incubate plates at 25°C and check for contamination and record at the time points: 24 hours and 7 days. Place three 2.5 cm $\times$ 2.5 cm pieces of Parafilm laboratory film in a sterile glass Petri dish. Place 50 mm $\times$ 50 mm samples from the center of the coating compositions onto each of the pieces of film. Four hundred μ L of inoculum (2.5×10^5 Colony Forming Units (CFU)) are then placed on the surface of each composition. After inoculation, the samples are covered with a 40 mm square glass coverslip and incubated for 24 hours at 35 °C. After 24 hours, a 10 ml solution of TSB is added to the petri dishes to wash the inoculum of the samples. The resulting suspension is serially diluted and then plated and the results read from differentiating dilution plates at equal serial dilutions. A total viable count (TVC) is performed on the eluent solution. Colony Forming

Units/milliliter (CFU/ml) of bacteria recovered from each sample are counted, if growth is uniform and evenly distributed over the face of a plate then a fraction of the plate is counted and the total CFU count can then be calculated.

[054] Examples 1-7. Examples 1-7 were treated with E.coli bacteria and tested in accordance with JIS Z 2801 as described in this disclosure. Example 1 was established as a control and utilized an untreated polyethylene film.

[055] The coatings of Examples 2-4 utilize a carboxy-functional polyester as the polymeric binder at about 54 wt%, a crosslinker of triglycidylisocyanurate (TGIC) of about less than 6 wt%, a white TiO₂ pigment of about 30 wt%, barium sulfate and calcium carbonate fillers of about 9%, and processing aids of about 1 wt%. Example 2 did not contain an antimicrobial agent. Example 3 contained bismuth aluminate at about 4 wt% with the barium sulfate and calcium carbonate fillers revised to about 4%. Example 4 included about 1 wt % SteriTouch antimicrobial agent from Alfa Chemicals Ltd, Berkshire Uk with the barium sulfate and calcium carbonate fillers reduced to about 3%. The results are shown in Table 1 and demonstrate that inorganic bismuth containing compounds are capable of impeding growth of colony forming units as compared to Example 1.

[056] The coatings of Examples 5-7 utilize a carboxy-functional polyester as the polymeric binder at about 57 wt%, a crosslinker of hydroxyalkylamide (PRIMID) of about less than 3 wt%, a white TiO₂ pigment of about 30 wt%, barium sulfate and calcium carbonate fillers of about 9%, and processing aids of about 1 wt%. Example 5 did not contain an antimicrobial agent. Example 6 contained bismuth aluminate at about 4 wt% with a corresponding reduction in fillers. Example 7 included about 1 wt % SteriTouch antimicrobial agent from Alfa Chemicals Ltd, Berkshire Uk and corresponding reduction in the amount of filler to compensate for the SteriTouch.

[057] The results for Examples 1-7 are shown in Table 1 and demonstrate that inorganic bismuth containing compounds are capable of reducing colony forming units on a powder coated article.

[058] Table 1: Escherichia coli

	Number of live organisms (Colony Forming Units)		% reduction of Colony Forming Units, expressed as comparison with Example 1
Example	0 Hours	24 hours	
1	110,000	12,000,000	NA
2	110,000	10,000,000	16%
3	110,000	2,200,000	81%
4	110,000	<10	99.99991%
5	110,000	14,000,000	-16%
6	110,000	5,000,000	25%
7	110,000	<10	99.99991%

[059] Examples 8-14. Examples 8-14 were treated with staphylococcus bacteria and tested in accordance with JIS Z 2801 as described in this disclosure. Example 8 was established as a control and utilized an untreated polyethylene film.

[060] The coatings of Examples 9-11 utilize the same compositions as those set forth in Examples 2-4 with Example 9 containing no antimicrobial, Example 10 containing bismuth aluminate, and Example 11 containing SteriTouch. The results are shown in Table 2 and demonstrate that inorganic bismuth containing compounds are capable of impeding the growth of colony forming units as compared to Example 8.

[061] Table 2: methicillin resistant staphylococcus

	Number of live organisms (Colony Forming Units)		% reduction of Colony Forming Units, expressed as comparison with Example 8
Example	0 Hours	24 hours	
8	120,000	150,000	NA
9	160,000	150,000	0%
10	160,000	130,000	13%
11	160,000	<10	99.99991%

[062] The complete disclosure of all patents, patent applications, and publications, and electronically available material cited herein are incorporated by reference. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described and variations apparent to one skilled in the art may be included within the invention defined by the claims. The invention illustratively disclosed herein suitably may be practiced, in some embodiments, in the absence of any element which is not specifically disclosed herein.

What is claimed is:

1. A method comprising:

- (a) providing a powder coating composition including an effective amount of at least one antimicrobial agent comprising at least one inorganic bismuth-containing compound;
- (b) depositing the powder coating composition onto at least a portion of an article; and
- (c) forming a film from the powder coating composition to create a coated article.

2. A composition comprising, a powder coating composition including an effective amount of at least one antimicrobial agent comprising at least an inorganic bismuth-containing compound.

3. A composition or method according to any of the preceding claims, wherein the inorganic bismuth-containing compound is a bismuth salt of a metal oxyanion.

4. The composition or method according to any of the preceding claims, wherein the inorganic bismuth-containing compound is bismuth aluminate.

5. The composition or method according to any of the preceding claims, wherein the antimicrobial agent further comprises an organic bismuth-containing compound.

6. The composition or method according to any of the preceding claims, wherein the powder coating composition comprises at least one thermoset polymer and forming a film comprises curing the at least one thermoset polymer.

7. The composition or method according to any of the preceding claims, wherein the powder coating composition comprises at least one thermoplastic polymer and forming a film comprises hardening the at least one thermoplastic polymer.

8. The composition or method according to any of the preceding claims, wherein the powder coating composition further comprises one or more pigments, crosslinking agents, dispersing agents, additives, fillers, carriers or combinations thereof.

9. The composition or method according to any of the preceding claims, wherein the powder coating composition comprises an epoxy, a polyamide, a polyepoxide, acrylic, polyurethane, polyester, polyvinyl chloride, fluoropolymer, silicone or combinations thereof.
10. The composition or method according to any of the preceding claims, wherein the coated article or the powder coating composition when applied and cured onto at least a portion of an article demonstrates at least a 10% reduction in growth of microbes over a coated article not having is at least one inorganic bismuth-containing compound.
11. The composition or method according to any of the preceding claims, wherein the antimicrobial agent is present in an amount of about 0.1 wt% to about 30 wt%.
12. The composition or method according to claim 6, wherein curing comprises the application of actinic radiation or thermal radiation.
13. Method of forming a powder coating composition, the method comprising:
- (a) melt processing at least one polymer, an effective amount of at least one inorganic bismuth-containing compound, and optionally one or more pigments, a crosslinking agent or one or more additives, to form a melt mixture;
 - (b) forming a solid coating composition from the melt mixture; and
 - (c) comminuting the solid coating composition to form a powder coating composition.
14. A method according to claim 13 wherein, melt processing comprises extruding.
15. A method according to claim 13, wherein polymer is a thermoset polymer, a thermoplastic polymer or a combination thereof.
16. A method according to claim 15, wherein the inorganic bismuth-containing compound is a bismuth salt of a metal oxyanion.

17. A method according to claim 15, wherein the inorganic bismuth-containing compound is bismuth aluminate.
18. A method according to claim 13, wherein the polymer comprises an epoxy, a polyamide, a polyepoxide, acrylic, polyurethane, polyester, polyvinyl chloride, fluoropolymer, silicone or combinations thereof.
19. A method according to claim 13, wherein the antimicrobial agent is present in an amount of about 0.1 wt% to about 30 wt%.
20. An article comprising an object at least partially coated with a powder coating composition having a polymeric binder and an effective amount of at least one antimicrobial agent comprising at least an inorganic bismuth-containing compound.
21. An article according to claim 20, wherein the at least one antimicrobial agent comprises at least an inorganic bismuth-containing compound of a bismuth salt of a metal oxyanion.
22. An article according to claim 20, wherein the inorganic bismuth-containing compound is bismuth aluminate.
23. An article according to claim 20, wherein the article comprises furniture, tables, chairs, benches, hospital equipment and fixtures, public transit equipment and fixtures, fitness equipment, laboratory equipment, manufacturing equipment, hand rails, restroom equipment and accessories, appliances, shower enclosures and cabinets, storage containers, shelves, tanks, vessels, kitchen equipment, recreational equipment, office equipment, automotive interiors and parts, and hotel equipment and fixtures.
24. An article according to claim 20, wherein the antimicrobial agent is present in an amount of about 0.1 wt% to about 30 wt%.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/033800

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2012 020392 A1 (MERCK PATENT GMBH [DE]) 24 April 2014 (2014-04-24) paragraph [0070] - paragraph [0080] paragraph [0111] - paragraph [0112] abstract; claims 1, 2, 16 -----	1-24
X	WO 03/006558 A2 (MERCK PATENT GMBH [DE]; AMBROSIUS KLAUS [DE]; ANSELMANN RALF [DE]; SCH) 23 January 2003 (2003-01-23) page 7, line 29 - page 9, line 4 page 16, line 3 - line 17 abstract; claims 1, 5, 8-10; examples 1-5 ----- -/-	1-24



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

29 August 2016

Date of mailing of the international search report

05/09/2016

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/033800

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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International application No

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