A corrosion-resistant coating which can be applied directly to a surface as self-priming topcoat comprising a polyurethane resin binder and a combination of pigments consisting essentially of a molybdate-modified zinc phosphate, zinc salts of benzoic acids, and an alkaline earth metal phosphate such as zinc-barium phosphate. In addition, the coating contains up to about 35 parts by weight of a titanium dioxide pigment, up to about 3.0 parts by weight of an oil soluble dispersant agent and up to about 50 parts by weight of at least one organic solvent.
A corrosion-resistant coating which can be applied directly to a surface as a self-priming topcoat comprising a polyurethane resin binder and a combination of pigments consisting essentially of a molybdate-modified zinc phosphate, zinc salts of benzoic acids, and an alkaline earth metal phosphate such as zinc-barium phosphate. In addition, the coating contains up to about 35 parts by weight of a titanium dioxide pigment, up to about 3.0 parts by weight of an oil soluble dispersant agent and up to about 50 parts by weight of at least one organic solvent.
POLYURETHANE SELF-PRIMING TOPCOATS

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

CONTINUATION APPLICATIONS

This application is a Continuation-In-Part of copending application Ser. No. 07/812,174 filed Dec. 20, 1991.

BACKGROUND OF THE INVENTION

This invention relates to novel coating compositions and more specifically to corrosion-resisting coatings which can be applied directly to various surfaces particularly metal either as a high or low gloss, self-priming topcoat.

Various surfaces and particularly metal surfaces require the protection of coatings especially when the surfaces are exposed to a corrosive environment. Metal surfaces of aircraft, for example, are exposed to seawater which requires protection from corrosion. Specifically, aircraft, e.g., Navy aircraft, are exposed to seawater spray in addition to various acid-forming gases such as sulfur dioxide, carbon dioxide, etc. Moreover, in addition to aircraft, various machinery and equipment in the industrial environments, where fossil fuels are used need protection against corrosion. It is important, therefore, that the coating be resistant to corrosion, various chemicals, the weather and at the same time be flexible and have good adhesion to the substrates.

Presently, coating systems comprise one or more films, i.e., an undercoat, a sealant and a topcoat. Aircraft, for example, traditionally have been coated with high performance two-component protective films consisting of an epoxy primer and a polyurethane topcoat. The type of epoxy primers used on the aircraft are designed to adhere to the metal surface and help to improve the adhesion of the topcoat and together prevent corrosion of the metal. However, these undercoats require a topcoat, since the undercoats lack flexibility especially at low temperatures (−60°F) resulting in extensive cracking particularly in highly flexed areas of the aircraft. Moreover, the undercoats usually lack weather resistance and generally cannot be formulated in different colors required for aircraft.

In comparison, the polyurethane coatings of this invention, provides the necessary corrosion resistance, the required degree of flexibility, the desired optical properties, and a resistance to weather and various chemicals. To obtain these characteristics, the multi-film coatings used heretofore generally required a dry-film thickness ranging up to about 0.005 inches, e.g., up to about 10 mils or more which added considerable weight to the aircraft. In addition, the multi coats are time consuming to apply particularly since there is a drying time between each application. Further, the removal of a two-coat system can be difficult and time consuming and generates high levels of volatile organic (VOC) emissions during the operations.

In accordance with this invention the corrosion-resistant coating comprise a polyurethane binder derived from the reaction of at least one polyol, e.g., polyester polyol and an isocyanate, e.g., hexamethylene disocyanate (HDI) or polyisocyanates in combination with a unique mixture of corrosion-inhibiting pigments consisting essentially of (1) an alkaline earth metal phosphate, e.g., zinc-barium phosphate, (2) zinc salts of benzoic acid or substituted benzoic acid, and (3) molybdate-modified zinc phosphates. All three of these compounds are essential, in the stated relative proportions, to provide a single high-gloss coating with the necessary corrosion resistance and adhesion characteristics required of a good top coat. In addition, titanium dioxide (TiO₂) including spherical TiO₂ particles, e.g., vesiculated beads of TiO₂ are included as a pigment together with these three alkaline earth metal or zinc salts. The coating compositions of this invention may be applied, as one coat, directly onto various hard surfaces such as metal and/or organic matrix composites, etc., and do not require an undercoat to provide a corrosion-resistant finish with desired optical and adhesion properties.

SUMMARY OF THE INVENTION

A corrosion-resistant coating which can be applied directly to a surface as a self-priming topcoat comprising from about 20 to 60 parts by weight and preferably 30–50 parts of a polymeric urethane resin binder and a combination of three corrosion-resistant pigments consisting essentially of a molybdate-modified zinc phosphate, zinc salts of benzoic acid, and alkaline earth metal and/or zinc phosphates such as a complex zinc-barium phosphate, together with dispersing agents, TiO₂ pigments, and organic solvents.

Accordingly, it is an object of this invention to provide a corrosion-resistant coating which can be applied directly to a surface, e.g., metal, as a single coat.

It is another object of this invention to provide a coating which is flexible, resistant to corrosion, chemicals, and weathering, and has good adhesion characteristics.

It is still a further object of this invention to provide a coating for use on military or civilian aircraft of reduced thickness to lower the weight thereon while at the same time providing the necessary corrosion resistance.

These and other objects of the invention are accomplished, in accordance with this invention, by providing a corrosion-resistant coating capable of being applied as a single coating with appropriate optical properties.

THE PREFERRED EMBODIMENTS

This invention is directed to a corrosion-resistant coating which functions as a primer and a topcoat. More specifically, this invention relates to a corrosion-resistant coating which comprises a major amount, e.g., 20 to 60 parts by weight of a urethane resin, i.e., polyurethane resin binders, and a minor amount of corrosion-inhibiting pigments, i.e., alkaline earth metal compounds and/or zinc salts. The unique combination of pigments consist essentially of from about 5 to 35 parts and preferably 10 to 30 parts by weight of an alkaline earth metal phosphate, e.g., zinc or zinc-barium phosphate, 0.5 to 5 parts and preferably 1 to 3 parts by weight of a zinc salt of a benzoic acid or substituted benzoic acid, and about 5 to 30 parts and preferably 10 to 25 parts by weight of a molybdate-modified zinc phosphate. In addition to the above metal compounds, depending on the opacity, etc., required of the coating, from 5.0 to 35 parts, and preferably from 5.0 to 15 parts by weight of titanium dioxide pigment, based on the total weight of the coating, is added as an additional pigment. Up to about 100% of the total amount of TiO₂...
may be in the form of vesicular beads, e.g., from 0 to 5\% of the TiO\textsubscript{2} in the coating are beads. Generally, the coating is applied as a high solids organic solution and therefore generally contains from 0 to 3.0 and preferably about 0.1 to 2.0 parts by weight of at least one oil soluble dispersing or wetting agent such as Anti-Terra-204 or BYK-320. Anti-Terra-204 is a carboxylic acid of polyamine-amides and BYK-320 is a polyether modified polyalkylpolysiloxane copolymers. Various other nonionic or anionic dispersing agents known as oil soluble dispersants or paint additives may be used in the coating. In addition, the coating contains from about 0 to 50 parts, e.g. as needed or from 10 to 25 parts by weight of the total coating of at least one organic solvent, e.g., Mil-T-61772 or various mixtures of paint solvents.

The organic binder of the coating comprises a polyurethane, and more particularly an aliphatic polyurethane derived from the reaction of a polyol and a multifunctional aliphatic polyisocyanate. The polyol is preferably used as a solution in an organic solvent e.g. toluene, xylene, n-butyl acetate, propylene glycol monomethyl ether acetate, methyl ethyl ketone, etc. The polyisocyanate is used as a 100\% solid but also can be diluted with any of the above organic solvents. The hydroxyl number of the polyol, i.e., polyester polyls and the isocyanate (NCO) content or the equivalent weights of the polyisocyanate and polyol are determined in order to obtain the desired polyurethane. The preferred polyols and polyisocyanates are reacted in approximately stoichiometric amounts so that the NCO to OH ratio ranges from about 0.85 to 1.4 equivalent of the NCO to 1.0 equivalent of the OH, or at about a 1.0 to 1.0 ratio of the NCO to OH. The combination of metal salts and/or pigments is unique and consists essentially of specific amounts of an alkaline earth metal phosphate, e.g., zinc phosphate or zinc-barium phosphate etc., zinc salts of benzoic acid or a substituted benzoic acid and a molybdate-modified zinc phosphate. These three metal salts or pigments used alone and in combination with TiO\textsubscript{2} provide outstanding corrosion protection and enables the coating to be used as a self-priming high-gloss or low-gloss topcoat. The particular alkaline earth metal complexes or zinc phosphates used in preparing the coating composition is preferably a zinc-barium phosphate. The preferred zinc salt of the benzoic acids has at least one hydroxyl substituent and one (NO\textsubscript{2}) group. Zinc salts of substituted benzoic acids and metal phosphates and complexes such as zinc and/or barium phosphates, zinc salts of substituted benzoic acids and Molybdate-modified Zinc Phosphates (e.g., MOLY-WHITE-MZAP or HEUCOPHOS-ZMP) or Dispersing agents, e.g., Anti-Terra-204 (Oil Soluble Anionic or Nonionic dispersants) provide out-

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>EXAMPLE 1 Parts by Weight (Ranges)</th>
<th>EXAMPLE 2 Parts by Weight (Ranges)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane Resin or Binder derived from polyester polyols and polyisocyanates</td>
<td>20-60</td>
<td>30-50</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>5.0-35</td>
<td>5-15</td>
</tr>
<tr>
<td>Titanium dioxide (vesiculated beads)</td>
<td>0-35</td>
<td>0.1-5.0</td>
</tr>
<tr>
<td>Alkaline earth metal phosphates and complexes such as zinc and/or barium phosphates</td>
<td>5-35</td>
<td>10-30</td>
</tr>
<tr>
<td>Zinc salts of substituted benzoic acids</td>
<td>0.5-5</td>
<td>1-3</td>
</tr>
<tr>
<td>Molybdate-modified Zinc Phosphates (e.g., MOLY-WHITE-MZAP or HEUCOPHOS-ZMP)</td>
<td>5-30</td>
<td>10-25</td>
</tr>
<tr>
<td>Dispersing agents, e.g., Anti-Terra-204 (Oil Soluble Anionic or Nonionic dispersants)</td>
<td>0-3</td>
<td>0.1-2.0</td>
</tr>
<tr>
<td>Organic solvents for coatings</td>
<td>As Needed</td>
<td>0-50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>EXAMPLE 3</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane Resin derived from polyester polyol in organic solvents (i.e., propylene glycol monomethyl ether acetate, n-butyl acetate) and polyisocyanate</td>
<td>39.2</td>
<td></td>
</tr>
<tr>
<td>Titanium Dioxide Pigment</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>Titanium Dioxide Vesiculated Beads</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Zinc-Barium Phosphate</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>Zinc Salt of a substituted Benzoic Acid (Sucorin RZ)</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Molybdate-Modified Zinc Phosphate (HEUCOPHOS-ZMP)</td>
<td>22.7</td>
<td></td>
</tr>
<tr>
<td>Dispersant (BYK-320)</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

Other molybdate-modified zinc phosphates include the metal complexes or mixtures of an alkaline earth metal from Group II of the Periodic Table such as a zinc molybdate-zinc phosphate, and more specifically a barium or calcium-zinc molybdate/zinc phosphate, such as CaMoO\textsubscript{4}, CaCO\textsubscript{3}, ZnO, Zn\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}. These complex or mixed metal phosphates are available commercially as MOLY-WHITE from the Sherwin Williams Co. of Cleveland, Ohio.

In addition to utilizing the above combination of metal pigments in the preferred ratios, titanium dioxide is added to the coating to provide reinforcing strength and to add color, hiding and opacity to the coating. Other additives that may be used include tinting or coloring agents which may be added to the coating in small but effective amounts such as zinc oxide, antimony oxides, barium sulfate, calcium carbonate and one or more of the organic pigments such as the phthalocyanine colors e.g. greens or blues, etc.

Specifically, the corrosion resistant coatings of this invention can be prepared by milling the ingredients set forth in the following Examples.
Examples 7-14, the polyester polyol blend was used as a solution, e.g., 79% solids in propylene glycol mono-methyl ether acetate and butyl acetate. The polyisocyanate was 100% solids, e.g., substantially containing no solvents.

Preferably, the coatings are prepared by mixing all of the ingredients, except the polyisocyanate and then milling the mixture to a fineness of about 5 for comouflage and 7 for high gloss colors on the Hegman scale according to ASTM D1210. Subsequently, the polyisocyanate is added before the application of the coating to the substrate. The coating is applied on the substrate at thickness ranging from about 0.001 to 0.003 inches e.g., from 0.5 to about 10 mls and preferably 1 to 3 mls. The coating may be applied by various methods including spraying, rolling, or brushing onto the surface depending on the viscosity. The viscosity of the coating for the particular application may be achieved by adjusting the content of the solvent within the ranges specified herein and by the selection of the particular reactants used to form the urethane resin. After the coating is applied to the surface, the solvent is evaporated at room or elevated temperatures and is allowed to cure to a film thickness having the desired properties. The pigments can be introduced into the coating by first forming a mill base with the polyester polyol. The mill base can be formed, for example, by conventional sand-grinding or ball-milling techniques, and then blended, by simple stirring or agitation with the other ingredients of the composition.

The combination of the molybdate-modified zinc phosphates, the zinc salts of benzoic acid, e.g., zinc benzoate and an alkaline earth metal phosphate, e.g., zinc or zinc-barium phosphates, improved the corrosion resistance while maintaining all the other desirable characteristics required of the coating. In other words, the specific combination of a zinc molybdate-zinc phosphate, a zinc salt of substituted benzoic acid and zinc or zinc-barium phosphates, in the ratios stated, improved the corrosion inhibition substantially when compared to the use of either one of these metal salts alone in the same coating.

More specifically in preparing the urethane resins, the preferred polyester polyols of this invention have equivalent weights ranging from about 260 to 970 with hydroxyl numbers ranging from 40 to 252 and an acid number less than 10. The polyols includes a variety of polyester polyhydroxyl compounds known in the art, including, for example, the condensation-reaction products of pentaerythritol and/or glycols with monocarboxylic acids or an aromatic or aliphatic dicarboxylic acid. Any branched-chain glycol may be used in the formation of the polyester, although it is preferred that these glycols contain no more than 8 carbon atoms. A useful polyol is formed where the molar ratio of glycol to pentaerythritol is from 2:1 to about 6:1. The carboxy-
The dicarboxylic acids useful in the formation of the polyester polyols have the general formula:

\[ \text{HOOC–R–COOH} \]

where R is aliphatic or aromatic group. Preferred are succinic acid, glutaric acid, adipic acid and pimelic acid. Useful are those in which R has 2 to 8 carbon atoms with the preferred being maleic acid and itaconic acid. The aromatic dicarboxylic acids are phthalic, isophthalic, and terephthalic, although other aromatic dibasic acids can be used.

It is known that the lower alkyl mono- or diesters of these acids and the anhydrides thereof can be used in place of the free acids. Other known polyester polyols can be obtained by the condensation reaction between a polybasic acid, such as adipic acid, phthalic anhydride, isophthalic acid, etc., and a diol or triol such as ethylene glycol, diethylene glycol, propylene glycol, trimethylol propane, glycerine, etc.

The hydroxyl numbers of the preferred polyester polyols should be at least 40 and preferably between 40 and 252. The polyesters, containing hydroxyl groups, are combined with the polyisocyanate. This combination can be carried out in several ways known to the art. For example, an organic solution of the polyester containing, if desired, a catalyst-promoting urethane formation such as an organo-tin compound, is added to an chemical equivalent amount of the isocyanate. This combination is made at ambient temperature but the heat of reaction usually causes an increase in temperature. The mixture is agitated preferably at room temperature until the urethane reaction is substantially completed. The course of the reaction can be followed by noting the viscosity of the mixture. When the viscosity becomes substantially constant, it may be concluded that the reaction is substantially completed. The resultant reaction product may contain insignificant amounts of free isocyanate and/or hydroxyl groups.

Alternatively, the polyester solution can be reacted with a small excess, e.g. about 10% excess of the isocyanate. After the urethane reaction is substantially completed, the excess NCO groups can be reacted with "chain-extending" substances, e.g. water, alcohols, etc. This procedure results in polymers of substantially equivalent character but permits the reaction to proceed at a faster rate, due to the mass action of the excess NCO groups. The term "small excess" is intended to be included within the meaning of the term "stochiometric amounts".

The polyisocyanates and particularly the aliphatic polyisocyanates based on HDI include various multifunctional aliphatic polyisocyanates having an isocyanate content (NCO) ranging from about 10 to 30% by weight with an equivalent weight (NCO) ranging up to about 300. Specific examples of the organic polyisocyanates used in this invention make up about 5 to 20% by weight of the blend. These compounds include aliphatic, alkaryl, aralkyl, heterocyclic, a trisocyanates. Specific compounds include polyisocyanates such as: diphenylmethane-4,4'-diisocyanate, diphenylmethane-4,4'-diisocyanate toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, 3,3'-dimethoxy-4,4'-diphenyle diisocyanate bis-(4-cyclohexyl isocyanate) tetramethylene diisocyanate, hexamethylene diisocyanate, decamethylene diisocyanate, ethylene diisocyanate, ethylenedimethylene diisocyanate, propylene-1,2-diisocyanate, cyclohexylene-1,2-diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 1,5-naphthalene bis-(2-isocyanatoethyl)dimurate, 1,3,5-benzene trisocyanate, para, para', para''-triphenylmethane triiso 3,3'-disiocyanatodipropyl ether, xlylene diisocyanate, B,B-diisocynal propene-4,4'-diisocynate, a 24 isophorone diisocynate. Preferred poly isocyanates include hexamethylene diisocyanate an bis-(4-cyclohexyl isocyanate) e.g. DES. By selecting the proper polyols and by NCO to OH ratio, the physical properties of the film, such as the strength of film: chemical resistance, solvent resistance, etc. trolled over a wide range. Compounds with to OH ratio ranges from 0.85 to 1.4 of N OH groups e.g. 1:2:1 are useful for the m coating in accordance with this invention. If the coating is derived from a two-pack the polyisocyanate is in one package and the polyol is in a separate package. The coating after applying the coating onto the surface of the two reactants is usually necessary s life" of some of the compositions is short. Cyanate (NCO) reacts with the hydroxyl / polyl at temperature as low as about 45 °C Regardless of the method by which the co- sition is prepared, the coating should con parts by weight of the polyurethane resi about 50 parts, e.g. 0-50 parts by weight of ove of the composition can be a mixture solvents wherein the constituents of the ur instead of the two-component or "n system, a "one package" coating can be reactive groups of the polyisocyanate are 5 a blocking agent such a methyl ethyl ket eliminates the need for keeping the polyo the polyisocyanate until just before use. W, with the blocked polyisocyanate, is
heated the blocking agent is released, permitting the polyisocyanate to react with the polyester polyol.

The blocking agents are used for purposes of masking the free isocyanate radical of the polyisocyanates. These agents include phenol, m-nitrophenol, p-chlorophenol, ethyl malonate, acetylacetonate, ethyl acetocetate, cresol, methanol, ethanol, ethylene, chlorophyrin, etc. Although the temperatures at which the above-mentioned blocking agents are dissociated varies with the agents, it is generally accepted that heating is required to deblock.

The coating composition also can contain ultraviolet light stabilizers, antioxidants, catalysts, wetting or dispersing agents, e.g., Anti-Terra-204 (carboxylic acid salts of polyamine-amides), flow modifiers e.g. BYK-320 (polyether modified methyldiallyl polyisoxane co-polymers), adhesion promoters, etc. The ultraviolet light stabilizer can be present in an amount of 1-10% by weight, based on the weight of the urethane binder. The antioxidants can be present also in amounts of 0.1-3% by weight of the urethane binder. Ultraviolet light stabilizers include benzophenones, triazoles, triazines, benzoates, substituted benzenes, organophosphorous sulfides, etc.

The coating composition of this invention may contain about 0.01-2.0% by weight, based on the weight of the polymer forming blend, of a curing catalyst. The catalysts are usually organ metallics such as dibutyl tin dilaurate and zinc octoate, dibutyl tin di-2-ethylhexoate, stannous octoate, stannous olate, zinc naphthenate, vanadium acetyl acetonate, and zirconium acetyl acetone. Also useful as catalysts are tertiary amines, such as, for example, triethylene diamine, triethyamine, pyridine, dimethylamine, and methyl morpholine. When a two-component system is used, the catalyst can be added to either the polyisocyanate or the solution of the polyester polyol.

The coating composition of this invention can be applied to a variety of substrates by conventional application methods such as spraying, dipping, brushing, or flow coating. Substrates that can be coated with the composition are, for example, metal, wood, glass, or plastics such as polypropylene, polystyrene, and the like. The coating is particularly suited for application over pretreated or unprimed metal. The coating can be cured at ambient temperatures or heated at 40°-120° C. for up to an hour or more. If the coating contains a blocked polyisocyanate, temperatures ranging up to about 160° C. may be necessary.

The solvent may include a mixture of organic solvents, e.g., benzene, toluene, xylene, and naphtha. Ester solvents include the acetates, e.g., ethyl acetate, butyl acetate, hexyl acetate, amyl acetate, etc., propionates such as ethyl propionate, butyl propionate, etc. Ketone solvents include acetone, methyl-ethyl ketone, methyl-isopropyl ketone, methyl-isobutyl ketone, diethyl ketone, cyclohexanone, etc. Glycol ester solvents include ethylene glycol, monomethyl-ethyl acetate, etc.

In testing the coatings prepared in accordance with this invention, the corrosion protection for an aluminum substrate was found to be over 2000 hours in 5% salt spray in accordance with ASTM Test Method B-117 and over 300 hours in SO2/salt spray in accordance with ASTM Test Method G-85. The coating was found to have outstanding performance when exposed to extreme heat conditions, high intensity of light and water, extreme cold conditions, hot lubricating oils and other chemicals normally found in aircraft operations. By utilizing the coating composition of this invention, a corrosion resistant film can be obtained on various substrates. The coating therefore has properties which function as a primer and more important as a single topcoat which is highly adherent, flexible, chemical resistant and resistant to all weather conditions. The coatings of this invention lower the risk of failure due to cracking especially at low temperatures and are easily touched-up since only one coating need be applied.

Since the coating requires only one coat, it requires less time for application and removal and thereby saves on manpower that would generally be needed in the preparation of a two coat system. Moreover, the present coating provides protection at lower film thicknesses thereby reducing the weight of the coating compared to a two-coat paint system which is an important factor when considering aircraft coatings.

It is obvious that there are other variations and modifications which can be made with respect to this invention without departing from the spirit and scope of the invention as particularly set forth in the appended claims.

We claim:

1. A corrosion-resistant self-priming coating comprising from about 20 to 60 parts by weight of a polyurethane resin binder, 5 to 35 parts by weight of an alkaline earth metal phosphate, 0.5 to 5 parts by weight of a zinc benzoate, 5 to 30 parts weight of a metal molybdate-modified zinc phosphate, 0.0 to 35 parts by weight of titanium dioxide, 0 to 3.0 parts by weight of an oil soluble dispersing agent and 0 to 50 parts by weight of at least one organic solvent.

2. The coating of claim 1 wherein the polyurethane ranges from about 30 to 50 parts by weight, titanium dioxide ranges from about 5 to 15 parts by weight, alkaline earth metal phosphate ranges from about 10 to 30 parts by weight, zinc benzoate ranges from about 1.0 to 3.0 parts by weight, metal molybdate-modified zinc phosphate ranges from about 10 to 25 parts by weight, the dispersing agent ranges from 0.1 to 2.0 parts by weight and the solvent ranges from about 10 to 25 parts by weight.

3. The coating of claim 1 wherein up to about 100 percent by weight of the total amount of titanium dioxide is in the form of vesiculated beads.

4. The coating of claim 2 wherein 0 to 50 percent by weight of the total amount of titanium dioxide is in the form of vesiculated beads.

5. The coating of claim 4 wherein the zinc benzoate is a salt of a substituted benzoic acid having one hydroxyl substituent and one nitro substituent.

6. The coating of claim 1 wherein the polyurethane is derived from hexamethylene disiocyanate and an aliphatic polyester polyol.

7. The coating of claim 6 wherein the polyurethane is derived from a polyisocyanate and a polyester polyol wherein the NCO to OH group ratios range from 0.85-1.4 to 1.0.

8. The coating of the claim 6 wherein the NCO to OH ratio of the hexamethylene disiocyanate and the aliphatic polyester polyol is about 1.2 to 1.0.

9. The coating of claim 8 wherein the zinc salt of the benzoic acid has one hydroxyl and one nitro (NO$_2$) substituent.

10. The coating of claim 7 wherein the polyester polyol and the polyisocyanate are reacted at a NCO to OH ratio of about 1.2 to 1.0.
11. The coating of claim 2 wherein the alkaline earth metal phosphate is a zinc-barium phosphate.
12. The coating of claim 2 wherein the alkaline earth metal phosphate is zinc phosphate.
13. The coating of claim 1 wherein the metal molybdate-modified zinc phosphate is an alkaline earth metal molybdate-modified zinc phosphate.
14. The coating of claim 1 wherein the metal molybdate-modified zinc phosphate is a zinc molybdate-zinc phosphate.
15. The coating of claim 13 wherein the metal molybdate-modified zinc phosphate is a calcium-zinc molybdate-zinc phosphate.