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## ZINC FILLED ALKYL TITANATE AND POLYVALENT METAL SALT COMPLEX GALVANIC COATING

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This invention relates to improvements in coating compositions and methods for preparing the same and in particular relates to a zinc filled coating vehicle which when applied to steel or other ferrous surfaces will provide cathodic or galvanic protection for the ferrous surface.

In the coating of this invention, the zinc being more reactive, that is less noble than the ferrous surface, will be sacrificed to protect less reactive but more noble ferrous surface. Thus, a very effective protection against corrosion is provided by this coating. The coating vehicle is characterized by tight adherence to the metal surface, insolubility in water, and all common solvents, and provides binding properties to hold the zinc particles together. In holding these zinc particles together and in contact with the ferrous surface, the coating vehicle does not form an insulative layer either between the individual zinc particles or the zinc particles and the ferrous surface, and a degree of porosity is thereby provided.

It is a feature of this invention that the coating vehicle employed has a long and stable shelf life, and provides a hard coating when cured. The coating vehicle has a high degree of stability and provides in use a coating vehicle which, when applied to metal surfaces, forms a hard, tough, and insoluble protective coating with the zinc filled particles.

It is a feature of this invention that the vehicle employed makes use of an alkyl titanate and a polyvalent metallic salt forming a complex to provide the stability desired. The alkyl titanate has an alkyl group from three to eight carbon atoms, while the polyvalent metallic salt has preferably a valence of two or three and the salt, desirably in the form of a halide, comprises at least one member of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride and zinc chloride. The vehicle with desirable solvents, and in some cases after partial hydrolysis of the alkyl titanate to the range of 0.05 to 0.95 equivalent weights of water, is used with finely divided metallic zinc dust as a filler, and any other conventional fillers that are desired to be added.

It is a feature of this invention that the hydrolysis of the alkyl titanate, where hydrolysis is employed, takes place in a special manner to avoid the precipitation of the titanate. This is accomplished by dissolving the titanate in an organic solvent, such as cellosolve, and then adding a mixture of water and cellosolve to the alkyl titanate solution to effect the hydrolysis.

It is a feature that through the employment of the vehicle composition and the method of making the same that the vehicle is insensitive to water within minutes after application and is substantially unaffected by sudden rainfalls, dew, high humidity, and the like. The hardness and hardening rate are only mildly, if at all, effected by humidity, and the coating will cure to a hard film. Further, the composition has a quite high flash point and can utilize all commercial grades of zinc dusts and does not require alkaline or special types of zinc dust.

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The coating is also characterized by a fast cure, even under humid conditions, and the vehicle exhibits a thixotropic character which prevents rapid settling of the fillers, which is quite desirable for shelf stability, and the shelf life is quite extended. Additionally, the pot life of the coating composition is quite long, exceeding four and one-half to five days.

The above features are objects of this invention and further objects will appear in the detailed description which follows.

Coatings available today have certain disadvantages which have been overcome by the present invention. Several different types of inorganic coating vehicles are presently in use. Sodium silicates, alkyl silicates and phosphates are all used as binders in "galvanic" coatings.

Sodium silicate vehicles have the disadvantages of being applicable only over heavily sand-blasted surfaces, susceptibility to freezing as such vehicles are aqueous and many of these vehicles require a second or additional curing coat.

The alkyl silicate based coatings exhibit poor to fair shelf stability as such films require hydrolysis to one extent or another. The greater the percentage of water used in this hydrolysis, the shorter the ensuing shelf life of the vehicle. Accordingly, the lower the percentage of water used, the softer the cast film will be. Although once applied and "cured," these coatings provide the desired properties, their "cure" is often quite slow, especially in drier regions, making it necessary to apply a "curing" or hardening solution before coated pieces may be handled. Unhydrolyzed alkyl silicates will not form a useful coating composition when filled with zinc powder. Such films are very soft, powdery, water and solvent soluble and often require several days to dry.

Phosphate vehicles give poor results in salt spray tests, exude salts to the coating surface which must be removed prior to top-coating and are subject to freezing as they are aqueous vehicles. Such vehicles are also quite sensitive to moisture for several hours after application.

The present invention involves the reaction of alkyl titanates forming polymeric titanates. Such polymeric titanates in combination with a salt of certain bi- or tri-valent metal salts form a suitable base which, when mixed with finely divided zinc powder and applied by conventional means, yields a film capable of providing the desired galvanic or cathodic protection.

In the present invention it is possible to prepare a coating which hardens readily to form a tough film adherent even to smooth steel surfaces. The present invention is insensitive to water within minutes after application, thus is unaffected by sudden rainfalls, dew, etc.

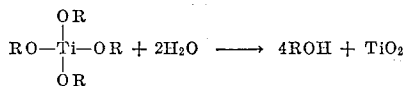
Dark pigments, such as carbon black, lamp black, or other inert materials may be and are used, in the present invention to give good contrast to sand blasted steel surfaces. Such pigments are not, however, necessary for proper functioning of the zinc filled inorganic coating vehicle.

The present composition invention hardens rapidly without the use of additional curing coats or hardening solutions. As the vehicle is prepared in low freezing point solvents, the present invention may be applied and will properly harden even at sub-zero temperatures. The coating will accept topcoats without difficulty, as there are no soluble salts that exude to the surface.

The coating is based on the formation of a partially hydrolyzed, polymeric alkyl titanate, bi or tri valent metallic salt complex in a suitable solvent, and the incorpora-

tion there with a finely divided metallic zinc dust. The coating may also employ non-hydrolyzed alkyl titanates in the formation of the complex as a special feature of the invention.

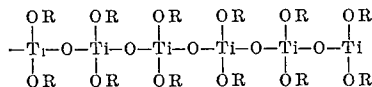
It is well known that alkyl titanates are readily hydrolyzed to form the corresponding alcohol and titanium dioxide in accordance with the following equation:



(R equals an alkyl radical having a chain length of 3 to 8 carbon atoms)

Exemplary of the alkyl titanates employed are tetraisopropyl titanate, tetrabutyl titanate and tetra 2-ethyl hexyl titanate. Several hydrates of varying composition are known. There appears to be little doubt that the hydrates orthotitanic acid  $\text{Ti}(\text{OH})_4$ , and metatitanic acid,  $\text{TiO}(\text{OH})_2$  exist, but in addition others have been prepared containing quantities of water intermediate between the amounts required for these two formulae, and also with less than that required by the latter formula. These may possibly be the hydrates corresponding to the complex titanic acids, but have not been obtained of sufficiently definite composition to enable this to be ascertained.

In the present invention, less than an equivalent weight, or stoichiometric quantity of water is used in the hydrolysis of the alkyl titanate where hydrolysis is employed. The amount of water employed is about 0.05 to 0.95 equivalent weight of water to the alkyl titanate. By controlling the concentration of water in a solvent system, a series of polymers of increasing molecular weight and titanium content can be produced. It is felt that titanium polymers of a chain length of six (6) to ten (10) titanium atoms yields optimum results in the present invention.



Titanium has a co-ordination number of six (6) which affords the alkyl titanates the property of entering into a series of complex co-ordination reactions with a number of compounds.

The addition of a quantity of 0.1 to 3 mols of bi or tri valent metal salt to 1 mol of the alkyl titanate affords

It has been repeatedly shown that various substituent groups of titanium could be interchanged and reacted, and that "mixed" compounds containing various combinations of elements and ester groups are possible.

If a quantity of alkyl titanate is added to a suitable bi or tri valent metallic salt, in an anhydrous solvent and said mixture or complex is mixed with finely divided metallic zinc dust and laid out in a film by conventional painting techniques, this film exhibits outstanding hardness and immediate water insensitivity.

All of the common alkyl titanates may be used in this invention and the properties of the coating composition and applied film can readily be regulated by the choice of alkyl titanate. Alkyl titanates having a very long or highly branched carbon chain tend to form a somewhat softer, more flexible film than do short chain alkyl titanates. The ultimate shelf stability of the coating composition is increased, however, through the use of such high molecular weight titanates.

All types of zinc dust may be used in the present invention. Manufacturers of zinc dust add calcium oxide to some grades of zinc dust to prevent gassing in organic vehicles. Although there may be some slight difference in the length of time required for films using various types of zinc dust to reach ultimate hardness, end properties of the resultant film are equal.

The hydrolysis of alkyl titanate where hydrolysis is employed must take place in a solvent system in order to avoid the precipitation of titanium dioxide. As distinguished from hydrolysis of other compounds, such as the hydrolysis of alkyl silicates, which takes place in solution without any visible precipitation, the addition of even a slight amount of water causes the precipitation of the alkyl titanate to the flocculant titanium dioxide precipitate. In order to avoid such precipitation, it was found that the hydrolysis of alkyl titanate can take place in solution by the use of two extremely dilute solutions which are a solution of the alkyl titanate on the one hand in a solvent such as Cellosolve and a solution of water in Cellosolve on the other hand, with the two solutions being added together to achieve the hydrolysis of the alkyl titanate. Exemplary of this finding of the requirement of use of a solvent system are the results shown in Table I below.

TABLE I

[Relative ratios in parts by weight]

| plus                |            | plus      |            | Results (clarity)               |
|---------------------|------------|-----------|------------|---------------------------------|
| Tetrabutyl Titanate | Cellosolve | add Water | Cellosolve |                                 |
| 34                  | -----      | .1        | -----      | (100%) H <sub>2</sub> O ppt.    |
| 34                  | -----      | .1        | .1         | (50%) ppt.                      |
| 34                  | -----      | .1        | .15        | (40%) ppt.                      |
| 34                  | -----      | .1        | .2         | (33 1/3%) cloudy.               |
| 34                  | -----      | .1        | .5         | (20%) cloudy.                   |
| 34                  | -----      | .1        | 1.0        | (10%) cloudy.                   |
| 34                  | -----      | .1        | 5.0        | (2%) cloudy.                    |
| 34                  | -----      | .1        | 10.0       | (1%) cloudy.                    |
| 34                  | 10         | .1        | -----      | (100%) H <sub>2</sub> O cloudy. |
| 34                  | 10         | .1        | 5.0        | (2%) cloudy.                    |
| 34                  | 10         | .1        | 10.0       | (1%) clear.                     |
| 34                  | 10         | .1        | 2.0        | (5%) cloudy.                    |
| 34                  | 15         | .1        | 2.0        | (5%) cloudy.                    |
| 34                  | 20         | .1        | 2.0        | (5%) sl. cloudy.                |
| 34                  | 25         | .1        | 2.0        | (5%) clear.                     |
| 34                  | 24         | .1        | 2.0        | (5%) clear.                     |
| 34                  | 23         | .1        | 2.0        | (5%) sl. cloudy.                |

properties to said mixture not evident in either the alkyl titanate or metallic salt alone. Although not wishing to be bound by theory, it is theorized that a bi-metallic complex of a composition similar to  $[\text{TiO}(\text{OH})_2]_x\text{A}$  (A being a bi or tri valent metallic salt of the type  $\text{SbCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{ZnBr}_3$ ,  $\text{CrCl}_3$ ,  $\text{AlCl}_3$ , etc., and X is from 6 to 10 to represent a cross-linked structure of from six (6) to ten (10) titanium atoms) is formed.

The separation of the zinc filler and complex vehicle composition of this invention is set forth below.

Example I

A molar solution of tetra butyl titanate representing 340 parts by weight of the titanate is dissolved in 250 parts of methyl isobutyl ketone. To this is added 530 parts by

weight of a 25% zinc chloride in cellosolve solution also containing 9 parts of water. The two solutions, after being added to one another, provide a partial hydrolysis of the titanate representing 25 percent hydrolysis based on one mol equivalent weight of water to that required for the complete hydrolysis. This final solution will provide a solids content of 20 to 50 percent, which in this example is 40 percent. Subsequently to this vehicle composition, finely divided zinc powder is added in the amount of 300 parts by weight to 100 parts by weight of vehicle solution. The zinc powder can be varied from 2 to 6 parts by weight based on the weight of the alkyl titanate metallic salt complex vehicle.

In the following formulations of Examples II through IX, the alkyl titanate and polyvalent complex vehicle was prepared in the same manner as set forth in Example I, and these examples show variations in the employment of the complex vehicle with the zinc filler and other fillers. The formulation of Example X below shows variations in the preparation of the complex vehicle.

*Example II*

|                                                              | Parts |
|--------------------------------------------------------------|-------|
| Partially hydrolyzed alkyl titanate/metal salt complex ----- | 10    |
| Zinc powder -----                                            | 60    |

*Example III*

|                                                              |    |
|--------------------------------------------------------------|----|
| Partially hydrolyzed alkyl titanate/metal salt complex ----- | 20 |
| Zinc powder -----                                            | 60 |

*Example IV*

|                                                              |    |
|--------------------------------------------------------------|----|
| Partially hydrolyzed alkyl titanate/metal salt complex ----- | 25 |
| Zinc powder -----                                            | 60 |

*Example V*

|                                                              |    |
|--------------------------------------------------------------|----|
| Partially hydrolyzed alkyl titanate/metal salt complex ----- | 10 |
| Zinc powder -----                                            | 40 |
| Carbon black -----                                           | 2  |

*Example VI*

|                                                              |    |
|--------------------------------------------------------------|----|
| Partially hydrolyzed alkyl titanate/metal salt complex ----- | 5  |
| Zinc powder -----                                            | 10 |
| Asbestos -----                                               | 1  |

*Example VII*

|                                                              |    |
|--------------------------------------------------------------|----|
| Partially hydrolyzed alkyl titanate/metal salt complex ----- | 15 |
| Zinc powder -----                                            | 50 |
| Platey mica -----                                            | 2  |

*Example VIII*

|                                                              |    |
|--------------------------------------------------------------|----|
| Partially hydrolyzed alkyl titanate/metal salt complex ----- | 20 |
| Zinc powder -----                                            | 50 |
| Carbon black -----                                           | 2  |
| Mica or calcium silicate -----                               | 3  |

*Example IX*

|                                                              |    |
|--------------------------------------------------------------|----|
| Partially hydrolyzed alkyl titanate/metal salt complex ----- | 20 |
| Zinc powder -----                                            | 60 |
| Carbon black -----                                           | 2  |
| Asbestos -----                                               | 3  |

In the following Example X, a liquid vehicle complex was prepared which is used with 2 to 6 parts by weight of the zinc filler to one part by weight of the alkyl titanate and polyvalent salt complex in the vehicle. In this example a non-hydrolyzed alkyl titanate is employed.

In this vehicle formulation, the manner of preparation was the same as set forth as for Example I.

*Example X*

A molar solution of isopropyl titanate representing 340 parts by weight of the titanate is dissolved in 250 parts of cellosolve, i.e., ethylene glycol monomethylether. To this is added 530 parts by weight of a 25% antimony chloride in cellosolve solution. This solution will provide a solids content of 20 to 50 percent, which in this example is 40 percent. Subsequently to this vehicle composition, finely divided zinc powder is added in the amount of 300 parts by weight to 100 parts by weight of vehicle solution. The zinc powder can be varied from 2 to 6 parts by weight based on the weight of the alkyl titanate metallic salt complex vehicle.

The above formulations employed with the zinc dust as pointed out above are laid down very simply by painting, spraying, swabbing, and the like, upon ferrous metal surfaces. These coatings cure very expeditiously and uniformly to provide a hard, tough, water soluble, coating.

The hardness is quite superior and ranges from 7H to 9H. Various changes may be made in the formulation of this invention as will be readily apparent to those skilled in the art. Such changes are within the scope and teaching of this invention as defined by the claims appended hereto.

What is claimed is:

1. A composition of matter comprising a liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said coating comprising a complex formed from an alkyl titanate and a polyvalent metallic salt, said vehicle consisting essentially of about 0.1 to 3 mols of a polyvalent metallic salt of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride and zinc chloride, and 0.1 to 1 mols alkyl titanate, said alkyl titanate having its alkyl groups of a carbon chain length of 3 to 8 carbon atoms.

2. A composition of matter comprising a liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said coating comprising a complex formed from an alkyl titanate and a polyvalent metallic salt, said vehicle consisting essentially of about 0.1 to 3 mols of a polyvalent metallic salt of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride and zinc chloride, and 0.1 to 1 mols alkyl titanate, said alkyl titanate having its alkyl groups of a carbon chain length of 3 to 8 carbon atoms, said vehicle and zinc filler being employed in the ratio of about 1 part vehicle to 2 to 6 parts by weight of zinc filler.

3. A composition of matter comprising a liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said coating comprising a complex formed from an alkyl titanate and a polyvalent metallic salt, said vehicle consisting essentially of about 0.1 to 3 mols of a polyvalent metallic salt of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride and zinc chloride, and 0.1 to 1 mols alkyl titanate, said alkyl titanate being partially hydrolyzed with about 0.05 to 0.95 equivalent weight of water, said alkyl titanate having its alkyl groups of a carbon chain length of 3 to 8 carbon atoms.

4. A composition of matter comprising a liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said coating comprising a complex formed from an alkyl titanate and a polyvalent metallic salt, said vehicle consisting essentially of about 0.1 to 3 mols of a polyvalent metallic salt of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride, and zinc chloride, and 0.1 to 1 mols alkyl titanate, said alkyl titanate being partially hydrolyzed with about 0.05 to 0.95 equivalent weight of water, said alkyl titanate having its alkyl groups of a carbon chain length of 3 to 8 carbon atoms, said vehicle and zinc filler being employed in the ratio

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of about 1 part vehicle to 2 to 6 parts by weight of zinc filler.

5. A method of making a galvanic action coating composition comprising a complex formed from an alkyl titanate, and a polyvalent metallic salt, said method comprising providing an organic solution of an alkyl titanate having a carbon chain length of 3 to 8 carbon atoms, adding thereto about 0.1 to 3 mols for each mol of titanate of a polyvalent metallic salt of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride and zinc chloride, diluting said mixture with an organic solvent and adding thereto finely divided zinc powder.

6. A method of making a galvanic action coating composition comprising a complex formed from an alkyl titanate, and a polyvalent metallic salt, said method comprising providing an organic solution of an alkyl titanate having a carbon chain length of 3 to 8 carbon atoms, adding thereto an amount ranging from .1 gram mol to 3 mols per gram mol of titanate of a polyvalent metal salt of the class consisting of zinc chloride, zinc bromide, aluminum chloride, antimony chloride, chromic chloride and iron chloride, diluting said mixture with an organic solvent to a solids content of 20 to 35% and incorporating therewith a filler component consisting of finely divided zinc powder.

7. A method of making a galvanic action coating composition comprising a complex formed from an alkyl titanate, and a polyvalent metallic salt, said method comprising providing an organic solution of an alkyl titanate having a carbon chain length of 3 to 8 carbon atoms, adding thereto an amount ranging from .1 gram mol to 3 mols per gram mol of titanate of a polyvalent metal salt of the class consisting of zinc chloride, zinc bromide, aluminum chloride, antimony chloride, chromic chloride and iron chloride, diluting said mixture with an organic solvent to a solids content of 20 to 35% and incorporating therewith a filler component consisting of finely divided zinc powder, said zinc powder being added in the amount of 2 to 6 parts by weight to each part of combined alkyl titanate and polyvalent metal salt.

8. A method of making a galvanic action coating composition comprising a complex formed from an alkyl titanate, and a polyvalent metallic salt, said method comprising partially hydrolyzing an alkyl titanate having a carbon chain length of 3 to 8 carbon atoms using about 0.05 to 0.95 equivalent weight of water, adding thereto about 0.1 to 3 mols for each mol of titanate of a polyvalent metallic salt of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride and zinc chloride, diluting said mixture with an organic solvent and adding thereto finely divided zinc powder.

9. A method of making a galvanic action coating composition comprising a complex formed from an alkyl titanate, and a polyvalent metallic salt, said method consisting of partially hydrolyzing an alkyl titanate having a carbon chain length of 3 to 8 carbon atoms, using about 0.05 to 0.95 equivalent weight of water in a mutually compatible organic solvent and adding thereto to an amount ranging from .1 gram mol to 3 mols per gram mol of titanate of a polyvalent metal salt of the class consisting of zinc chloride, zinc bromide, aluminum

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chloride, antimony chloride, chromic chloride and iron chloride, diluting said mixture with an organic solvent to a solids content of 20 to 35% and incorporating therewith a filler component consisting of finely divided zinc powder.

10. A method of making a galvanic action coating composition comprising a complex formed from an alkyl titanate, and a polyvalent metallic salt, said method consisting of partially hydrolyzing an alkyl titanate having a carbon chain length of 3 to 8 carbon atoms, using about 0.05 to 0.95 equivalent weight of water in a mutually compatible organic solvent and adding thereto an amount ranging from .1 gram mol to 3 mols per gram mol of titanate of a polyvalent metal salt of the class consisting of zinc chloride, zinc bromide, aluminum chloride, antimony chloride, chromic chloride and iron chloride, diluting said mixture with an organic solvent to a solids content of 20 to 35% and incorporating therewith a filler component consisting of finely divided zinc powder, said zinc powder being added in the amount of 2 to 6 parts by weight to each part of combined alkyl titanate and polyvalent metal salt.

11. A method of making a galvanic action coating composition comprising a complex formed from an alkyl titanate, and a polyvalent metallic salt, said method comprising dissolving an alkyl titanate having a carbon chain length of 3 to 8 carbon atoms in an organic solvent adding thereto a solution of water in an organic solvent, said water being employed in an amount to provide 0.05 to 0.95 equivalent weight to the alkyl titanate for partial hydrolysis thereof, adding to the partially hydrolyzed alkyl titanate about 0.1 to 3 mols for each mol of titanate of a polyvalent metallic salt of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride and zinc chloride, diluting said mixture with an organic solvent and adding thereto finely divided zinc powder.

12. A method of making a galvanic action coating composition comprising a complex formed from an alkyl titanate, and a polyvalent metallic salt, said method comprising dissolving an alkyl titanate having an alkyl chain of 3 to 8 carbon atoms in an organic solvent, adding thereto a solution of water in an additional separate quantity of a mutual solvent for water and said titanate, said water being employed in an amount to provide 0.05 to 0.95 equivalent weight to the alkyl titanate for partial hydrolysis thereof, adding to the partially hydrolyzed alkyl titanate about 0.1 to 3 mols for each mol of titanate of a polyvalent metallic salt of the group consisting of zinc bromide, aluminum chloride, antimony chloride, chromic chloride, iron chloride and zinc chloride, diluting said mixture with an organic solvent and adding thereto finely divided zinc powder, said zinc powder being added in the amount of 2 to 6 parts by weight to each part of combined alkyl titanate and polyvalent metal salt.

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