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ZINC FILLED GALVANIC COATING

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This invention relates to improvements in coating compositions and method 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 is anhydrous, that is it contains no water, and involves no hydrolysis reaction which substantially enhances its stability to provide in use a coating vehicle which, when applied to metal surfaces, forms a hard, tough, and insoluble protective coating with the zinc filled particles. Since there is no hydrolysis of the coating vehicle, there is provided virtually an unlimited shelf life.

It is a feature of this invention that the vehicle employed makes use of a complex bimetallic amine salt with an alkyl silicate forming a polymeric silylene amine metallic salt to provide the stability desired. This vehicle is obtained through the employment of zinc chloride, antimony trichloride with an amine or alkanolamine to form the complex bimetallic amine salt which, with an alkyl silicate, forms the polymeric silylene amine metallic salt vehicle combination. This vehicle is used then with finely divided metallic zinc dust as a filler and any other conventional fillers that are desired to be added.

It is a feature through the employment of the vehicle composition and the method of making the same that, since no hydrolysis takes place, manufacturing procedures are not highly critical and the vehicle is easily controlled. Thus, the vehicle is insensitive to water within minutes after application and is unaffected by sudden rain falls, dew, high humidity, and the like. Thus, the hardness and hardening rate is only mildly, if at all, affected by humidity and will cure to a hard coating even in arid regions without the use of additional curing coats or hardening solutions.

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

In the preparation of the coating vehicle of this invention with which the zinc dust filler is employed, it has been found that an anhydrous vehicle, employing no hydrolysis reaction, comprised of a complex bimetallic amine salt with an alkyl silicate forming a polymeric silylene amine metallic salt produces a firm, tough, hard and insoluble protective coating in which the cure is rapid and definite and substantially independent of weather conditions. Further, the coating vehicle has a long shelf life and can be stored quite well without loss for long periods of time. Further, it has been found that a higher solids

content can be obtained than that heretofore obtainable, which is quite advantageous in this field. Essentially, it is believed that the coating vehicle ultimately obtained is a unique triple complex of zinc, antimony and an anhydrous alkyl silicate with an amine. This complex is prepared by means of the preparation of a complex bimetallic amine salt employing zinc chloride, antimony trichloride and an amine which is then reacted with an alkyl silicate forming the polymeric silylene amine metallic salt. With the coating vehicle and the zinc dust filler, other fillers may be employed, such as dark pigments, including carbon black, lamp black or other inert materials which may be employed to give good contrast to sand blasted surfaces where the vehicle coating is applied by painting, spraying, or other conventional application techniques. In addition, asbestos fibers, calcium silicate, mica, and the like, may be utilized.

The zinc chloride employed is employed in the vehicle in the range of 1 to 2 mols. It is employed with a known anhydrous solvent for the zinc chloride such as an alcohol, ketone, Cellosolve, etc. Exemplary of such solvents is Cellosolve, i.e., ethylene glycol monoethyl ether.

The antimony trichloride is employed in the range of 0.025 to 0.1 mol.

The amine employed may be either a primary or secondary amine or alkanolamine. Exemplary of such amines are 2-ethyl hexyl amine, di(2 ethyl hexyl) amine, monoethanolamine, dimethylaminopropylamine, diethylaminopropylamine, 2-amino-2 meythl-1 propanol and morpholine. These amines are used in the general range of 1 to 2 mols in the coating vehicle. The limit of the alkyl group chain length is limited only by its solubility in the solvent employed and for this purpose it is generally desired that the carbon chain length be 1 to 10 carbon atoms. The properties of the applied film vehicle can readily be regulated by the choice of the amine. Long chain alkylamines tend to form a somewhat softer and more flexible film than do short chain amines. The very low molecular weight compounds, however, tend to require a longer period to reach a stage of water insolubility.

The alkyl silicates employed may be the common alkyl silicates normally found where the alkyl group ranges from 2 to 9 carbon atoms in chain length either straight or branched chain. Exemplary of such alkyl silicates are isopropyl silicate, n-butyl silicate and all three types of ethyl silicate. Due to the higher silica (SiO_2) content, the ethyl silicates have been utilized in this invention. The three types of ethyl silicate most commonly employed are pure tetra ethyl ortho silicate, condensed ethyl silicate and 40% ethyl silicate. The first is a reagent type grade and too expensive for commercial use. Condensed ethyl silicate is a grade containing 26 to 28% silica as SiO_2 and is used in zinc filled inorganic coatings. The 40% ethyl silicate contains 40% silica (SiO_2) and may be employed making this advantageous because of its high silica content. Previously this 40% ethyl silicate had not been satisfactorily employed in zinc filled coatings, because of its difficulty in partially hydrolyzing as the silica is readily precipitated, because the shelf stability is poor as strong acids must be used to catalyze the hydrolysis, and because the applied film does not have the hardness afforded by condensed ethyl silicate and such films were powdery.

It has been established that zinc, antimony, aluminum, and other metallic salts form complexes with amines and that antimony in particular forms crystalline double salts with a variety of metallic chlorides. These salts are quite water soluble. It has also been established that zinc chloride, in particular, forms soluble complexes of the composition $Zn°A_4$ with amine compounds. In this invention it has been found that zinc chloride in an anhydrous

solvent, reacted with various molar ratios of amine forms such a compound and that the addition of antimony trichloride forms a bi-metallic complex of the theoretical composition $ZnCl_2$—$SbCl_3$—A, where A is a primary or secondary amine or alkanolamine. This system must be maintained in an anhydrous state as the presence of water causes immediate precipitation of antimony oxychloride (SbOCl or $Sb_4O_5Cl_2$). The presence of tartaric, oxalic or free hydrochloric acid prevents such precipitation. If the above complex composition is mixed with zinc dust and laid out in a film, the film is hard, powdery and retains its water sensitivity and cannot satisfactorily be employed as a protective coating.

However, it has been found through this invention that when alkyl silicate is added to the metallic complex and the mixture is mixed with finely divided zinc dust and laid out in a film, this film exhibits outstanding hardness and immediate water insensitivity and provides a protective coating of a high degree of advantage. Although not wishing to be bound by theory, it is theorized that the alkyl silicate reacts with the excess of amine assuming polymeric forms of the type $(H_2Si—NH—)_x$ which may or may not form complex triple salts with the zinc antimony amine chelate or complex already present. It has been shown that the various substituent groups of silicon could be interchanged and reacted according to rules based on ionic radii, and that many "mixed" compounds containing various combinations of elements and ester groups are possible. Of the many amines examined, virtually all form complex compounds with zinc and antimony chlorides, but, for proper use, the amine complexes should be soluble in all common solvents.

The zinc dust employed with the complex vehicle may be of the general commercial type. Manufacturers of the zinc dust, however, add calcium oxide to some grades of zinc dust to prevent gassing in organic vehicles. Although these grades of zinc may be used, it has been found that the presence of calcium oxide lengthens the period of time required for the film to reach ultimate hardness and should be avoided, although end products are ultimately satisfactory.

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

Example I

A molar solution of zinc chloride in ethylene glycol monoethyl ether is reacted with 1.5 mols of 2-ethyl-hexyl amine. This mixture is adjusted to a pH of about 2 to 3 with an anhydrous acid. Antimony trichloride in the amount of 0.025 mol is added slowly to prevent precipitation which may occur with too rapid an addition. Subsequently, 0.1 mol of 40% ethyl silicate is added. The entire complex is then diluted to 38–40% solids with a conventional solvent such as Cellosolve, Cellosolve acetate, ethyl acetate, and the like. This complex is then ready for use and the zinc dust may be added to it in the amount of 6 parts by weight of the zinc dust to 1 part by weight of the complex vehicle.

In the following formuations of Examples II through VIII, the complex was prepared in the same manner as set forth in Example I and show variations in the employment of the complex with the zinc filler and other fillers. The formulations of Examples IX through XIII below show variations and ranges in the preparation of the complex.

Example II

	Parts
Complex vehicle from Example I	20
Zinc powder	60

Example III

Complex vehicle from Example I	25
Zinc powder	60

Example IV

	Parts
Complex vehicle from Example I	10
Zinc powder	40
Carbon black	3

Example V

Complex vehicle from Example I	5
Zinc powder	10
Asbestos	1

Example VI

Complex vehicle from Example I	15
Zinc powder	50
Platey mica	2

Example VII

Complex vehicle from Example I	20
Zinc powder	50
Carbon black	2
Mica	3

Example VIII

Complex vehicle from Example I	20
Zinc powder	60
Carbon black	2
Asbestos	2

In the following Examples IX through XIII, a liquid vehicle complex was prepared which is used with two to six parts by weight of zinc filler to one part by weight of the complex vehicle.

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

Example IX

1 mol zinc chloride
1.2 mol 2-amino-2-methyl-1-propanol
0.025 mol antimony trichloride
1 mol ethyl silicate, condensed

Example X

1.5 mol zinc chloride
1.5 mol monoethanol amine
0.1 mol antimony trichloride
0.5 mol n-butyl silicate

Example XI

2 mol zinc chloride
2 mol diethylaminopropylamine
0.05 mol antimony trichloride
0.3 mol isopropyl silicate

Example XII

1 mol zinc cholride
1.2 mol morpholine
0.025 mol antimony trichloride
0.2 mol ethyl silicate 40%

Example XIII

1 mol zinc chloride
1 mol 2-amino-2-methyl-1-propanol
0.03 mol antimony trichloride
1 mol ethyl silicate, condensed

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 formulations 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 an anhydrous liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said vehicle being prepared by the addition of about 1 to 2 mols zinc chloride to 1 to 2 mols amine selected from the group consisting of primary and secondary amines and alkanolamines having a carbon chain length of 1 to 10 carbon atoms, followed by the addition of 0.025 to 0.1 mol antimony trichloride and 0.1 to 1 mol alkyl silicate in which the alkyl group has from 2 to 9 carbon atoms.

2. A composition of matter comprising an anhydrous liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said vehicle being prepared by the addition of about 1 to 2 mols zinc chloride to 1 to 2 mols amine selected from the group consisting of primary and secondary amines and alkanolamines having a carbon chain length of 1 to 10 carbon atoms, followed by the addition of 0.025 to 0.1 mol antimony trichloride and 0.1 to 1 mol alkyl silicate in which the alkyl group has from 2 to 9 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 an anhydrous liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said vehicle being prepared by the addition of about 1 mol zinc chloride to 1.2 mols 2-amino-2 methyl-1-propanol, followed by the addition of 0.025 mol antimony trichloride and 1 mol ethyl silicate, condensed.

4. A composition of matter comprising an anhydrous liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said vehicle being prepared by the addition of about 1.5 mols zinc chloride to 1.5 mols monoethanol amine, followed by the addition of 0.1 mol antimony trichloride and 0.5 mol n-butyl silicate.

5. A composition of matter comprising an anhydrous liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said vehicle being prepared by the addition of about 2 mols zinc chloride to 2 mols diethylaminopropylamine, followed by the addition of 0.05 mol antimony trichloride, and 0.3 mol isopropyl silicate.

6. A composition of matter comprising an anhydrous liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said vehicle being prepared by the addition of about 1 mol zinc chloride to 1.2 mols moropholine, followed by the addition of 0.025 mol antimony trichloride, and 0.2 mol ethyl silicate 40%.

7. A composition of matter comprising an anhydrous liquid vehicle and a zinc powder filler providing a zinc galvanic coating for surfaces when applied thereto, said vehicle being prepared by the addition of about 1 mol zinc chloride to 1 mol 2-amino-2-methyl-1-propanol, followed by the addition of 0.03 mol antimony trichloride and 1 mol ethyl silicate, condensed.

8. A method of preparing a zinc filled liquid galvanic coating composition capable of forming a protective film upon surfaces to which it is applied, comprised of a zinc filler and a liquid vehicle which comprises adding 1 to 2 mols of an amine selected from the group consisting of primary and secondary amines and alkanolamines having a carbon chain length of 1 to 10 carbon atoms to 1 to 2 mols of zinc chloride to form a mixture, adding about 0.025 to 0.1 mol antimony trichloride to the mixture, subsequently adding 0.1 to 1 mol of an alkyl silicate in which the alkyl group has from 2 to 9 carbon atoms to the mixture to obtain the liquid vehicle and then mixing powdered zinc filler with said liquid vehicle.

9. A method of preparing a zinc filled liquid galvanic coating composition capable of forming a protective film upon surfaces to which it is applied, comprised of a zinc filler and a liquid vehicle which comprises adding 1 to 2 mols of an amine selected from the group consisting of primary and secondary amines and alkanolamines having a carbon chain length of 1 to 10 carbon atoms to 1 to 2 mols of zinc chloride to form a mixture, adding about 0.025 to 0.1 mol antimony trichloride to the mixture, subsequently adding 0.1 to 1 mol of an alkyl silicate to the mixture to obtain the liquid vehicle, said alkyl silicate having its alkyl groups of a carbon chain length of 2 to 9 carbon atoms and then mixing powdered zinc filler with said liquid vehicle, 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.

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