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ZINC-RICH COATINGS CONTAINING CONDUCTIVE CARBON BLACK

Filed July 13, 1966

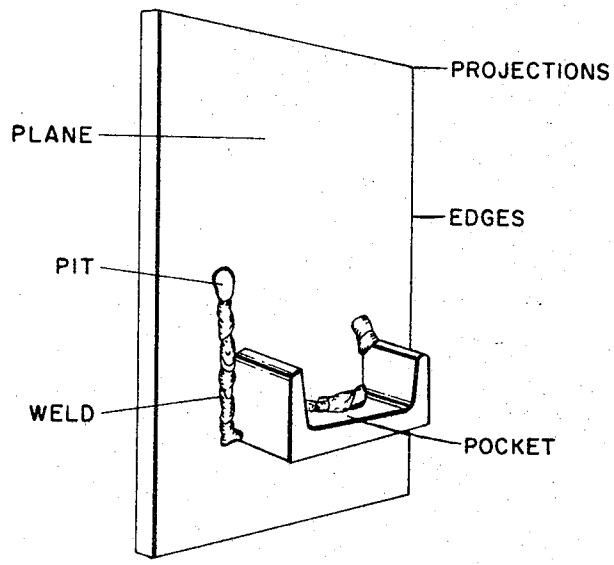


FIG. 1

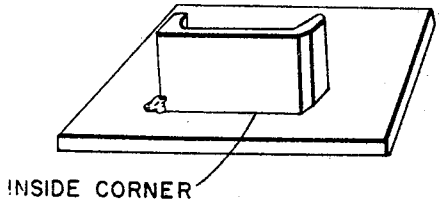


FIG. 2

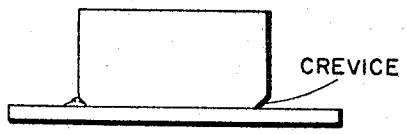


FIG. 3

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ZINC-RICH COATINGS CONTAINING CONDUCTIVE CARBON BLACK

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ABSTRACT OF THE DISCLOSURE

Improved corrosion resistant coatings for ferrous metals comprise 12 to 32½% by weight binder, 65 to 87% zinc dust and 0.9 to 2.6% electrically conductive carbon black.

This invention relates to corrosion resistant coatings for ferrous metals. In particular, it relates to such coatings in the form of a paint or primer containing metallic zinc.

It is well known that metals, particularly steel, can be protected against the rapid deteriorative effects of corrosion by the elements in its environment by applying thereto a coating of metallic zinc. This protection is provided in several ways. One way is that zinc itself is much more durable under most service conditions that is steel. Thus, the zinc coating forms a barrier on the surface of the steel which corrodes only very slowly while shielding the steel from the corrodent.

Another, and equally significant, protection is the electrochemical or sacrificial action of the zinc. This effect is exterted when the steel and the zinc particles are electrically coupled and in contact with a conductive aqueous solution. In such a case, the steel is protected at the expense of the zinc since the electrical potential of the zinc is sufficiently higher than that of the steel (iron) to direct the flow of electrons to the steel, maintaining a negative charge on the steel surface and preventing the formation of the ferrous ions which represent rust. This effect results in the formation of zinc hydroxide on the zinc which in turn reacts with chlorine or carbon dioxide in the surrounding environment to form basic zinc salts. These basic zinc salts plate out on the bare steel surface to form a protective coating which affords good barrier protection to the steel. When this effect is taking place, the metallic zinc is, of course, being consumed by the salt formation; thus the term "sacrificial action." The typical case where this process comes into play is that where a steel structure is coated with zinc and a scratch or other discontinuity develops in the coating. The sacrificial action then continues until the damaged area has been sufficiently plated to yield protection. In effect, the zinc acts as the anode of a galvanic cell while the steel acts as the cathode. This effect is well known as the source of the expression "galvanized iron."

The application of a zinc coating directly to steel is a rather cumbersome and expensive operation. In the past this has been accomplished by hot dip coatings or electroplating, both of which are to some extent objectionable for the above reasons.

More recently, it has become the practice to coat the metal item sought to be protected with a paint containing a sufficient amount of metallic zinc to impart the desired resistance to corrosion. These paints have proven very effective in providing both the cathodic or galvanic type protection and the barrier type as well. However, in order to provide the desired degree of cathodic protection, a certain minimum electrical conductivity of the coating solution is required. In order to provide the required level of conductivity, a very high level of zinc in the coating is

required. In most cases this is as high as 85 to 95% by weight of the total solids content of the coating.

The previously known zinc containing coating compositions suffer at least two major shortcomings as a result of the high zinc loading. For one, the high zinc content pushes the cost of these coatings to an undesirable level. Even more troublesome, however, is the fact that the low level of binder material relative to that of the metallic zinc results in the formation of relatively weak films which disintegrate or degrade rather readily when subjected to even normal usage.

In accordance with the instant invention, coating compositions containing zinc are provided which exhibit the same high level of cathodic protection against corrosion as is shown by prior art compositions, but which do so at greatly reduced zinc loading. These compositions comprise a film-forming binder or vehicle, metallic zinc, and conductive carbon black. More specifically, these compositions comprise about 12 to 32.5% by weight binder, based on total weight of components, 65 to 87% by weight metallic zinc, and 0.9 to 2.6% by weight conductive carbon black.

Whereas, as previously noted, prior art compositions of this nature, in order to be effective, required zinc loadings as high as 85 to 95% by weight, drastically reducing the allowable binder content therein, the total content of zinc and carbon black combined need not exceed 85% in the instant compositions. Thus, these compositions contain sufficient binder to impart a high level of strength and durability to the coatings which was not always the case with prior art coatings.

The compositions of this invention, when used as prime coatings, have been found to be less prone to cause bubbling in a subsequently applied topcoat than are the more highly loaded compositions of the prior art. This is likewise believed to be closely related to the lower pigment concentration in these compositions.

Compositions according to this invention can be prepared using any of the binders normally used in preparing corrosion resistant coatings or outdoor coatings generally. Such binders include chlorinated rubber, polyisoprene, poly(vinyl acetate), vinyl chloride—vinyl acetate copolymers, polyurethanes, catalyzed epoxy and epoxy-ester resins, chlorinated polyolefins, alkyd resins and inorganic binders, to name a few. The type of binder depends to some extent upon the type of service anticipated. A particularly good binder, and a preferred one, is chlorinated rubber containing about 63 to 69% chlorine. This particular binder is effective under a wide variety of conditions and is quite extensively used due to its environmental stability and durability.

Normally the coating compositions according to this invention are employed as primers or undercoatings under one or more finish coats. Their utility is, of course, not limited to this application, although the coloration due to the carbon black may limit their utility in many cases. Where the black color is not a deterrent, these compositions can be employed as finish coats if they are otherwise properly formulated.

The metallic zinc in these compositions is in small particle form. These particles can be in the form of extremely small flakes having thickness between about 0.1 and 0.5μ which can be prepared by atomizing extremely pure zinc (about 99.7% Zn or more) followed by ball milling. Equally preferable are spherical particles having diameter between about 0.1 and 0.5μ. These can be prepared by distillation and subsequent condensation of the high purity Zn metal. No further treatment of the zinc is required prior to incorporation thereof into the coating composition.

Any of the commercially available electrically conductive carbon blacks can be employed. Preferably, the black is made from the thermal degradation of acetylene and

will have a particle size between about 0.005 and 0.200μ. A particularly useful black is that known as acetylene black, prepared by thermal decomposition of acetylene without combustion thereof.

For application to a substrate, the components are incorporated into a liquid medium which is, in most cases, a solvent for the binder material and a suspending medium for the zinc and carbon black. A film of the binder material with the pigments dispersed therethrough is formed by evaporation of the solvent liquid. In some cases, the binder material can be an uncured or partially polymerized resin which forms a film by completing its polymerization after the solvent or carrier has evaporated. In either case, the selection of the liquid medium depends upon the binder to be used. Selection of the binder-liquid combination to be used is within the skill of the art and forms no part of this invention.

Generally speaking, the compositions of this invention are otherwise comprised of combinations of ingredients known to the art. For example, various plasticizers known to be effective or desirable with the selected binder material are frequently used, as well as additional resins, to yield specific properties desired. It is also sometimes desirable to include wetting agents to assist in suspending the solid, insoluble pigments, as well as additives, to modify the drying rate or curing rate of the composition following its application to a substrate.

The coating compositions of necessity must exhibit a certain minimum conductivity in order to provide the necessary cathodic protection to the metal which is to be coated therewith. The conductivity is a function of the total concentration of zinc and carbon black in the composition and the degree of interdispersion of the two. Thus, the carbon black and the zinc must be intimately mixed throughout the composition during the preparation thereof. Such mixing is readily accomplished by known methods of mixing. Normally, the composition, including the solvent, is passed through a conventional paint mill or the like to effect intimate mixing.

The solvent-containing material can be applied to the metal by spraying, brushing, or in any other convenient way. The viscosity or flow characteristics of the solution will depend upon the method to be used for applying the coating.

In the attached drawing, FIGS. 1, 2 and 3 illustrate a standard test panel used in exposing coating compositions to the atmosphere. The critical points of exposure are designated on the panel. This type panel was employed in the testing of the formulation of Example 1.

Example 1

A zinc rich primer containing carbon black and a control primer were prepared having the following formulations:

	Control	Ex. 1
Chlorinated rubber (Ca 65% chlorine (parts)	2.12	7.19
Chlorinated biphenyl (parts)	1.16	3.91
Chlorinated triphenyl (parts)	.57	1.93
Zinc dust (7 microns)	62.79	45.50
Zinc oxide	6.71	4.83
Al powder	3.96	----
Organic modified Mg montmorillonite	.42	.35
Dibasic lead phosphite	.28	.23
Acetylene black	----	1.06
Xylene	17.60	27.00
VM & P naphtha	4.40	8.00

Aluminum powder was in flake form. Flakes were approximately 0.13μ thick. Not less than 90% of the flakes will pass through a 325 mesh standard screen having 44μ openings.

The formulations were prepared by pebble milling the mixture for 8 hours.

Standard steel test panels of the type shown in the drawing were sandblasted to white metal and spray coated with the two formulations to a thickness of about 2.5 to 3.5 mils. These were then sprayed with a chlorinated rubber midcoat to a thickness of 2 to 3 mills and then with a TiO_2 pigmented chlorinated rubber topcoat of about 2 to 3 mils.

A third set of test panels was treated with a commercial zinc rich primer believed to be comprised of zinc particles suspended in a sodium silicate binder and overcoated similarly.

The coated test panels were exposed to a highly corrosive industrial atmosphere of a plant in Brunswick, Ga., where chlorinated camphene is produced. After six months exposure to this corrosive atmosphere, the panels were inspected for evidence of rust and corrosion. A qualitative and quantitative evaluation of each panel at each of the critical spots was made as follows:

Good (G)=no apparent change in coating=2 points
Fair (F)=some change, <5% of surface attacked=1 point
Bad (B)=film failure has occurred, rust appeared=0 point

The ratings of the three coatings were as in the following table.

		Area								Overall rating	
Coating	Panel No.	Projection	Plane	Edge	Pit	Weld	Crevice	Inside corner	Pockets	Individual panels	Composite
Control A	1	G	G	G	G	B	B	F	B	9	17
	2	G	G	F	F	F	B	F	B	8	
Control B	1	G	G	B	G	G	B	G	F	11	22
	2	G	G	B	G	G	B	F	G	11	
Example 1	1	G	G	G	G	G	B	G	G	14	29
	2	G	G	G	G	G	F	G	G	15	

The overall number ratings clearly show that the test panels primed with the compositions of this invention resist the corrosive effects of the atmosphere better than those coated with either of the compositions which do not contain carbon black.

Substantially similar results were achieved when other test panels containing these same coatings were subjected to a tidal exposure in Miami, Florida for six months. Again, the best corrosion resistance was exhibited by those panels which were primed with the compositions of this invention.

Example 2

A series of chlorinated rubber based zinc rich primers was prepared to demonstrate the improved sacrificial or galvanic protection afforded by the zinc rich coatings containing carbon black. In each case, the film-forming vehicle was composed of:

	Parts
Chlorinated rubber	53.0
Chlorinated biphenyl	14.2
Chlorinated triphenyl	28.4
Organic modified magnesium montmorillonite	2.6
Dibasic lead phosphate	1.8

This vehicle was formulated into a paint by dissolving in an 80/20 mixture of toluene and VM&P naptha, incorporating the zinc and carbon black therein and mixing well in a pebble mill. The following compositions were prepared (parts by weight):

No.	Vehicle	Zinc dust	Acetylene black	Solvent
A	20.83	39.17		40
B	19.42	39.10	1.48	40
C	17.75	52.25		30
D	16.56	52.10	1.34	30
E	14.78	65.22		20
F	13.83	65.07	1.10	20
G	10.50	69.50		20
H	9.81	69.40	0.79	20
I	7.52	77.48		15
J	7.03	77.40	0.57	15
K	4.56	80.44		15
L	4.26	80.39	0.35	15

Each of the primer compositions was spray coated onto a 2 x 4 inch, degreased, cold-rolled, steel panel. Each coated panel was electrically coupled to a second uncoated panel of the same size. Coupling was accomplished by insulated copper wires connected at the top of each panel.

The coupled plates were then immersed to a depth of 2¾ inches in a 1% aqueous sodium chloride solution. Voltage differences and current flow between the two panels were measured periodically with a meter connected directly across the panels. The results of these readings are recorded in the following table which clearly shows that the efficiency of the calvanic cell decreases less rapidly in all cases where the carbon black is present than in the corresponding controls where zinc is used at the same level without carbon black. The breakdown of the galvanic cell leads to corrosion of the metal, thus the presence of the carbon black clearly yields improved corrosion resistance.

Also observed and noted in these tests was the time elapsed before the first sign of rust appeared on the panel. These times were as follows:

Primer number	Time elapsed (days)
A	1
B	4
C	<1
D	2
E	1
F	2
G	2
H	3
I	2
J	6
K	6
L	7

Here again, in each instance, the corrosion resistance was improved by the presence of the carbon black.

Example 3

The compositions prepared for the testing of Example 2 were subjected to a series of physical tests to demonstrate the improvement in physical properties which can be achieved by reducing the zinc loading.

Film integrity was determined on coatings sprayed onto clean, 4 x 6 inch panels, which had not been sand-blasted. The test consisted of scratching the panels with the rounded end of a paper clip. The results were evaluated and assigned subjective ratings as follows:

(1)—Very good resistance to abrasion
(2)—Fair resistance to abrasion
(3)—Poor resistance to abrasion
(4)—Very poor resistance to abrasion

The conical mandrel elongation test was performed according to ASTM standard D-525-60.

Results of these tests are recorded in the following

Formulation	A	B	C	D	E	F	G	H	I	J	K	L
Immediate:												
Potential	2.00	2.21	2.20	2.40	2.50	2.50	2.10	2.30	2.50	2.60	2.50	2.60
Current	.55	.52	.55	.50	.57	.50	.50	.50	.52	.50	.50	.50
7 hrs.:												
Potential	1.70	1.85	1.95	2.15	2.09	2.05	2.02	2.50	2.35	2.25	1.80	.195
Current	.50	.51	.48	.50	.50	.52	.51	.48	.52	.46	.51	.45
24 hrs.:												
Potential	1.50	1.70	.35	1.35	1.00	1.40	1.30	1.60	1.60	2.10	1.70	1.50
Current	.35	.45	.20	.37	.45	.35	.45	.33	.37	.32	.33	.40
2 days:												
Potential	.035	1.40	.040	1.20	.062	.90	.095	1.40	.13	1.85	1.80	1.80
Current	.05	.48	.10	.33	.10	.27	.15	.25	.15	.252	.25	.36
3 days:												
Potential		.90	.013	1.30	.016	.02	.043	1.00	.025	1.52	1.70	1.57
Current		.49	.06	.51	.07	.03	.10	.20	.06	.24	.23	.24
4 days:												
Potential		.04		.17			.03	.04	.01	1.42	.95	1.30
Current		.05		.10					.05	.24	.20	.24
5 days:												
Potential									.02	1.45	1.20	1.61
Current									.05	.21	.21	.23
6 days:												
Potential										.19	.98	1.31
Current										.15	.26	.23
7 days:												
Potential										.125	.27	.99
Current										.15	.24	.24
8 days:												
Potential										.12	.235	.92
Current										.18	.22	.23
9 days:												
Potential										.105	.175	.82
Current										.13	.18	.23
10 days:												
Potential										.115	.16	.220
Current										.15	.19	.18
12 days:												
Potential										.062	.11	3.0
Current										.10	.15	.11
14 days:												
Potential											.08	.09
Current											.11	.11

table in which the specimen identifications correspond to those in Example 2.

Specimen	Film integrity	Percent elongation
A	1	30
B	1	21
C	1	22
D	1	19
E	2	21
F	1	9
G	3	14
H	2	10
I	3	4
J	2	3
K	4	3
L	3	0

The data clearly show that the compositions of relatively low zinc content containing carbon black (A through F) have definitely improved physical properties over those (G through L) having the higher zinc loadings required of prior art zinc rich corrosion resistant coatings. Coatings G through L were observed to be brittle, flaking or powdering when scratched. Their performance was characteristic of coatings containing too little binder for adequate film cohesion.

Example 4

The coatings described as A, B, C and D in Example 2 above were applied in triplicate to sand-blasted 3 x 5 inch steel panels having an inverted V-shaped area masked out so as to remain unpainted according to Steel Structures Painting Council Paint Specification 12–64P. The masked out area runs from top to bottom of the panel, tapering from ½ inch in width at one end to 0 at the other.

To test the corrosion resistance of panels thus coated, the panels were subjected to 96 hours salt fog exposure. The efficacy of the coating is judged by the degree of rust build up; the coated panel should show no rust on the top 1 inch of the masked out area or on the coated area, but should show moderate rust 1 inch from the bottom of the masked out area.

In this test, both of the zinc rich primers containing carbon black passed, both without carbon black failed in that they showed considerable rust in the upper 1 inch of the masked out area.

What I claim and desire to protect by Letters Patent is:

1. A corrosion resistant metal coating composition having a non-volatile phase comprising about 12 to 32.5% of binder by weight, 65 to 87% by weight of high purity, metallic zinc in small particle form and 0.9 to 2.6% by weight of electrically conductive carbon black in the form of 0.005 to 0.2 micron particles.

2. The composition of claim 1 where the binder material is chlorinated rubber containing a minimum of 63% chlorine.

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