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METAL PRIMERS AND COATING COMPOSITIONS MODIFIED WITH LOWER ALKYL ESTERS OF UNSATURATED ALIPHATIC ACIDS

Kenneth F. Atwood, Atlanta, Ga., and Austin K. Long, Bay Village, and Owen F. Shobe, Lakewood, Ohio, assignors to The Glidden Company, Cleveland, Ohio, a corporation of Ohio

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This invention relates to improved organic coating compositions such as metal primers, i.e. coating compositions whose protective qualities adapt them particularly for impeding and delaying the corrosion of corrosion-prone metals when applied directly to the surfaces of such metals. Ferrous metals are most often thought of in connection with metal primer coatings since, as is well known, ferrous metals are prone to develop rust and corrosion fairly rapidly when exposed to the atmosphere. The improved coatings of this invention are particularly useful on ferrous metals, and are especially useful as either initial primers on clean metal or as recoating primers where the ferrous metal surface which is to be primed has already become covered with rust. As is well known, many fabricated ferrous metal structures such as bridges, storage tanks, oil refinery superstructures, ship superstructures, etc. are wholly and continuously exposed to the weather. Such structures have long been protected by painting and it has long been known that the protective paint must be renewed periodically. Such structures, when first erected are primed and top-coated. Such use of a metal primer is what is here termed an initial priming. As the initial protective coating system weathers away, some areas of the structure become inadequately protected and rust soon forms in such areas. Maintenance painting seeks to recoat the structures before this occurs, but many factors may interfere with the maintenance program to the end that the structure becomes rusted at least in some areas before the new maintenance coatings have been applied. Such maintenance coating systems usually involve the application of a metal primer as the initial coating. Such use of a metal primer is what we here term a recoating priming.

Initial and recoating primers are formulated to give the best possible protection against rusting of the underlying ferrous metal, and initial primers ordinarily do a better job than do recoating primers, mainly because the ferrous metal surface underlying the initial primer is fairly smooth and free of scaly rust. This latter type of rust is ordinarily encountered in the application of recoating primers and it has long been a recognized problem that even the best recoating primer and top-coat systems presently known ordinarily fail first in areas where such scaly, badly rusted areas are recoated. Sometimes determined efforts are made, as in the recoating of ships, to scrape off, sand blast, or otherwise remove as much of the rust as is practical, and especially to remove the scaly rust formations. Where this is done, the recoating protective primer/topcoat systems ordinarily give good protection against further rusting. The removal of all of the rust is, however, an expensive task especially in structures like bridges where much surface is exposed to the weather and where many lapped joints are involved. Consequently, the operation of removing all of the rust is frequently omitted and the structure is recoated without thorough surface preparation. Where such is the case, coating formulators seek to supply a primer/topcoat system which will still offer good protection, but at the present time, as far as we are aware, the art recognizes that present primers with few exceptions are deficient in their ability to penetrate into and through the loose rust so as to carry the corrosion-inhibiting pigments of the primers down

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to the plane of the interface between the clean metal and its overlying layer of rust.

We have now discovered that a restricted group of esters prepared from monohydric alcohols of up to 8 carbon atoms and monocarboxylic acids such as the fatty acids of drying and semidrying oils or tall oil having a low (less than about 5% by weight) rosin content are additives which confer to primers a greatly enhanced ability to wet and penetrate the rust on ferrous metal and similarly to wet and penetrate the corrosion found on other corroded metals. At least about five percent of the esters, by weight on the primers, appears to be necessary to this end with 6–10% preferred. Greater amounts can be used, however, especially where the acids of the esters are such that the esters possess oxidizing film-forming qualities of their own. Typical esters of the types mentioned above are methyl linoleate, butyl linoleate, butyl esters of tall oil, 2-ethyl hexyl esters of tall oil, methyl esters of linseed oil acids, ethyl esters of soybean oil acids, mixtures of the foregoing, etc.

Accordingly, it is an object of this invention to provide improved pigmented organic coating compositions characterized by having present in their formulations at least about five percent of said lower alcohol esters of the kinds mentioned above.

A further object is to provide improved coated metal articles protected with coating systems employing coating compositions of the character set forth in the preceding object.

Still another object is to provide improved recoating primers for corroded metals, which primers exhibit improved wetting.

Another object is to provide improved recoating primers especially adapted for application to ferrous metal, at least some exposed surface portions of which are covered with rust.

These and other objects will be apparent from the following and preceding description of our invention.

It has long been recognized that most primers in common use have exhibited a tendency to merely cover the surface of a rusty area on ferrous metal without penetrating deeply thereinto. This lack of wetting and penetrating qualities leaves much porosity in the underlying layers of rust. The porosity entraps air and moisture, so that the rust-forming reactions can continue under the film. In time, the coating system overlying the rusty area becomes blistered and soon thereafter flakes off. We have now found that the ester additives referred to above, when incorporated in the primer or like organic coating in an amount of at least five percent and preferably 6 to 10% by weight, markedly improve the wetting and penetrating properties of the resulting primer, while conferring other benefits such as flexibilization of the film, improved gloss in the dried films, improved durability on exposure and modifications in rheological properties of the wet film.

The following examples illustrate the merits of our coatings for providing protective coating systems on clean (non-pre-rusted) and on pre-rusted ferrous metal. The examples include the best modes presently known to us for applying and practicing the principles of our present invention.

EXAMPLE 1.—METHYL LINOLEATE IN PRIMERS APPLIED TO CLEAN (NON-RUSTY) FERROUS METAL

Tests for salt spray resistance, sea water immersion resistance and humidity were carried out on clean ferrous metal panels which had been coated with various primers containing or free of added methyl linoleate, and coating systems employing said primers plus top coats.

The following is a list of the primers employed. The

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methyl linoleate used in some of the primers was a commercial product analyzing over 90% methyl linoleate, balance methyl esters of other octadecanoic acids.

Primer A.—Alkyd/linseed oil/red oxide chromated primer

Pigments:	
Metallic brown.....	4 lb.
Zinc chromate.....	2 lb.
Chrome orange, light, C.P.....	1 lb.
Zinc oxide, lead-free.....	.75 lb.
Magnesium silicate.....	2.5 lb.
Kieselguhr.....	.25 lb.
Silica powder.....	1.75 lb.
Powdered litharge.....	.10 lb.
Film-forming solution and modifiers:	
Raw linseed oil.....	2.375 pints.
Alkyd resin solution ¹	1.0 pint.
Paint oil ²	1.25 pints.
Diacetone alcohol.....	.50 pint.
T.S. 28 solvent.....	1.625 pints.
Lead/manganese drier solution ³	3 liq. oz.
Lead drier solution ⁴	3 liq. oz.
Diammonium mono-hydrogen phosphate.....	.5 liq. oz.
Thickening agent (Bentone No. 38).....	1.5 oz. av.
Phenolic resin/tung oil varnish solution ⁵	1.25 pints.

¹ Glycerine, 64 lbs./phthalic anhyd., 100 lbs./distilled linseed oil fatty acids, 1645 lbs. in mineral spirits, 253 gal.; 63-65% solids by weight, acid number of 5-7, weighs 7.76 lbs./gallon.

² Rosin, 75 lbs./litharge 24 lbs./tung oil, 150 gal./mineral spirits 105 gal./dipentene, 24 gal.

³ Solution contains 4.5% Pb derived from lead naphthenate (24% Pb) and .96% Mn derived from manganese naphthenate (6% Mn). Mineral spirits as solvent.

⁴ Mineral spirits solution containing 6.94% Pb derived from lead naphthenate (24% Pb).

⁵ Prepared from 200 lbs. commercial resin BR-254 (100% oil-soluble paraphenyl phenol/formaldehyde resin of 100% solids); 26 gals. tung oil. Resin and oil cooked at 450° F. for 10-15 minutes, then cooled and reduced with 80 gals. xylol; varnish solution weighs 7.8 lbs./gal.

Primer A'—Alkyd resin/phenolic resin varnish/methyl linoleate

Pigments:	
Metallic brown No. 1105.....	3.5 lb.
Zinc oxide, lead-free.....	.375 lb.
Silica powder.....	1.5 lb.
Magnesium silicate No. 399 SF.....	1.125 lb. (av.).
Basic lead silico chromate (M-20).....	3.75 lb.
Zinc chromate.....	3.5 oz. (av.).
Bentone No. 38 (modified bentonite).....	.5 oz. (av.).
Nuact paste ¹ (44% Pb; 77% solids).....	.75 oz. (av.).
Film-forming components and modifiers:	
Alkyd resin solution of Primer A.....	3.25 pints.
Methyl linoleate.....	1.25 pints.
T.S. 28 solvent ²	1.5 pints.
Guaiacol.....	0.5 liq. oz.
Phenolic resin varnish solution ³	1.5 pints.
T.S. 28 solvent.....	0.5 pint.
Cobalt drier solution ⁴	.25 liq. oz.
Manganese drier solution ⁵	.375 liq. oz.
Lead drier solution ⁶	.375 liq. oz.

¹ A commercial product, said to be a lead organic compound functioning as a drier/activator or drier absorption agent; contains 44% lead; solids content of 77%.

² Contains 82-76% aromatics, has a kauri-butanol value of 63-74 and weighs 7.102-7.115 lbs./gal. at 60° F.; initial B.P. 310° (min.) to 360° F. (max.); 60% B.P. 364°-370° F.

³ Prepared from 200 lbs. pure phenol/formaldehyde resin/50 lbs. of 100% oil-soluble alkylated phenol/formaldehyde resin/62 gals. China-wood oil/6.75 gals. of best-bodied (visc. Z_1-Z_2) mixed linseed oil (44 lbs.) China-wood oil (6 lbs.)/10 gals. T.S. 28 solvent/65 gals. mineral spirits. Weighs 7.65 lbs./gal., has solids content of 64%; acid number of 20-21; and Gardner-Holdt viscosity of K at 25° C.

⁴ Mineral spirits solution containing 38-40% solids by weight of cobalt octoate containing 6% Co.

⁵ Mineral spirits solution containing 65% solids by weight of manganese naphthenate containing 6% Mn.

⁶ The lead drier solution of Primer A.

Primer B.—Epon ester primer, short oil type

Pigments:	
Red lead 95%.....	207 lb.
Zinc chromate.....	97 lb.
Barytes.....	44 lb.
Magnesium silicate No. 399 SF.....	199 lb.
Bentone No. 38.....	2 lb.
Leiothin.....	4 lb.
Nuact paste (see Primer A supra).....	4 lb.
Anti-skinning agent.....	1 gal.
Aluminum paste (65% solids in mineral spirits).....	72 gal.
Film-forming components and modifiers:	
Xylol solution of DCO acid ester of Epon 1004 resin (60% Epon/40% DCO acids) at 50% solids by wt.; A.N. 7-10 (100% solids basis, viscosity (Gardner-Holdt) V-W at 77° F.; 7.9 lb./gal. (DCO-dehydrated castor oil).....	44.75 gal.
Solvesso solvent No. 150.....	29.5 gal.
Isopropyl alcohol.....	5.0 gal.
Cobalt octoate solution (38-40% solids by wt.; 6% Co in octoate).....	.5 gal.

¹ Epon 1004 is a bisphenol/epichlorhydrin polyether condensation product having terminal epoxy groups and reactive hydroxyl groups.

Primer B'

This primer duplicates Primer B except that the "film-forming components and modifiers" thereof are reduced

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in total amount to about 81% (6.5 parts in 8) and methyl linoleate is added in an amount of about 19% (1.5 parts in 8). Thus Primer B' has the following proportions of

5 Film-forming components and modifiers:	
Epon ester solution, supra.....	36.4 gal.
Solvesso solvent No. 150.....	24.0 gal.
Isopropyl alcohol.....	4.0 gal.
Cobalt octoate solution.....	40 gal.
Methyl linoleate.....	14.95 gal.

Primer C.—Epon ester primer long oil type

10 Pigments:	
Iron oxide pigment (88% Fe ₂ O ₃).....	3 lb.
Zinc chromate.....	1.625 lb.
Zinc oxide, lead-free.....	.875 lb.
Silica powder.....	1.25 lb.
Asbestine.....	.75 lb.
15 Film-forming components and modifiers:	
Epon ester solution; 50% solids.....	7 pints.
Epon 1004 resin.....	1,000 lb.
Soy bean oil fatty acids, (dist'd.).....	1,210 lb.
T.S. 28 solvent (supra).....	1,050 lb.
Mineral spirits.....	1,050 lb.
First two materials reacted at about 500° F. under CO ₂ until body of F-G attained; then cooled and reduced.	
Ethylene glycol monoethylether acetate.....	1 pint.
Cobalt octoate solution (6% cobalt, supra).....	.25 liq. oz.
Anti-skinning agent (containing wood phenols).....	.25 liq. oz.

This primer can be reduced for spraying at rate of 4:1 with xylol. It air dries overnight.

Primer C'

This primer duplicates Primer C except that the 8 pints of Epon ester solution and glycol ether acetate were reduced to 6.5 pints, and 1.5 pints of methyl linoleate was added. Thus the formulation in Primer C' was:

30 Film-forming components and modifiers:	
Epon ester solution, supra.....	5.67 pints.
Ethylene glycol monoethylether acetate.....	.82 pint.
Methyl linoleate.....	1.5 pints.
Cobalt octoate solution, supra.....	.25 liq. oz.
Anti-skinning agent, supra.....	.25 liq. oz.

TOP COATS

I. SELF CLEANING WHITE TANK PAINT

Pigments:	
TiO ₂ rutile.....	1.625 lb.
TiO ₂ anatase.....	1.75 lb.
Magnesium silicate (No. 399 SF).....	.875 lb.
Modified bentonite (Bentone No. 38).....	.03 lb.
Nuact paste, supra.....	.047 lb.
Film-forming component and modifiers:	
Linseed oil modified glyceryl phthalate alkyd (847 lbs. oil/100 lbs. glycerine/210 lbs. phthalic anhyd.), 8.3 lbs./gal.; 100% solids; A.N. 9-12; T-U visc. Gardner-Holdt).....	1 pint.
Soya oil (60%)/pentaerythritol (13.7%)/phthalic anhydride (26.3%), alkyd resin varnish reduced to 60% solids in mineral spirits (7.85 lbs./gal.).....	2.875 pints.
Hi Flash coal tar naphtha.....	1.0 pint.
Grind all above and then add:	
Soya oil (60%)/pentaerythritol (13.7%)/phthalic anhydride (26.3% wt.) alkyd resin reduced in xylol to 70% solids.....	2.5 pints.
Hi Flash coal tar naphtha.....	.625 pint.
Zinc naphthenate (8% zinc).....	.125 oz.
Lead/manganese naphthenate (24% Pb; 6% Mn) in mineral spirits at 20% solids.....	.125 oz.
Lead naphthenate (24% Pb) in mineral spirits at 14% solids.....	.125 oz.
Guaiacol.....	.016 oz.

55 NOTE.—Reduce 10:1 with xylol for spraying; air dries in 24 hours.

II. ALKYD/VINYL COPOLYMER RESIN WHITE TANK PAINT

Fatty acid (34% wt.)/ethylene glycol (9.6%)/phthalic anhydride (37.5%)/pentaerythritol (18.6%) alkyd resin reduced in xylol to 60% solids content; 8.4 lbs./gal.; A.N. 5-6.	
Hi Flash coal tar naphtha.....	2.5 pints.
Diacetone alcohol.....	2.0 pints.
Vinyl stabilizer (low M.W. epoxy resin of bisphenol/epichlorhydrin, C.P. type).....	.06 lb.
Vinyl chloride/dialkyl maleate/monoalkyl maleate/trichloroethylene copolymer conforming to Ex. 1 of U.S. 2,731,449.....	1.5 lb.
65 All of the above dissolved, then add:	
Pigment/alkyd resin paste of 65.3% pigment.....	2.125 pints.
TiO ₂ rutile.....	13 lb.
TiO ₂ anatase.....	3 lb.
DCO-fatty acid modified glycerine/rosin alcohol/phthalic anhydride/p-tert. butyl benzoic acid alkyd at 60% solids in xylol; A.N. 10; 44.5% oil acids; 29.5% phthalic anhyd./5.9% benzoic acid/70% excess polyol; 8.2 lb./gal; visc. C-D Gardner-Holdt).....	7 pints.
Xylol.....	1 pint.
Leiothin.....	.125 lb.
Dimethyl silicone anti-silking fluid, 2% solids in toluol.....	.75 liq. oz.

NOTE.—This tank paint weighs 10.2 lbs./gal; 54% solids; visc. 70-80° at 80° F. (No. 4 Ford cup); air dries over night; reduce 16:1 with toluol for spraying.

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The following tabulation indicates the results secured from evaluations of the indicated tests of steel panels coated with the above primers alone or with systems composed of one of said primers with one of said top coats. In numerical ratings, 0=failure, 10=excellent.

1000 HOURS HUMIDITY

Top-coated systems using:

Primer A	Completely blistered.
Primer A'	Excellent.
Primer B	Excellent.
Primer B'	Excellent.
Primer C	Blistered.
Primer C'	Excellent.

430 HOURS' IMMERSION IN SEA WATER

Top-coated systems using:

Primer A	Failed by blistering in 120 hrs.
Primer A'	Excellent after 430 hrs.
Primer B	Badly blistered.
Primer B'	Excellent.
Primer C	Failed by blistering after 340 hrs.
Primer C'	Blistering after 430 hrs.

Panels coated with:

Primer C only	Completely blistered.
Primer C' only	Slightly blistered at end of 430 hrs.

1030 HOURS' IMMERSION IN SEA WATER

Primer	Top-Coated ¹	Primer Only
A	0	0
A'	7	6
B	7	0
B'	8	10
C	0	0
C'	5	8

SALT SPRAY TESTS

Primer	350 Hours—Top-Coated ¹	830 Hours	
		Top-Coated	Primer Only
A	6	0	0
A'	9	6	2
B	9	7	0
B'	10	9	10
C	9	7	6
C'	9	8	10

SALT SPRAY 575 HOURS

Primer	Plain, Clean Steel		Pre-Rusted Steel	
	Top-Coated ¹	Primer Only	Top-Coated ¹	Primer
A	3	7	8	9
A'	6	7	9	10
B	6	7	7	5
B'	7	8	10	10

¹ Primed with indicated primer, dried, then top-coated.

SEA WATER IMMERSION 575 HOURS

Primer	Plain, Clean Steel		Pre-Rusted Steel	
	Top-Coated ¹	Primer Only	Top-Coated ¹	Primer
A	0	0	5	10
A'	10	10	10	10
B	6	0	7	7
B'	6	6	6	6

HUMIDITY 250 HOURS; TOP-COATED¹

Primer	Plain Steel	Pre-Rusted
A	0	0
A'	6	8
B	6	8
B'	6	8

¹ Primed with indicated primer, dried and then top-coated.

EXAMPLE 2

Primers A and A' were used as "controls" in the fol-

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lowing tests of coated steel panels wherein three analogous primers A2, A3 and A4 were used differing only in that the methyl linoleate of Primer A' was replaced with an equal weight of the wetting additive identified below:

SALT SPRAY 980 HOURS

Primer	Wetting Additive	Top Coated ¹	Primer Only
10 A	None	0	0
A'	Methyl linoleate	5	5
A2	Butyl esters of linseed oil acids	3	3
A3	Butyl esters of unsaturated fatty C18 acids	4	4
15 A4	Butyl esters of tall oil (about 2% rosin content by weight).	5	5

Primer	Sea Water—1,000 Hours		Humidity—150 Hours Top-Coated ¹
	Top-Coated ¹	Primer Only	
A	1	0	0
A'	7	7	7
25 A2	9	10	8
A3	9	9	8
A4	8	9	8

¹ Same meaning as in Example 1.

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EXAMPLE 3

To illustrate the universality of the invention, a Federal Specification paint TT-P-86A was tested along with three modifications of it. A first modification, here identified as TT-P-86A modified, involved the formulation shown below. The second and third modifications consisted of removing the phenolic resin/tung oil solids to an extent of 6% of the total paint solids and adding methyl linoleate to a level of 6% by weight on the coating in TT-P-86A and in TT-P-86A modified. The resulting four coatings were applied as primers, dried and then were top coated partially. The top coat was a commercial tank intermediate paint whose formulation is given below. The coated panels were dried and some of them were then exposed outdoors for four months and others were exposed in a conventional weatherometer test cabinet for 350 hours (which period of time is roughly equivalent to a year of outdoor exposure). The exposed panels were then scraped with a knife to see how poorly or how firmly the coatings adhered to the panel. The panels having no methyl linoleate in their primers were easily flaked off by scraping, both coatings coming off in wide strips and exposing the metal underneath. In contrast, the comparative test panels having methyl linoleate in their primers were difficult to penetrate by scraping, and demonstrate that the coating composition has penetrated deeply into the rusted surface and has securely bound the rust to the metal surface.

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PANEL LABELLED "1-TT-P-86A"

Red lead (97% grade)	777 lb.
Aluminum stearate	3 lb.
Leicithin	4 lb.
Raw linseed oil	14.25 gal.
Bodied linseed oil	4.25 gal.
Mineral spirits	10.00 gal.
65 Mixed rosin soap drier ¹	1.50 gal.
Anti-skinning agent	.0625 gal.
Yield—41.5 gals.	

¹ A mineral spirits solution of 25% solids by weight; contains 0.25% Ca; 1.42% Pb; 0.97% Mn by weight.

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PANEL LABELLED "1+6% WA"

The above formulation was modified by withholding 26% of the raw linseed oil and 26% of the bodied linseed oil, and by replacing the withheld oils with an equal volume of methyl linoleate.

PANEL LABELLED "2 MOD. TT-P-86A"

Basic lead silico chromate.....	1,000 lb.
Bentone 34, supra.....	6 lb.
Raw linseed oil.....	40 gal.
Alkyd resin TTR-266, type 1, 70% solids (below).....	14 gal.
Mineral spirits.....	13 gal.
Lead naphthenate drier, supra (24% Pb).....	41 gal.
Manganese naphthenate drier, supra (6% Mn).....	23 gal.

PANEL LABELLED "2+6% WA"

Above formulation modified by replacing 26% of the raw linseed oil with methyl linoleate.

TANK INTERMEDIATE PAINT

Pigment:	
TiO ₂ rutile.....	212 lb.
Barytes.....	231 lb.
Magnesium silicate.....	154 lb.
Powd. litharge.....	7 lb.
Nuact paste of Primer A'.....	5 lb.
Bentone No. 38.....	5 lb.
Green pigment.....	5 lb.
Film-formers and modifiers:	
Alkyd resin prepared from soybean oil (2944 lbs.)/pentaerythritol (672 lbs.)/phthalic anhyd. (1290 lbs.)/powdered litharge (1.75 lbs.) and reduced in mineral spirits to 60% solids.....	33.75 gal.
T.S. 28 solvent (supra).....	4.75 gal.
Mineral spirits.....	10.00 gal.
Enamel vehicle prepared from pure phenol-formaldehyde resin (200 lbs.)/100% oil-soluble alkylated phenol/formaldehyde resin (footnote 3, Primer) supra (50 lbs.)/tung oil (62 gals.)/T.S. 28 solvent (10 gals.)/heat bodied mixture of linseed oil (88%)/tung oil (12%) of Z ₁ -Z ₂ viscosity (6.75 gals.)/mineral spirits (65 gals.).....	14.5 gal.
Raw linseed oil.....	9.625 gal.
Mineral spirits.....	4.5 gal.
Mixed lead naphthenate (24% Pb)/manganese naphthenate (6% Mn)/mineral spirits drier solution supra.....	1.25 gal.
Zinc naphthenate solution (8% zinc) (65% solids).....	1.875 gal.
Guaiacol.....	.125 gal.
Diphenyl Mercury dodeceny succinate; 22% solids; 10% Hg.....	.75 gal.

EXAMPLE 4

This example has reference to a group of panels which have been tested for fracture resistance of the applied coatings. The panels were all of iron which had been pre-rusted and which then had been primed with Primer A of Example 1 modified in the manner shown in Primer A' to contain 0, 3, 5, 6, and 10% of methyl linoleate by weight on the total paint solids. The upper 1/3 of each primed panel was then coated with the white intermediate tank paint of Example 3. When this coat was dry, the upper two-thirds of each panel was coated with a grey commercial tank top-coat whose formulation is set forth below. All the panels were then conditioned for testing by exposing in the weatherometer for 350 hours, and then were bent about a conical mandrel and examined for fractures in the coatings. It became evident that 5-6% of methyl linoleate was conducive to minimum fracturing.

GREY TOP COAT TANK PAINT

TiO ₂ rutile.....	202 lb.
Magnesium silicate No. 389.....	85 lb.
Yellow oxide of iron.....	5 lb.
Antimony black No. 1.....	16 lb.
Bentone No. 38 supra.....	2.5 lb.
Nuact paste supra.....	4.0 lb.
H ₂ Flash coal tar naphtha.....	10.625 lb.
Soybean oil / pentaerythritol / phthalic / litharge / mineral spirits solution, of tank intermediate paint, supra.....	30.5 lb.
Linseed/glycerine/phthalic/litharge varnish of Primer A.....	10.625 lb.
Grind above, then add:	
Soybean oil (2,944 lbs.)/pentaerythritol (672 lbs.)/phthalic anhydride (1290 lbs.)/powd. litharge (1.75 lbs.)/xylol (2000 lbs.), alkyd resin solution.....	26.6 gal.
H ₂ Flash coal tar naphtha.....	6.625 gal.
Mixed lead/manganese drier solution of tank intermediate paint.....	1.3 gal.
Lead naphthenate drier (24% Pb) in mineral spirits at 14% solids.....	1.3 gal.
Zinc naphthenate drier (8% Zn) at 65% solids.....	1.3 gal.
Super Ad it supra.....	.3 gal.
Guaiacol.....	.16 gal.

From the foregoing examples it will be clear that our coating compositions can be formulated from a variety of conventional film-forming vehicles and pigments with or without film-forming modifiers. The following is a representative but not necessarily complete list of film-forming or binding materials which can be used in our coating compositions.

(1) Any of the many known oleoresinous varnishes

prepared from (a) drying and/or semi-drying oils in their various bodied and unbodied, modified and unmodified forms with (b) conventional varnish resins in conventional proportions of oil(s) to resin(s).

(2) Alkyd resins modified with triglyceride oil(s) and/or varnish resins, with the modifiers in proportions corresponding to the range covered by long to short oil length.

(3) Phenolic/aldehyde condensation products reacted with or otherwise modified with triglyceride (usually drying and semi-drying) oils and/or varnish resins, to give air-drying varnish-type materials.

(4) Varnishes which are a blend of alkyd resins (2 above) and the modified phenolic condensation products (3 above), with or without added triglyceride drying and/or semi-drying oils.

(5) Epoxy esters, i.e. epoxy resins of the bis-phenol/epichlorhydrin type which have been reacted with rosin acids, resin acids, and/or saturated and unsaturated fatty acids of drying and semi-drying oils, thereby to yield substantially full esters having substantially zero epoxy and/or hydroxy equivalent but being air drying by reason of ethylenic unsaturation in the esters.

(6) Triglyceride-oil-base binders with or without modifying proportions of alkyd resins blended therewith.

(7) In some special instances, vinyl/alkyd blends can be used, e.g. copolymers of vinyl chloride and vinyl acetate blended with alkyd resins which have been modified with drying and/or semi-drying oils. These blends are preferably top-coats, however.

Coating compositions utilizing binders such as those listed above can be pigmented with anticorrosive pigments such as the following:

Red lead.....	Blue lead.....
Lead chromate.....	Zinc dust/zinc oxide.....
Zinc chromate.....	Basic lead silico chromate.....
Calcium chromate.....	Barium chromate.....
Calcium plumbate.....	Strontium chromate.....
Iron oxide(s).....	Zinc tetroxy chromate.....

Conventional color pigments and/or fillers (inerts) can be included if desired to yield pigment volumes between about 25-60%.

While the resulting coatings are preferably applied to metal as initial or recoating primers, they can be employed as temporary top-coats because of their moderate weatherability.

In coating systems employing our compositions as either initial or recoating primers, then the dry prime coat can be top-coated with any known air-drying paints of established weatherability. The film-forming materials listed above for our compositions find use also in top-coats but are then pigmented mainly for color and durability rather than for anticorrosive qualities.

Following is a typical formulation of coating compositions utilizing the present inventions.

TYPICAL FORMULATION

	Minimum, percent	Maximum, percent
60		
Pigment:		
Anticorrosive.....	18	77
White.....	14	75
Color.....	1	8
Inert.....	1	15
65 Vehicle:		
Alkyd varnish ¹	57	62
Phenolic resin penetrating liquid ²	15	17
Phenolic varnish ³	0	9
Aromatic mineral spirits.....	7	8
Diacetone alcohol.....	6	7
Driers and anti-skinning.....	2	3

Example formulations within the "Typical Formulation" are as follows:

¹ Soya oil (60%)/pentaerythritol (13.7%)/phthalic anhydride (26.3%) alkyd resin varnish reduced to 60% solids in mineral spirits (7.85 lbs./gal.).

² A mixture of methyl linoleate and air-drying oil-modified phenolic/aldehyde condensation product, in the proportions of 52 gallons of methyl linoleate to 48 gallons of said air-drying condensation product.

³ The varnish described in note 3 or Primer A'

Quick drying red lead primer for priming bridges, tanks and structural steel

This is a fast drying red lead primer with good chemical resistance and excellent resistance to blistering from exposure to high humidity and moisture. The phenolic resin penetrating liquid is included to give better wetting of rusty or porous surfaces than can be accomplished with a primer made with a pure linseed oil vehicle. Its controlled luster and Cellosolve component of the vehicle are designed to prevent crawling trouble in cold weather applications. It is believed that further field testing will show this product to have superior durability.

Composition	Percent	Weight	Volume
Pigment:			
Red lead (97% Grade).....	88.00	1,391.00	18.900
Asbestine (Nytal 300 or equal).....	7.91	125.00	5.265
Celite.....	2.26	35.70	2.127
Aluminum stearate.....	.42	6.70	.800
Litharge (powdered).....	1.13	17.85	.223
Nuact paste (supra).....	.28	4.46	.319
	100.00		
Vehicle:			
Alkyd varnish T-T-R-266, Type II, Class A ¹	33.00	183.0	23.43
Phenolic resin penetrating liquid ²	37.54	208.0	27.89
Tung oil.....	4.73	26.2	3.35
Aromatic mineral spirits.....	13.30	74.8	10.03
Cellosolve (ethyleneglycol monoethyl ether).....	9.35	51.8	6.68
Guaiacol.....	.45	2.5	.279
Lead naphthenate (24% Pb) supra.....	1.21	6.7	.698
Manganese naphthenate (6% Mn) supra.....	.42	2.2	.279
	100.00		

¹ Alkyd varnish of "Typical formulation" supra.

² Penetrating liquid of "typical formulation" supra.

Pigment.....	68%
Vehicle.....	32%
Wt./gal.....	21.33 lbs.
P.V.....	40.5%
Non volatile by volume.....	68%
Non volatile by weight.....	89.4%
Viscosity.....	85-90 K.U.
Grind.....	5-6.
Theoretical coverage.....	816 sq ft./gal. at 1.5 mils dry.
Dry to recoat.....	24 hours.
Reduce to spray.....	8-1 with VM & P naphtha.
Brush.....	Full body.

GRAY-GREEN FINISH COAT

Composition	Percent	Pounds	Gallons
Pigment:			
Basic lead silico chromate.....	77.00	391.5	11.4
Rutile titanium dioxide (non-chalking).....	14.25	72.4	2.6
Carbon black.....	.38	1.936	.1
Phthalocyanine blue.....	.75	3.87	.3
C.P. chromium oxide.....	6.10	31.0	.6
Bentone 38.....	.76	3.87	.3
Nuact paste.....	.76	3.87	.3
	100.00		
Vehicle:			
Alkyd varnish ¹	61.0	393.0	50.2
Phenolic resin Penetrating liquid ²	16.5	106.15	14.2
Phenolic varnish ³	7.52	48.6	6.2
Aromatic mineral spirits (320°-380° F.).....	7.4	48.0	6.4
Diacetone alcohol.....	6.05	39.2	5.1
Lead naphthenate (24% Pb).....	.72	4.64	.5
Manganese naphthenate (6% Mn).....	.20	1.30	.2
Zinc naphthenate (8% Zn).....	.16	1.045	.13
Guaiacol anti-skin agent.....	.45	2.92	.3
	100.00		

¹ Alkyd varnish of "typical formulation" supra.

² Penetrating liquid of "typical formulation" supra.

³ Phenolic varnish of "typical formulation" supra.

Pigment.....	44%
Vehicle.....	56%
Wt. per Gallon.....	11.5 lb.
Pv.....	24.9%
Non Volatile by Volume.....	63.6%
Non Volatile by Weight.....	78.2%
Viscosity.....	74-77 K.U.
Grind.....	6-7.
Dry to Recoat.....	24 hours.
Reduce.....	8 to 1 VM & P to spray.
Brush.....	Full Body.

From the foregoing description of our invention it will be clear that the principles thereof can be embodied in a variety of specifically different formulations in which our identified lower alcohol esters of monocarboxylic acids can function for the hereindescribed benefits.

Having now described our invention, what we claim is:

1. A coating composition adapted for use as a protective coating in direct contact with corroded metal such as rusty ferrous metal, said composition consisting essentially of: an organic-solvent solution of film-forming weather-resistant material of the air-drying type, dispersed pigment including anticorrosive pigment in an amount sufficient to bring the pigment volume into the range of about 25% to 60% of the total volume of said coating composition, and a liquid wetting additive in an amount corresponding to about 5-10% by weight of said coating composition, said wetting additive being at least one ester of (A) monohydric alcohol selected from the group consisting of aliphatic and cycloaliphatic monohydric alcohols having up to eight carbon atoms, and (B) monocarboxylic acids selected from the group consisting of (a) the fatty acids of triglyceride drying and semi-drying oils, and (b) mixtures of said fatty acids with small amounts of rosin acids.

2. A coating composition as claimed in claim 1 wherein the weather resistant film-forming material is selected from the group consisting of air-drying oleoresinous varnishes, air-drying alkyd resins containing modifiers in an amount corresponding to the range covered by long to short oil length, air-drying oil-modified type of phenolic/aldehyde condensation product, mixtures of said alkyd resins and phenolic/aldehyde condensation products, mixtures of said alkyd resins with said phenolic/aldehyde condensation products and triglyceride drying and semi-drying oils, air-drying monocarboxylic acid esters of bisphenol/epichlorohydrin epoxy resins, said epoxy esters having substantially zero epoxy and hydroxy equivalents, triglyceride oils of the drying and semi-drying classes, mixtures of said triglyceride oils with said alkyd resins, and mixtures of vinyl chloride/vinyl acetate copolymers with oil-modified air-drying alkyd resins.

3. A coating composition as claimed in claim 2 wherein said wetting additive is present in an amount between about 6% and 10% by weight of said coating composition.

4. A coating composition as claimed in claim 3 wherein anticorrosive pigment is present in amounts between about 18-77% of the total pigment.

5. A coating composition as claimed in claim 4 wherein the wetting additive is methyl linoleate.

6. A coating composition as claimed in claim 5 wherein the wetting additive is a mixture of methyl linoleate and air-drying oil modified phenolic/aldehyde condensation product, in the proportions corresponding to 52 gallons of methyl linoleate to 48 gallons of said air-drying condensation product.

7. A wetting additive adapted for use in protective coating compositions for metal, said additive being a blend of methyl linoleate and air-drying oil-modified phenolic/aldehyde condensation product in which said materials are present in the proportions of about 52 gallons of methyl linoleate to 48 gallons of said air-drying condensation product.

8. A pigmented coating composition consisting essentially of: an organic-solvent solution of film-forming weather resistant material of the air-drying type, dispersed pigment, and a liquid wetting additive in an amount corresponding to about 5-10% by weight of said coating composition, said wetting additive being at least one ester of (A) monohydric alcohol selected from the group consisting of aliphatic and cycloaliphatic monohydric alcohols having up to eight carbon atoms, and (B) monocarboxylic acids selected from the group consisting of (a) the fatty acids of triglyceride drying and semi-drying

oils, and (b) mixtures of said fatty acids with small amounts of rosin acids.

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