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(57) Claim

1. An anticorrosive pigment composition which comprises zinc oxide and a trivalent metal silicate material selected from the group consisting of (i) a material obtained by reacting a trivalent metal compound with a silicate (ii) a naturally occurring aluminium silicate material or a synthetic equivalent thereof, (iii) a naturally occurring or synthetic aluminium silicate surface-modified by ion exchange, and (iv) mixtures thereof, said metal silicate material being the major proportion by weight of the composition.

2. A composition according to claim 1, wherein the trivalent metal is selected from the group consisting of aluminium, iron and chromium.

12. A substantially water-soluble-salt-free pigment comprising, as the major component in proportion by weight, a pigment material obtained by reacting an aluminium salt and a silicate in aqueous solution, and then separating, washing and drying the reaction product, and also comprising zinc oxide.

13. A salt-free pigment according to claim 12, in which the aluminium salt used is a phosphate or sulphate.

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18. A coating composition which comprises a film forming material and a pigment composition according to any of the preceding claims.

19. A coating composition according to claim 18 wherein the film forming material is an alkyd primer.

623938

Form 10

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# COMPLETE SPECIFICATION

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Complete Specification for the invention entitled:

SURFACE TREATMENT

The following statement is a full description of this invention, including the best method of performing it known to :- us

This invention relates to surface treatment and more particularly to compositions for the surface treatment of metals and other materials.

Our earlier copending British Patent application, published as GB 2,201,157 A describes the treatment of surfaces of metals and other materials with coating compositions which are aqueous dispersions containing acidic trivalent metal compounds e.g. phosphates and silica of fine particle size. These compositions are intended to be applied as a surface pre-treatment to deposit a corrosion-inhibiting coating before a subsequent organic coating is applied. Our prior application also describes the preparation of corrosion-inhibiting pigments obtained by reacting the acidic trivalent metal compound with a silicate in aqueous solution. The corrosion-inhibiting materials produced by this method are recovered and formulated as anticorrosive pigments for use as such in paints. The compositions according to our prior application for subsequent coating with an organic layer confer excellent corrosion resistance on metal surfaces and excellent adhesion properties on metal and other surfaces.

One type of coating composition according to our prior application comprises a paint vehicle (film-forming polymer or other material) and a pre-formed material obtained by reacting, in aqueous solution, a trivalent metal compound, in which the metal is iron, aluminium, or chromium or a mixture thereof, and a silicate. In the material the silicon to trivalent metal atom ratio is in the range 0.2 - 30:1, such as 1.5 - 20:1, including 3.5 - 9.5:1 and 5.5 - 9.5:1. A group of examples of such a composition is described in Example 13 of our prior application. Where the trivalent metal used is aluminium the pre-formed anticorrosive pigment formed by reaction of the aluminium salt with the silicate is believed to be a type of aluminium silicate material and, for convenience, the terms "metal silicate" "aluminium silicate" or "aluminium silicate material" will be used hereinafter to indicate a material of this kind although it will be understood that the chemical composition of the pigment is not precisely known. For the preparation of coating compositions for use as paint finishes i.e. containing a suitable film-forming material, anticorrosive pigments formed by the reaction of aluminium sulphate with a silicate give especially good protection and are less costly than those prepared from aluminium phosphate.

It has been found that anticorrosive compositions, based on the aluminium or other metal silicate materials obtained by reacting the acidic trivalent metal compounds with a silicate especially those described in our earlier application mentioned above can be still further improved by the addition or incorporation of zinc oxide. Moreover, the combination of zinc oxide with the aluminium or other metal silicate material shows synergism in relation to the level of corrosion resistance conferred on treated metal surfaces.

Full details of the trivalent metal silicate materials are described in our earlier application. The preferred trivalent metals are chromium, iron and especially aluminium. The preferred acidic compounds are acid phosphates eg. metal tris dihydrogen phosphates as such or mixed with extra phosphoric acid, and sulphates eg. acid sulphates and sulphates and other salts giving an acidic reaction in aqueous solution. The trivalent metal compounds may be reacted with an alkali metal silicate in aqueous phase i.e. in solution or dispersion to produce a precipitate which, after filtration and water washing to reduce the content of water soluble materials, is then subsequently dried at elevated temperature eg. at 100-250°C or 200-250°C for 0.1-6 hours eg. 2-6 hours. Higher drying temperatures e.g. up to 350°C may also be used. The product at this stage is thus a preformed product useful as a pigment for incorporation in an appropriate coating composition. The product is substantially free of the anions present in the acidic trivalent metal compound e.g. phosphate or sulphate ions, and is thus substantially free of water-soluble salts. Products prepared in this way are the highly preferred anticorrosive materials used in the present invention.

Other types of aluminium silicate material for which a beneficial effect of combination with zinc oxide has been found are certain naturally occurring aluminium silicates and related materials obtained synthetically. These materials may be compounds or mixtures of oxides and/or hydroxides or other compounds of silicon, and aluminium optionally containing hydrogen bound as $H_2O$. The silicate material may also contain alkali metals, such as sodium or potassium, preferably chemically bound or alkaline earth metals such as calcium but, apart from impurities, the silicate material advantageously contains essentially only silicon, oxygen, aluminium and optionally hydrogen; most preferably the silicate material contains aluminium and hydrogen. A similar enhancement of anticorrosion properties resulting from the incorporation of zinc oxide is obtained with pigments based on metal silicate material optionally surface-modified by ion exchange eg. with calcium or otherwise. The material to which the zinc oxide is added may be as described in US Patent 4687595 and EP46057.

Therefore the present invention provides an anticorrosive pigment composition which comprises zinc oxide and a trivalent metal silicate material selected from the group consisting of (i) a material obtained by reacting a trivalent metal compound with a silicate (ii) a naturally occurring aluminium silicate material or synthetic equivalent thereof, (iii) a naturally occurring or synthetic aluminium silicate surface-modified by ion exchange, and (iv) mixtures thereof, said metal silicate material being the major proportion by weight of the composition.

The preferred trivalent metal for use according to this invention is aluminium. The preferred composition is a substantially water-soluble-salt-free pigment comprising, as the major component in proportion by weight, a material obtained by reacting an aluminium salt and a silicate in aqueous solution, and then separating, washing and drying the reaction product, and also comprising zinc oxide.

The aluminium and other trivalent metal silicates useful for the purposes of this invention preferably contain silicon to metal in atom ratios of 0.2-30:1 eg. 0.5-10:1 preferably 0.5-5:1 and especially 0.5-3:1 or 1.5-3.5:1 or 0.5-1.5:1.

A range of silicate materials may be used for the purposes of the invention including synthetic materials obtained by chemical reaction and naturally occurring aluminium silicates. The silicate materials are preferably in the form of particles which usually have an average size of less than 10 micro metres eg. 0.1-5 micrometres especially 0.1-1 micrometres, may or may not be colloidal and may have a plate like structure; preferably they do not substantially thicken any paint or other coating composition in which they are formulated.

More preferred silicate materials are those for whose particles at least 40% pass a 2 micron screen eg. 40-98% and especially 70-98%, and especially at least 70% pass a 1 micron screen. The silicate material is preferably one with a total water soluble content of less than 1% eg. 0.05-1% such as less than 0.5% or 0.3% eg 0.02-0.5% or 0.02-0.3%. Examples of ions contributing such water solubility are sodium, chloride and sulphate. Preferred silicate materials are hydrated aluminium silicates, which may be capable of acting as ion exchangers. Examples of suitable aluminium silicates are clays such as China clay (Kaolin, $Al_2O_3.2SiO_2.2H_2O$) which is particularly preferred and gives excellent performance at low cost, and bentonite $Al_2O_3.4SiO_2.2H_2O$. Mixtures of clays may be used; the clays may have been calcined but are preferably uncalcined. The particle size and water solubility characteristics given above are particularly suitable for the clays and also for the reaction products of the acidic trivalent metal compound and the silicate.

The zinc oxide and other ingredients of compositions according to this invention may be combined by any convenient method such as by mixing a water slurry of zinc oxide with the other milled solids, or by milling the dry materials together, or by water slurrying them together.

The improvement in corrosion-resisting properties obtained by the combination of zinc oxide and the aluminium silicate material is particularly noticeable with coating compositions comprising a film-forming material, as in a paint composition, and which are water-based or solvent-based. The former may be for example, aqueous emulsions or dispersions of suitable alkyd resins or vinyl polymers or vinyl-acrylic co-polymers; the latter may be alkyd resins e.g. long, medium or short oil alkyd, phenolic alkyd resins, 2-component epoxies, and chlorinated rubber, epoxy primers, epoxyester/melamine formaldehyde primers, short oil alkyd/urea formalehyde primer, 2 pack epoxy polyamide primers, epoxy/urea formaldehyde coil coating primers and electrophoretic primers.

The incorporation of the improved pigments of the present invention into the final organic finishing composition permits the desired protective effect to be obtained with a paint or lacquer applied directly to the surface without chemical pre-treatment, that is, without any treatment other than cleaning and drying of the surface.

In comparison with known anticorrosion coating compositions, those according to the present invention show a pronounced improvement in corrosion resistance and resistance to scribe-line corrosion and blistering of the final organic coating as determined in conventional test procedures. The level of protection achieved by the composition of the invention based on zinc oxide with the trivalent metal silicate material is often superior to that obtained using either component in the absence of the other. For long term corrosion protection, the combination of the zinc oxide with the metal silicate pigment obtained from the reaction of the trivalent metal salt with the silicate appears to give better results than the combination of the clays and zinc oxide.

The relative proportions of zinc oxide and the metal silicate pigment in the compositions of this invention can be varied over a wide range. It has been found that it is usually undesirable to incorporate zinc oxide in amounts exceeding about 30% and preferably not exceeding 25% by weight of the total anticorrosive pigment in the coating composition. At higher proportions of zinc oxide the results are even more inferior. At least an effective amount of the zinc oxide is preferably used; it is preferred not to use significantly less than about 2% of zinc oxide (based on the total weight of pigment), so advantageously amounts of 2-30% or 2-25% such as 10-25% especially 5-25% are used (based on the total weight of the zinc oxide and the metal silicate component). For many purposes a convenient range of proportions of zinc oxide is from 5 to 20% for solvent-based as well as water-based formulations.

The final coating compositions for application to the metal or other surface may contain up to 50% preferably 0.1-20% eg. 1-15% such as 4-10% by weight of anticorrosive pigment based on the weight of the coating composition.

The zinc oxide incorporated as described above is desirably of particle size up to about 0.2mm preferably from 0.001 to 0.05 or 0.1mm. Even smaller particle sizes may be advantageous e.g. from 0.1 to 10 microns eg. 0.0-1 micron especially 0.3-0.4 microns. The substrates to which the coating composition may be applied are described in our earlier application mentioned above and are usually metal surfaces. The substrates are usually first cleaned, if necessary, to remove oil, dirt and corrosion products with subsequent rinsing with water prior to coating.

The invention is illustrated in the following Examples 1 - 15. Examples A - E are comparative. Parts and percentages are by weight.

**Example 1**

Sodium silicate ($SiO_2$: $Na_2O$ 2:1) (162g) was dissolved in deionised water (1L). Aluminium dihydrogen orthophosphate solution (48% w/w) (80ml) together with phosphoric acid (S.G. 1.75) (47ml) was added with stirring to the sodium silicate solution. The solid was filtered off, washed well with water and dried at 230°C for 4hr. The solid was milled in a Retsch mill using a 0.08mm sieve and then incorporated with 20% zinc oxide of particle size 0.34-0.38 microns, based on the total weight of pigment. The resulting solid was incorporated at 6.6% by weight into a water-based alkyd primer. After applying the paint to a clean mild steel panel to a thickness of 35 microns, the panel was stoved at 60°-160°C for 10 minutes, allowed to age for 7 days, diagonally scribed and subjected to neutral salt spray for 200hr. Scribe line corrosion was good with no blistering under the paint film.

**Example 2**

The procedure of Example 1 was followed using 4% of the zinc oxide (instead of 20%) in the anticorrosive pigment. Excellent scribe line resistance was obtained with little blistering under the paint film.

**Example 3**

The pigment was prepared from aluminium orthophosphate solution (48% w/w) (80ml) and sodium silicate (12g) as described in Example 13C of our prior application mentioned above. Mixing of the pigment with zinc oxide at 20% and 4% w/w in the total solid gave results comparable with those in Examples 1 and 2. The paint was prepared as described in Example 1 and applied to the panel as in Ex 1.

**Example 4**

The process of Ex 3 was repeated with a pigment was prepared as in example 13E of our prior application mentioned above. Incorporation of 10% w/w of the zinc oxide (based on the total weight of pigment and zinc oxide) resulting in a coated panel with substantially reduced blistering without detrimental effect on scribe line corrosion.

**Example 5**

The procedures described in Examples 1 to 4 were repeated using a solvent based air-drying phenolic/alkyd primer paint. Similar results were obtained.

**Example A** (Comparative)

Aluminium sulphate 16 hydrate (84g) in water (300ml) was added with stirring to a solution of sodium silicate ($SiO_2.Na_2O$ 2:1) (72g) in water (800ml) at room temperature. The slurry was filtered, washed well with water until the filtrate had a pH greater than 5 and finally dried for 4 hrs at 230°C. The product was milled in a Retsch mill using a 0.08mm sieve.

The resulting aluminium silicate material was incorporated at 7.7% by weight into a solvent-based phenolic/alkyd primer. After applying the paint to a clean mild steel panel to a thickness of 35-40 microns the panel was allowed to age for 72 hrs, diagonally scribed and subjected to neutral salt spray for 200 hrs. Scribe line corrosion was good with some blistering under the paint film.

**Example 6**

The aluminium silicate material according to Example A was mixed with 20% zinc oxide of particle size 0.34-0.38 microns based on the total weight of pigment solid (ie aluminium silicate material and zinc oxide). This solid was incorporated at 7.7% by weight in the solvent-based phenolic/alkyd primer and the same procedure carried out as in Example A. Scribe line corrosion was excellent with no blistering under the paint film.

**Example B** (Comparative)

The procedure of Example A was repeated using Kaolin in place of the synthetic aluminium silicate material. Light Kaolin, acid-washed, was incorporated at 7.7% by weight into the solvent-based phenolic/alkyd primer and tested as described in Example A. The results showed average scribe line corrosion with blistering under the paint film.

**Example 7**

Zinc oxide was mixed with the light Kaolin of Ex. B to give a solid containing 20% by weight of the zinc oxide. This solid was incorporated at 7.7% by weight into the solvent-based phenolic/alkyd primer and the procedure of Example B was repeated. The results showed excellent scribe line corrosion with no blistering under the paint film.

**Example C** (Comparative)

Precipitated aluminium silicate (ex BDH, Poole, England) (with an atomic ratio of Si: Al of 7:1 and a content of 0.2% Na, 0.1% Cl and 0.5% sulphate ie 0.8% total water soluble material) was incorporated at 7.7% by weight into the solvent-based phenolic/alkyd primer and the composition was tested as described in Example A. The results showed poor scribe line corrosion with severe blistering under the paint film.

**Example 8**

Zinc oxide was mixed with the precipitated aluminium silicate used in Example C to give a solid containing 20% by weight of zinc oxide. This solid was incorporated at 7.7% by weight into the solvent-based phenolic/alkyd primer and the test procedure of Example A repeated. The resulting scribe line corrosion and blistering under the paint film were better than in Example C.

**Example 9** and Comparative Ex. D.

The procedures of Example A and 6 were repeated separately with 5 different types of China clay instead of the synthetic aluminium silicate and with and without the zinc oxide (20% w/w on the total of zinc oxide and clay). The clays were obtained from English China Clays Ltd, Cornwall, England and were as follows. Clay I was Light Kaolin pharmaceutical (Brit Pharm.) grade which had been purified and acid washed to have a low heavy metal content and 0.1% total water soluble material; the particle size was such that 75% passed a 2 micron screen. Clay II was a Supreme grade of high brightness with about 0.2% total water soluble material and a particle size such that 90% passed a 1 micron screen. Clay III was a calcined grade "Polestar 200P" with about 50% of the particles passing a 2 micron screen. Clay 1V was sold under the Speswhite mark with high brightness, and a 0.2% water solubles content, and at least 60% of the particles passed a 1 micron screen, while clays V and VI were sold as Grades D and E powder with 45% of the particles less than 2 microns (for clay V) and 25% less than 2 microns (for clay VI); both clays V and VI have water soluble contents of about 0.15%. The results of the tests were as follows:

| **CLAY** | **BLISTERING UNDER FILM** | | **SCRIBE LINE CORROSION** | |
|---|---|---|---|---|
| | **WITHOUT ZnO** (Comp. Ex. D) | **WITH ZnO** (Ex. 9) | **WITHOUT ZnO** (Comp. Ex. D) | **WITH ZnO** (Ex. 9) |
| I | 3-4 | 0 | 2 | 0-1 |
| II | 3 | 0 | 1-2 | 0-1 |
| III | 3-4 | 1 | 2 | 1 |
| IV | 3 | 2 | 1-2 | 1 |
| V | 4 | 2 | 3 | 2 |
| VI | 4 | 2 | 3 | 2 |
| No Clay | - | 4 | - | 2 |

**NOTE In the Table 0 gives the best results and 5 the worst results.**

**Example 10** and Comparative Example E

The procedures of Ex. 9 and comparative Ex. D were repeated with the clays, with and without zinc oxide applied at 6.6% total weight of clay and (if present zinc oxide) in an air drying water based alkyd primer as used in Ex. 1 The results in the absence of zinc oxide were average scribe line corrosion with blistering under the paint film, whereas with zinc oxide there was improved scribe line corrosion and reduced blistering under the paint film. Clays I and II gave the best results.

**Examples 11-15**

The pigments of the present invention were compared with equal volumes of other pigments for corrosion inhibiting properties in commercial paint formulations. All parts are by weight.

**Example 11** - Two pack epoxy-polyamide primer (green)

A two-pack composition was prepared containing in one pack a paint base of composition A in which the nature of the pigment was varied and in another pack a catalyst of composition B.

**Composition A:**

| Materials | Quantity (parts) |
|---|---|
| EPOXY RESIN (Epikote 1001 x 75 - Shell Chemicals) | 403 |
| METYL ISO BUTYL KETONE (MIBK) | 204.1 |
| METHOXY PROPYL ACETATE (MPA - BP Chemicals) | 61.1 |
| TITANIUM DIOXIDE (Tiona 472 - SCM) | 83.6 |
| MAGNESIUM SILICATE (Micro-Talc 20/M/2 - Luzenac Talc) | 144 |
| YELLOW IRON OXIDE (Bayferrox 3920 - Bayer) | 10.5 |
| CHROMIUM OXIDE 39K3 (Blythe) | 10.4 |
| POLYETHER-MODIFIED DIMETHYL SILOXANE CO-POLYMER (Byk 300 - Byk-Chemie) | 2.52 |
| BUTANOL | 20.8 |
| XYLENE | 103.7 |
| PIGMENT - as in (i) - (v) below | |

**Composition B:**

| Materials | Quantity (parts) |
|---|---|
| POLYAMIDE RESIN (Versamid 115 x Cray Valley Products) | 210 |
| POLYAMIDE RESIN (Versamid 140 - Cray Valley Products) | 49.1 |
| SILANE A1120 (Union Carbide) | 12.3 |
| BUTANOL | 331 |
| XYLENE | 268 |

The contents of the two packs were mixed together in a ratio of 2:1 by volume of base:catalyst to give the paint.

Five paints 11 (i)-(v) of the above composition were prepared each containing a different pigment (i)-(v) below:

| | Pigment | Quantity (parts) |
|---|---|---|
| (i) | K-White 84 (Zinc Oxide/Aluminium tripolyphosphate) | 245 |
| (ii) | Zinc Phosphate | 289 |
| (iii) | Aluminium Silicate Material as described in Example 5A | 245 |
| (iv) | Shieldex AC-5 (W.R. Grace) | 158 |
| (v) | Aluminium Silicate Material as described in Example 5A (196 pts) plus zinc oxide (49 pts) | 245 |

After applying each of the paints to a clean mild steel panel, to a thickness of 35 microns, the panels were air dried at room temperature for seven days, diagonally scribed and subjected to a neutral salt spray for 312 hr. The results are presented in the following Table in which 0 represents the best result and 5 the worst:

| | Pigment | Scribe Line Corrosion | Blistering Under Film |
|---|---|---|---|
| (i) | K-White 84 | 2-3 | 0 |
| (ii) | Zinc Phosphate | 2 | 0 |
| (iv) | Shieldex AC-5 | 3 | 0 |
| (iii) | Aluminium Silicate Material | 1-2 | 0 |
| (v) | Aluminium Silicate Material plus zinc oxide | 1 | 0 |

**Example 12** Two-pack epoxy polyamide maintenance primer

Paints 12 (i)-(v) were prepared according to the following formulation, by mixing the base and catalyst in the amounts quoted.

BASE

| | Quantity (parts) | | | | |
|---|---|---|---|---|---|
| Material | (i) | (ii) | (iii) | (iv) | (v) |
| EPOXY RESIN (Epikote 1001-x-75 / Shell Chemicals) | 274 | 274 | 274 | 274 | 274 |
| AMINOFORMALDEHYDE RESIN (Beetle BE 640-BIP) | 17.6 | 17.6 | 17.6 | 17.6 | 17.6 |
| WETTING AGENT (EFKA-63-Croxton and Garry, Agents) | 5.70 | 5.70 | 5.70 | 5.70 | 5.70 |
| MAGNESIUM SILICATE (Microtalc ATI-Norwegian Talc) | 225 | 225 | 225 | 225 | 225 |
| BARIUM SULPHATE (H. Haeffner & Co. Ltd.) | 328 | 328 | 328 | 328 | 328 |
| TITANIUM DIOXIDE RCR 2 (Tioxide UK) | 253 | 253 | 253 | 253 | 253 |
| XYLENE:BUTANOL (1:1) (BP Chemicals) | 303 | 303 | 303 | 303 | 303 |
| K-WHITE 84 | 65.0 | 0 | 0 | 0 | 0 |
| ZINC PHOSPHATE | 0 | 76.5 | 0 | 0 | 0 |
| ALUMINIUM SILICATE MATERIAL (as in ex. 11) | 0 | 0 | 65.0 | 0 | 0 |
| SHIELDEX AC-5 (W.R. Grace) | 0 | 0 | 0 | 44.1 | 0 |
| ALUMINIUM SILICATE MATERIAL (52 pts.) PLUS ZINC OXIDE (13 pts.) | 0 | 0 | 0 | 0 | 65.0 |
| CATALYST | | | | | |
| Versamid 115 (Cray Valley Products) in Xylene/Butanol (1:1) (65% Solution) | 148 | 148 | 148 | 148 | 148 |

The paints were applied to mild steel panels, cured and tested in the same way as the paints of Example 11, except that neutral salt spray was applied for 240 hrs. The results are present below where 0 represents the best result and 5 the worst:

| | Pigment | Scribe-Line Corrosion | Blistering Under Film |
|---|---|---|---|
| (i) | K-White 84 | 2 | 1 |
| (ii) | Zinc Phosphate | 4 | 2 |
| (iv) | Shieldex AC-5 | 2 | 1 |
| (iii) | Aluminium Silicate Material | 2-3 | 2 |
| (v) | Aluminium Silicate Material plus zinc oxide | 2 | 1 |

**Example 13** - Short oil alkyd/urea formaldehyde industrial primer (yellow)
Two-pack compositions were formulated as follows:

**PACK A:**

| Material | Paint 13: (i) | (ii) | (iii) | (iv) | (v) |
|---|---|---|---|---|---|
| | Quantity (parts) | | | | |
| SHORT OIL ALKYD (Synolac 9090X Cray Valley Prod. Ltd) | 369 | 369 | 369 | 369 | 369 |
| ORGANIC SOLVENT (Solvesso 100 - Esso Chemicals) | 136 | 136 | 136 | 136 | 136 |
| POLYOXYALKYLENEMETHYLALKYL POLYSILOXANE CO-POLYMER (Byk 320 - Byk-Chemie) | 1.83 | 1.83 | 1.83 | 1.83 | 1.83 |
| BARIUM SULPHATE (Micronised Barytes-H. Haeffner) | 111 | 111 | 111 | 111 | 111 |
| MAGNESIUM SILICATE (Micro-Talc 10/M/2-Luzenac Talc) | 76.6 | 76.6 | 76.6 | 76.6 | 76.6 |
| YELLOW IRON OXIDE (Bayferrox 3920-Bayer) | 59.8 | 59.8 | 59.8 | 59.8 | 59.8 |
| TITANIUM DIOXIDE (Tioxide RCR 2-Tioxide) | 15.9 | 15.9 | 15.9 | 15.9 | 15.9 |
| ORGANIC DERIVATIVE OF A MONTMORILLONITE CLAY (Bentone SD 2-NL Chemicals) | 2.96 | 2.96 | 2.96 | 2.96 | 2.96 |
| XYLENE | 38.5 | 38.5 | 38.5 | 38.5 | 38.5 |
| BUTANOL | 79.5 | 79.5 | 79.5 | 79.5 | 79.5 |
| K-WHITE 84 | 162 | 0 | 0 | 0 | 0 |
| ZINC PHOSPHATE | 0 | 190 | 0 | 0 | 0 |
| ALUMINIUM SILICATE MATERIAL (as in Ex. 11) | 0 | 0 | 162 | 0 | 0 |
| SHIELDEX AC-5 (W.R. Grace) | 0 | 0 | 0 | 104 | 0 |
| ALUMINIUM SILICATE MATERIAL (as in Example 11, 32 parts) PLUS ZINC OXIDE (32 parts) | 0 | 0 | 0 | 0 | 162 |

**PACK B:**

| Material | | Quantity (parts)-in each paint 13 (i)-(v) |
|---|---|---|
| UNPLASTICISED UREA RESIN | (Resamine HF Hoechst/RCL) | 15.3 |
| SOLVESSO 100 | (Esso Chemicals) | 25.7 |
| BUTANOL | | 21.4 |

The contents of packs A and B were mixed together to give the paints 13 (i)-(v). After applying each paint to a clean mild steel panel to a thickness of 35 microns, the panels were cured for 30 minutes at a temperature of 150°C, diagonally scribed and subjected to a neutral salt spray for 192 hrs. The results are presented in the following table in which 0 represents the best result and 5 the worst:

| | Pigment | Scribe-Line Corrosion | Blistering Under Film |
|---|---|---|---|
| (i) | K-White 84 | difficult to assess | 5 |
| (ii) | Zinc Phosphate | 1-2 | 0 |
| (iv) | Shieldex AC-5 | 1-2 | 0 |
| (iii) | Aluminium Silicate Material | 2 | 0 |
| (v) | Aluminium Silicate Material plus zinc oxide | 1 | 0 |

**Example 14** - Epoxy - ester/melamine - formaldehyde industrial primer.

Paints 14 (i) - (v) were prepared by mixing the materials below and then adding unplasticised melamine formaldehyde resin (Maprenal 580 Hoechst/RCL) (209 pts.) and Solvesso 100 (Esso Chemicals) (24.7 pts.).

| Material | Paint 14: (i) | (ii) | (iii) | (iv) | (v) |
|---|---|---|---|---|---|
| SHORT OIL OXIDISING EPOXY ESTER (Synolac 463-Cray Valley Prod. Ltd) | 446 | 446 | 446 | 446 | 446 |
| ORGANIC SOLVENT (Solvesso 100 - Esso Chemicals) | 103 | 103 | 103 | 103 | 103 |
| POLYOXYALKYLENEMETHYLALKYL POLYSILOXANE CO-POLYMER (Byk 320 - Byk-Chemie) | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| BARIUM SULPHATE (Micronised Barytes-H. Haeffner) | 97.5 | 97.5 | 97.5 | 97.5 | 97.5 |
| MAGNESIUM SILICATE (Micro-Talc 20/M/2-Luzenac Talc) | 69.7 | 69.7 | 69.7 | 69.7 | 69.7 |
| TITANIUM DIOXIDE (Tioxide RCR 2-Tioxide) | 21.7 | 21.7 | 21.7 | 21.7 | 21.7 |
| ORGANIC DERIVATIVE OF A MONTMORILLONITE CLAY (Bentone SD 2-NL Chemicals) | 4.04 | 4.04 | 4.04 | 4.04 | 4.04 |
| RED OXIDE 130 M (Bayer) | 95.6 | 95.6 | 95.6 | 95.6 | 95.6 |
| XYLENE | 12.9 | 12.9 | 12.9 | 12.9 | 12.9 |
| BUTANOL | 12.5 | 12.5 | 12.5 | 12.5 | 12.5 |
| K-WHITE 84 | 209 | 0 | 0 | 0 | 0 |
| ZINC PHOSPHATE | 0 | 246 | 0 | 0 | 0 |
| ALUMINIUM SILICATE MATERIAL (as in Ex. 11) | 0 | 0 | 209 | 0 | 0 |
| SHIELDEX AC-5 (W.R. Grace) | 0 | 0 | 0 | 134 | 0 |
| ALUMINIUM SILICATE MATERIAL (as in Example 11, 167 parts) PLUS ZINC OXIDE (42 parts) | 0 | 0 | 0 | 0 | 209 |

Quantity (parts)

After applying each paint to a clean mild steel panel to a thickness of 35 microns, the panels were cured for 30 minutes at 150°C, diagonally scribed and subjected to a neutral salt spray for 300 hr. The results are presented below in which 0 represents the best results and 5 the worst:

| | Pigment | Scribe-Line Corrosion | Blistering Under Film |
|---|---|---|---|
| (i) | K-White 84 | 2 | 1-2 |
| (ii) | Zinc Phosphate | 2 | 2-3 |
| (iv) | Shieldex AC-5 | 1-2 | 0-1 |
| (iii) | Aluminium Silicate Material | 2 | 2 |
| (v) | Aluminium Silicate Material plus zinc oxide | 1 | 1 |

**Example 15** - Water-based maintenance primer

A two-pack composition was prepared and the contents mixed together to form paints 15 (i)-(v)

**PACK 1:**

| Material | Paint 15: (i) | (ii) | (iii) | (iv) | (v) |
|---|---|---|---|---|---|
| | Quantity (parts) | | | | |
| WATER | 8.9 | 8.9 | 8.9 | 8.9 | 8.9 |
| METHYL CARBITOL | 12.5 | 12.5 | 12.5 | 12.5 | 12.5 |
| DISPERSANT (Tamol 165) | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 |
| WETTING AGENT (Triton CF-10) | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| FOAM CONTROL AGENT (Drewplus TS - 4380) | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| RHEOLOGY MODIFIER (Acrysol RM 825) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| RED IRON OXIDE (Bayferrox 120NM) | 13.9 | 13.9 | 13.9 | 13.9 | 13.9 |
| CALCIUM CARBONATE (Atomite) | 37.5 | 37.5 | 37.5 | 37.5 | 37.5 |
| K-WHITE 105 | 6.1 | 0 | 0 | 0 | 0 |
| ZINC PHOSPHATE | 0 | 6.9 | 0 | 0 | 0 |
| SHIELDEX AC-3 | 0 | 0 | 0 | 4.5 | 0 |
| ALUMINIUM SILICATE MATERIAL (as in Ex. 11) | 0 | 0 | 6.1 | 0 | 0 |
| ALUMINIUM SILICATE MATERIAL (as in example 11 - 4.9 parts) PLUS ZINC OXIDE (1.2 pts.) | 0 | 0 | 0 | 0 | 6.1 |

**PACK 2:**

| Material | Quantity (parts)-for each paints 15 (i)-(v) |
|---|---|
| AQUEOUS POLYURETHANE DISPERSION (Maincote HG - 54) | 147.9 |
| SOLVENT (Texanol) | 3.75 |
| FOAM CONTROL AGENT (Drewplus 4310) | 0.75 |
| AMMONIUM HYDROXIDE ($NH_4OH$ - 28% $NH_3$) | 1.0 |
| BUTYL CARBITOL | 8.1 |
| DIBUTYL PHTHALATE | 3.75 |
| SODIUM NITRITE (15%) | 2.0 |

After applying each paint to a mild steel panel to a thickness of 35 microns, the panels were air dried at room temperature for seven days, diagonally scribed and subjected to a neutral salt spray for 240 hr. The results are presented in the following table in which 0 represents the best result and 5 the worst:

| | Pigment | Scribe Line Corrosion | Blistering Under Film |
|---|---|---|---|
| (i) | K-White 105 | 3 | 1-2 |
| (ii) | Zinc Phosphate | 0-1 | 0 |
| (iv) | Shieldex AC-3 | 2-3 | 2 |
| (iii) | Aluminium Silicate Material | 0-1 | 2 |
| (v) | Aluminium Silicate Material plus zinc oxide | 0-1 | 0 |

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An anticorrosive pigment composition which comprises zinc oxide and a trivalent metal silicate material selected from the group consisting of (i) a material obtained by reacting a trivalent metal compound with a silicate (ii) a naturally occurring aluminium silicate material or a synthetic equivalent thereof, (iii) a naturally occurring or synthetic aluminium silicate surface-modified by ion exchange, and (iv) mixtures thereof, said metal silicate material being the major proportion by weight of the composition.

2. A composition according to claim 1, wherein the trivalent metal is selected from the group consisting of aluminium, iron and chromium.

3. A composition according to claim 2, wherein the trivalent metal is aluminium.

4. A composition according to claim 3, wherein the metal silicate material is a reaction product prepared in aqueous solution from an aluminium salt selected from an acid phosphate, a sulphate or mixture thereof and a soluble silicate.

5. A composition according to any of claims 1 to 3, in which the metal silicate material is hydrated aluminium silicate clay.

6. A composition according to claim 5, in which the metal silicate material is china clay.

7. A composition according to any of claims 1 to 6, wherein the zinc oxide comprises 2-30% by weight of the composition.

8. A composition according to claim 7, wherein the zinc oxide comprises 2-25% by weight of the composition.

9. A composition according to claim 7, wherein the zinc oxide comprises 10-25% by weight of the composition.

10. A composition according to claim 7, wherein the zinc oxide comprises 5-25% by weight of the composition.

11. A composition according to any of the preceding claims, wherein the zinc oxide has a particle size of 0.1-10 microns.

12. A substantially water-soluble-salt-free pigment comprising, as the major component in proportion by weight, a pigment material obtained by reacting an aluminium salt and a silicate in aqueous solution, and then separating, washing and drying the reaction product, and also comprising zinc oxide.

13. A salt-free pigment according to claim 12, in which the aluminium salt used is a phosphate or sulphate.

14. A composition according to any of the preceding claims, in which the silicon to trivalent metal atom ratio is in the range of 0.2 - 30:1.

15. A composition according to claim 14, in which the silicon to trivalent metal atom ratio is in the range 0.5 - 10:1.

16. A composition according to 15, in which the silicon to trivalent metal atom ratio is in the range 0.5 - 5:1.

17. A composition according to claim 16, in which the silicon to trivalent metal atom ratio is in the range of 0.5 - 3:1.

18. A coating composition which comprises a film forming material and a pigment composition according to any of the preceding claims.

19. A coating composition according to claim 18 wherein the film forming material is an alkyd primer.

20. A coating composition according to claim 18 or 19, which is water based.

21. A coating composition according to claim 18 or 19, which is organic solvent based.

22. A process for protecting a surface which comprises applying to the surface a composition according to claim 18.

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