

PATENT SPECIFICATION

(11) 1 276 008

NO DRAWINGS

- (21) Application No. 24105/69 (22) Filed 12 May 1969
 (31) Convention Application No. 32095 (32) Filed 13 May 1968 in
 (33) Japan (JA)
 (45) Complete Specification published 1 June 1972
 (51) International Classification C09D 3/48, 5/08

(52) Index at acceptance

C3P 4C12A 4C14A 4C17 4C20A 4C20D1 4C20D3 4C8B
 4D3B1 8C12A 8C14A 8C17 8C20A 8C8B 8D2A
 8D2B2 8K8
 B2E 193 197 19Y 20Y 410 416 41X 41Y 44Y 473 485
 486 487 498 505 507 50Y 515 516 517 52Y 533
 545 546 547 565 567 56Y 575 576 577 58Y



(54) STRIPPABLE AND ANTI-CORROSIVE FILM-FORMING COMPOSITIONS

(71) We, KURITA WATER INDUSTRIES LTD., a Japanese body corporate of No. 1, Koraibashi 3-chome, Higashi-ku, Osaka-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a chemical composition for use in forming strippable and anticorrosive films for protecting the surface of metal workpieces and the like.

Metal workpieces and the like are liable to get scratched or gather rust on their surfaces when stored or transported, and therefore it has been usual to protect their surfaces by forming a protective film thereon. It has been common to employ an emulsion of a plastics material as the film forming composition for this purpose. However, inasmuch as this emulsion contains emulsifier, employment of the emulsion, as it is, would result in the formation of a hydrophilic film and would not prevent a rapid gathering of rust.

For instance, emulsions of polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyacrylates, polymethacrylates, and corresponding copolymers have been popularly employed in forming protective films on the surfaces of such materials as metal, glass, stone and plastics. But these emulsions, particularly oil-in-water type emulsions, contain much water and emulsifier so when they are applied to metals, especially mild steel, they are apt to cause corrosion even under ordinary indoor conditions, not to speak of such conditions as high temperature and high humidity.

Not only that, but polyvinyl chloride and polyvinylidene chloride are unstable when

exposed to the ultraviolet rays of sun-light and to heat. This drawback may be accelerated by degeneration of plasticizer incorporated therein and it is not unusual for the resin film to change in quality and thus to cause corrosion of the metal and detract from the stripability of the film when placed in the open air or exposed to a high temperature.

Corrosion inhibition may be obtained by employing film-forming compositions prepared by mixing a conventional metal-corrosion inhibitor such as a chromate or phosphate with the aforesaid emulsion so as to prevent the gathering of rust as stated above. However, the film forming composition comprising such a corrosion inhibitor is apt to adhere so firmly to the surfaces of metals that it is difficult to remove the film when the metal workpiece comes to be used and the working efficiency is reduced accordingly.

The present invention provides a strippable and anti-corrosive film-forming composition which is a mixture of a water-soluble metal composition which is a mixture of a water-soluble metal-corrosion inhibitor, e.g. a nitrite, chromate, bichromate or phosphate with an aqueous emulsion of a film-forming synthetic resin, e.g. a polymer or copolymer of vinyl chloride, vinyl acetate, vinylidene chloride or of an acrylate ester or methacrylate ester and 0.5 to 5% and preferably 0.5 to 3% based on the weight of synthetic resin, of oleic acid and/or a sodium, potassium, ammonium or amine salt of oleic acid. The resin film formed on the surfaces of various metals by coating them with the emulsion and drying has very good anti-corrosiveness and stripability.

The composition of the present invention is preferably prepared by adding a water-soluble

corrosion-inhibitor, which may be a water-soluble nitrite, sodium benzoate, a water-soluble chromate, a water-soluble bichromate or a sodium polyphosphate, to the aforesaid resin emulsion in a proportion amounting to from 2 to 5% by weight of the resin employed. Mild steel coated with this emulsion and having an anti-corrosive resin film formed thereon has been found to be free from any trace of gathering rust even after 6 months' exposure to ordinary indoor conditions or more than 1 month's exposure to such unfavourable conditions as a temperature of 60°C and a relative humidity of more than 95%.

However, the presence of corrosion inhibitors in a synthetic resin film tends to render it lacking in strippability, and this tendency becomes particularly conspicuous in cases where the surface of the object material is not smooth or the resin or plasticizer degenerates under the influence of light and heat.

But when the oleic acid and/or an oleic acid salt of the kind referred to above is included in the resin emulsion in an amount of 0.5 to 5%, and preferably 0.5 to 3% by weight of the resin employed and the mixture is well blended, and then applied to the surface of a metal and dried, the strippability of the film formed is improved without substantially reducing the anti-corrosiveness thereof. The strippability of the film thus obtained proves remarkably superior to that of a film which contains no oleic acid or oleic acid salt of the kind specified, and consequently even a resin film having a high adhesive property becomes strippable.

The addition of the oleic acid or salt thereof does not make it necessary to modify the quantity of the corrosion inhibitor used.

Examples of compositions according to the invention (wherein all the parts and percentages are by weight) will now be given.

EXAMPLE 1

0.2 part of oleic acid was mixed with 100 parts of an aqueous emulsion of polymethyl acrylate (comprising 30% of resin), and then an aqueous solution, prepared by dissolving 1.5 parts of sodium nitrite in 5 parts of water, was added to the resultant mixture and thoroughly blended. The resin emulsion obtained was applied to a ground, clean surface of mild steel and to an etched surface of mild steel and dried to form transparent resin films. Subsequently, both film-carrying surfaces of mild steel were exposed to a temperature of 60°C and a relative humidity of more than 95%. Comparison of anti-corrosiveness (based on visual estimation) and strippability (based on stripping tests by hand) of the film formed by applying the basic resin emulsion (shown as comparative example A) and that formed by applying an emulsion comprising the same basic resin emulsion plus the sodium nitrite only (shown as comparative example B) resulted in the findings shown in Table 1, together with the results for the film according to the invention. In this context, the number appearing in the anti-corrosiveness column indicates the rating number of JIS D 0201-1964. (The same applies hereinafter).

JIS (Japanese industrial standard) D 0201-1964 is based on the "general rules of electroplating for automobile parts" and is a method for rating the degree of corrosion of the surface of metals in terms of the rate of corroded area. To put it more concretely, there are provided standard charts corresponding to the respective rating numbers for the sake of comparison, and the number is determined by evaluation of the post-test state of metal surface by means of visual estimation in comparison with the charts. These standard charts are summarized as follows:

Rating No.	Rate of Corroded Area (%)
10	0
9	less than 0.1
8	from 0.1 to less than 0.25
7	from 0.25 to less than 0.5
6	from 0.5 to less than 1.0
5	from 1.0 to less than 2.5
4	from 2.5 to less than 5.0
3	from 5.0 to less than 10
2	from 10 to less than 25
1	from 25 to less than 50
0	50 and over

TABLE 1

	Strippability	Anti-corrosiveness
Comparative Example A	Not strippable because of rust	Rust all over the surface in a day. Rating No. after 3 days0
Comparative Example B	Film on the ground surface is barely strippable Film on the etched surface is not strippable at all	No rust for 1 month. Rating No. after 1 month.....10
Example 1	Film on either surface is easily strippable	Ditto

EXAMPLE 2

5 In this case, 1.5 parts of N-alkyl-trimethylene diamine dioleate was added to 100 parts of an aqueous emulsion of polyvinyl acetate (comprising 55% of resin, of which 20/100 is dibutyl phthalate plasticiser and blended, and then an aqueous solution prepared by dissolving 2.5 parts of sodium chromate in 7 parts of water was added to the resultant mixture and thoroughly blended by stirring. The resin emulsion thus obtained was applied onto the surface of mild steel and dried to form a resin

film. Subsequently, the treated mild steel surface was subjected to indoor exposure to evaluate the anti-corrosiveness and strippability of the film.

Tests were also conducted on the respective film formed by employing the basic resin emulsion only (shown as comparative example C) and the basic resin emulsion plus sodium chromate only (shown as comparative example D) in the same manner as above, and the results thereof were as shown in the following Table 2.

TABLE 2

	Strippability	Anti-corrosiveness
Comparative Example C	Film once dried is not strippable	Rust all over the surface within 1 month. Rating No. after 1 month4
Comparative Example D	Ditto	No rust for more than 3 months. Rating No. after 3 months10
Example 2	Film is easily strippable even after 3 months.	As in comparative Example D

EXAMPLE 3

30 0.5 parts of sodium oleate was mixed with 100 parts of an aqueous emulsion (comprising 45% of solid matter) of an ethyl acrylate-methyl methacrylate (60:40) copolymer, and then an aqueous solution prepared by dissolving 2 parts of a mixture comprising sodium nitrite and sodium benzoate (1:1) in 7 parts of water was added to the resultant mixture and thoroughly blended by stirring. The emulsion obtained was applied onto a ground mild

steel surface and dried to form a film thereon, and the test of anti-corrosiveness was conducted at a temperature of 60°C and relative humidity of 97%.

Tests were also conducted on the respective films formed by employing the basic resin emulsion only (shown as comparative example E) and basic resin emulsion plus the corrosion inhibitor only (as shown as comparative example F) in the same manner as above; the results thereof are shown in Table 3.

TABLE 3

	Strippability	Anti-corrosiveness
Comparative Example E	Film once solidified is hard to strip	Rust all over the surface after 3 days. Rating No. after 3 days0
Comparative Example F	Ditto	No rust even after 1 month. Rating No. after 1 month10
Example 3	Film is easily strippable even after 1 month	As in comparative Example F

WHAT WE CLAIM IS:—

1. A strippable and anti-corrosive film-forming composition which comprises an aqueous emulsion of a film-forming synthetic resin mixed with a water-soluble metal-corrosion inhibitor, and 0.5 to 5% based on the weight of synthetic resin of oleic acid and/or a sodium, potassium, ammonium or amine salt of oleic acid.
2. A composition as claimed in claim 1, wherein the resin component of the synthetic resin emulsion is a polymer or copolymer of an acrylate ester.
3. A composition as claimed in claim 1, wherein the resin component of the synthetic resin emulsion is a polymer or copolymer of a methacrylate ester.
4. A composition as claimed in claim 1, wherein the resin component of the synthetic resin emulsion is a polymer or copolymer of vinyl acetate.

5. A component as claimed in any preceding claim wherein the content of water-soluble metal-corrosion inhibitor is from 2 to 5% by weight of the resin employed.

6. A composition claimed in any of claims 1 to 5, wherein the proportion of oleic acid or of the sodium, potassium, ammonium or amine salt thereof is 0.5 to 3% based on the weight of the synthetic resin.

7. A strippable and anti-corrosive film-forming composition substantially as described in Example 1, 2 or 3.

Agents for the Applicants,
STANLEY, POPPLEWELL, FRANCIS
& ROSS,
Chartered Patent Agents,
20/21 Tooks Court, Cursitor Street,
London E.C.4A 1LB.

TABLE 3

	Strippability	Anti-corrosiveness
Comparative Example E	Film once solidified is hard to strip	Rust all over the surface after 3 days. Rating No. after 3 days0
Comparative Example F	Ditto	No rust even after 1 month. Rating No. after 1 month10
Example 3	Film is easily strippable even after 1 month	As in comparative Example F

WHAT WE CLAIM IS:—

1. A strippable and anti-corrosive film-forming composition which comprises an aqueous emulsion of a film-forming synthetic resin mixed with a water-soluble metal-corrosion inhibitor, and 0.5 to 5% based on the weight of synthetic resin of oleic acid and/or a sodium, potassium, ammonium or amine salt of oleic acid.

2. A composition as claimed in claim 1, wherein the resin component of the synthetic resin emulsion is a polymer or copolymer of an acrylate ester.

3. A composition as claimed in claim 1, wherein the resin component of the synthetic resin emulsion is a polymer or copolymer of a methacrylate ester.

4. A composition as claimed in claim 1, wherein the resin component of the synthetic resin emulsion is a polymer or copolymer of vinyl acetate.

5. A component as claimed in any preceding claim wherein the content of water-soluble metal-corrosion inhibitor is from 2 to 5% by weight of the resin employed.

6. A composition claimed in any of claims 1 to 5, wherein the proportion of oleic acid or of the sodium, potassium, ammonium or amine salt thereof is 0.5 to 3% based on the weight of the synthetic resin.

7. A strippable and anti-corrosive film-forming composition substantially as described in Example 1, 2 or 3.

Agents for the Applicants,
STANLEY, POPPLEWELL, FRANCIS
& ROSS,
Chartered Patent Agents,
20/21 Took's Court, Cursitor Street,
London E.C.4A 1LB.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *