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⑤④ **Corrosion inhibiting composition.**

⑤⑦ A corrosion inhibiting composition comprising a mixture of
(A) at least one basic metal sulfonate and
(B) at least one aliphatic dicarboxylic acid or anhydride
containing no more than 38 carbon atoms excluding the
carbon atoms in the carboxylic acid groups or a metal salt
thereof is useful in temporary anticorrosion coatings for
metal having improved anticorrosion properties weathering and
removability characteristics.

Description

CORROSION INHIBITING COMPOSITION

This invention concerns corrosion inhibiting compositions which are useful as light duty or temporary corrosion preventatives and heavy duty or permanent corrosion preventatives.

In particular the invention relates to coatings which may be applied to metal for protection during storage between fabrication and use. Such coatings are generally applied from oil solution by spraying or dipping and must adhere to the metal sufficiently to give the desired anti-corrosion effect during the storage period which can be up to 6 months whilst at the same time being readily removable generally by washing with aqueous alkaline detergent to enable the metal to be painted. It is therefore important that the coatings have adequate light stability to ensure they are not converted to a laquer during storage which cannot then be easily removed.

Corrosion inhibiting compositions based on alkali or alkaline earth metal salts are known.

US Patent No. 3 453 124 relates to a product for inhibiting the corrosion of metal surfaces prepared by the reaction of (A) a non-Newtonian colloidal dispersed system comprising alkali or alkaline earth metal carbonates predispersed in dispersing medium and, as a third essential component, an alkali or alkaline earth metal salt of a carboxylic or sulphonic acid with (B) an acidic ester of a phosphoric acid.

US Patent No. 3 730 895 concerns greases thickened with conventional grease thickeners and containing a cloudy type overbased alkali metal or alkaline earth metal sulphonate or carboxylate dispersant and a water-soluble corrosion inhibiting salt, that is an alkali metal nitrite or an alkali metal chromate.

US Patent No. 3 850 823 discloses a method for producing corrosion inhibiting compositions comprising lubricating oil, a cloudy type overbased alkali metal and/or alkaline earth metal dispersant and at least one water-soluble salt effective as a corrosion inhibitor, that is an alkali metal nitrite or an alkali metal chromate.

US Patent No. 3 897 350 relates to anti-rust lubricating and hydraulic oil compositions containing a naphthol, a metal sulphonate selected from neutral alkali metal sulphonate, neutral alkaline earth metal sulphonate, neutral zinc sulphonate, overbased alkali metal sulphonate, overbased alkaline earth metal sulphonate, and overbased zinc sulphonate, and a detergent selected from alkenyl succinimides, alkenyl succinic esters, alkyl lactone amides, alkyl lactam amides, and Mannich bases.

PCT Application WO 86/03513 concerns corrosion inhibiting compositions comprising a mixture of (A) an oil-soluble neutral or basic alkali metal or alkaline earth metal salt or complex of an organic acid, and (B) a nitrogen- and boron- containing composition which is the reaction product of an amino alcohol, a boric acid or boron trioxide, and an organic carboxylic acid.

Mixture of basic sulphonates and naturally occurring unsaturated carboxylic acids such as linoleic acids are also used as temporary anti-corrosion coatings, these have poor light stability.

It is known to treat overbased complexes with high molecular weight aliphatic carboxylic acids or acid derivatives.

US Patent No 3 714 042 discloses a composition prepared by a process comprising mixing (A) a basic metal complex selected from sulphonate, sulphonate-carboxylate and carboxylate complexes with up to an amount equivalent to the total basicity thereof of (B) a high molecular weight aliphatic carboxylic acid or anhydride wherein there are at least about 25 aliphatic carbon atoms per carboxy group in (B), such mixing is generally effected at temperatures that will cause the products to react.

It is generally assumed that the presence of both water and oxygen is essential for the oxidation of ferrous metal articles. Oxidation can be prevented or at least in large measure inhibited, by relatively impermeable coatings which have the effect of excluding moisture and/or oxygen from contact with the metal surface. Such coatings are often exposed to high humidity, corrosive atmosphere, etc, and to the extent that these coatings are penetrated or otherwise harmed by such influences they become ineffective for the desired purpose. A satisfactory corrosion-proof coating must have the ability to resist weathering, high humidity and corrosive atmospheres, such as air contaminated with industrial waste, so that a uniform protective film is maintained on all or most of the metal surface.

It is an object of the present invention to provide corrosion inhibiting compositions for metals, especially ferrous metals, and a process for their preparation.

It is also an object of the invention to provide corrosion inhibiting coating compositions for metals, which compositions are resistant to weathering including light stability and may be easily and inexpensively applied to metal surfaces and can also be readily removed to permit painting of the metal. It is a further object to provide metal coated with such corrosion inhibiting compositions.

According to the present invention a corrosion inhibiting composition comprises a mixture of (A) at least one basic metal sulphonate and (B) at least one aliphatic dicarboxylic acid or anhydride containing no more than 38 carbon atoms excluding the carbon atoms in the carboxylic acid or anhydride groups or a metal salt thereof.

Surprisingly the combination of basic metal sulphonate and aliphatic dicarboxylic acid and anhydride has a much stronger anti-corrosive effect than the basic metal sulphonate alone. Some sort of synergism between components (A) and (B) enhances the resistance to weathering and humidity of the protective film on the metal surface.

The metal salts of component (A) may be a group I or group II metal such as lithium, sodium, potassium, magnesium, calcium, strontium or barium. An alkaline earth metal and especially calcium is preferred, sodium

salts are less preferred since their light resistance is inferior.

Component (A) may be the salt of a natural or synthetic sulphonate and is preferably a metal salt of an alkyl substituted aromatic sulphonic acid. The product should have a residual basicity and we prefer it have a TBN of at least 40 preferably greater than 60. Blends of neutral and basic sulphonates may also be used. Preferably the sulphonic acid is a benzene sulphonic acid having 1-3 alkyl substituents in the meta and para positions of the benzene ring or a naphthalene sulphonic acid. Said alkyl substituents may be branched or linear or cyclic alkyl residues. Preferably at least one of said alkyl substituents of the benzene sulphonic acid is a "long-chain residue" containing from 12-50 carbon atoms. The additional alkyl substituents may also be long-chain residues or they may be short-chain residues containing less than 12 carbon atoms, for example, methyl or ethyl groups. Many processes have been described for the production of basic metal salts of such sulphonic acids and the choice of process is not important although the thixotropic forms of the sulphonates, particularly calcium sulphonate, are not preferred since they can be difficult to remove from the metal.

Preferably component (A) consists of a mixture of different alkyl benzene sulphonates which mainly differ in the size of their long-chain alkyl substituents. It is especially preferred that an even distribution of alkyl substituents continuously increasing in size is present in component (A). The substituents may increase in size over a range of 20 carbon atoms, especially from C₁₀ to C₃₀. Compositions according to this invention containing such mixtures of alkyl benzene sulphonates yield films on metal surfaces which are especially resistant to weathering and humidity.

Component (B) is preferably an alkyl or alkenyl succinic acid or anhydride or a salt therefore preferred salts are the alkyl or alkenyl succinic acids or anhydrides containing from 6-32 aliphatic carbon atoms particularly those 10 to 24 especially 10 to 14 carbon atoms excluding those in the carboxylic acid groups or their salts.

It is preferred that the component (B) be present as the free acid or anhydride rather than the salt prior to application to the metal protected since it is believed that the presence of the free acid or anhydride can give improved adhesion to the metal.

The composition according to the present invention may further comprise a minor amount of a monocarboxylic metal salt, for example a formic acid salt.

It is preferred that the mixture contains from 95% to 75% by weight of the basic metal sulphonate and from 5% to 25% by weight of the component B although the relative amounts will depend upon the use to which the composition is put. It is especially preferred that component (B) makes up 10-50 wt% of the total amount of components (A) and (B). It is preferred that the composition have residual basicity.

Usually the corrosion inhibiting compositions are employed as coating compositions which are solutions in a liquid vehicle. Examples of liquid vehicles are hydrocarbon oils and the various petroleum distillates which generally contain up to 15 wt% of the corrosion inhibiting composition, particularly up to 10 wt% generally between 0.5 and 5 wt% active ingredient content of the composition of the invention. If the composition contains a non-polar vehicle there may additionally be present some metal in solid (colloidal) form associated with components (A) and (B) action as dispersants.

The vehicle may also be a water-based system, for example a mixture of polyisobutylene, wax and water.

The coating composition including the vehicle is usually grease-like material having a consistency from fluid to semi-solid. The corrosion inhibiting films of this invention may be applied to metal surfaces by any of the ordinary methods such as brushing, spraying, dip-coating, flow-coating, roller coating and the like. The viscosity of the corrosion inhibiting coating composition may be adjusted for the particular method of application selected by adding a suitable amount of diluent.

The corrosion inhibiting compositions according to the present invention may be prepared in different ways, for example, by preparing the metal salts independently and mixing them subsequently. Alternatively a solution of an overbased metal sulphonate complex can be prepared to which an aliphatic dicarboxylic acid or its anhydride is added.

It is preferred that the products are mixed in a manner that they do not react, i.e. the temperature is maintained below about 50°C although reaction products of components (A) and (B) are within the scope of the invention. The amount of the aliphatic dicarboxylic acid or its anhydride added to the overbased metal sulphonate complex should be such that the resulting mixture is overbased. Such overbased mixtures are also useful as corrosion inhibiting compositions.

The composition may be supplied as a concentrate preferably a solution of the mixture of (A) and (B) in oil in which case it is preferred that the solution contains from 20% to 60% active ingredient. Alternatively the components may be supplied separately for incorporation into the final coating medium.

We have found that the corrosion coatings of the present invention have improved weather resistance particularly resistance to light and can be readily removed from the metal to enable painting etc. The coatings may be used on metal sheets to be used for automobile manufacture, constructional steelwork in building and bridge building etc.

The compositions may also contain other additives such as antioxidants, antifoams, etc. The invention is further illustrated by the following examples.

Compositions according to the present invention and comparative compositions were prepared and their corrosion inhibiting effects were determined according to the methods of DIN 51 386 and DIN 50 017.

Steel panels of identical size were washed, rinsed, and dried. The dry panels were coated with the respective composition by dip coating. The coated panels were then stored in a climatic chamber.

The climate in the chamber was varied in cycles. Each cycle consisted of an eight hour period at a

temperature of $40 \pm 3^\circ\text{C}$ and a relative humidity of 100% followed by a 16 hour period at a temperature in the range of from $18-28^\circ\text{C}$ and a relative humidity of less than 75%.

It was determined how many cycles could be run before the first rust spot appeared on the panel. A larger number of cycles indicates a better anti-corrosion performance of the product tested.

Each composition was tested on two steel panels. The numbers given for each composition in Examples 1 to 5 are the average of two tests.

All compositions tested were based on mineral oil. They consisted of 94 wt.% mineral oil and 6 wt.% active ingredient (that is anything different from mineral oil). All compositions tested had a total base number in the range of from 6-10 milligram KOH/gram.

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Example 1 (Comparative Example)

The corrosion inhibiting performance of a mineral oil (130 neutral base stock) without active ingredient was tested. The number of cycles before appearance of the first rust spot was 0.

15 Example 2 (Comparative Example)

A composition was prepared containing 94 wt.% of mineral oil (130 neutral base stock) and 6 wt.% of a mixture of calcium sulphonates. The calcium sulphonates employed were the neutral salt of 4-(C₁₂-alkyl)-3,5-dimethyl benzene sulphonic acid and the basic salt of 4-(C₂₄-alkyl) benzene sulphonic acid having a TOTAL BASE NUMBER (TBN) of 250 to give a blend of TBN 60. C₁₂ and C₂₄ indicate the average number of carbon atoms in the long-chain residue of the respective benzene sulphonic acid.

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Steel panels coated with this composition were tested in the climatic chamber. The number of cycles before appearance of the first rust spot was 13.

Example 3 (Comparative Example)

A composition was prepared containing 94 wt.% of mineral oil (130 neutral base stock), 5.5 wt.% of a mixture of calcium sulphonates and 0.5 wt.% of solid calcium carbonate in colloidal form. The calcium sulphonates employed were salts of 4-(C₁₂-alkyl)-3,5-dimethyl benzene sulphonic acid, 4-(C₁₈-alkyl) benzene sulphonic acid and 4-(C₂₄-alkyl) benzene sulphonic acid of TBN 250 to provide the colloidal calcium carbonate. C₁₂, C₁₈ and C₂₄ indicate the average number of carbon atoms in the long chain residue of the respective benzene sulphonic acid.

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Steel panels coated with this composition were tested in the climatic chamber. The number of cycles before appearance of the first rust spot was 15.

Example 4

A composition was prepared containing 94 wt.% of mineral oil (130 neutral base stock), 3.1 wt.% of a mixture of sodium sulphonates, 1.0 wt.% of a mixture of calcium sulphonates, and 1.9 wt.% of a calcium carboxylate. The sodium sulphonates employed were salts of 4-(C₁₂-alkyl)-3,5-dimethyl benzene sulphonic acid and 4-(C₂₄-alkyl) benzene sulphonic acid. The calcium sulphonates were the same as in Example 2. The calcium carboxylate was a salt prepared from an alkenyl succinic anhydride with an average number of 12 carbon atoms in the alkenyl residue.

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Steel panels coated with this composition were tested in the climatic chamber. The number of cycles before appearance of the first rust spot was 25.

Example 5

A composition was prepared containing 94 wt.% of mineral oil (130 neutral base stock), 4.0 wt.% of a mixture of calcium sulphonates used as in Example 3, and 2.0 wt.% of calcium carboxylate used in Example 4.

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Steel panels coated with this composition were tested in the climatic chamber. The number of cycles before appearance of the first rust spot was 30.

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This Example demonstrates the improved resistance to weathering and humidity of a composition according to the present invention. A comparison of Example 5 with Examples 2 and 3 shows the synergism between calcium sulphonates and calcium carboxylate.

Example 6

The products of the invention were compared with a similar composition containing the calcium salt of an C₆₈ Alkenyl succinic acid, the products tested were prepared by adding the following formulations to oil (130 neutral base stock) to give the total active ingredient levels set out in Table 1.

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<u>Formulation 1</u>	26 wt% calcium sulphinate) as in 3% colloidal calcium carbonate) Example 2 6% C ₁₂ Alkenyl succinic acid 65% oil	5
<u>Formulation 2</u>	26 wt% calcium sulphinate) as in 3 wt% colloidal calcium carbonate) example 2 6 wt% C ₆₈ Alkenyl Succinic Acid 65 wt% oil	10 15

The formulations were tested as metal anti-corrosion coatings in the humidity cabinet (ASTM D 1748) and salt spray cabinet (ASTM B117) tests with the following results 20

	HUMIDITY CABINET ASTM D 1748		SALT SPRAY CABINET ASTM B117	25
Wt% Active Ingredient	<u>1.5%</u>	<u>2.5%</u>	<u>10%</u>	30
Formulation (1)	>472 Hrs	>500 Hrs	70 Hrs	
Formulation (2)	300 Hrs	>472 Hrs	12 Hrs	35

Claims

1. A corrosion inhibiting composition comprising a mixture of
 - (A) at least one basic metal sulfonate and
 - (B) at least one aliphatic dicarboxylic acid or anhydride containing no more than 38 carbon atoms excluding the carbon atoms in the carboxylic acid or anhydride groups or a metal salt thereof.
2. A composition according to Claim 1 wherein the organic part of the aliphatic dicarboxylic acid metal salt makes up 10 to 50 wt.% of the total amount of components (A) and (B). 50
3. A composition according to Claim 1 or Claim 2, wherein the metal is selected from Group I metals and Group II metals.
4. A composition according to any of the preceding Claims, wherein the metal is calcium.
5. A composition according to any of the preceding Claims wherein the metal sulfonate (A) is selected from alkyl aryl sulfonates. 55
6. A composition according to Claim 5 wherein the alkyl aryl sulfonates are selected from benzene sulfonates having 1 to 3 alkyl substituents in the meta and para positions of the benzene ring.
7. A composition according to any of the preceding claims in which the component (B) is an alkenyl succinic acid or anhydride. 60
8. A composition according to Claim 7 in which
 - (B) contains 10 to 16 carbon atoms excluding the carbon atoms in the carboxylic acid or anhydride groups.
9. A composition according to any of the preceding claims containing 95% to 75 wt% of component (A) and 5% to 25% of component (B). 65

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10. A concentrate comprising an oil solution of a composition according to any of the preceding claims.

11. A coating composition comprising a solution containing from 0.5 to 5 wt% of a composition according to any of claims 1 to 9.

12. Metal whenever coated with a composition according to any of claims 1 to 9.

13. The use of a composition according to any of claims 1 to 9 for the temporary protection of metals against corrosion.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 5292

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB-A-2 131 444 (DAI-ICHI KOGYO SEIYAKU) * Claims 1-3; page 2, lines 6-20,39-54; examples *	1-13	C 23 F 11/10 C 10 M 163/00 // (C 10 M 163/00 C 10 M 129:42 C 10 M 135:10 C 10 M 159:24) C 10 N 30:12
A	GB-A-1 265 969 (NIPPON STEEL CORP.) * Claims 1-20 *	1-13	
D,A	US-A-3 714 042 (P.E. GREENOUGH) * Claims 1-8,10-11,17 *	1-13	
A	US-A-3 422 013 (R.W. SCHER) * Claim 1; column 3, lines 49-75 *	1	
A	US-A-3 004 917 (J.A. FEFER)		
D,A	US-A-3 897 350 (E.I. HEIBA et al.)		
D,A	US-A-3 453 124 (R.G. WURSTNER)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 23 F C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31-08-1988	Examiner DE ANNA P.L.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			