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(54) Corrosion protection.

(57) Water-based corrosion protector for metals consisting of a solution of polyphosphate 23%, alcohol 2% and water 73%, and a solution consisting of tallow diamine ethoxylate 5%, alcohol 2% and water 93%. The corrosion protector is preferably intended for automobiles and is used after washing by spraying the first solution in mist form on the still wet automobile for about 15 seconds and then, after a time interval, spraying the second solution. The corrosion is reduced by this treatment by more than 50% as compared to the corrosion on unprotected automobile sheet metal.

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Corrosion Protection

Annual losses due to destruction by rust and other corrosion are enormous, and this destruction is rising rapidly due to the increasing content of corrosive substances such as road salt, sulphur compounds etc. in the modern environment.

Particular attention has been given to the problem of rust in automobiles, and the present invention will be described with reference to automobiles even if it can, to be sure, also be used with advantage for similar problems in other constructions of iron and steel such as bridges, ships etc.

For rust protection of automobiles, undercarriage treatments of various types have been used, usually based on petroleum products, and the so-called ML method has been used for rust protection inside beams and other cavities.

Much has been done directly at the factory to give the automobile an initial basic protection; the sheet metal has been galvanized, various plastic coatings have been tried and various types of sealants have been tested.

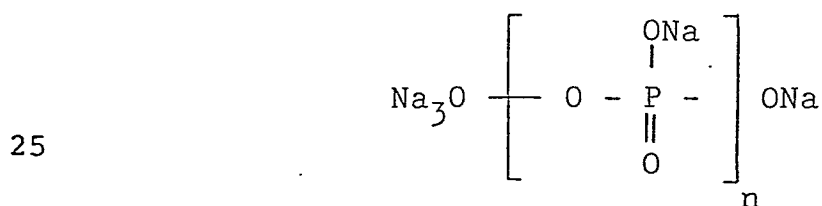
In retreating the car, it must first be carefully cleaned and washed and then carefully dried in order for the protective petroleum products to adhere correctly. Cars are usually washed prior to undercarriage treatment with steam and hot water and are then dried carefully before the rust protection is applied. According to the present invention, however, a water-based anti-rust agent is used thus eliminating the need for drying but still having the anti-rust agent diffuse into and passivate the metal surface.

It is previously known to use water-based anti-rust agents, but the results have up to now not been satisfactory and the present invention is the first to achieve practically acceptable results.

The invention will be described in more detail below with reference to examples relating to rust protection in automobiles, but similar advantages can of course also be

achieved in other iron and steel constructions.

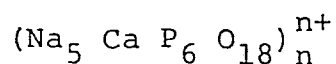
An automobile is washed in the usual manner in an automatic carwash and immediately after washing, while the automobile is still wet, it is sprayed with an aqueous solution of a first anti-rust agent and, after a period of time, with an aqueous solution of a second anti-rust agent. The solutions are sprayed on in mist form, suitably with spray pistols or in automatic carwashes with fixed nozzles which spray the anti-rust agents in mist form. The solutions are applied on the one hand from below in a moving ramp, and on the other hand from above and from the side via the movements of the carwash portals. Under the present conditions, a spraying time of about 15 seconds for each solution was found to be suitable. The first anti-rust agent consists of an aqueous solution of an anionic corrosion inhibitor, which disperses very easily and rapidly over the moist, clean metal and forms a protective film. A number of different anionic corrosion inhibitors have been used and tested, but particularly good results have been obtained with polyphosphates. Polyphosphate is a linear polymer with the general formula



in which n is 2 or more. Optimal values of n for corrosion protection lie between 3 and about 20.

Especially good results have been obtained with sodium hexametaphosphate, "Graham's salt", which contains tri- and tetrametaphosphate and high polymer polyphosphate ions.

The negative hexametaphosphate ion can also form, under special conditions, positive ions of the type



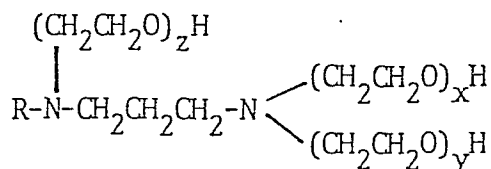
thus having a cathodic inhibiting effect.

The polyphosphate film formed increases the cathodic polarisation markedly. The second cationic rust inhibitor sprayed on thereafter is fixed with its hydrophilic portion in the polyphosphate film thus imparting water-repellant characteristics to the resulting film. The second spraying also covers "greasy" portions of the metal, remaining paint, spots etc. A number of cationic compounds were investigated and the best result was achieved with amines, especially long-chained, quaternary ammonium compounds, preferably tallow amine ethoxylate.

Highly hydrophobic amines have proved to produce the best results. Shorter fatty acid chains increase the water solubility and the effect is poorer. Water solubility also increases with the ethylene oxide content. Diamines have proved to be more effective than monoamines.

The best results have been obtained with Ethoduomine T 13; a reaction product between N-alkyl-trimethylene diamines and ethylene oxide.

The molecular structure for this compound is



in which R is derived from a fatty acid and $x+y+z$ varies between 3 and 10 or higher. The presence of two amino groups in the molecule increases the cationic properties.

Non-ionic surfactants have also been tested, since they have certain advantages in handling, e.g. less tendency to foam, but the results have not been as favourable.

By virtue of the fact that the anti-rust agent according to the invention is water-based and has a very low surface tension, it has a very good spreading ability and penetrates easily into all places where it is at all possible for moisture to reach such as joints, cracks in the undercarriage surface, beneath layers of dirt, etc.

The simplicity of the treatment makes it possible to repeat it often, thus protecting the areas most subjected to mechanical stresses, stones hitting the automobile and wheel spray.

- 5 The composition of the solutions can be varied within very wide limits, and below will be given only an example of two solutions and the test results with them.

Testing of the corrosion properties

The composition of the solutions:

10	<u>Corrosion protection 1</u>	<u>Corrosion protection 2</u>
	Polyphosphate 23%	Tallow diamine ethoxylate 5%
	Alcohol 2%	Alcohol 2%
	Water 73%	Water 93%

The execution of the test:

- 15 Corrosion test. The test was carried out with weighed test panels, protectively painted on the reverse side, of cold-rolled steel with dimensions and surface treatment according to the following.

- (a) dim. 150 x 100 x 1 mm, clean, degreased surfaces
- 20 (b) dim. 150 x 100 x 1 mm, rusty surfaces (precorroded test panels according to SS 18 60 19)
- (c) dim. 150 x 60 x 0.8 mm, phosphating, electro-dipping, varnishing and anti-rust treatment (factory treatment)
- (d) dim. 150 x 70 x 1 mm, degreased surface coated with cavity liquid and undercarriage liquid (currently marketed treatment)
- 25

The test panels under (c) and (d) were provided with a cross-scratch down to the sublayer.

Exposure

- 30 The test panels were exposed lying on a rack in a chamber with the bottom surface covered with water. In the chamber, which was provided with a misting nozzle, a water mist was sprayed for 10 minutes per day without spraying the test surface directly, but allowing water mist to fall
- 35 down freely on all test surfaces. The test temperature was $23 \pm 2^{\circ}\text{C}$, and the relative humidity was 85-90% except during the spray periods when it was 100%. The total exposure time was 28 days.

The testing procedure

- 5 A. Two test panels each from groups (a), (b) and (d), and one test panel from group (c) were moistened with tap water, were sprayed with inhibitor solution 2 and thereafter with inhibitor solution 1 in a total amount of about 35 g/m². The test panels were then coated with a 2-3 mm thick layer of synthetic road dirt. The synthetic road dirt was prepared as follows: Washed quartz sand 112 g of No. 65, 26 g of No. 30 and 50 g of No. 18 as well as 12 g of kaolin powder was added to 20 ml of a 15% aqueous solution of sodium chloride and was mixed thoroughly. After an exposure time of one week the test panels were cleaned by high-pressure spraying with water and new inhibitor solutions were applied as well as well as new road dirt. The process was repeated at one week intervals throughout the entire exposure period. A pair of plates from each of the groups (a), (b) and (d) were treated in the same manner but at two week intervals and a pair of plates from each group were treated only once prior to the beginning of the exposure.
- 20 B. Test panels from group A were first coated with road dirt, were moistened with tap water and sprayed with the inhibitor solutions. Without removing the road dirt, the test panels were then sprayed with the inhibitor solutions according to the same schedule as under A.
- 25 C. The testing was carried out as according to A without coating the test panels with road dirt.
- D. The panels from groups (a), (b), (c) and (d), with and without road dirt, were used as control panels. They were exposed without treatment during the entire exposure.
- 30 E. Two test panels from groups (c) and (d) were moistened and treated with the inhibitor solutions. After exposure for one day, the test panels were rinsed off with tap water and returned to the test chamber. After six days of further exposure, one test panel, E 1 of each type, was removed and treated again according to the above. This was repeated once per week during the entire test period. The two other test panels, E 2, were exposed without further treatment.
- 35

After completed exposure, the road dirt was removed and the test surfaces were examined with regard to the extent of rust, any defects in the anti-rust treatment, and under-film corrosion at the scratches.

5 The protective coating was then removed from the reverse side of the test panels from groups (a) and (b), and the metal loss was calculated by derusting in Clarke's solution and subsequent weighing.

10 The effect on metals was determined according to SS 18 60 13. Two plates each of aluminium, copper, cold-rolled steel and galvanized steel with known weight were immersed in a mixture of equal parts of corrosion protectors 1 and 2 for 7 days at 50°C.

15 Two other plates of each type with known weight were first sprayed with corrosion protector 2 and then with corrosion protector 1. After drying at room temperature for 1 day, the plates were stored for 7 days in air at 50°C. After completion of the testing, all of the plates were cleaned and examined with regard to pitting. The plates were
20 then weighed and the weight reduction in g/m^2 was calculated.

 Penetration into cracks was determined according to SS 18 60 17. Eight blasted plates were screwed together two by two somewhat staggered in relation to each other. The blasted surfaces faced each other and had point contact
25 over the common surface. The plates were placed vertically and were sprayed perpendicular to the downwardly facing blasted side. After 7 days at $23 \pm 2^\circ\text{C}$ the plates were separated and the penetration was determined.

30 Spraying with the inhibitor solutions and water proceeded as according to the following:

 A pair of plates was sprayed once with corrosion protector 2 and corrosion protector 1.

 A pair of plates was first sprayed with water; then with corrosion protector 2 and corrosion protector 1.

35 A pair of plates was sprayed with corrosion protector 2 and corrosion protector 1, the treatment being repeated after 2 and 5 days.

- 7 -

A pair of plates was first sprayed with water and then with corrosion protector 2 and corrosion protector 1, the treatment being repeated after 2 and 5 days.

The rust protection on a moist surface was determined according to SS 18 60 18. 0.1 ml of corrosion protector 2 and of corrosion protector 1 was dropped on a blasted plate surface which was moistened with 3% sodium chloride solution. After storage at $23 \pm 2^{\circ}\text{C}$ and $50 \pm 5\%$ relative humidity for 48 hours, the test plates were examined with regard to corrosion of the surfaces coated with inhibitor solutions. The spread of the inhibitor solutions on the plate surface was measured and the mean diameter was calculated.

Test results

Corrosion testing, weight loss after exposure for 28 days.

Test panels from group (a), clean, degreased surfaces.

Test procedure	Test panel	Treatment with inhibitor solution number of times			
		1	2	3	0 (Control panels)
A Treatment with inhibitor	1	141.9	123.9	146.2	216.2
- coating with road dirt	2	114.2	136.1	154.0	239.4
Average value		128.1	130.0	150.1	227.8
B Coating with road dirt - treatment with inhibitor	1	89.0	115.4	141.5	
	2	98.0	59.8	134.5	
Average value		93.5	87.6	138.0	
C Only treatment with inhibitor	1	42.1	7.1	6.0	91.3
	2	6.9	4.7	2.9	230.4
Average value		24.5	5.9	4.5	160.9
Test panels from (b), precorroded surfaces					
A Treatment with inhibitor	1	36.5	32.6	13.2	50.6
- coating with road dirt	2	29.3	13.9	12.7	56.4
Average value		32.9	23.3	13.0	53.5
B Coating with road dirt - treatment with inhibitor	1	23.4	2.0	44.0	
	2	19.1	8.2	1.4	
Average value		21.3	5.1	22.7	
C Only treatment with inhibitor	1	2.7	8.3	10.3	54.5
	2	0	0.2	0	53.2
Average value		1.4	4.3	5.2	53.9

The effect on metals

Total immersion test in equal parts of corrosion protectors 1 and 2 at 50°C for 7 days.

5	Metal	Al	Cu	Fe	Zn
	Weight loss g/m ²	11.6	3.7	25.2 ¹⁾	81.1 ²⁾

Sprayed and air-dried test plates after storage at 50°C for 7 days.

10	Weight loss g/m ²	0.05	0.5	0.7	0.7
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1) Pits in phase boundary between precipitate and liquid lying on top.

2) Zinc completely dissolved in the precipitate phase.

15 Penetration in cracks

Maximum penetration 3-5 mm upon spraying 1 or 3 times.

Anti-rust protection on moist surface

No rusting.

20 Extent, diameter 35 mm.

The test performed has demonstrated that the inhibitor system, under the conditions prevailing in the test chamber, on an average was able to bring down the rate of corrosion of unprotected pure steel coated with synthetic road dirt by about 45%, for unprotected pure steel without coating with road dirt by about 90%, for rusty steel coated with road dirt by 40-75% and for rusty steel without coating with road dirt by about 90%.

As regards the protected panels in groups (c) and (d), the testing time was too short to reveal any reliable differences between test and control panels.

As can be seen from the results, the inventive corrosion protector is also very effective on other metals than iron, as the results with aluminium, copper and zinc demonstrate. It is mentioned above that the spreading capacity of the inventive water-based corrosion protector makes it possible to protect all places where moisture can

penetrate. The entire rust film also provides improved adhesion for the underseal which can be applied e.g. in the wheel housing to protect against stones.

5 Thus the anti-rust agents according to the invention provide a synergetic anti-rust effect from the two inhibitors when applied in the manner described above. The effect is however totally eliminated if the anti-rust agents are mixed prior to spraying, or if the spraying is done in another order.

10 This method makes it possible to rust-protect an automobile simply and inexpensively without the customer having to relinquish his automobile. The treatment can be easily done as a standard step in washing.

Corrosion testing, rust spreading, on surfaces according to SIS 18 51 11 (Rsg) where 10 = no rust and 1 = the entire surface rusty, in scratches in % of the total length of the scratch and maximum spreading in either direction in mm.

Test procedure	Test panel	Treatment with inhibitor solution, number of times:				(Control panels)				
		Rsg	%	mm	Rsg	%	mm	Rsg	%	mm
Test panels group (c), factory treated										
A Inhibitor - road dirt	1	-	-	-	-	10	80	0	100	0
B Road dirt - inhibitor	1	-	-	-	-	10	60	0	90	0
C Only pretreatment with inhibitor	1	-	-	-	-	10	5	0	-	-
	2	-	-	-	-	10	10	0	-	-
E Without road dirt, rinsing with water one day after treatment with inhibitor	1	-	-	-	-	10	90	0	-	-
	2	10	95	1	-	-	-	-	-	-

Corrosion testing, rust spreading, on surfaces according to SIS 18 51 11 (Rsg) where 10 = no rust and 1 = the entire surface rusty, in scratches in % of the total length of the scratch and maximum spreading in either direction in mm.

Test procedure	Test panel	Treatment with inhibitor solution, number of times:								(Control 0 panels)			
		2				4							
		Rsg	%	mm	Rsg	%	mm	Rsg	%		mm		
Test panels group (d), "currently marketed treatment"													
A Inhibitor - road dirt	1	8	70	0	8	50	0	8	90	3	8	90	1
	2	8	50	2	8	5	0	7.5	0	0	8.5	80	1
B Road dirt - inhibitor	1	7	90	0	9	100	3	9	60	1			
	2	7	100	6	9	10	4	9	100	2			
C Only treatment with inhibitor	1	8	10	4	9	10	2	10	0	0	10	0	0
	2	9	0	0	8	80	5	10	0	0	10	10	0
E Without road dirt, rinsing with water one day after treatment with inhibitor	1	-	-	-	-	-	-	10	0	0			
	2	10	10	0	-	-	-	-	-	-			

CLAIMS

1. Method of protecting metals against corrosion, characterized in that there is applied to the metal surface, with an intervening period of time, a solution of an an-
5 ionic corrosion inhibitor and a solution of a cationic corrosion inhibitor.
2. Method according to claim 1, characterized in that the anionic corrosion inhibitor solution is sprayed on first
10 and then, after a period of time, the cationic corrosion inhibitor solution.
3. Method according to claim 1, characterized in that the inhibitors are present in aqueous solutions.
4. Method according to claims 1-2, characterized in
15 that the solutions are sprayed in mist form on water-washed, still wet surfaces one after the other.
5. Method according to claim 1, characterized in that the corrosion protection is used for automobiles in conjunction with washing.
- 20 6. Corrosion protection for spraying on metals, characterized in that a first solution consists of polyphosphate 23%, alcohol 2% and water 73%, and that a second solution for subsequent spraying consists of tallow diamine ethoxylate 5%, alcohol 2% and water 93%.



European Patent
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EUROPEAN SEARCH REPORT

0043360

Application number

EP 81 85 0119

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	GB - A - 1 133 385 (FUJI IRON & STEEL) * claim 1; example 10; page 5 * --	1,3	C 23 F 11/08
	FR - A - 1 532 639 (R. TOURNIER) * abstract points 2 ^o , 5 ^o * --	1	
	DE - A - 1 521 869 (METALLGESELLSCHAFT) * claim 1; page 4, lines 16-20 * --	1,3	TECHNICAL FIELDS SEARCHED (Int. Cl.3)
	BE - A - 535 818 (J.H. SCHULMAN) * claims 1,5,6; example II; page 2 * --	1,2,3	C 23 F 11/00 11/08 11/10 7/10
	A US - A - 3 412 025 (A.G. OSTROFF) -----		CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	2-10-1981	TORFS	