



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification³ : C09D 5/08, 3/74</p>	<p>A1</p>	<p>(11) International Publication Number: WO 84/ 00973 (43) International Publication Date: 15 March 1984 (15.03.84)</p>
<p>(21) International Application Number: PCT/GB83/00211 (22) International Filing Date: 26 August 1983 (26.08.83) (31) Priority Application Number: 8224789 (32) Priority Date: 31 August 1982 (31.08.82) (33) Priority Country: GB (71) Applicant (for all designated States except US): DOUBLE H INTERNATIONAL LIMITED [GB/GB]; 27B Central Trading Estate, Staines, Middlesex TW18 4XQ (GB). (72) Inventor; and (75) Inventor/Applicant (for US only) : ROBERTS, Daniel, Clarkson [GB/GB]; Pemberley, Lamborough Hill, Wooton, Abingdon, Oxfordshire (GB). (74) Agent: R.F. HASLAM; Lower Wainhill Farmhouse, Chinnor, Oxford OX9 4AB (GB).</p>		<p>(81) Designated States: AT, AT (European patent), AU, BE (European patent), CH, CH (European patent), DE, DE (European patent), DK, FI, FR (European patent), GB, GB (European patent), JP, LU, LU (European patent), NL, NL (European patent), NO, SE, SE (European patent), US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: COMPOSITIONS FOR RUST TREATMENT (57) Abstract A composition for rust treatment comprises an aqueous film-forming emulsion and an effective amount of pyrogallol as a chelating agent for iron oxides.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	LI	Liechtenstein
AU	Australia	LK	Sri Lanka
BE	Belgium	LU	Luxembourg
BR	Brazil	MC	Monaco
CF	Central African Republic	MG	Madagascar
CG	Congo	MR	Mauritania
CH	Switzerland	MW	Malawi
CM	Cameroon	NL	Netherlands
DE	Germany, Federal Republic of	NO	Norway
DK	Denmark	RO	Romania
FI	Finland	SE	Sweden
FR	France	SN	Senegal
GA	Gabon	SU	Soviet Union
GB	United Kingdom	TD	Chad
HU	Hungary	TG	Togo
JP	Japan	US	United States of America
KP	Democratic People's Republic of Korea		

- 1 -

Compositions for rust treatment

The present invention relates to compositions for rust treatment for use on articles made of iron and steel, whether free from oxidation or not, of the kind comprising a dispersion or
5 emulsion of a film-forming agent such as a polymer emulsion together with a chelating agent for chelating iron oxides.

Compositions of this kind have already been proposed, for example in German Offenlegungsschrift
10 No. 25 55 597, Swiss Patent Specification 580 152 and British Patent Specification No. 1 494 212. In these prior disclosures gallic acid and tannin, among others, are disclosed as suitable chelating agents for chelating iron oxides.

15 Pyrogallol (1, 2, 3-trihydroxybenzene) has also been proposed as a chelating agent for chelating iron oxides in such compositions.

It is the aim of this invention to provide a water-based corrosion-inhibiting paint or varnish



- 2 -

which, when applied to steel (whether rusted or not), will give a coating capable of substantially preventing further oxidation or corrosion and durable under severe conditions of damp and frost and durable against oil,
5 acid or alkaline or other corrosive environments.

To be effective in practice a corrosion-inhibiting paint or varnish should be compatible with surface coatings in general use. The adhesion and fastness of the varnish film when properly applied should not
10 be less than those of surface coatings in general use and superior in providing a primed surface to allow good finishes to be obtained. The varnish must be of low toxicity and not in itself strongly acid or caustic, not inflammable and must not give off
15 inflammable, explosive or toxic vapours. It must be applicable by painting, spraying or dipping and should cure and dry at ambient temperatures and humidities in a relatively short time.

It has been found that particularly useful film-
20 forming emulsions (or latices) for the purposes of the present invention are those described in the paper by A. J. Burgess, D. Caldwell and J.C. Padget in the Journal of the Oil and Colour Chemists' Association Volume 64, May 1981 pages 175-185, and
25 also in the British Patent Specification No. 1558 411 and European Patent Application 0 030 080 A1. These documents are incorporated herein by reference. Products of the kind there described are sold by Imperial



- 3 -

Chemical Industries Ltd as Haloflex 202 and Haloflex 208
("Haloflex" is a registered Trade Mark).

The invention described and claimed in the
aforesaid British patent is an aqueous latex comprising
5 a copolymer derived from (i) vinylidene chloride, (ii)
vinyl chloride, (iii) one or more alkyl acrylates
having 1 to 12 carbon atoms in the alkyl group and/or
one or more alkyl methacrylates having from 2 to 12
carbon atoms in the alkyl group and (iv) one or more
10 aliphatic alpha-beta-unsaturated carboxylic acids,
the proportion of vinylidene chloride being from 65
to 90 parts by weight the proportion of the said
alkyl acrylates and/or methacrylates being from 2 to
15 parts by weight and the proportion of the said
carboxylic acids being from 0.2 to 8 parts by weight,
per hundred parts by weight of the total vinylidene
chloride and vinyl chloride.

The aforesaid European patent application describes
and claims an aqueous latex comprising a copolymer of
20 (i) vinylidene chloride, (ii) vinyl chloride and (iii)
one or more alkyl acrylates or alkyl methacrylates
having from 1 to 12 carbon atoms in the alkyl group,
characterised in that:-

(a) the proportion of vinylidene chloride is from
25 20 to 95 parts by weight per hundred parts
by weight of total vinylidene chloride and
vinyl chloride,



- 4 -

- (b) the proportion of vinylidene chloride is not more than 75 parts by weight per hundred parts by weight of total vinylidene chloride, vinyl chloride and the said acrylate(s) and/or methacrylate(s) and
- (c) the proportion of the said acrylate(s) and/or methacrylate (s) is more than 15 but less than 45 parts by weight per hundred parts by weight of total vinylidene chloride and vinyl chloride.

The present invention therefore in one embodiment provides a corrosion-inhibiting paint or varnish comprising a film-forming latex as defined in the preceding paragraphs together with an effective amount, as chelating agent, of pyrogallol.

The permeability of water varnishes based on this latex was in the order of $\frac{1}{100}$ of similar latices not containing vinylidene.

The addition of Pyrogallic acid introduced remarkable corrosion resisting qualities not otherwise easily obtained, for instance by the use of quarternary compounds or phosphoric acid.

Butyl Glycol ethers and ester alcohols were used to produce lower setting temperature effects and greater salt resistance.

Considerable difficulty was experienced with other chelating agents such as Tannic acid in that the



- 5 -

latex became unstable without other additives which reduced efficiency.

One embodiment of the invention comprises the following composition:

5	Haloflex 202	80 - 98%
	Pyrogallol	2 - 5%
	Water	0 - 10%

The preferred composition is that in which the pyrogallol is present at 3.0% and the pH is less than 10 6, preferably less than 4 the optimum being 1.8 - 2.5.

This product was subject to the testing procedures described below.

Tests were carried out on mild steel plates 6 inches x 4 inches and on motor car body panels.

- 15 1. The compositions tested were in two main groups.
(a) an acrylic/methacrylic copolymer emulsion containing 3% pyrogallol and (b) a vinylidene chloride/vinyl/copolymer emulsion containing 3% pyrogallol (the preferred composition described above).
- 20 2. The plates used were from the same stock of bright mild steel, some of which had been exposed to 2% salt spray and extensive exposure out of doors to promote heavy rusting and pitting.
- 25 3. All plates were wire brushed and rubbed with coarse sandpaper prior to applying the protective coatings.



- 6 -

Both sides of the plates were treated.

4. The rusted motor car body panel was brushed and sandpapered then washed with clean water.

5 A one inch wide bristle paint brush was used to apply the protective emulsion except when an air sprayer was used for the car panel and some of the topcoats.

The first coat of the protective emulsion was allowed to dry thoroughly before any subsequent
10 coats were applied.

A dark blue-black colour developed on the treated plates indicating the complexing of the iron surface.

Comparisons were made after treating the painted plates to 100 hours in a salt spray cabinet using a
15 2% sodium chloride solution at 20 - 30°C.

Those plates treated with the acrylic polymer preparation:-

1 coat showed rusting in 24 hours

2 coats " " " 36 hours

20 Those plates treated with the vinylidene/chloride/vinyl chloride copolymer

1 coat showed slight rusting in 90 hours

2 coats showed No rusting in more than 100 hours

25 Those plates which were pre-rusted did not show significant differences from the bright metal plates.

Where the second coat was allowed 24 hours to



- 7 -

dry and then smoothed with wet sandpaper the surface was rust free for more than 100 hours in the salt spray.

The second part of these tests involved the assessment of compatibility of (b) with various types of paint and was applied to both bright steel and rusted steel plates.

In general all varieties of paints tried showed good adhesion.

10 More specifically:

Aerosol paints both cellulose and synthetic varnish gave excellent results.

Automotive finishes in cellulose and 2 part acrylic, applied by brush and by spraying were completely satisfactory.

20 A rusted car panel was sprayed with 2 coats of the vinylidene copolymer preparation, the black surface was allowed 24 hours to harden before spraying with an epoxy type filler, this was built up to cover the rust pitting and rubbed down before applying a cellulose decorative paint - after 48 hours drying the section was immersed in a water tank for 7 days when no blistering or loosening of the filler was observed.

25 In further tests, treated plates with 2 coats of the vinylidene preparation were subjected to 2 hours stoving at 80°C and then painted with an acrylic resin paint and stoved for a further 2 hours. The



- 8 -

resulting finish was found to be as durable as the paint makers' claims, in resisting damp, attrition and bending. There being no apparent difference between the bright metal and the rusted plates.

5 The composition of the present invention, when applied to articles already rusted, showed superior adhesion to Haloflex alone.

Another embodiment of the invention is as follows :

10	Haloflex 202	preferred 82.6%	variation 75 - 85%
	Water	3.6%	0 - 4%
	Pyrogalllic acid	1.8%	5 - 3%
	Butyl Ethoxol	4.0%	0 - 5%
	Isopropanol	8.0%	5 - 12%
15		<hr/> 100.0	

Haloflex 208 may be used in place of Haloflex 202.

TEST RESULTS

1. Plates of grit blasted steel painted with two coats of the preferred formula.
 - 20 a) were tested in a salt spray cabinet at 25°C after 1000 hrs a few very small blisters occurring near cut edges were observed.
 - b) Similar plates coated with cellulose, acrylic and alkyd paints showed serious rusting.
- 25 Plates coated with two coats of the inhibiting paint



- 9 -

before painting with these finishing enamels showed no significant corrosion after 1000 hrs saltspray.

c) Water permeability of the latex used has been assessed and found to be in the order of 1% of that of most other emulsion latices, and comparable to or better than chlorinated rubber paints.

d) Grit blasted plates coated with 2 coats of the preferred formula were immersed in water for three months without showing signs of deterioration or rust creeping in from cut edges.

The latex used has a very low toxicity and does not cause eye damage or respiratory hazard.

The finished dried film is flame retardant.

There may be added to the compositions of the present invention other substances well known as additives to paints and varnishes such as fillers, extenders, wetting agents, surfactants and the like.

Compositions according to the invention can be painted over damp or wet rusted metal. The water is absorbed from the iron or steel surface but is prevented from returning as the composition dries.



CLAIMS

1. A composition for rust treatment comprising an aqueous film-forming emulsion and an effective amount of pyrogallol as a chelating agent for iron oxides.
- 5 2. A composition as claimed in Claim 1 wherein the aqueous film-forming emulsion is an aqueous latex comprising copolymers of vinylidene chloride.
3. A composition as claimed in Claim 2 wherein the emulsion is a copolymer of vinylidene chloride, vinyl
10 chloride and one or more alkyl acrylates or methacrylates.
4. A composition as claimed in any of claims 1 to 3 wherein the proportion of pyrogallol lies between 0.5 to 5%.
5. A composition as claimed in any of the preceding
15 claims and containing 0 to 5% butyl ethoxol.
6. A composition as claimed in any of the preceding claims and containing from 5 to 12% isopropanol.
7. A composition substantially as herein described.
8. A composition substantially as herein described in
20 Example 1.
9. A composition substantially as herein described with reference to Example 2.
10. A method of applying a protective coating to a substrate characterised in that there is employed an
25 aqueous latex claimed in any of claims 1 to 8.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 83/00211

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ³ : C 09 D 5/08; C 09 D 3/74		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC ³	C 09 D 5/08; C 09 D 3/74	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	GB, A, 2075538 (APPLIED COATINGS TECHN.) 18 November 1981 see claims 1,7; page 4, lines 55-60; page 5, lines 54-55; page 6, lines 11-41	1-10
	--	
X,Y	DE, A, 2555597 (NOVEROX) 8 June 1977 see claims 1,9,10; page 7, para- graph 2; examples 5 and 6 (cited in the application)	1-10
	--	
Y	EP, A, 0035316 (IMPERIAL CHEM. IND.) 9 September 1981 see claim 1	1

<p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ¹	
24th November 1983	02 JAN. 1984	
International Searching Authority ¹	Signature of Authorized Officer ¹⁹	
EUROPEAN PATENT OFFICE	G.L.M. Kruidenberg	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 83/00211 (SA 5677)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 20/12/83

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2075538	18/11/81	FR-A- 2481710	06/11/81
		JP-A- 57018766	30/01/82
		DE-A- 3116736	21/01/82
		AU-A- 6995081	05/11/81
DE-A- 2555597	08/06/77	NL-A- 7612839	01/06/77
		US-A- 4086182	25/04/78
		AU-A- 1962376	25/05/78
		JP-A- 52065731	31/05/77
		SE-A- 7613039	28/05/77
EP-A- 0035316	09/09/81	JP-A- 56122874	26/09/81
		AU-A- 6631781	06/08/81

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82