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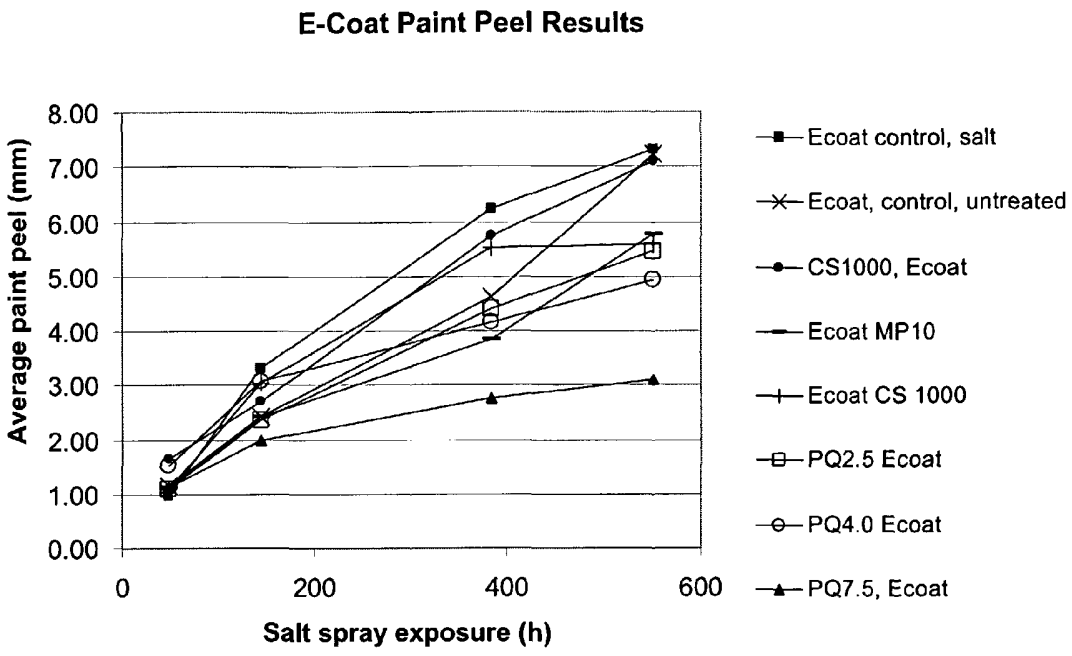
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(54) Title: QUATERNARY AMMONIUM SALTS AS A CONVERSION COATING OR AS ANTICORROSIVE ADDITIVE IN PAINTS



(57) Abstract: Disclosed are quaternary ammonium salts containing non-halogen anions such as carbonates, bicarbonates, phosphates, glycolates and mixtures thereof as conversion coatings or additives imparting anti-corrosive properties to paints. The invention relates to a method for inhibiting the corrosion of metal surfaces by applying a composition containing one or more quaternary ammonium carbonate or bicarbonate. The disclosure is also directed to anti-corrosive coatings for metal substrates containing these compounds and to metal substrates having these anticorrosive coatings.

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QUATERNARY AMMONIUM SALTS AS A CONVERSION COATING OR AS ANTICORROSIVE ADDITIVE IN PAINTS

FIELD OF THE INVENTION

The present invention relates to the use of quaternary ammonium salts containing non-halogen anions such as carbonate, bicarbonate, phosphate and glycolate as active ingredients of conversion coatings and as additives for paints and coatings.

BACKGROUND OF THE INVENTION

In processes where metal surfaces come in contact with water, whether as liquid water or humid air, there is always the danger of corrosion. This is particularly problematic when the metal itself is prone to corrosion and is not coated.

Examples of metals prone to corrosion are found in stamped metal car parts made from ferrous alloys, abraded surfaces such as machined steel parts, and machine components made from cast iron.

Conversion coatings are used to inhibit corrosion and to assure good adhesion of paint to a metal surface, in particular to steel. Bare steel does not form a good bond with organic coatings. To improve the metal/organic coating bond, chromate or phosphate conversion coatings are chemically reacted with the steel to form a rough surface structure with metal-phosphate platelets that provide both mechanical and chemical keying (adhesion) of the organic polymer to the metal surface. See, for example, Watson, J. *"A refresher: Understanding pretreatment"*, *Powder Coating* **1996**, *7*(3) and Ferguson, D.; Monzyk, B., "Nonpolluting replacement for chromate conversion coating and zinc phosphate in powder coating applications", *Powder Coating* **2001**, *12*(7). Here and hereinbelow, a conversion coating is to be understood to mean a protective barrier film or layer on the metal substrate surface simultaneously capable of both corrosion inhibition and paint adhesion and comprised of either (i) an organic film, (ii) an inorganic oxide resulting from a metal etching and redeposition process, (iii) an inorganic oxide resulting from a true deposition process, or (iv) any mixture of inorganic and organic materials from (i), (ii) and (iii). The most widely used conversion coatings are chromating, phosphochromating and zinc phosphatizing processes. It is believed that chromating gives better corrosion inhibition, while phosphochromating gives better paint adhesion. Prior to applying the conversion coating to the metal surface, the metal surface must be cleaned in order to remove any grease on the metal surface. The conversion coating can then be applied by either immersion or spraying. Chromate and phosphochromate conversion

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coatings are the most common chemical conversion coatings, but because of health, safety and environmental concerns other types of conversion coatings are needed.

SUMMARY OF THE INVENTION

It has been discovered that quaternary ammonium salts containing non-halogen anions such bicarbonate, carbonate, phosphate and glycolate, more specifically, dialkyl dimethyl ammonium salts containing bicarbonate, carbonate, phosphate or glycolate as the anion, and various combinations thereof, have applicability as a conversion coating for metal surfaces and steel in particular. Additionally it has been discovered that said quaternaries are capable of effecting a desirable surface transformation such as the growth of desirable surface oxides (i.e. magnetite, Fe_3O_4) on steel substrates. This oxide formation results in distinct crystallite domains which adhere to the metal substrate and to which coatings such as paints are expected to exhibit improved adhesion. In addition, said quaternary ammonium salts can be added directly to paints to provide better adhesion of the paint to the metal surface and thereby improving corrosion resistance.

The corrosion inhibition properties of quaternary ammonium carbonates and bicarbonates have been disclosed in copending U.S. Patent Application Serial No. 10/810279 (US 2005/0003978 A1). Additionally it has now been discovered that under the inhibitor film, a protected steel surface grows desirable surface oxides (i.e., magnetite, Fe_3O_4). This oxide formation creates domains to which organic coatings such as paints are expected to exhibit improved adhesion.

DETAILED DESCRIPTION OF THE INVENTION

Surprisingly, it has been found that certain quaternary ammonium salts containing non-halogen anions, such as di-*n*-decyldimethylammonium carbonate, when applied to the surface of iron and iron alloys such as steel, have a propensity to effect a known, desirable transformation on the surface of iron and iron alloys such as steel under much milder conditions of temperature than previously known. While thermally induced transformations of steel surfaces at >110 °C are known in the art, the high temperatures required to effect those transformations have heretofore limited their commercial exploitation. However the above mentioned quaternary ammonium salts appear capable of effecting a similar transformation of steel surfaces at temperatures as low as room temperature.

Additionally, the unique nature of the above quaternary ammonium salts (either neat or in formulation) allows for a one step metal surface preparation process prior to final coating

applications. It has been found that metal exposure to their solutions will simultaneously clean, corrosion inhibit, and primer coat metal surfaces in preparation for final coating applications. This represents a significant improvement over current processes which perform the following independent functions in a stepwise fashion and with significantly greater amounts of industrial effluents which must be disposed of:

a) the raw metal is passivated with oil to prevent flash rust.

b) the passivation oil is removed and disposed of

c) the metal surface is treated with conversion coating solutions (acidic, heavy metal containing chemicals) and cured before the final coating is applied.

It has also been found that steel surfaces treated according to the present invention are resistant to flash rusting. Flash rusting occurs when a newly formed bare steel surface is exposed to water and reacts to form a red iron hydroxide rust layer.

Coiled sheet steel treated with according to the present invention is resistant to the edge staining that occurs when moisture condenses on the edges of the coils. Presently steel sheet is sprayed with a light oil prior to storage or transportation. This oil must be removed prior to additional surface treatments or coatings.

The oxide film formed in according to the present invention has the potential of being an under-paint conversion coating or primer for steel. Bare steel does not form a good bond with organic coatings. To improve the metal/organic coating bond, chromate or phosphate conversion coatings are chemically reacted with the steel to form a rough surface structure with metal-phosphate platelets that provide both mechanical and chemical keying (adhesion) of the organic polymer to the metal surface.

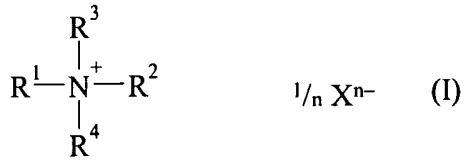
It has also been found that the conversion coatings and anticorrosive paints of the present invention exhibit certain self-healing properties on scratching, which means that even the "bare" metal surface in a scratch shows some passivation that may be due to migration of the quaternary ammonium salt from the surrounding coating. In some cases, a permanent oxide transformation is also observed resulting in long term passivation of a scratched area. This is an effect that is similar to the self-healing observed on chromium coated metal surfaces.

In particular, the present invention relates to a method for applying a conversion coating to the surface of a metal substrate, said method comprising the step of contacting the substrate with a composition comprising

(a) at least one quaternary ammonium salt containing a non-halogen anion and

(b) optionally, a solvent.

Preferably, the quaternary ammonium salt has the formula



$$R^1-\overset{R^3}{\underset{R^4}{N^+}}-R^2 \qquad {}^1/_n X^{n-} \qquad (I)$$

wherein R^1 is an optionally aryl-substituted C_{1-20} alkyl group, and R^2 is an optionally aryl-substituted C_{1-20} alkyl group, R^3 and R^4 independently of each other are C_{1-4} alkyl groups, X^{n-} is an anion selected from the group consisting of hydroxide, carbonate, bicarbonate, phosphates, phosphites, hypophosphite, nitrate, sulfates, borates, anions of saturated and unsaturated acyclic C_{1-20} monocarboxylic acids, anions of saturated and unsaturated C_{2-20} dicarboxylic acids, and anions of hydroxy-substituted carboxylic acids, and n denotes the appropriate number of negative charges of said anion.

Here and hereinbelow, C_{1-20} alkyl groups are linear or branched alkyl groups having 1 to 20 carbon atoms, including, but not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl, *tert*-butyl, pentyl, isopentyl, hexyl, heptyl, octyl, nonyl, isononyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and icosyl. Aryl-substituted C_{1-20} alkyl groups are any of the above groups bearing an aryl group, in particular phenyl, as a substituent. Preferred examples of aryl-substituted C_{1-20} alkyl groups are benzyl, phenylethyl and phenylpropyl.

The term "phosphates" is to be understood as including both acid and neutral salts of phosphoric acid, namely, dihydrogenphosphates ($H_2PO_4^-$), monohydrogenphosphates (HPO_4^{2-}) and phosphates (PO_4^{3-}), as well as salts of oligo- and polyphosphoric acids such as diphosphates (pyrophosphates) and triphosphates.

Phosphites are salts of phosphorous acids containing the anions $H_2PO_3^-$ and/or HPO_3^{2-}.

Sulfates are hydrogensulfate (HSO_4^-) and sulfate (SO_4^{2-}) as well as disulfate ($S_2O_7^{2-}$) and related anions.

Borates are any anions derived from boric acid (H_3BO_3) and the various polyboric acids.

Saturated and unsaturated acyclic C_{1-20} monocarboxylic acids are in particular alkanoic acids, such as formic, acetic, propionic, butyric, pentanoic, hecanoic, octanoic, decanoic, dodecanoic, tetradecanoic, hexadecanoic, octadecanoic and icosanoic acids, or alkenoic acids, such as acrylic, methacrylic, oleic and linolic acid.

Saturated and unsaturated acyclic C_{2-20} dicarboxylic acids are in particular alkanedioic acids, such as oxalic, malonic, succinic, glutaric and adipic acid, or alkenedioic acids such as fumaric or maleic acid.

Hydroxy-substituted carboxylic acids are any carboxylic acids bearing at least one hydroxy group in addition to the carboxylate group(s), such as glycolic, malic, citric or salicylic acid.

More preferred quaternary ammonium salts exhibiting the effect described above are quaternary ammonium carbonates, quaternary ammonium bicarbonates, quaternary ammonium phosphates and quaternary ammonium glycolates.

Still more preferably, R^3 and R^4 in the quaternary ammonium salt of formula I are methyl groups.

In a preferred embodiment, R^1 is methyl.

In a more preferred embodiment, R^2 is benzyl or phenylethyl.

In another preferred embodiment, R^1 and R^2 are the same C_{1-20} alkyl groups.

In a more preferred embodiment, R^1 and R^2 are C_{10} alkyl groups.

In an even more preferred embodiment, R^1 and R^2 are *n*-C_{10} alkyl groups.

In a particularly preferred embodiment, the quaternary ammonium salt is di-*n*-decyldimethylammonium carbonate and/or di-*n*-decyldimethylammonium bicarbonate.

Preferably, the metal substrate is steel.

More preferably, the steel is coiled sheet steel.

Another object of the invention is an article of manufacture comprising a metal substrate treated according to the above described method or any of its preferred embodiments.

Again, the preferred metal substrate is steel.

Still another object of the invention is an anticorrosive paint comprising

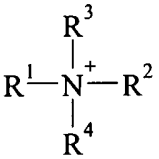
(a) at least one quaternary ammonium salt containing a non-halogen anion,

(b) a binder,

(c) optionally, a solvent and

(d) optionally, a pigment.

As in the method described above, the quaternary ammonium salt in the anticorrosive paint preferably has the formula



$$\ {}^{1}/_{n}\, X^{n-} \qquad \text{(I)}$$

wherein R^1 is an optionally aryl-substituted C_{1-20} alkyl group, and R^2 is an optionally aryl-substituted C_{1-20} alkyl group, R^3 and R^4 independently of each other are C_{1-4} alkyl groups, X^{n-} is an anion selected from the group consisting of hydroxide, carbonate, bicarbonate, phosphates, nitrate, sulfates, borates, anions of saturated and unsaturated acyclic C_{1-20} monocarboxylic

acids, anions of saturated and unsaturated C_{2-12} dicarboxylic acids, and anions of hydroxy-substituted carboxylic acids, and n denotes the appropriate number of negative charges of said anion.

The further preferred embodiments of the quaternary ammonium salt in the above described method apply analogously to the anticorrosive paint.

Preferably, the binder is selected from the group consisting of acrylic resins, casein (milk protein), vinyl resins, latex resins, acetate resins, epoxy resins and mixtures thereof.

In a preferred embodiment, the anticorrosive paint is a latex paint.

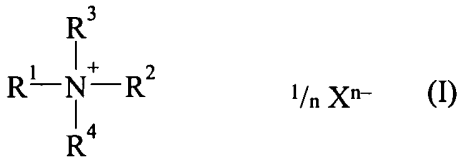
In another preferred embodiment, the anticorrosive paint is an enamel spray paint.

In a further preferred embodiment, the anticorrosive paint is an E-Coating paint.

In still another preferred embodiment, the anticorrosive paint is an acrylic paint.

Still another object of the invention is an article of manufacture comprising a metal substrate painted with the above described anticorrosive paint. All preferred embodiments regarding the nature of the anticorrosive paint, the ammonium salt being comprised in said paint, and the metal substrate apply likewise to said article of manufacture.

Still another object of the invention is the use of a quaternary ammonium salt having the formula



$$1/n\ X^{n-} \qquad (I)$$

wherein R^1 is an optionally aryl-substituted C_{1-20} alkyl group, and R^2 is an optionally aryl-substituted C_{1-20} alkyl group, R^3 and R^4 independently of each other are C_{1-4} alkyl groups, X^{n-} is an anion selected from the group consisting of hydroxide, carbonate, bicarbonate, phosphates, phosphites, hypophosphite, nitrate, sulfates, borates, anions of saturated and unsaturated acyclic C_{1-20} monocarboxylic acids, anions of saturated and unsaturated acyclic C_{2-20} dicarboxylic acids and anions of hydroxy-substituted carboxylic acids, and n denotes the appropriate number of negative charges of said anion as an anticorrosive additive in paints or coatings.

The further preferred embodiments of the quaternary ammonium salt in the above described method apply analogously to the use as an anticorrosive additive.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a SEM micrograph of a steel surface after two weeks immersion in 3.5% aqueous NaCl solution containing 0.1% di-*n*-decyldimethylammonium carbonate. Note the formation of hexagonal platelets on the surface.

Figure 2 is a SEM micrograph of a steel surface after two months immersion in 3.5% aqueous NaCl solution containing 0.1% di-*n*-decyldimethylammonium carbonate. The surface is covered with platelets and spherical particles. One of these phases is ferromagnetic (magnetite, Fe_3O_4).

Figure 3 is a SEM micrograph of a steel surface after 48 h immersion at 70 °C in a 0.1% solution of di-*n*-decyldimethylammonium glycolate in tap water.

Figure 4 is a SEM micrograph of a steel surface after 1 h immersion at 70 °C in tap water (control experiment).

Figure 5 depicts the results of paint peel back tests with several E-coated steel samples after salt spray exposure.

Figure 6 depicts the results of salt spray tests of steel samples painted with latex paint made anticorrosive by addition of quaternary ammonium salts.

Figure 7 depicts the results of salt spray tests of steel samples painted with gloss protective spray enamel with various amounts of quaternary ammonium salts.

The following examples illustrate the invention, but are not limiting thereof. All parts and percentages are given by weight unless otherwise stated.

Example 1

A Conversion Coating Study (Reference: NB5751-001 through 018) was done with the objective to prepare steel panels (S-46, purchased from Q-Panel Lab Products, Cleveland, Ohio) with various aqueous treatments of either CarboShield® 1000 (di-*n*-decyldimethyl-ammonium bicarbonate/carbonate), "Phosphoquat" (di-*n*-decyldimethylammonium phosphates), and various related controls.

A plastic tank being 27.9 cm (11″) in diameter and 27.9 cm (11″) in height was used to treat the panels. The plastic tank was filled with 9,600 grams of test solution. 10.16 cm×15.24 cm×1.59 mm (4″×6″×$^1/_{16}$″) steel (S-46) panels with a hole of 6.35 mm (¼″) in diameter located 6.35 mm (¼″) from the top edge were treated by placing a plastic pipette through the hole in the panel. Up to three panels were skewed using the same pipette. This allowed for the panels to stand upright, with only the bottom of the panel touching the bottom of the tank. The tank was then placed in an oven which was at 70 °C for one hour. After one hour, the panels were removed from the tank, dried with a paper towel and then wrapped in a plastic wrap and labeled. The test solutions prepared can be found in the list below. All

concentrations are given in percents by weight. The concentrations stated for CarboShield® and Phosphoquat are the true concentrations of the active compound(s):

Test Solutions

Deionized Water

Tap Water (Allendale, NJ)

5% Salt (NaCl) Water

0.1% CarboShield® 1000*) in Deionized Water

0.1% CarboShield® 1000 in Tap Water (Allendale, N.J.)

0.1% CarboShield® 1000 in 5% Salt (NaCl) Water

0.1% Phosphoquat**) (pH = 2.5) in Deionized Water

0.1% Phosphoquat (pH = 4.0) in Deionized Water

0.1% Phosphoquat (pH = 7.5) in Deionized Water

0.1% Glycoquat***) (pH = 7.5) in Deionized Water

*) CarboShield® 1000 is a 50% aqueous solution of di-*n*-decyldimethylammonium (bi)carbonate (90 mol% bicarbonate, 10 mol% carbonate).

**) Phosphoquat is a solution of di-*n*-decyldimethylammonium (hydrogen)phosphate(s) prepared by adding the amount of 85% aqueous phosphoric acid required to obtain the specified pH to CarboShield® 1000.

***) Glycoquat is a solution of di-*n*-decyldimethylammonium glycolate(s) prepared by adding the amount of glycolic acid required to obtain the specified pH to CarboShield® 1000.

After the steel panels were treated with the test solutions, they were painted using three different painting processes. Two panels were painted for each painting process. In one of the painting processes, the steel panels were spray painted using Rust-Oleum®'s Professional High Performance Enamel (Hunter Green) spray paint. Four steel panels were laid flat end to end and spray painted with approximately 18 g of paint applied to the top surface of the steel panels and allowed to dry overnight. The bottom of the panels were treated in a similar manner the next day. A second set of panels were painted using Rust-Oleum®'s Painters Touch® (Hunter Green) latex paint. The paint was applied with a foam roller to the steel panels. A total of two coats of paint were applied to each side of the steel panels. A third set of panels were painted using a commercial painting process known as E-Coating (a polymer based coating). These samples were painted at Royal E-Coat (Costa Mesa, California), using a proprietary process. A fourth set of steel panels (untreated) were also painted using Rust-Oleum®'s Painters Touch® (Hunter

Green) latex paint to which CarboShield® 1000 was added at either 0.1%, 0.5% or 1.0%. A fifth set of steel panels (untreated) were also painted using Rust-Oleum®'s Gloss Protective Spray Enamel (Hunter Green) paint to which CarboShield® 1000, phosphoquat, or glycoquat was added at indicated levels.

All of the painted samples were sent to Assured Testing Services (224 River Rd., Ridgeway, PA 15853) for salt spray testing (ASTM B117). One set of panels were scored with an "X" in the center of the panel. The amount of paint pull back for the scored X was measured (in mm) in 5 different locations. The measurements were then averaged. The lower the average value, the better was the performance of the treatment. The samples were measured at different time intervals during the course of the testing. The second set was edge coated with wax to prevent edge effects. The undisturbed panel surface was periodically evaluated for total visible rust and rated from 0 to 100%.

Conversion Coating/Paint/Salt Spray Testing Results:

The panels that were spray painted (enamel) exhibited the largest improvement in paint adhesion relative to the control samples. For most of the test samples evaluated, the latex paint samples did not show differences between test sample and the corresponding controls. The E-Coat samples exhibited the least amount of paint pull back after 144 hours. The relevant results where differences exist between the test sample and the control are compiled in Tables 1 and 2 below.

Table 1

Type of Water Used	Additive Treatment	Paint Type	Rating*) (after 144 hours) (Amount of Paint Pull Back)
5% Salt Water	CarboShield® 1000	Enamel Spray Paint	7.36
5% Salt Water	None	Enamel Spray Paint	12.36 (Control)
None	None	Enamel Spray Paint	13.89 (Control)
Deionized Water	Phosphoquat (pH = 7.5)	Enamel Spray Paint	5.71
Deionized Water	CarboShield® 1000	Enamel Spray Paint	7.63
Deionized Water	Phosphoric Acid (pH = 4.0)	Enamel Spray Paint	8.86
Deionized Water	Phosphoquat (pH = 2.5)	Enamel Spray Paint	9.87
Deionized Water	Phosphoquat (pH = 4.0)	Enamel Spray Paint	9.98
None	None	Enamel Spray Paint	13.89 (Control)
Deionized Water	None	Enamel Spray Paint	15.20 (Control)
Tap Water	CarboShield® 1000	Enamel Spray Paint	10.04
Tap Water	None	Enamel Spray Paint	11.86 (Control)
None	None	Enamel Spray Paint	13.89 (Control)
Tap Water	CarboShield® 1000	Latex Paint	7.65
Tap Water	None	Latex Paint	9.10 (Control)
Tap Water	None	Latex Paint	9.12 (Control)
Deionized Water	Phosphoquat (pH = 2.5)	Latex Paint	5.95
Deionized Water	None	Latex Paint	6.87 (Control)

*) Average paint peel in mm.

This data clearly demonstrates dramatic improvements to paint peel in the case of a commercial spray enamel when the test panel is pre-treated with CarboShield® 1000 and phosphoquat materials.

Table 2: Summary of average paint peel back data for E-coated samples.

		Salt Spray Hours			
Sample ID	**Description**	**48**	**144**	**384**	**552**
B10	Ecoat control, salt	0.97	3.31	6.22	7.32
A10	Ecoat, control, untreated	1.15	2.42	4.61	7.24
E32	Phosphoric Acid, control	0.79	2.49	5.57	6.22
B16	CS1000, Ecoat	1.65	2.71	5.74	7.11
F8	Ecoat MP10	1.12	2.43	3.85	5.76
D16	Ecoat CS 1000	1.07	3.04	5.53	5.59
E14	PQ2.5 Ecoat	1.10	2.36	4.40	5.46
E16	PQ4.0 Ecoat	1.53	3.07	4.15	4.93
E18	PQ7.5, Ecoat	1.12	2.00	2.76	3.09

PQ = Phosphoquat; CS = CarboShield®; DI = deionized water.

The results listed in Table 2 are also depicted in Figure 5.

A duplicate set of unscored paint panels was prepared and subjected to salt spray exposure testing. Table 3 below is a summary table of the key results where differences exist between the test sample and the control.

Table 3: Summary of key undisturbed test panel surfaces salt spray testing

Water Used	Additive Treatment	Paint Type	% Visual Rust	Time (h)
Deionized Water	Phosphoquat (pH = 2.5)	Latex	20%	288
Deionized Water	Phosphoquat (pH = 4.0)	Latex	20%	288
Deionized Water	Phosphoquat (pH = 7.5)	Latex	40%	288
Deionized Water	Phosphoric acid (pH = 4.0)	Latex	10% (Control)	288
Deionized Water	None	Latex	75% (Control)	288
5% Salt Water	CarboShield® 1000	Enamel Spray	20%	288
5% Salt Water	None	Enamel Spray	75% (Control)	288
Deionized Water	Phosphoquat (pH = 2.5)	Enamel Spray	10	456
Deionized Water	CS MP10	Enamel Spray	15	456
Deinonized Water	CarboShield® 1000	Enamel Spray	15	456
Deionized Water	Phosphoquat (pH = 4.0)	Enamel Spray	40	456
Deionized Water	Phosphoric acid (pH = 4.0)	Enamel Spray	40% (Control)	456
Deionized Water	None	Enamel Spray	40	456
Deionized Water	Phosphoquat (pH = 7.5)	Enamel Spray	50	456
Tap Water	CarboShield® 1000	Enamel Spray	5	624
Tap Water	None	Enamel Spray	15	624

Collectively, this data demonstrates a dramatic ability of both CarboShield® 1000 and the phosphoquat version "conversion coating" pretreatments to significantly reduce total rust of a commercial latex and a spray enamel treatment in salt spray testing.

Table 4: Peel back data for CarboShield® 1000 added to brush latex

"Spiking" Treatment	Peel Rating (144 h)
1.0% CarboShield® in Latex Paint	3.79
0.1% CarboShield® in Latex Paint	5.97
0.5% CarboShield® in Latex Paint	6.98
0.0% CarboShield® in Latex Paint	9.12

This data shows dramatic improvements in paint peel when CarboShield® 1000 is incorporated directly into a commercial paint formulation.

In another test, the amount of visual rust (in %) was determined for undisturbed test panel surfaces painted with latex paint spiked with various amounts of CarboShield® 1000 (CS) after salt spray exposure for 24 to 456 h. The data is compiled in Table 5 below and depicted in Figure 6.

Table 5: Undisturbed test panel surfaces for latex paint spiked with CarboShield® 1000.

Time (h)	Sample G1 0.1% CS Spike, Brush	Sample G3 0.5% CS Spike	Sample G5 1% CS Spike	Sample A5 Brushed, Untreated
24	1	1	1	1
48	1	1	1	1
120				20
144	15		20	30
192			25	
216	25			45
288	35	3		80
312		5	35	
336		10		
360	45			85
456	75	15	40	95

Samples were prepared by brush application.

In another test, the amount of visual rust (in %) was determined for undisturbed test panel surfaces painted with gloss protective spray enamel with various amounts of CarboShield® 1000 (CS), phosphoquat, and glycoquat after salt spray exposure for 24 to 168 h. The data is compiled in Table 6 below and depicted in Figure 7.

Table 6: Undisturbed test panel surfaces for gloss protective spray enamel (GPE) spiked with CarboShield® 1000 (CS), phosphoquat (PQ), and glycoquat (GQ).

	Time (h)				
Sample Description	**24**	**48**	**72**	**96**	**168**
GPE spray enamel (control)	0.5	15	45	80	87.5
0.25% GQ (spiked)	0	0	0	0	12.5
0.50% GQ (spiked)	0	0	0	0	2.5
0.25% CS (spiked)	0	0	0	0.5	12.5
0.50% CS (spiked)	0	0	0	0	1.5
0.25% PQ4.0 (spiked)	0	0	0.5	0	3
0.50% PQ4.0 (spiked)	12.5	12.5	0	35	77.5

All samples were prepared by brush application in order to allow for spiking where applicable.

The data in tables 5 & 6 shows dramatic improvements in corrosion resistance when CarboShield® 1000 or related phosphoquat or glycoquat materials are incorporated directly into commercial paint formulations.

Example 2 & Comparative Example 1

Two latex paints were formulated according to the amounts and order of ingredients and process steps listed in Table 7. One formulation (Example 2) contained CarboShield® 1000 while the other one (Comparative Example 1) contained a combination of a nonionic surfactant (Triton X-100) and a conventional corrosion inhibitor (Canguard® 327).

Table 7: Summary of Formulated Ingredients

Material / *Process Step*	**Comp. Example 1**	**Example 2**
Water	57.34 L	57.34 L
Propylene glycol	15.42 kg	15.42 kg
Natrosol® 250 HBR	816.5 g	816.5 g
Mix 30 minutes		
Tamol® 850	4.536 kg	4.536 kg
Triton® X-100	1.043 kg	—
CarboShield® 1000	—	**1.043 kg**
Drewplus® L-493	861.8 g	861.8 g
Canguard® 327	1.021 kg	—
AMP-95™	453.6 g	453.6 g
Mix		
Ti-Pure® R-931	87.32 kg	87.32 kg
Imsil® A-15	87.32 kg	87.32 kg
High speed stir at 4,000 RPM for 30 min, then decrease speed to 1,000 RPM		
UCAR® 123 latex	154.0 kg	154.0 kg
Texanol®	3.080 kg	3.080 kg
Drewplus® L-493	997.9 g	997.9 g
Acrosol® RM-825	907.2 g	907.2 g
Water	81.29 L	81.29 L
Allow to sit for 48 hours to test for stability and dispersion before testing material		

Natrosol® 250 HBR is a water soluble hydroxyethylcellulose of Hercules Inc., Wilmington, Delaware.

Tamol® 850 is a sodium polyacrylate of Rohm and Haas Co., Philadelphia, Pennsylvania.

Triton® X-100 is an octylphenol ethoxylate of The Dow Chemical Company.

Drewplus® L-493 is a defoamer of Ashland Specialty Chemical Co., Boonton, New Jersey.

Canguard® 327 is an oxazolidine-based corrosion inhibitor of ANGUS Chemical Company, a subsidiary of The Dow Chemical Company.

AMP-95™ is 2-amino-2-methyl-1-propanol containing 5% water, obtainable from ANGUS Chemical Company.

Ti-Pure® R-931 is a rutile titanium dioxide pigment of DuPont Titanium Technologies, Wilmington, Delaware.

Imsil® A-15 is a microcrystalline silica of Unimin Specialty Minerals Inc., Tamms, Illinois.

UCAR® 123 is a high-solids styrene-acrylic binder of UCAR Emulsion Systems, Cary, North Carolina.

Texanol® is 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate of Eastman Chemical Company, Kingsport, Tennessee.

Acrosol® RM-825 is an acrylate copolymer-based rheology modifier of BASF AG, Ludwigshafen, Germany.

The formulations of Table 7 were tested for storage stability and viscosity as well as scrub resistance and hide of paint films on metal surfaces.

The formulation of Example 2 was stable for several days, even better than that of Comparative Example 1, with less separation. The formulation was also "creamier" (more desirable) than the comparative formulation. This observation confirms that CarboShield® 1000 is compatible in latex systems.

Hide, which is the ability of a coating to hide black marks, was 96.8% in the comparative example 97.2% in the example according to the invention. This indicates that CarboShield® 1000 works better than the surfactant Triton® X-100. Hide was measured by contrast ratio using a bird bar draw down (76.2 μm = 3 mil) on a standard Leneta (type 2C) card and are expressed as a ratio of black and white L-values (LAB color system).

The scrub resistance of the paint film prepared from the formulation of Example 2 was 480 cycles to failure while that of the film prepared from the formulation of Comparative Example 1 was only 370 cycles to failure. This is a significant ca. 30% improvement. Scrub resistance was measured using standard ASTM D2486 methodology.

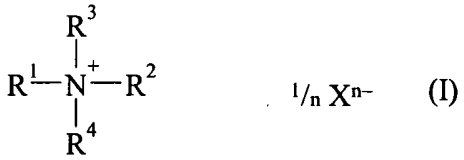
Gloss measurements indicated no significant difference between the coatings prepared from both formulations.

The Stormer viscosity of the Formulation of Example 2 was significantly higher than that of Comparative Example 1, 83 KU vs. 73 KU. This allows to reduce the amount of associative thickener added to the formulation.

Claims

1. A method for applying a conversion coating to the surface of a metal substrate, said method comprising the step of contacting the substrate with a composition comprising
   (a) at least one quaternary ammonium salt containing a non-halogen anion, and
   (b) optionally, a solvent.

2. The method of claim 1, wherein the quaternary ammonium salt has the formula



$$R^1-\overset{\overset{R^3}{|}}{\underset{\underset{R^4}{|}}{N^+}}-R^2 \qquad {}^1/_n X^{n-} \qquad (I)$$

wherein R^1 is an optionally aryl-substituted C_{1-20} alkyl group, and R^2 is an optionally aryl-substituted C_{1-20} alkyl group, R^3 and R^4 independently of each other are C_{1-4} alkyl groups, X^{n-} is an anion selected from the group consisting of hydroxide, carbonate, bicarbonate, phosphates, phosphites, hypophosphite, nitrate, sulfates, borates, anions of saturated and unsaturated acyclic C_{1-20} monocarboxylic acids, anions of saturated and unsaturated acyclic C_{2-20} dicarboxylic acids and anions of hydroxy-substituted carboxylic acids, and n denotes the appropriate number of negative charges of said anion.

3. The method of claim 2, wherein X^{n-} is selected from the group consisting of carbonate, bicarbonate, phosphates and glycolate.

4. The method of claim 2 or 3, wherein R^3 and R^4 are methyl groups.

5. The method of any of claims 2 to 4, wherein R^1 is methyl.

6. The method of any of claims 2 to 5, wherein R^2 is benzyl or phenylethyl.

7. The method of any of claims 2 to 4, wherein R^1 and R^2 are the same C_{1-20} alkyl groups

8. The method of claim 7, wherein R^1 and R^2 are C_{10} alkyl groups.

9. The method of claim 8, wherein R^1 and R^2 are *n*-C_{10} alkyl groups.

10. The method of claim 9, wherein the quaternary ammonium salt is di-*n*-decyldimethyl-ammonium carbonate and/or di-*n*-decyldimethylammonium bicarbonate.

11. The method of any of claims 1 to 10, wherein the metal substrate is steel.

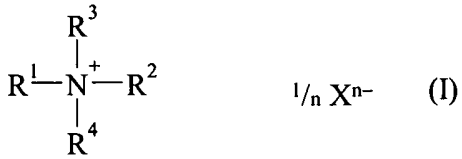
12. The method of claim 11, wherein the steel is coiled sheet steel.

13. An article of manufacture comprising a metal substrate treated according to the method of any of claims 1 to 12.

14. The article of manufacture of claim 13 wherein the metal substrate is steel.

15. An anticorrosive paint comprising
    (a) at least one quaternary ammonium salt containing a non-halogen anion,
    (b) a binder,
    (c) optionally, a solvent and
    (d) optionally, a pigment.

16. The anticorrosive paint of claim 15, wherein the quaternary ammonium salt has the formula



$$R^1\text{—}N^+(R^3)(R^4)\text{—}R^2 \quad {}^1/_n X^{n-} \qquad (I)$$

wherein R^1 is an optionally aryl-substituted C_{1-20} alkyl group, and R^2 is an optionally aryl-substituted C_{1-20} alkyl group, R^3 and R^4 independently of each other are C_{1-4} alkyl groups, X^{n-} is an anion selected from the group consisting of hydroxide, carbonate, bicarbonate, phosphates, phosphites, hypophosphite, nitrate, sulfates, borates, anions of saturated and unsaturated acyclic C_{1-20} monocarboxylic acids, anions of saturated and unsaturated acyclic C_{2-20} dicarboxylic acids and anions of hydroxy-substituted carboxylic acids, and n denotes the appropriate number of negative charges of said anion.

17. The anticorrosive paint of claim 15 or 16, wherein the binder is selected from the group consisting of acrylic resins, casein (milk protein), vinyl resins, latex resins, acetate resins, epoxy resins and mixtures thereof.

18. The anticorrosive paint of claim 15 or 16, which is a latex paint.

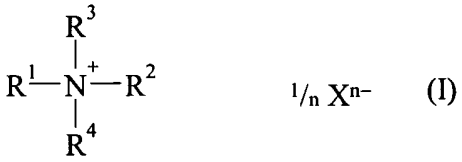
19. The anticorrosive paint of claim 15 or 16, which is an enamel spray paint.

20. The anticorrosive paint of claim 15 or 16, which is an e-coating paint.

21. The anticorrosive paint of claim 15 or 16, which is an acrylic paint.

22. An article of manufacture comprising a metal substrate painted with the anticorrosive paint of any of claims 15 to 21.

23. Use of a quaternary ammonium salt having the formula



$$\frac{1}{n} X^{n-} \qquad (I)$$

wherein R^1 is an optionally aryl-substituted C_{1-20} alkyl group, and R^2 is an optionally aryl-substituted C_{1-20} alkyl group, R^3 and R^4 independently of each other are C_{1-4} alkyl groups, X^{n-} is an anion selected from the group consisting of hydroxide, carbonate, bicarbonate, phosphates, phosphites, hypophosphite, nitrate, sulfates, borates, anions of saturated and unsaturated acyclic C_{1-20} monocarboxylic acids, anions of saturated and unsaturated acyclic C_{2-20} dicarboxylic acids and anions of hydroxy-substituted carboxylic acids, and n denotes the appropriate number of negative charges of said anion as an anticorrosive additive in paints or coatings.

Fig. 1

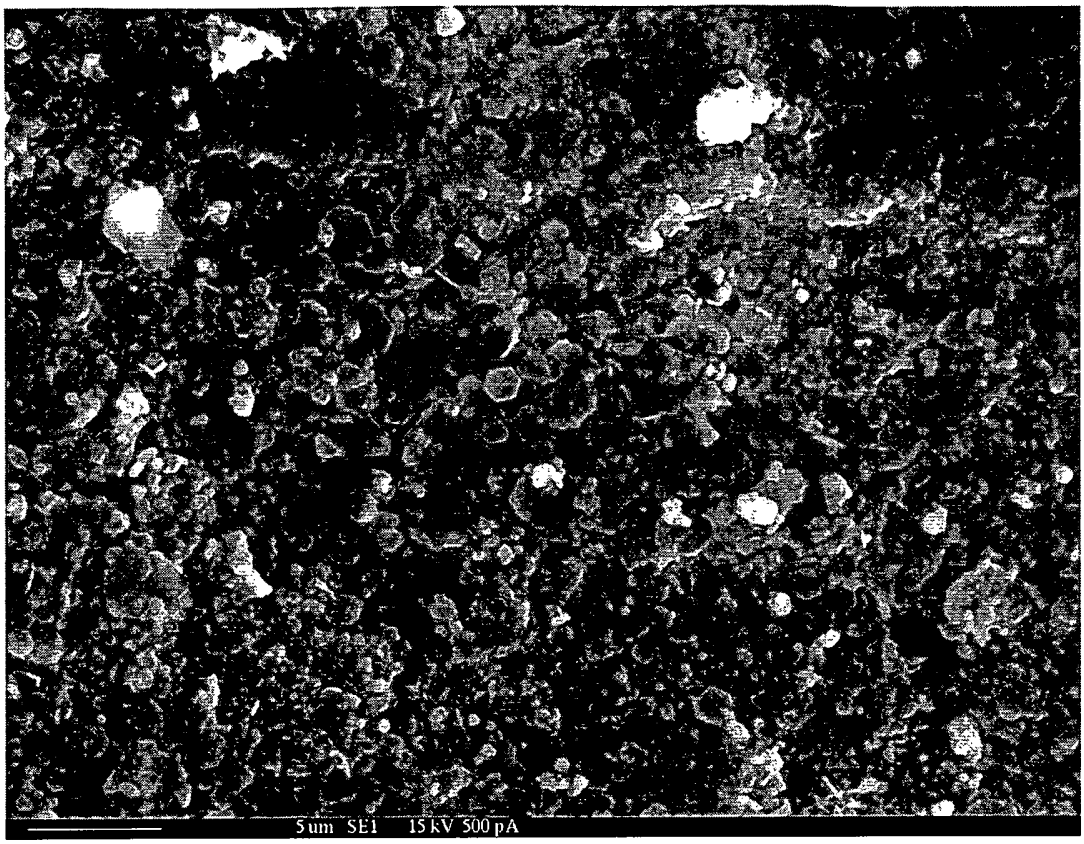


Fig. 2



Fig. 3



Fig. 4

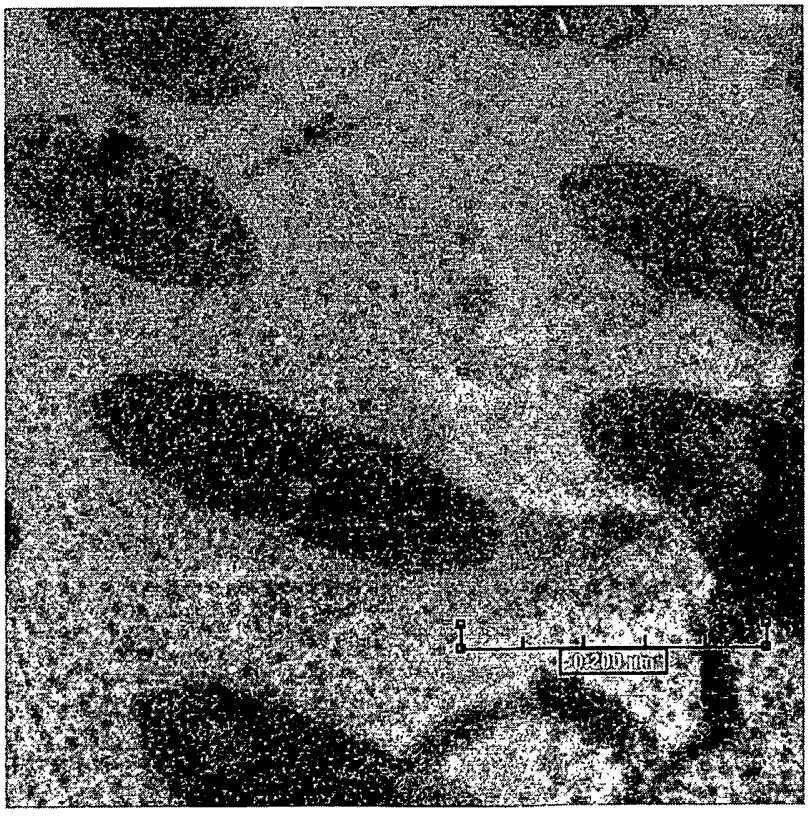


Fig. 5

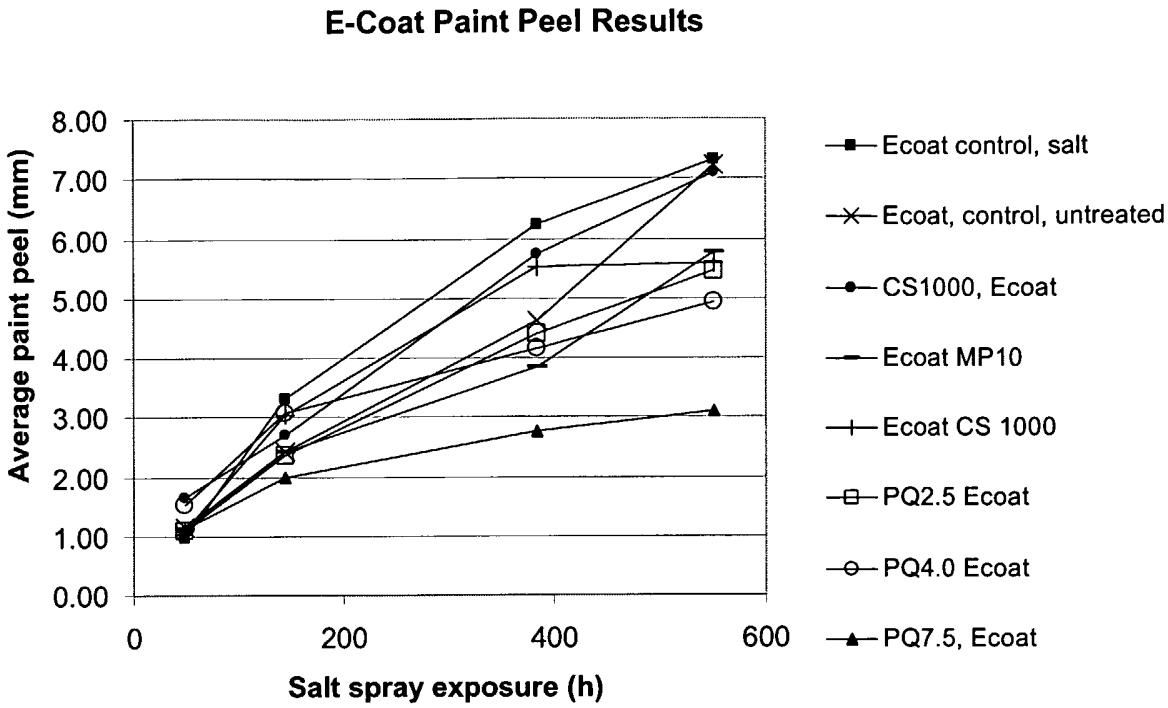

E-Coat Paint Peel Results
Average paint peel (mm)
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0
200
400
600
Salt spray exposure (h)
Ecoat control, salt
Ecoat, control, untreated
CS1000, Ecoat
Ecoat MP10
Ecoat CS 1000
PQ2.5 Ecoat
PQ4.0 Ecoat
PQ7.5, Ecoat

Fig. 6

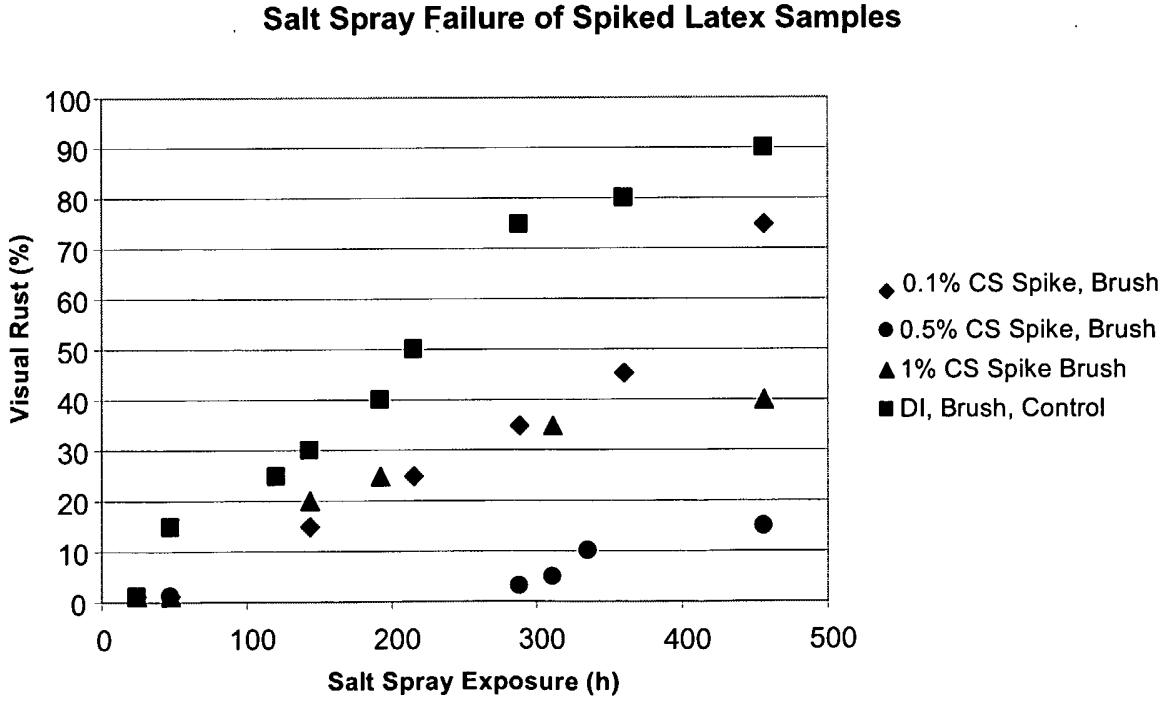
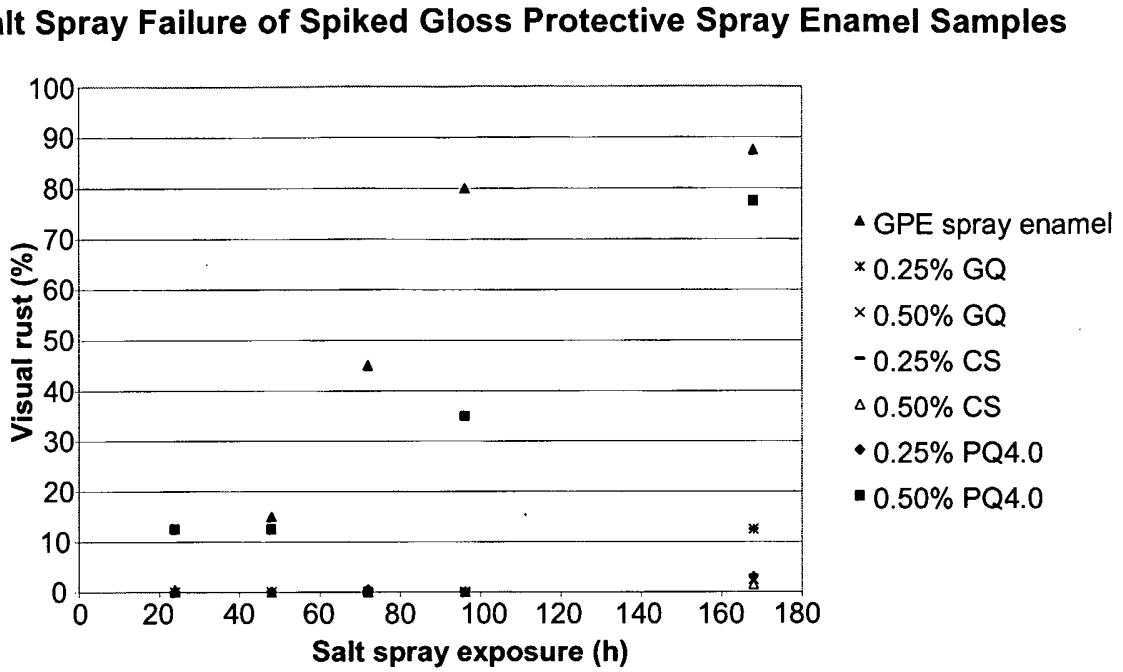

Salt Spray Failure of Spiked Latex Samples
Visual Rust (%)
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
Salt Spray Exposure (h)
0.1% CS Spike, Brush
0.5% CS Spike, Brush
1% CS Spike Brush
DI, Brush, Control

Fig. 7


Salt Spray Failure of Spiked Gloss Protective Spray Enamel Samples
Visual rust (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
Salt spray exposure (h)
GPE spray enamel
0.25% GQ
0.50% GQ
0.25% CS
0.50% CS
0.25% PQ4.0
0.50% PQ4.0

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/013191

A. CLASSIFICATION OF SUBJECT MATTER
C23C22/68 C23C22/50 C23F11/14 C09D5/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C C23F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2004/106589 A (LONZA INC; LONZA AG; CHIANG, MICHAEL, Y; HALL, LARRY, K; KIMLER, JOSEP) 9 December 2004 (2004-12-09) example 2; table 2 page 6, lines 13-24 claims 1-10,17-23	1-17,22, 23
P,X	US 2005/003978 A1 (HALL LARRY K ET AL) 6 January 2005 (2005-01-06) example 2; table 2 page 3, paragraph 42-44 claims 1-10,17-19	1-17,22, 23

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
22 March 2006	31/03/2006

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/013191

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 2005/012077 A1 (HALL LARRY K ET AL) 20 January 2005 (2005-01-20) example 2; table 2 page 3, paragraph 42-44 claims 1-10,17-19	1-17,22, 23
X	US 3 121 091 A (GREEN JEROME) 11 February 1964 (1964-02-11) column 2, lines 7-20,35-40 column 5, lines 15-19 column 7, line 63 - column 8, line 6; example VI column 9, lines 5-29,39	1-9,11, 13,14,23
X	WO 99/12889 A (SK CHEMICALS; HAHN, SOON, JONG; SHIN, JEONG, JOO; HA, JAE, MIN; CHO, C) 18 March 1999 (1999-03-18) pages 10-15; examples 1-3,comparative	1-4,6, 11,13, 14,23
X	US 4 859 418 A (OHLENDORF ET AL) 22 August 1989 (1989-08-22) examples 1-4,6-8	1,2,4,5, 11,13, 14,23
X	EP 0 227 179 A (ENICHEM SINTESI S.P.A; ENICHEM SYNTHESIS S.P.A) 1 July 1987 (1987-07-01) page 2, lines 1-3,19-40 page 4, lines 5,6,13-17 page 5; examples 1-3; table 1	1-6,13, 23
X	EP 0 946 788 B (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN; COGNIS DEUTSCHLAND GMBH) 25 July 2001 (2001-07-25) page 6, paragraphs 37,38; examples 1-3; table 1 sentence 55; table 2 sentences 16,21; table 3	1-6,11, 13,14,23
X	US 5 409 528 A (WALTHER ET AL) 25 April 1995 (1995-04-25) column 2, lines 20-30 column 3, lines 8-33 column 4, lines 15,21-30	15,17,22
Y	examples 1-3; tables I,(F-K) column 5, lines 24-29 tables II,(F-K) column 5, lines 36-64 column 3, lines 65-68	18-21

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/013191

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 365 313 A (JR. GEORGE LEATHWHITE ROBERTS, ET AL) 23 January 1968 (1968-01-23) column 1, lines 14-17 column 3, lines 1-13	15,17,22
Y	examples 1-7,13-15,17 claims 1-3	18-21
X	WO 02/092880 A (WAYNE PIGMENT CORPORATION) 21 November 2002 (2002-11-21) claims 13-16,18,19	1,15
A	WO 95/11324 A (ALBRIGHT & WILSON LIMITED; DAVIS, KEITH, PHILIP; WILLIAMS, MICHAEL, JO) 27 April 1995 (1995-04-27) the whole document	15-23
A	US 4 505 748 A (BAXTER ET AL) 19 March 1985 (1985-03-19) the whole document	15-23
A	US 4 226 624 A (OHR ET AL) 7 October 1980 (1980-10-07) the whole document	1-23
A	US 2 759 975 A (CHIDDIX MAX E ET AL) 21 August 1956 (1956-08-21) the whole document	1-23
A	EP 0 284 000 A (HODOGAYA CHEMICAL CO., LTD) 28 September 1988 (1988-09-28)	1-23

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/013191

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004106589 A	09-12-2004	AU 2004243559 A1	09-12-2004
		CA 2526667 A1	09-12-2004
US 2005003978 A1	06-01-2005	US 2005012077 A1	20-01-2005
US 2005012077 A1	20-01-2005	US 2005003978 A1	06-01-2005
US 3121091 A	11-02-1964	NONE	
WO 9912889 A	18-03-1999	DE 69811917 D1	10-04-2003
		DE 69811917 T2	18-12-2003
		EP 1012134 A1	28-06-2000
		JP 2001515880 T	25-09-2001
		US 2002065251 A1	30-05-2002
US 4859418 A	22-08-1989	DE 3523088 A1	08-01-1987
		EP 0206311 A2	30-12-1986
		JP 62004888 A	10-01-1987
		NO 862608 A	29-12-1986
EP 0227179 A	01-07-1987	DE 3672976 D1	30-08-1990
		IT 1207517 B	25-05-1989
		JP 62156279 A	11-07-1987
		US 4849170 A	18-07-1989
		US 4792417 A	20-12-1988
EP 0946788 B	25-07-2001	AT 203575 T	15-08-2001
		AU 726726 B2	16-11-2000
		AU 5553298 A	22-06-1998
		CA 2273268 A1	04-06-1998
		DE 19649285 A1	04-06-1998
		DK 946788 T3	24-09-2001
		WO 9823792 A1	04-06-1998
		EP 0946788 A1	06-10-1999
		ES 2160979 T3	16-11-2001
		HU 0000370 A2	28-06-2000
		NO 992563 A	27-05-1999
		TR 9901153 T2	21-10-1999
		US 6261346 B1	17-07-2001
US 5409528 A	25-04-1995	NONE	
US 3365313 A	23-01-1968	NONE	
WO 02092880 A	21-11-2002	GB 2391237 A	04-02-2004
WO 9511324 A	27-04-1995	AU 7938694 A	08-05-1995
		EP 0728226 A1	28-08-1996
		ZA 9408312 A	17-01-1996
US 4505748 A	19-03-1985	CA 1199786 A1	28-01-1986
US 4226624 A	07-10-1980	NONE	
US 2759975 A	21-08-1956	NONE	
EP 0284000 A	28-09-1988	DE 3874176 D1	08-10-1992
		DE 3874176 T2	08-04-1993

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/013191

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0284000 A		JP 2624755 B2	25-06-1997
		JP 64000054 A	05-01-1989
		KR 9306193 B1	08-07-1993