(12) UK Patent (19) GB (11) 2527640 (13) B

(45) Date of B Publication **21.09.2022**

(54) Title of the Invention: Corrosion inhibitors, improved paint and corrosion protection coating

(51) INT CL: ***C09D 5/08*** (2006.01) ***B01J 41/12*** (2017.01) ***C08F 8/30*** (2006.01) ***C08L 27/06*** (2006.01)
C08L 33/08 (2006.01) ***C09D 201/02*** (2006.01)

(21) Application No: **1506696.2**

(22) Date of Filing: **21.04.2015**

(30) Priority Data:

(31)	**102014207517**	(32)	**21.04.2014**	(33)	**DE**
(31)	**1411848.3**	(32)	**02.07.2014**	(33)	**GB**
(31)	**102014216233**	(32)	**14.08.2014**	(33)	**DE**
(31)	**62/066301**	(32)	**20.10.2014**	(33)	**US**
(31)	**102014223651**	(32)	**19.11.2014**	(33)	**DE**
(31)	**62/085637**	(32)	**30.11.2014**	(33)	**US**
(31)	**1421440.7**	(32)	**02.12.2014**	(33)	**GB**

(43) Date of A Publication **30.12.2015**

(56) Documents Cited:

GB 2081275 A	**WO 2014/038810 A1**
WO 2012/089649 A1	**WO 1997/014751 A1**
CN 103147104 A	**US 4612049 A**

(58) Field of Search:
As for published application 2527640 A viz:
INT CL **B01J, C08F, C09D**
Other: **EPODOC, WPI, TXTA, CASONLINE**
updated as appropriate

Additional Fields
Other: **None**

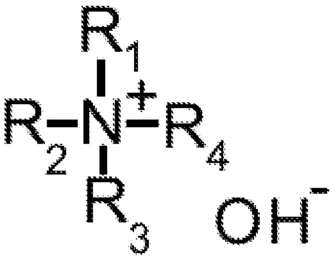
(72) Inventor(s):
Friedrich Wilhelm Wieland

(73) Proprietor(s):
Friedrich Wilhelm Wieland
Koelner Str. 38 B, Luedenscheid 58509, D, Germany

Wieland KG
Koelner Str. 38 B, Luedenscheid 58509, D, Germany

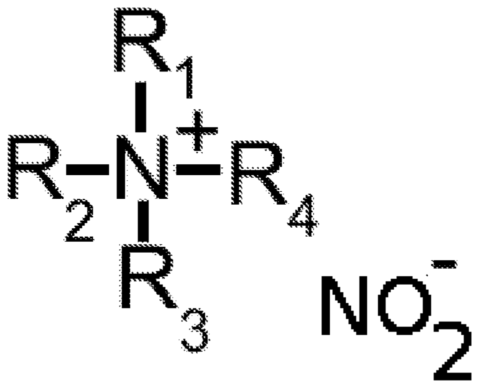
(74) Agent and/or Address for Service:
Friedrich Wilhelm Wieland
Koelner Str. 38 B, Luedenscheid 58509, D, Germany

Fig. 1A



$$R_2-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{\overset{|}{\underset{|}{N^+}}}}-R_4 \quad OH^-$$

Fig. 1B



$$R_1R_2R_3R_4N^{+}\ NO_2^{-}$$

Fig. 2A

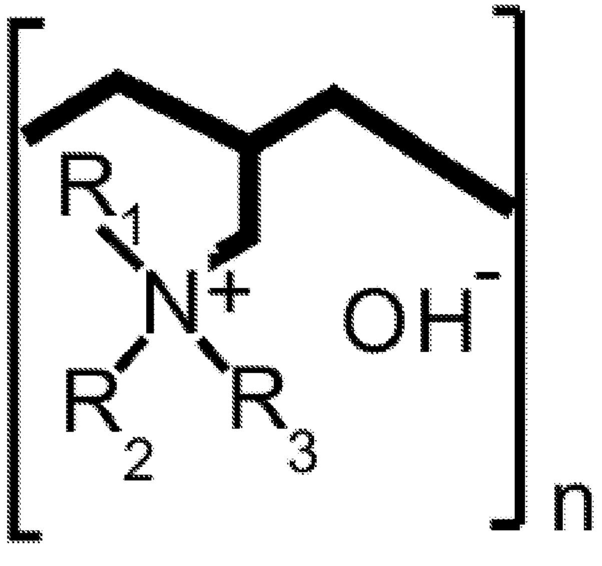


Fig. 2B

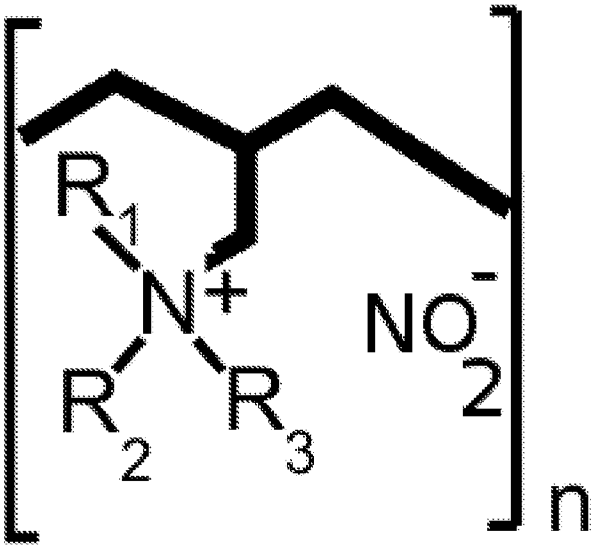


Fig. 3A

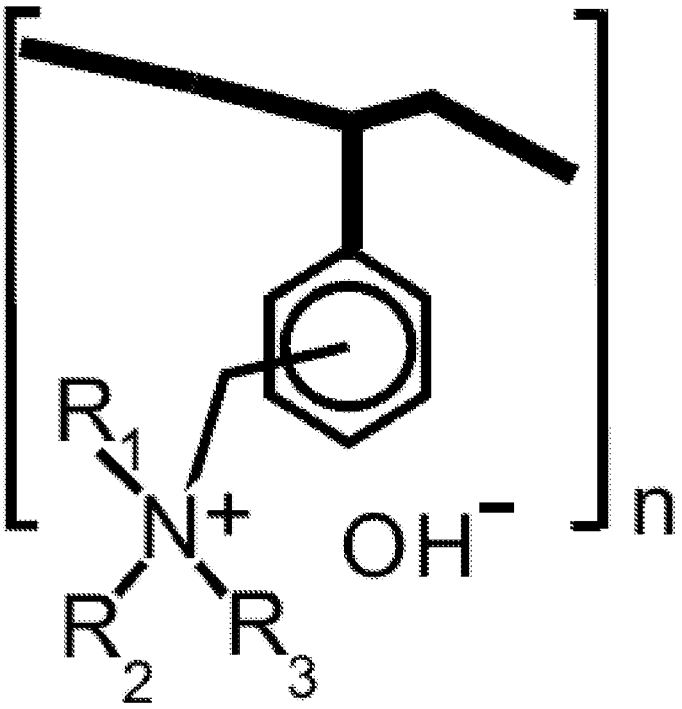


Fig. 3B

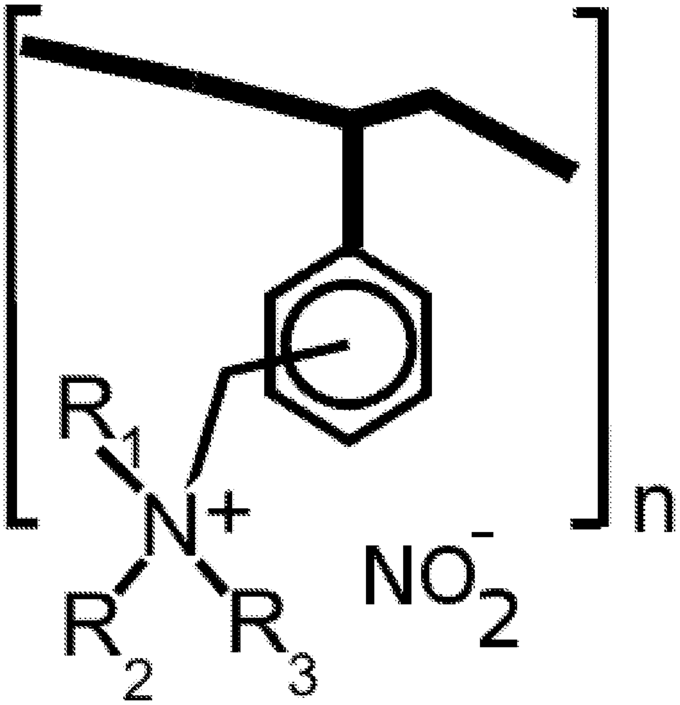


Fig. 4A

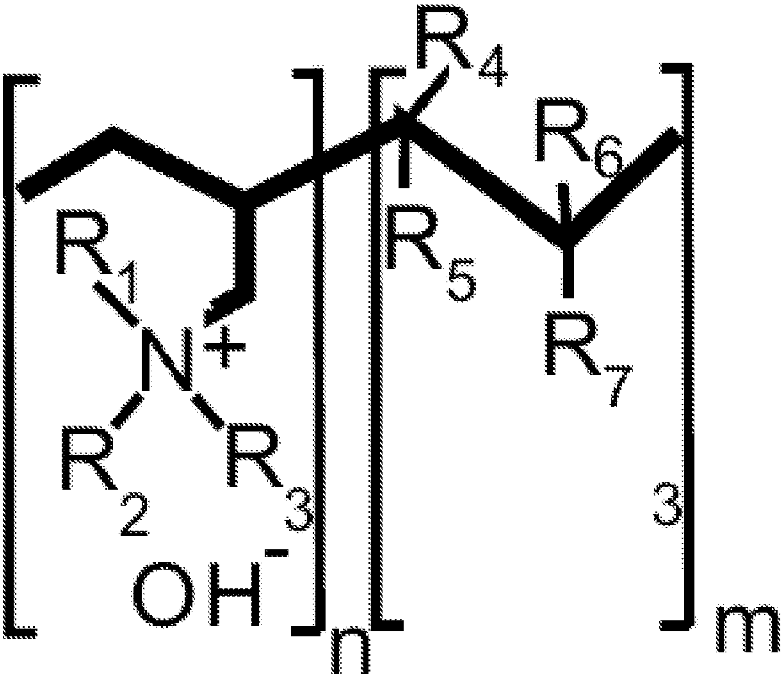


Fig. 4B

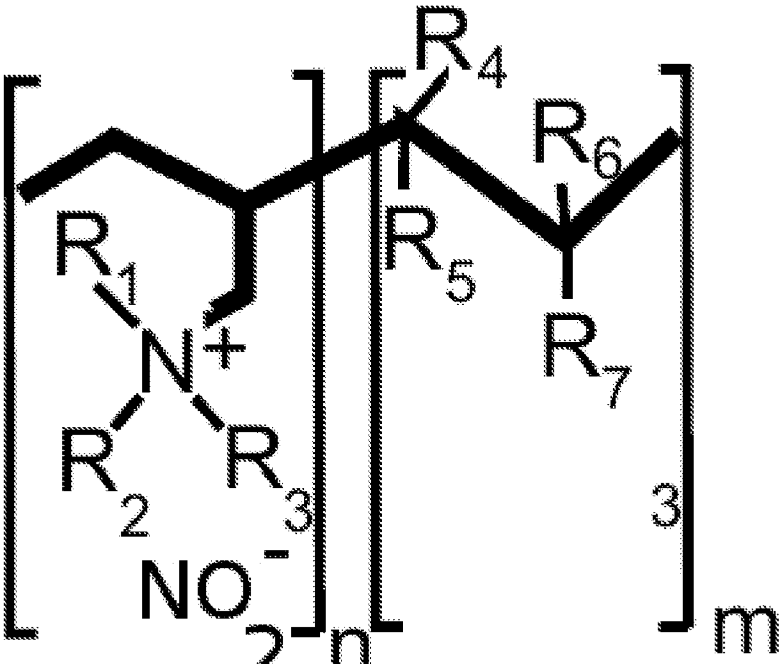


Fig. 4c

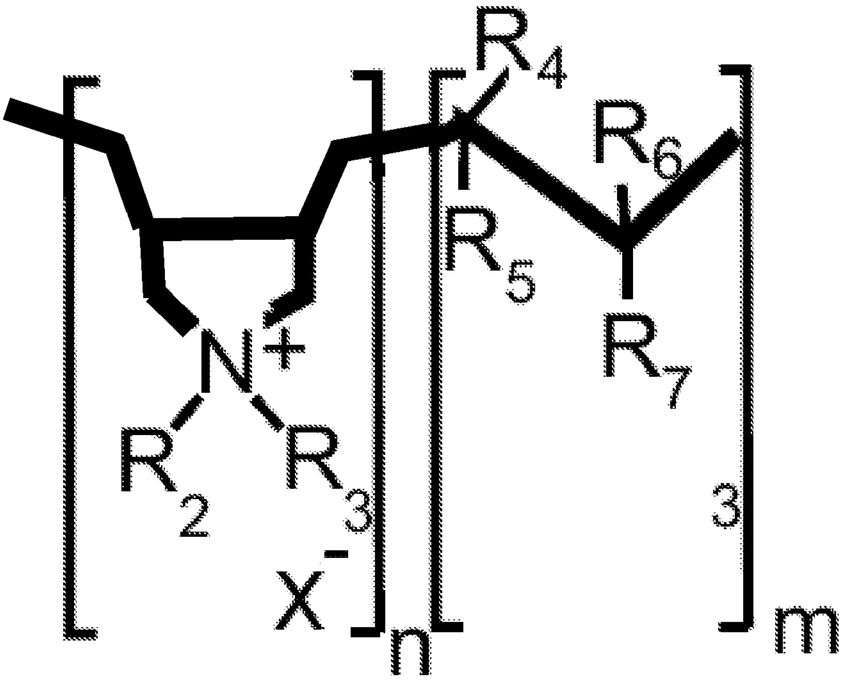


Fig. 5 A

13 07 15

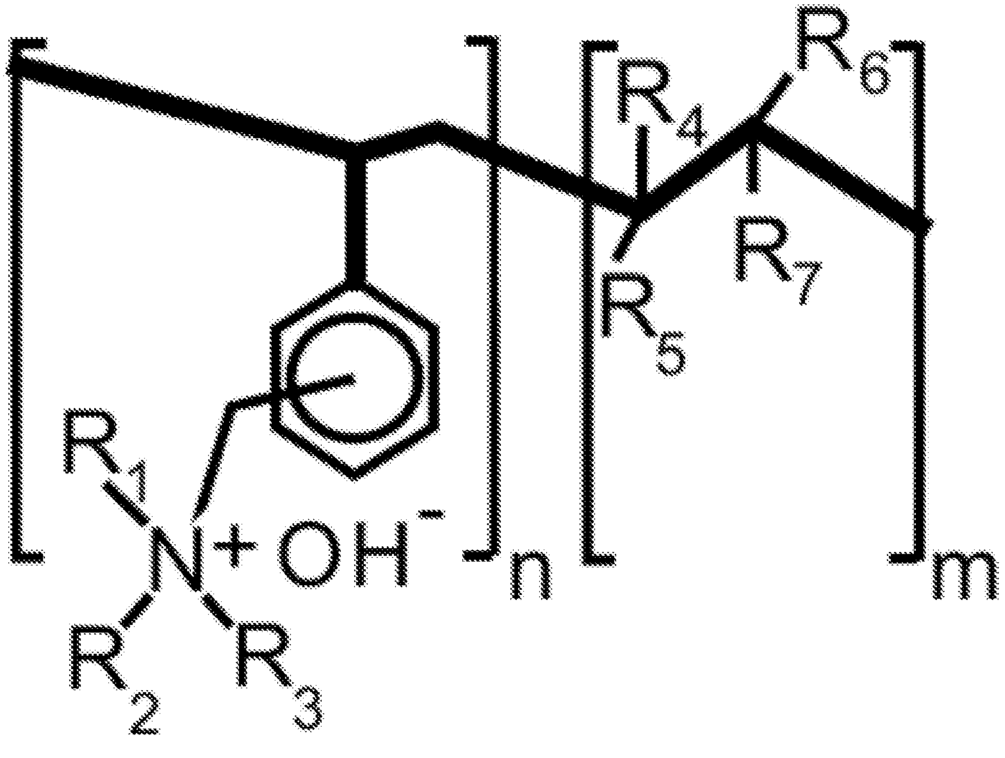


Fig. 5B

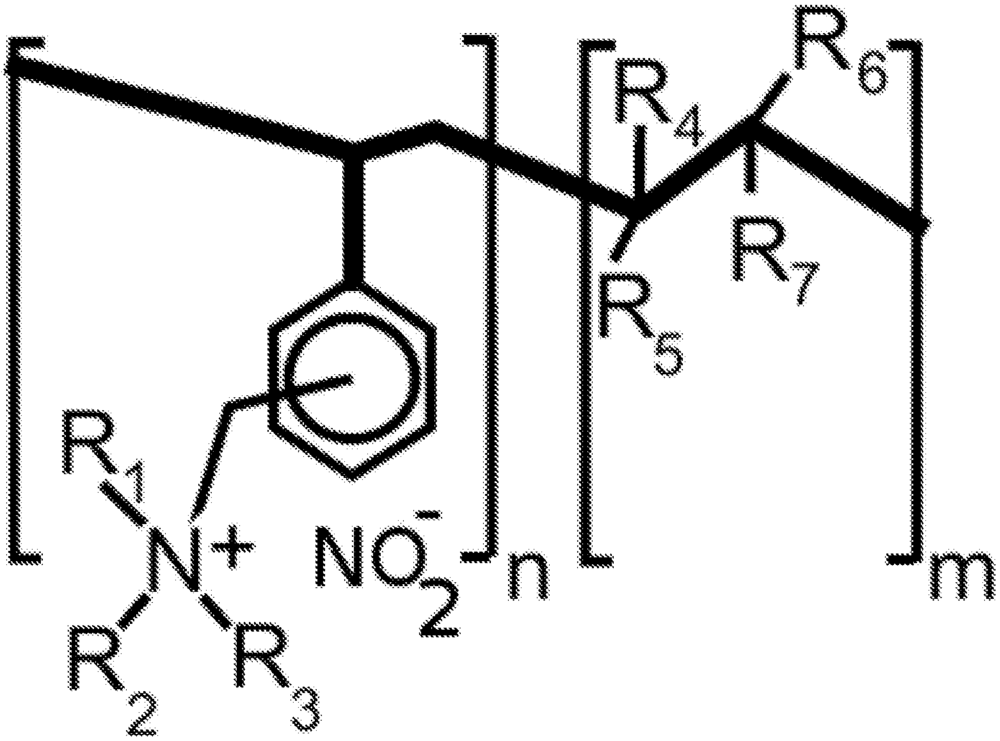


Fig. 6

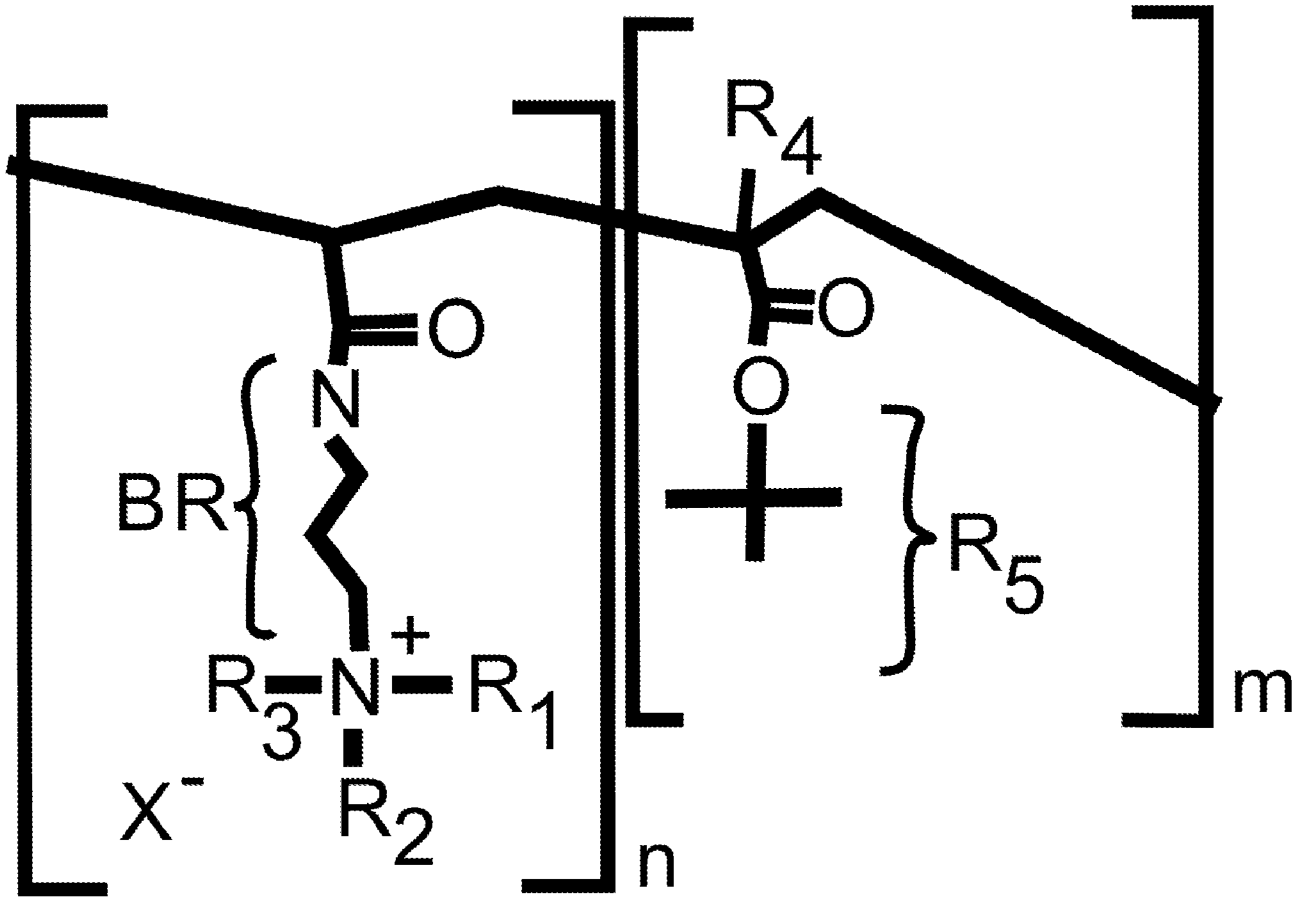


Fig. 7

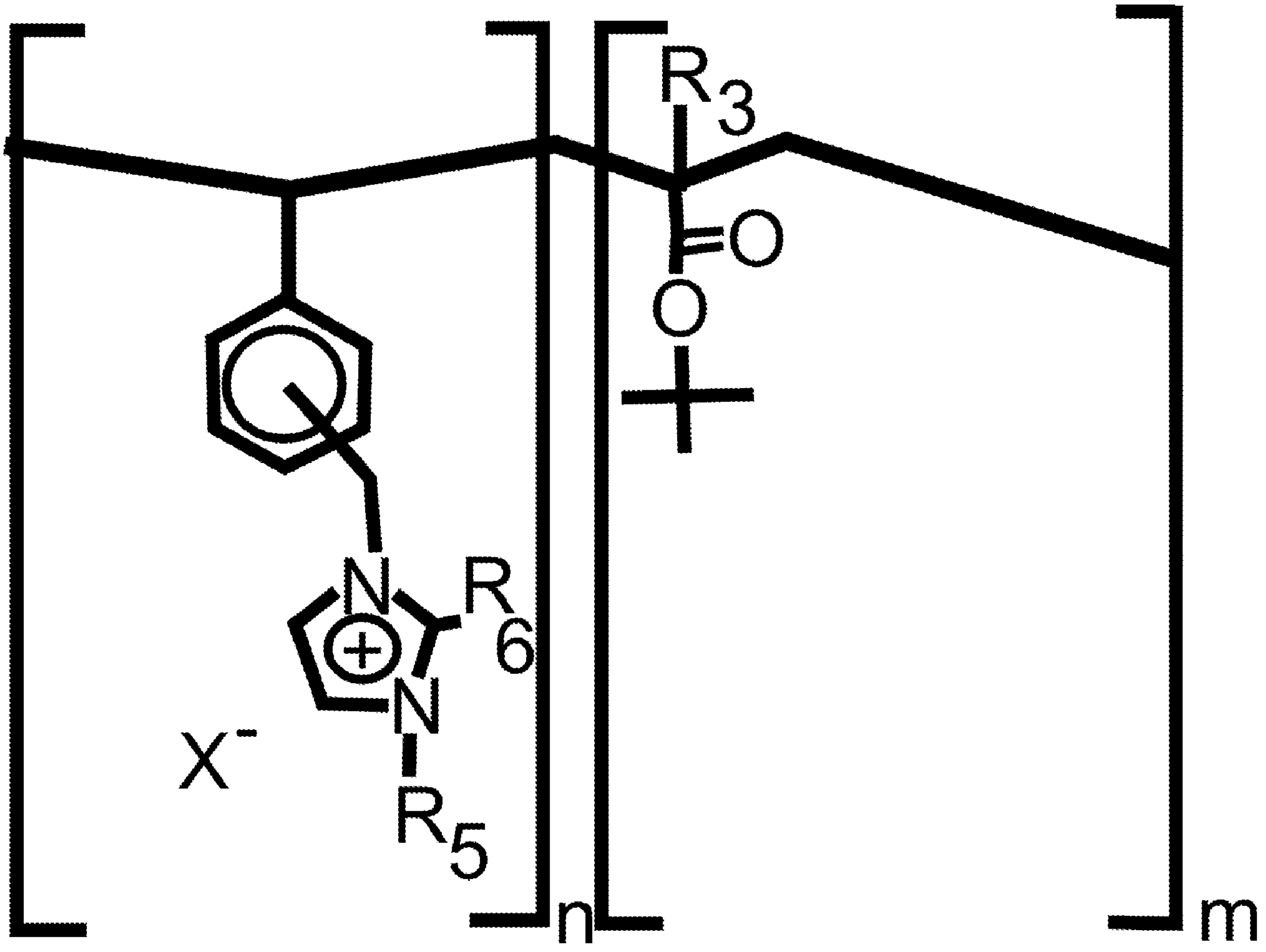


Fig. 8

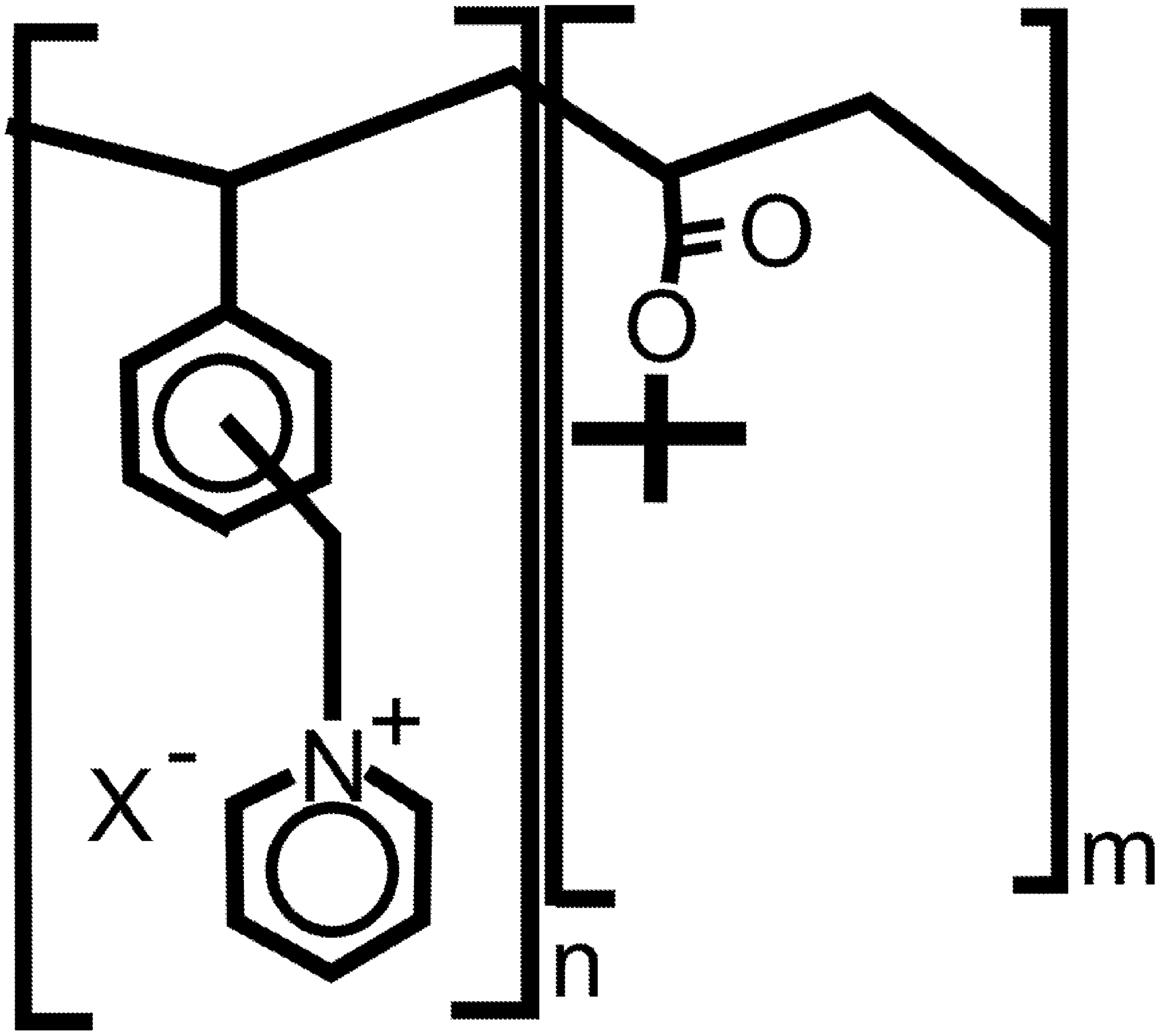


Fig. 9

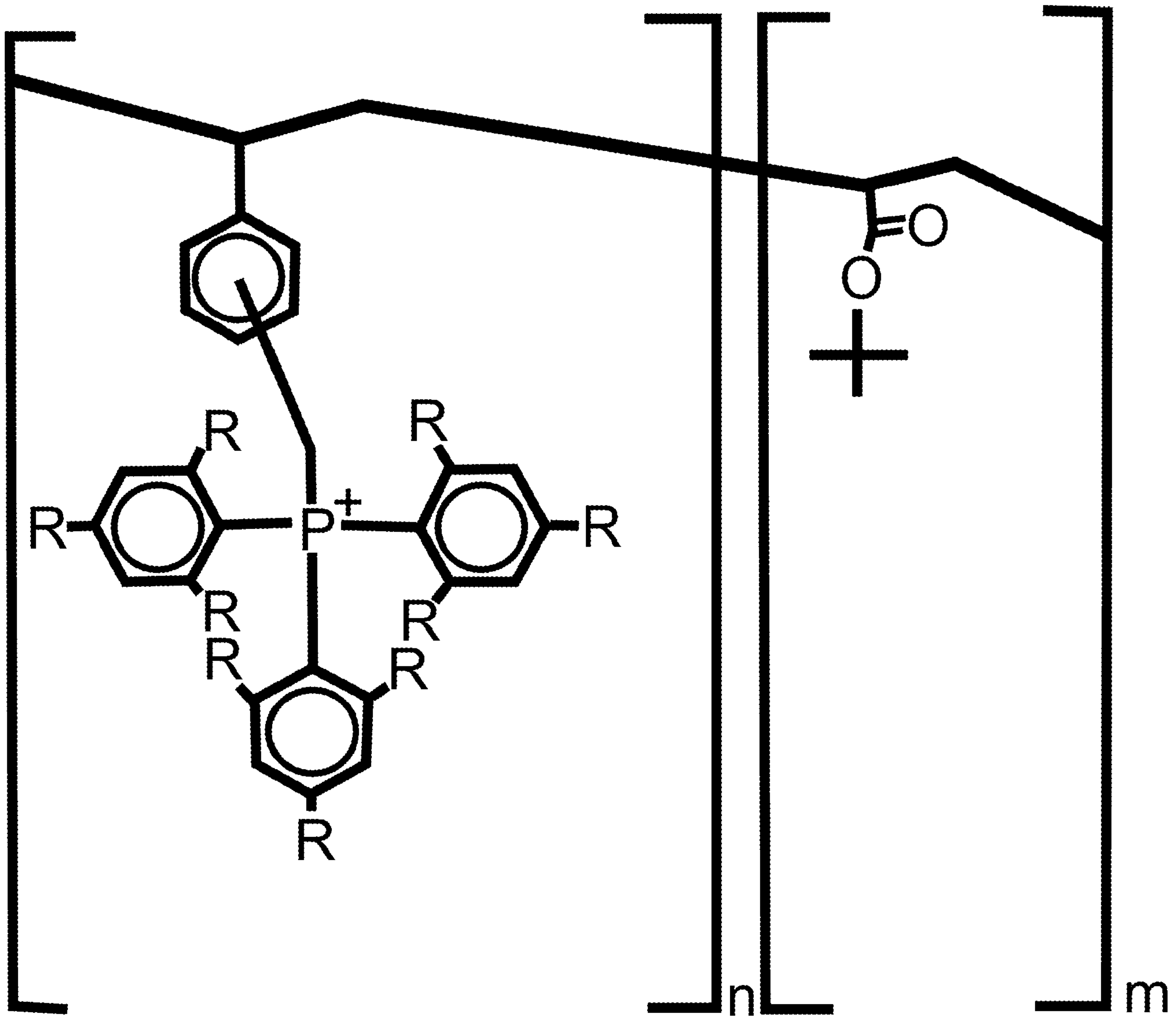


Fig. 10

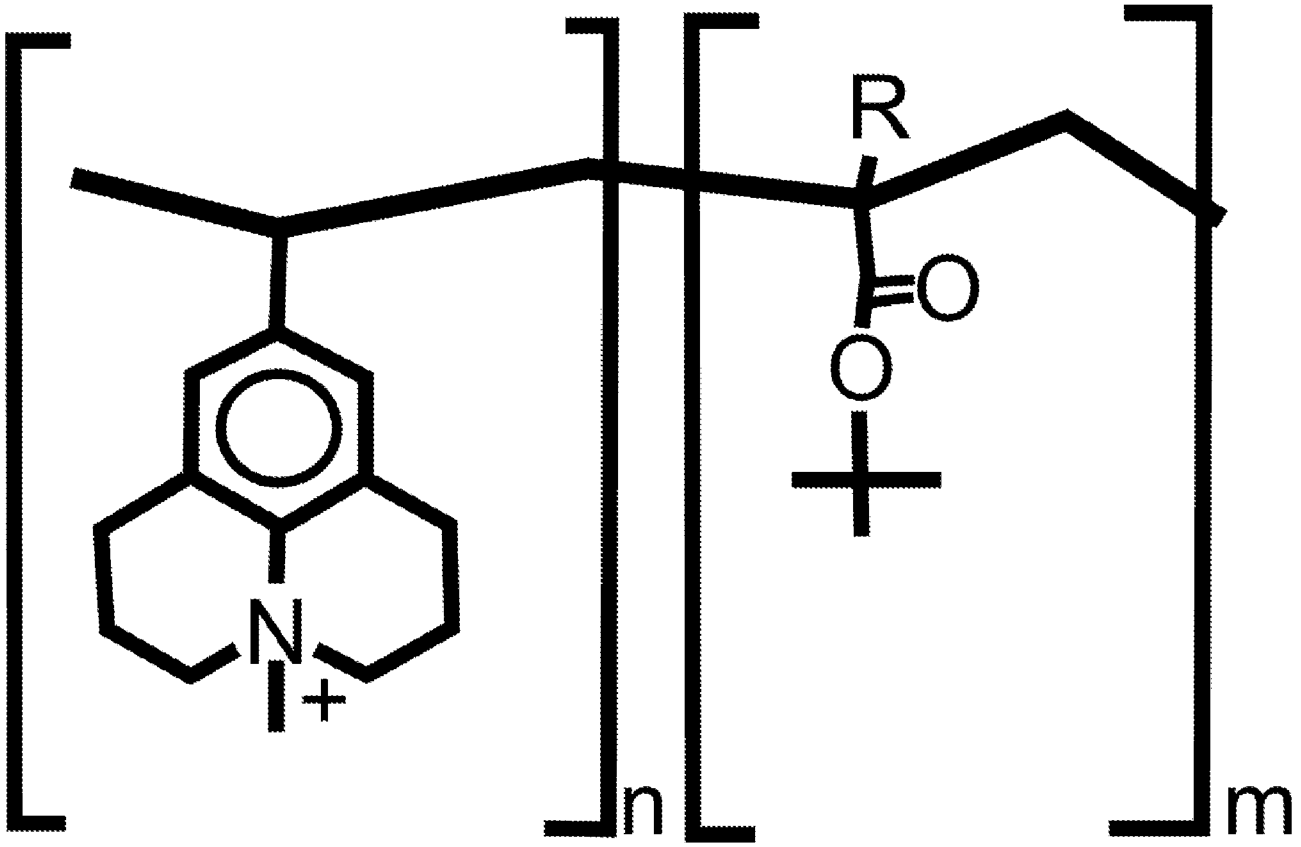
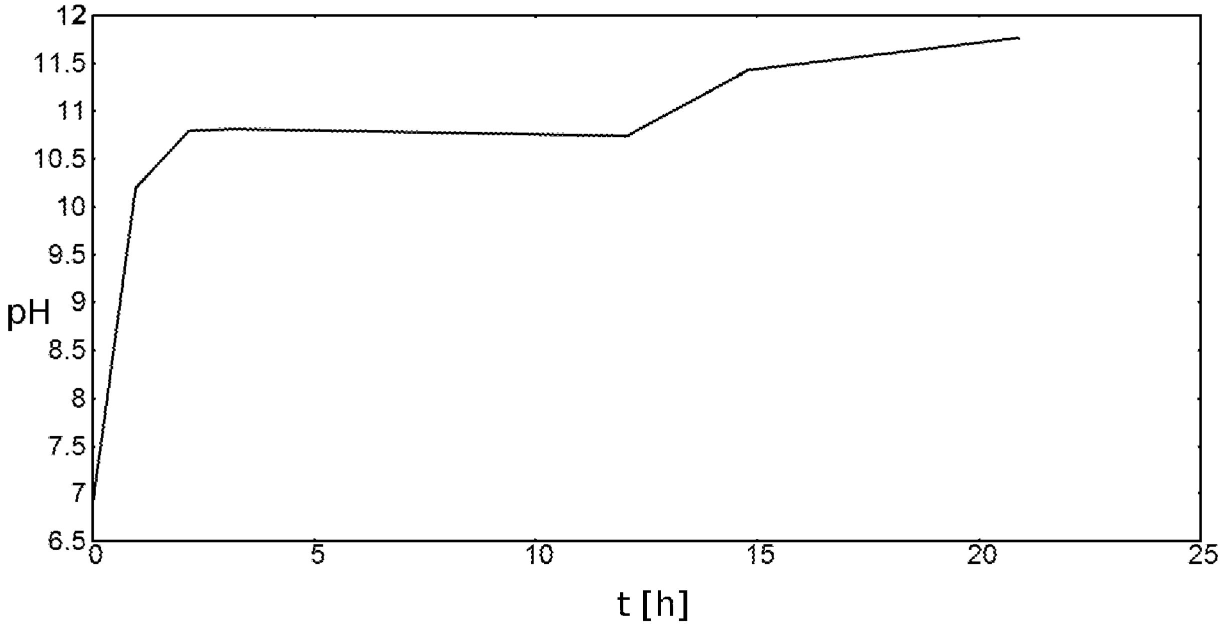


Fig. 11



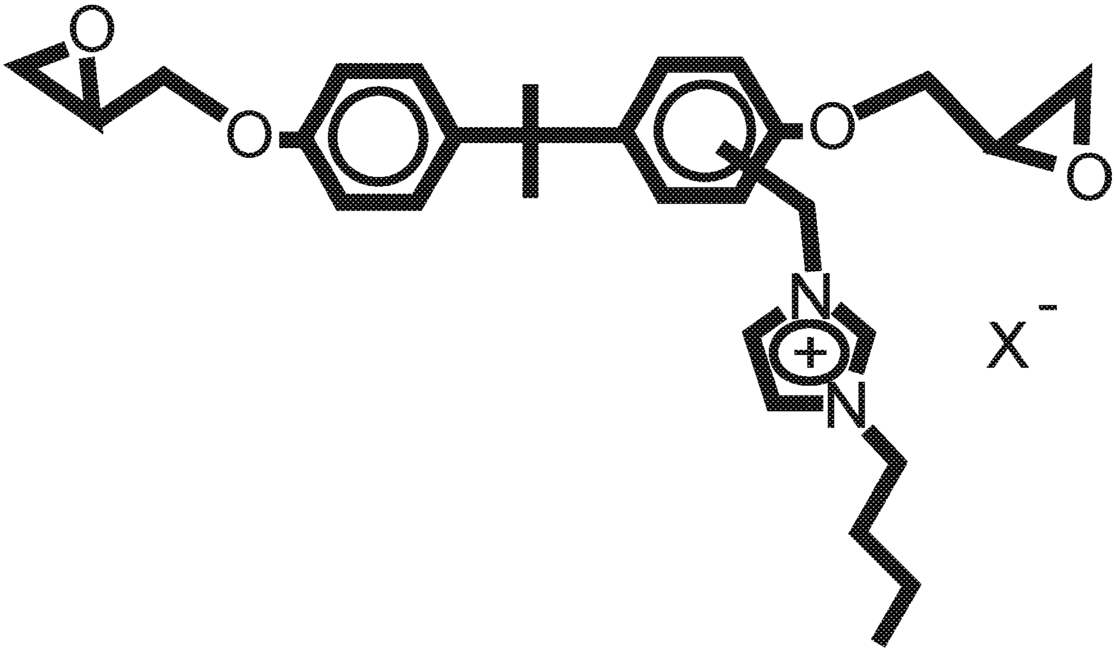


Fig. 12A

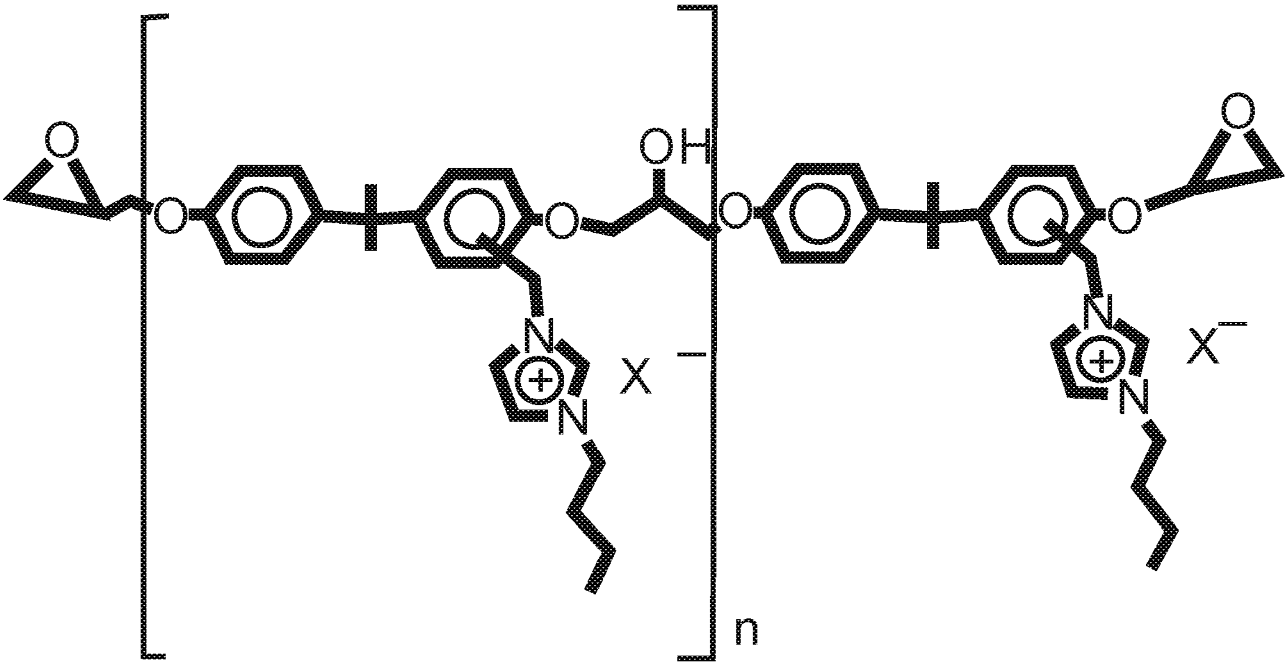


Fig. 12B

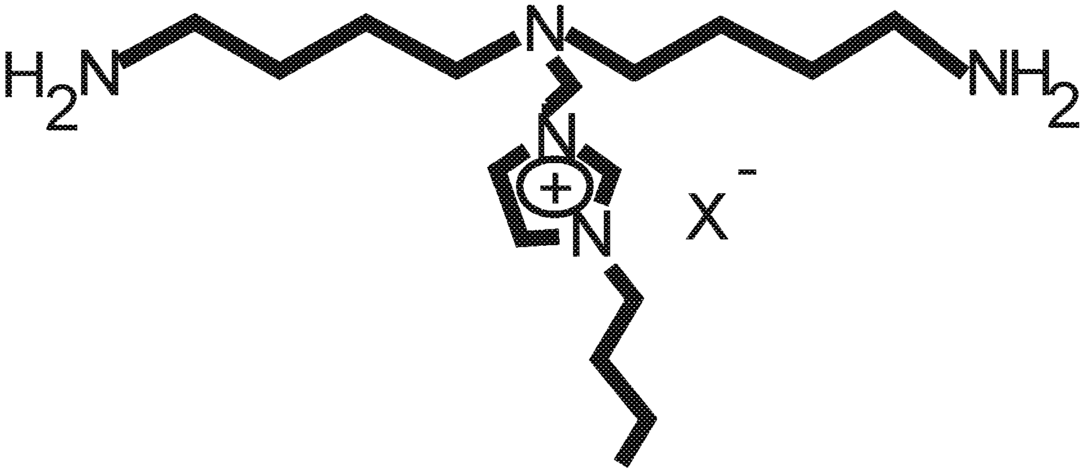
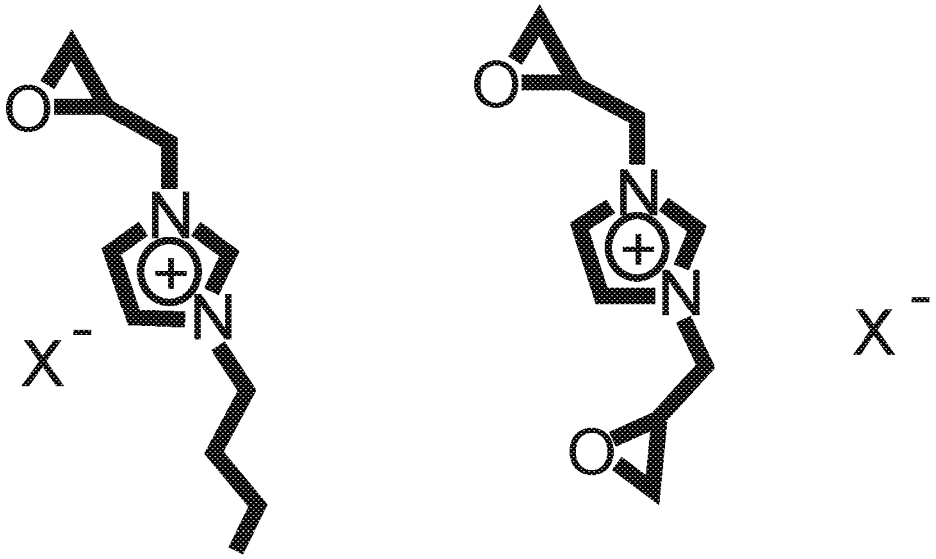


Fig. 13

Fig. 14



Title: Corrosion Inhibitors, Improved Paint and Corrosion Protection Coating

by

Friedrich W. Wieland

FIELD OF THE INVENTION

[0001] This invention relates to corrosion protection coatings. More specifically the invention relates to corrosion protection coatings for iron, steel and alloys comprising iron.
The invention also relates to the production of corrosion protection additives for priming coats.

BACKGROUND

[0002] Iron and steel are affected by corrosion and considerable costs are produced by corrosion of iron or steel components that are affected by rain and oxygen of the air.

[0003] Effective conventional corrosion protection coatings comprise materials such as cadmium, lead oxide Pb_3O_4, calcium plumbate or chromium(VI)-compounds such as strontium chromate or zinc chromate that are banned or restricted because of environmental protection or occupational safety reasons.

[0004] Other corrosion protection coatings comprise heavy metals such as zinc with reduced toxicity but are difficult to apply in the form of a key lacquer as many of the metal particles in a lacquer are not electrically connected to the base metal that shall be protected against corrosion so these paints are less effective than electroplated or hot-dip galvanized zinc layers. Since it is not possible to electroplate zinc or deposit a zinc layer by hot-dip galvanizing on a steel structure that is in use e.g. as a balustrade or other components e.g. of a building it is not possible to provide an effective corrosion protection to such parts comprising iron alloys.

[0005] Moreover many environmentally beneficial corrosion inhibitors and lacquers are much less effective than these corrosion protection coatings and iron or steel parts coated with such primers are readily affected by corrosion.

[0006] For the foregoing reasons, there is a need for an improved corrosion protection key lacquer that effectively inhibits corrosion and can be applied easily like a conventional paint.

SUMMARY

[0007] The present invention is directed to a corrosion protection priming coat that solves these problems.

[0008] It was found that inexpensive quaternary alkyl ammonium hydroxides and quaternary alkyl phosphonium hydroxides as well as anion-exchanging polymers with these functional groups effectively inhibit corrosion or iron alloys and steel. Oxydizing additives such as nitrites considerably improve the corrosion protecting properties of corrosion-inhibitors according to the present invention. As source of nitrite-ions quaternary alkylammonium nitrites or strong basic anion exchange resins in nitrite-form may be used according to another embodiment of the present invention. This corrosion-inhibiting action is improved by a sparingly-soluble salt such as calcium phosphate ($Ca_3(PO_4)_2$).

[0009] Without being bound to any theory it is assumed that the corrosion-inhibiting action of polymers and compositions according to the present invention relies on

1. the interception of corrosive anions such as chloride-ions by the polymer-layer,
2. the exchange of corrosive anions by corrosion-inhibiting anions such as nitrite-ions and alkaline hydroxide-anions by anion-exchange that are passivating iron alloys,
3. an additional corrosion-inhibiting effect of the quaternary Nitrogen-compounds such as quaternary ammonium-compounds that are also acting as a biocide,
4. the admixture of a sparingly water-soluble salt such as an alkaline earth phosphate yields a system for the slow release of alkaline hydroxide-anions (and nitrite-anions) in the presence of water with a low ion-content such as rainwater. The anion-exchange polymer removes the small trace amounts of phosphate-ions that are released by the slight partial dissolution of alkaline earth phosphate-particles in paint according to the present invention in contact with water and exchanges them against alkaline hydroxide-anions and nitrite-anions. The alkaline solution that is formed by the contact of water with the corrosion-inhibiting paint keeps the coated metal and even uncoated metal parts in a pH-range that allows passivation of said iron alloys (see Fig. 11) in order to prevent corrosion. So said metal part is even protected in uncoated areas near the coating by paint according to the present invention. This system for corrosion-protection is only active when said coating is affected by water or moisture. If said coating is used as a priming coat under an intact hydrophobic lacquer the system for slow release of passivating anions is not releasing any ions because corrosion-protection by the lacquer is still sufficient.

[0010] Moreover the corrosion-inhibiting composition is environmentally benign because polymers according to the present invention are insoluble in water and are not leached out into the environment by water.

[0011] It was also found that corrosion inhibitors comprising polymers with quaternary alkylammonium-groups or quaternary arylalkylammonium-groups in nitrite-form or other quaternary ammonium nitrites and sparingly soluble salts such as calcium phosphate ($Ca_3(PO_4)_2$) offer effective corrosion protection for iron, steel and other iron alloys when these compositions also comprise anion-exchange resin polymers (or copolymers) with quaternary ammonium groups in the form of a weak basic anion instead of the hydroxide-form. As weak basic anions anions of carboxylic acids such as acetate ions or benzoate ions may be used.

So a paint comprising these compounds or polymers offers an effective corrosion protection.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] These and the other features, aspects and advantages of the present invention will become better understood with regard to the following description, appended claims and accompanying drawings, where:

[0013] Fig. 1A shows the structure of quaternary ammonium hydroxide corrosion-inhibitors according to the first embodiment of the present invention;

[0014] Fig. 1B shows the structure of quaternary ammonium nitrite corrosion-inhibitors according to the first embodiment of the present invention;

[0015] Fig. 2A shows the structure of functional polymer corrosion-inhibitors with quaternary ammonium hydroxide groups obtained from polymerization of allyl amines according to the second embodiment of the present invention;

[0016] Fig. 2B shows the structure of functional polymer corrosion-inhibitors with quaternary ammonium nitrite groups obtained from polymerization of allyl amines according to the second embodiment of the present invention;

[0017] Fig. 3A shows the structure of functional polymer corrosion-inhibitors with quaternary ammonium hydroxide groups obtained from polymerization of vinylbenzyl chloride according to the second embodiment of the present invention;

[0018] Fig. 3B shows the structure of functional polymer corrosion-inhibitors with quaternary ammonium nitrite groups obtained from polymerization of vinylbenzyl chloride according to the second embodiment of the present invention;

[0019] Fig. 4A shows the structure of functional copolymer corrosion-inhibitors with quaternary ammonium hydroxide groups obtained from copolymerization of allyl amines with other monomers according to the third embodiment of the present invention;

[0020] Fig. 4B shows the structure of functional copolymer corrosion-inhibitors with quaternary ammonium hydroxide groups obtained from copolymerization of allyl amines with other monomers according to the third embodiment of the present invention;

[0021] Fig. 4C shows the structure of functional copolymer corrosion-inhibitors with quaternary ammonium hydroxide groups ($X^-=OH^-$) or ammonium nitrite ($X^-=NO_2^-$) groups obtained from copolymerization of diallyl amine with other monomers according to third embodiment of the present invention;

[0022] Fig. 5A shows the structure of functional copolymer corrosion-inhibitors with quaternary ammonium hydroxide groups obtained from copolymerization of vinylbenzyl chloride with other monomers according to the third embodiment of the present invention;

[0023] Fig. 5B shows the structure of functional copolymer corrosion-inhibitors with quaternary ammonium nitrite groups obtained from copolymerization of vinylbenzyl chloride with other monomers according to third embodiment of the present invention;

[0024] Fig. 6 shows the structure of another class of copolymers with quaternary alkylammonium-groups in acetate-form (or hydroxide-form) and in nitrite form as part of a corrosion-inihibiting composition according to an embodiment of the present invention;

[0025] Fig. 7 shows the structure of another copolymer with imidazolium groups in the acetate- (or hydroxide-) form and nitrite-form and t-butylacrylate (or t-butylmethacrylate) according to an other embodiment of the present invention;

[0026] Fig. 8 shows the structure of copolymers with pyridinium-groups in acetate-form (X^- =acetate or hydroxide-form $X^-=OH^-$) and nitrite-form ($X^-=NO_2^-$) and t-butyl acrylate (or t-butyl methacrylate) according to a further embodiment of the present invention;

[0027] Fig. 9 shows the structure of copolymers with triphenylphosphonium-groups (e.g. in the acetate-form (or hydroxide-form) and nitrite-form) and t-butyl acrylate (or t-butyl methacrylate) according to a further embodiment of the present invention;

[0028] Fig. 10 shows the structure of copolymers with julolidinium-groups (e.g. in the acetate-form (or hydroxide-form) and nitrite-form) and t-butyl acrylate (or t-butyl methacrylate) according to a further embodiment of the present invention; and

[0029] Fig. 11 shows the change of pH produced by a corrosion-inhibiting composition of an anion-exchange polymer with quaternary ammonium groups in hydroxide form further comprising strontium phosphate according to an embodiment of the present invention.

[0030] Fig. 12A and Fig. 12B show an epoxy-resin with imidazolium-functional groups in nitrate- ($X^-=NO_3^-$) or in form of basic anions X^- such as in acetate-form ($X^-=CH_3COO^-$);

[0031] Fig. 13 shows a curing agent with an imidazolium-functional group in nitrate-form ($X^-=NO_3^-$) or in form of basic anions X^- such as in acetate-form ($X^-=CH_3COO^-$); and

[0032] Fig. 14 shows a reactive component (a reactive diluent) with imidazolium-functional groups in nitrate- ($X^-=NO_3^-$) or in form of basic anions X^- such as in acetate-form ($X^-=CH_3COO^-$).

[0033] These and the other features, aspects and advantages of the present invention are better understood with respect to the following description and appended claims.

DETAILED DESCRIPTION

[0034] An effective corrosion protection is crucial for the useability of components comprising iron alloys that are affected by corrosion. Many well known corrosion protecting coatings comprise toxic heavy metals such as cadmium, lead oxide (minium, Pb_3O_4), calcium plumbate or carcinogenic chromium(VI)-compounds such as strontium chromate or zinc chromate that are banned or restricted because of environmental protection or occupational safety reasons e.g. in the European Union RoHS (2002/95/EC) and REACH-regulations (1907/2006).

[0035] Other corrosion inhibitors comprise metals such as zinc that are applicable by hot-dip plating or electroplating only during manufacture but not when installed as a building. For example it is nearly impossible to deposit such a layer on iron parts of a bridge. Paints comprising zinc are less effective than layers of metallic zinc because only a fraction of the zinc particles in a paint has electrical contact to the base metal, i.e. the iron.

[0036] Other corrosion inhibitors such as hydrazine, hydrazinium salts or ascorbic acid that are used for example in water of a cooling systems are also incompatible to the use on an iron part or in a paint because they are highly water soluble.

[0037] However it was found that polymers comprising quaternary ammonium alkyl ammonium hydroxides and quaternary alkyl phosphonium hydroxides as well as polymers with these functional groups effectively inhibit corrosion or iron alloys and steel. Paints comprising these quaternary ammonium alkyl ammonium hydroxides or quaternary alkyl phosphonium hydroxides or polymers obtainable by polymerization of monomers with at least one quaternary alkyl ammonium hydroxide group or at least one quaternary alkyl phosphonium hydroxide groups effectively protect iron and iron alloys against corrosion. This is especially true if they are combined with sparingly soluble salts such as alkaline earth phosphates.

[0038] Within this patent application quaternary arylalkylammonium hydroxides shall be treated as equivalent to quaternary alkylammonium hydroxides. Moreover quaternary alkyl phosphonium hydroxide groups or tertiary alkyl sulphonium hydroxide groups shall be treated as equivalent to quaternary alkylammonium hydroxide groups. Quaternary arylalkyl phosphonium hydroxide groups shall be also treated equivalent to quaternary alkylammonium hydroxide groups. This applies to quaternary ammonium or quaternary phosphonium salts and all monomers as well es polymers with quaternary alkylphosphonium hydroxide groups that shall be also treated as equivalent to polymers with quaternary alkylammonium hydroxide groups.

[0039] The presence of nitrite ions strongly improves the corrosion protecting properties.

[0040] According to the first embodiment of the invention paints comprising at least one quaternary ammonium alkyl ammonium hydroxide and an quaternary alkylammonium nitrite as shown in Fig. 1A and Fig. 1B, respectively, are effectively inhibiting corrosion. The addition of quaternary alkylammonium nitrites or nitrite ions strongly enhance the anti-corrosive properties. According to the second embodiment of the invention paints comprising at least one polymer obtainable by polymerization of monomers with at least one quaternary alkyl ammonium hydroxide group as shown in Fig. 2A and Fig. 3A are more preferred. Such polymers may be used in a form of a fine dispersion of small polymer particles obtainable by grinding polymer beads by milling.
For such polymers the use of an additional source of nitrite-ions such as a strong basic anion exchange polymer with quaternary alkylammonium groups as shown in Fig 2B and Fig. 3B in the nitrite-form the anti-corrosive action is strongly improved, too.

[0041] However paints comprising only anion-exchange-resins in the nitrite-form with tribasic Calcium phosphate only a short corrosion-protecting action was observed so the use of a combination with anion-exchange resins in the hydroxide-form is preferred.

[0042] Preferred corrosion-protecting additives according to the present invention comprise a molar ratio of strong basic anion-exchange resins in the nitrite-form to strong basic anion-exchange resins in the hydroxide-form between 20:1 to 1:20. Preferred is a molar ratio between 10:1 to 1:10. A molar ratio of 5:1 to 1:5 is most preferred. A molar ratio of 1:1 to 3:1 is optimum (i.e. with a slight molar excess of anion-exchange resin in nitrite form). Additives with a molar ratio of anion-exchange resin in nitrite-form to the hydroxide-form of more than 20:1 are not very effective for long-term protection while additives with a molar ratio of over 1:20 offer no sufficient corrosion protection at all.

[0043] Paints according to this embodiment of the present invention are especially environmentally beneficial because the anion-exchange polymers are insoluble in water. There is no danger that an organic component that would be detrimental for the environment is leeched out.

[0044] Paints comprising a solution of a polymer obtainable by polymerization of monomers with at least one quaternary alkyl ammonium hydroxide group and such a copolymer in the nitrite-form in a suitable solvent as shown in Fig. 4A/Fig. 4B/Fig. 4C and Fig. 5A/Fig. 5B are most preferred. In such a form it is possible to protect the whole surface of a part comprising iron.

[0045] Those quaternary alkyl ammonium salts and polymers obtainable by polymerization of monomers with at least one quaternary alkyl ammonium hydroxide group are environmentally benign. Therefore, paints comprising these corrosion inhibitors may replace conventional corrosion protecting paints that are affected by recent EC regulations.

[0046] Quaternary alkylammonium hydroxides such as Tetrabutylammonium hydroxide, Tetramethylammonium hydroxide or Benzyltrialkylammonium hydroxides may be used together with tetrabutylammonium nitrites, tetramethylammonium nitrite or benzyltrialkylammonium nitrite or the equivalent nitrates as preferred corrosion inhibitors according to the first embodiment of the present invention although other quaternary alkylammonium hydroxides or quaternary alkylphosphonium hydroxides may be used as corrosion inhibitors, too.

[0047] Paints comprising a dispersion of milled chloromethylated polystyrene with quaternary alkylammonium hydroxide groups or alkylammonium nitrite groups as shown in Fig. 2A/Fig. 2B and Fig. 3A/Fig. 3B such as strong basic anion exchange resins commonly sold under the trademark such as “DOWEX MONOSPHERE 550A UPW”(RTM) by Dow Chemical Company, Midland, MI, USA or “AMBERLITE IRA 402” (RTM) or “AMBERSEP 900” (RTM) by Rohm&Haas Company, Philadelphia, PA, USA according to the second embodiment of the present invention are more preferred.

[0048] A maximum particle size of the anion exchanger particles of less than 250 µm is preferred, a particle size of less than 30 µm is more preferred and a particle size of less than 10 µm is most preferred. A particle size of less than 3 µm is optimum. Particles with a diameter of larger than 250 µm tend to produce uneven coatings.

[0049] Corrosion-protecting paints according to the second and third embodiment of the present invention comprise at least one polymer comprising quaternary alkylammonium hydroxide groups. Moreover such anion exchange polymers in the hydroxide-form may be used that are partially converted to the nitrite-form. A composition comprising several different polymers may be used.

[0050] The use of a polymer with quaternary alkylammonium hydroxide-groups and a polymer with quaternary alkylammonium nitrite-groups according to the third embodiment of the invention that is soluble in a solvent is most preferred. Polymers that are soluble in organic solvents such as acetone, toluene, xylene, tetrahydrofurane, dimethylsulfoxide, dimethylformamide or alcohols, ethers or a mixture thereof are preferred although polymers that are soluble in other solvents such as N-methylpyrrolidinone or a mixture thereof may be useable, too.

[0051] Instead of the above copolymers that harden by evaporation of a solvent reactive copolymers with additional epoxy groups that require a chemical curing reaction may be also used.

[0052] According to a further embodiment of the invention such polymers may comprise reactive functional groups that allow hardening by polymerization, polyaddition or polycondensation such as expoxy groups and amino groups. Such reactive groups should not react with hydroxide ions and nitrite ions. Polymers comprising reactive hardening groups may be soluble in water if the condensation product is insoluble in water.

[0053] Copolymers according to the third embodiment of the invention comprising quaternary alkylammonium groups in hydroxide and nitrite form may be further manufactured by a polymerization reaction of a monomer with quaternary alkylammonium group such as diallyldialkylammonium salts shown in Fig. 4C or quaternary arylalkylammonium-group as shown in Fig.5A or Fig. 5B and at least one base-resistant monomer such as styrene, 1,3-butadiene. A copolymer produced by polymerization with 1,3-butadiene in order to yield a flexible resin is preferred. A block copolymer is also preferred.

[0054] Moreover anti-corrosive compositions according to the third embodiment of the invention may be further comprising alkali-resistant polymers such as polyolefines such as polystyrene, polystyrene-copolymers such as polystyrene-butadiene-copolymers such as SEBS or SBS, polyethylene-copolymers such as e.g. poly(vinylalcohol-co-ethylene), although other alkali-resistant polymers such as epoxy-resins or polyurethane-resins or polyacrylamide polymers may be suitable, too.

[0055] Moreover the molar ratio of polymers with quaternary alkylammonium hydroxide groups and quaternary alkylammonium nitrite groups to the total molar amount of polymers in coatings according to the second embodiment of the present invention is appropriately chosen. A weight capacity of the polymer composition of 10^{-3} meq/g to 7.1 meq/g is preferred for commercial anion-exchange-resins although larger weight capacities may be useable, too. A weight capacity of 10^{-2} meq/g to 1.2 meq/g is more preferred, a weight capacity of 0.1 meq/g to 1.2 meq/g is most preferred. Compositions with weight capacities of less than 10^{-3} meq/g do not inhibit corrosion over longer periods while production of compositions with a weight capacity of over 7.1 meq/g may be difficult.

[0056] Functional polymers obtainable by polymerization and subsequent alkylation of allylamine and conversion to the free hydroxide or by polymerization of quaternary allylammonium salts and subsequent conversion to the hydroxide form as shown in Fig. 4A according to the third embodiment of the present invention are preferred. Alternatively such functional polymers as shown in Fig. 5A/Fig. 5B are obtainable by the reaction of a polymer with an alkylhalogenide-group such as poly(vinylbenzyl chloride) with an amine such as trimethylamine solution. Copolymers obtainable by copolymerization of allylamine with a monomer that is compatible to strong bases such as an alkene such as styrene and subsequent alkylation and conversion to a free quaternary ammonium hydroxide that have limited or no solubility in water are optimum. These copolymers may be also produced by copolymerization of quaternary allylalkylammonium salts with monomers such as styrene and subsequent conversion to the hydroxide form. Similar functional copolymers are obtainable by radicalic copolymerization of vinylbenzyl chloride with alkali-resistant alkenes such as styrene and and subsequent reaction with trimethylamine solution and conversion to free hydroxide form.

[0057] Corrosion-protecting paints according to the present invention comprise at least one copolymer comprising quaternary alkylammonium hydroxide groups. A composition comprising several different copolymers may be used.

[0058] In order to ensure compatibility of the above prime-coatings according to the present invention with subsequent paint layers an intermediate paint layer or a topcoat that is resistant to strong bases such as a paint based on polyolefines such as polystyrene or alkali-resistant epoxy resins that are cured with amines is preferred although other paints such as polyurethane-based paints may be useable, too.

[0059] Most preferred are paints that comprise corrosion inhibitors according to the present invention and an alkali-resistant paint (comprising at least one alkali-resistant polymer system such as expoxy resins cured with amines that may further comprise at least one pigment, at least one plasticizer and at least one UV stabilizer).

[0060] The above corrosion-protecting paints according to the present invention may be also applied by powder coating using thermoplastic or thermosetting polymers.

[0061] Preferred catalysts for the production of functional polymers according to the present invention are azo compounds such as azodiisobutyronitrile or peroxides such as dibenzoylperoxide, t-butylhydroperoxide, alkali persulfates or hydrogen peroxide. More preferred are azo compounds such as 2,2'-azobis(methyl 2-methylpropionate).

[0062] Preferred quaternary alkylammonium hydroxides according to the first embodiment of the present invention as shown in Fig. 1A have substituents R_1-R_3 of C_1-C_8 alkyl. R_1 may be also chosen as an aryl system such as benzene, substituted benzene, and naphthalene. More preferred are substituents R_1-R_3 chosen as C_1-C_4 alkyl groups. Most preferred are symmetrically substituted quaternary ammonium salts with $R_1=R_2=R_3$ chosen as C_1-C_4 alkyl although other substituents such as R_1=hydroxyethyl might be useable, too.

[0063] Preferred polymers for coating compositions according to the second embodiment of the present invention comprise polymers with quaternary alkylammonium hydroxide groups such as polymers that are commercially available as strong basic anion exchange resins or soluble anion exchangers as shown in Fig. 2A and Fig. 3A.

[0064] Preferred quaternary alkylammonium hydroxide groups of polymers according to the third embodiment of the present invention as shown in Fig. 4A and Fig. 5A also have alkyl groups R_1-R_3 of C_1-C_8 alkyl . R_1 may be also chosen as an aryl system such as benzene, substituted benzene, and naphthalene. More preferred are lower alkyl groups R_1-R_3 of C_1-C_4.alkyl. R_4-R_7 depend on the other monomer of the copolymer. For example R_4-R_6 may be chosen as hydrogen and R_7 may be benzene for a styrene monomer of the copolymer. A preferred ratio of monomers is chosen that the obtained copolymer is soluble in an organic solvents such as toluene, acetone or butylacetate and insoluble in water. Moreover a suitable molar ratio of monomers with quaternary alkylammonium hydroxide groups ($x(M\text{-}N^+OH^-)=n(M\text{-}N^+OH^-)/n_{ges.}$) , respectively quarternary Alkylammoniumnitrite-groups or Alkylammoniumnitrate-groups, to the total molar amount of monomers of the copolymers is chosen. A weight capacity of the resulting copolymers comprising quaternary ammonium groups of 10^{-5} meq/g to 1 meq/g is preferred although larger weight capacities may be useable, too. A weight capacity of 10^{-3} meq/g to 1.0 meq/g is preferred, a weight capacity of 10^{-2} meq/g to 0.5 meq/g is more preferred. A weight capacity of 0.1 meq/g to 0.5 meq/g is most preferred. The same total weight capacities are selected if a composition of several of such copolymers or a composition of a copolymer and a quaternary ammonium hydroxide-anion exchange resin is used. Weight capacities of lower than 10^{-3} meq/g are less effective for inhibiting corrosion over long periods while copolymers with weight capacities of over 1.0 meq/g are more difficult to produce.

[0065] Preferred corrosion-inhibiting compositions according to the third embodiment of the present invention comprise copolymers with a molar ratio of polymers with quaternary ammonium groups in nitrite-form $x(M\text{-}N^+NO_2^-)$ to copolymers with quaternary ammonium groups in hydroxide-form $x(M\text{-}N^+OH^-)$ based on those functional groups between $x(M\text{-}N^+NO_2^-)$: $x(M\text{-}N^+OH^-)$ of 20:1 to 1:20 although ratios of more than 20:1 or less than 1:20 such as 100:1 or 1:100 may be useable, too. More preferred is a molar ratio of 10:1 to 1:10, most preferred 5:1 to 1:5. A molar ratio of 1:1 to 3:1 is optimum with a slight excess of polymers in nitrite form. Copolymers with a molar ratio above 20:1 show only a corrosion-inhibiting effect for a short time period while a composition with a molar ratio below 1:20 show no sufficient corrosion-inhibiting effect. Of course a copolymer in hydroxide-form that is partially converted to the nitrite-form with the above molar ratios may be used, too.

[0066] When other non-functionalized polymers are present in said corrosion-protecting paint or coating the weight capacity of the above copolymers have to be increased so that the weight capacity of the total composition is in the ranges specified above. For example if a non-functionalized polymer is added that the paint comprises 30 mole-% copolymers and 70 mole-%

non-functionalized polymer the weight capacity of the above copolymers has to be increased by a factor of three, i.e. for example a range of $3\ 10^{-3}$ meq/g to 3 meq/g would be preferred and a range of 0.3 meq/g to 1.5 meq/g would be most preferred.

[0067] The second monomer of the above monomer is chosen as monomer that yields an alkali-resistant polymer. Preferred monomers are alkenes such as styrene, unsubstituted or substituted ethylene, propylene, tetrafluoroethylene, hexafluoropropylene or vinylidene fluoride, vinyl chloride or methylpentene although other monomers may be useable, too.

[0068] The above copolymers may be combined with other alkali-resistant polymers and alkali resistant pigments such as titanium dioxide or phthalocyanines in a paint or as a component of a priming coat.

[0069] According to a further embodiment of the present invention a corrosion-protecting paint comprising anion exchange polymers with groups $-NR_3^+ X^{q-}$ (such as those in the hydroxide-form, i.e. $X^- = OH^-$ or the nitrite-form $X^- = NO_2^-$, respectively) is further comprising at least one sparingly water-soluble salt Me_nY_m with a different anion Y^{z-} of a higher retention strength referring to said anion exchangers. Within this patent application the term “auxiliary corrosion-inhibitors” is used for said sparingly soluble salts Me_nY_m.

[0070] In a preferred embodiment of the invention the anion X^{q-} as well as the anion Y^{z-} are both acting as corrosion inhibitors for iron alloys. The use of a strong basic anion exchange resin or copolymer comprising strong basic anion exchange groups in the hydroxide-form (i.e. anions $X^{q-} = OH^-$) and nitrite form ($X^{q-} = NO_2^-$) with anions such as phosphate (i.e. $Y^{z-} = PO_4^{3-}$) is preferred. The use of anion exchange resins in other forms with corrosion inhibiting anions such as anion exchange resins in the nitrite or nitrate form or hydrogen phosphate form or acetate form (i.e. $X^{q-} = NO_2^-, NO_3^-, HPO_4^{2-}$) and sparingly soluble salts such as chromates (i.e. $Y^{z-} = CrO_4^{2-}$), citrates or other trivalent organic acids such as aconitic acid or titanates or molybdates may be usable too. The use of anion-exchange resins in acetate-form is more preferred.

[0071] According to a more preferred embodiment of the invention an earth alkali salt is used as sparingly water-soluble salt although other metal salts such as transition metal salts may be useable, too. Tribasic calcium phosphate $Ca_3(PO_4)_2$ and tribasic barium phosphate $Ba_3(PO_4)_2$ and zinc phosphate $Zn_3(PO_4)_2$ are more preferred although other metal phosphates or hydrogen phosphates may be usable, too. Tribasic strontium phosphate $Sr_3(PO_4)_2$ is most preferred.

[0072] Without being bound to any theory it is assumed that the sparingly water-soluble salt slowly dissolves when water is in contact to the salt particles in the paint. It is assumed that the anions Y^{z-} are slowly exchanged against the anions X^{q-} of the anion exchange resin (or copolymer with anion exchange functionalities) and that the resulting eluat comprising anions X^{q-} inhibits corrosion on the metal surface. With a sufficiently low solubility ($c(Y^{z-}) \approx 10^{-7}$ mole/l) this process can be delayed to long periods in order to maintain a corrosion-inhibiting environmental conditions over long periods by retarded release of corrosion-inhibiting anions X^{q-}.

[0073] Equilibrium concentrations of anions Y^{z-} of $c(Y^{z-}) \approx 10^{-5}$ mole/l to 10^{-7} mole/l for pure salt in pure water are preferred, concentrations of $c(Y^{z-}) \approx 10^{-6}$ mole/l to 10^{-7} mole/l are more preferred. For metal salts with metal cations Me^{2+} such as alkaline earth salts (z=2) the preferred values correspond to solubility products $L=K_{sp}$ of $L=8/27\ c(Y^{z-})^5$ of about $3\ 10^{-26}$ $(\text{mole/l})^5$ to $3\ 10^{-36}$ $(\text{mole/l})^5$. Equilibrium concentrations $c(Y^{z-})$ larger than 10^{-5} mole/l and corresponding solubility products of over $3\ 10^{-26}$ $(\text{mole/l})^5$ yield a composition that rapidly produce a too large concentration of inhibiting anions X^{q-} while equilibrium concentrations $c(Y^{z-})$ below 10^{-7} mole/l and corresponding solubility products below $3\ 10^{-36}$ $(\text{mole/l})^5$ retard the delivery of inhibiting anions X^{q-} too much.

[0074] A ratio of the molar amount n per gram of anion exchange resin of the amount of the auxiliary corrosion-inhibitors to the weight capacity w of the anion exchange resin of n/w=0.01 to 2/3 is preferred for an alkaline earth phosphate $Me_3(PO_4)_2$, a ratio of 0.1 to 0.5 is more preferred and a ratio of 0.1 to 0.25 is most preferred. For other salts with anions Y^{z-} of a salt Me_nY_m the preferred ratio n/w is 0.01 to 1/(m z), the more preferred ratio is 0.1 to 1/(m z). A ratio n/w of over 1/(m z) is of little value as it would yield only the small equilibrium concentration of corrosion inhibiting anions Y^{z-} while a ratio n/w of less than 0.01 would yield only retarded release of corrosion inhibiting anions X^{q-} over a short period of time.

[0075] Instead of alkaline earth phosphates such as calcium phosphate ($Ca_3(PO_4)_2$) , strontium phosphate, barium phosphate, magnesium phosphate lithium phosphate and other sparingly water-soluble alkaline earth salts such as carbonates, chromates, molybdates or oxalates with a charge of ≥ 2 may be used, too. Alkaline earth phosphates are however preferred.

[0076] Paints or prime-coatings according to the present invention may be further comprising additional corrosion inhibitors such as zinc particles. Paints or prime-coatings according to the present invention may be further comprising UV-stabilizers and plasticizers.

[0077] Paints or prime-coatings according to the present invention may be also used on iron alloys that are coated by electroplating or hot-dip galvanized with a zinc layer although an uncoated metal sheet is more preferred.

[0078] It was also found that anion-exchange resins in hydroxide-form or in the form of a weakly basic anion in addition to an anion-exchange resin in nitrite-form may be used in a corrosion-inhibiting composion further comprising a sparingly soluble salt such as an earth alkaline phosphate in order to yield an effective corrosion inhibition.

[0079] As weakly basic anions in anion-exchanging resins according to the present invention anions of carboxylic acids are preferred.

[0080] More preferred are anions of carboxylic acids that form readily water-soluble salts with the cation of the sparingly soluble salt of the composition, i.e. calcium-, strontium- or Zinc-ions.

[0081] Most preferred are anions of weak carboxylic acids with pK_s that ist as large as possible (i.e. a small value of K_s), most preferred above 4.0. A $pK_s > 4.7$ is optimum.

[0082] More preferred are also anions of aliphatic and aromatic dicarboxylic acids such as azelaic acid and phthalate-anions, althought anions of other dicarboxylic acids may be suitable, too.
The dicarboxylic acids may be branched or linear, may comprise double bonds, triple bonds, nitro-groups or cyano-groups.

[0083] Most preferred are anions of weak dicarboxylic acids (pKs>4.0 for the second carboxylic group) that form readily water-soluble salts with the cation of the sparingly soluble salt of the composition, i.e. calcium-, strontium-, barium-, magnesium-, lithium- or zinc-ions such as tartrate-anions, maleate-anions, fumarate-anions, or phthalate-anions.

[0084] Anions of tricarboxylic acids that form readily water-soluble salts with earth-alkaline cations or zinc cations are also preferred if they are eluable by anions of the sparingly soluble salt (such as phosphate anions).

[0085] Anions of tetracarboxylic acids are usually not sufficiently eluable and are less suitable although some anions of such acids may be useable, too.

[0086] More preferred are anions of monocarboxylic acids because of good eluability, good solubility in aqueous solutions and because of the favorable pKs-value of the carboxylic acid (except for formic acid) i.e. quite basic carboxylate salts.

[0087] Most preferred are short-chained monocarboxylic acid anions of C_1-C_5-carboxylic acids (formiate- to valeriate-anions) such as acetate-ions or propionate-anions and anions of aromatic monocarboxylic acids such as benzoate-ions although carboxylic acids with a longer chain may be useable, too. The above anions of carboxylic acids may be branched or unbranched and may have substitutents such as hydroxyl-groups or halogens. The above carboxylic anions may comprise double bonds or triple bonds such as cinnamic acid.

[0088] The use of copolymers with quaternary alkylammonium-groups, arylalkylammonium-groups, positively charged heterocyclic groups such as imidazolium-groups or pyridinium-groups or phosphonium-groups or sulfonium-groups in acetate-form is optimum.

[0089] The use of polymers with anion-exchange-groups in the form of other basic anions such as carbonate-ions, hydrogenphosphate-ions, phosphate-ions, silicate-ions, hydrogencarbonate-ions,

borate-ions is also preferred according to another embodiment of the present invention. Polymers in the form of anions such as molybdate-ions, tungstate-ions or vanadate-ions are also preferred although other anions such as chromate-anions may be useable, too.
More preferred is the use of hydrogencarbonate-ionen, hydrogenphosphate-ionen hydrogenborate-anions and silicate-ions such as $Si_3O_7^{2-}$.

[0090] According to a further preferred embodiment of the present invention polymers in nitrite-form may be completely or partially replaced by polymers in nitrate-form that are more stable. Polymers in the form of other oxydizing anions such as permanganate- or manganate-anions may be suitable, too.

[0091] Preferred corrosion-inhibiting compositions according to the present invention comprise a molar ratio of polymers with quaternary ammonium groups (or equivalent phosphonium- or imidazolium-groups) in nitrite-form to polymers with quaternary ammonium groups (or equivalent phosphonium- or imidazolium-groups) in hydroxide- or acetate-form based on these functional groups between 20:1 and 1:20. More preferred is a molar ratio between 10:1 and 1:10, most preferred a molar ratio between 5:1 and 1:5 and a molar ratio of 1:1 to 3:1 with a slight excess of polymer in nitrite-form is optimum. Compositions with a molar ratio above 20:1 show a corrosion-inhibiting properties for only a short-time while compositions with a molar ratio below 1:20 show no sufficient corrosion-inhibiting action although molar ratios of 100:1 or 1:100 may show some corrosion-inhibiting action for a short time.

[0092] Basic anions (e.g. hydroxide-ions, acetate-ions) and nitrite-Ions may be bound to one anion-exchange-polymer-resin instead of two resins according to a preferred further embodiment of the present invention.

[0093] Moreover corrosion-inhibiting compositions according to an embodiment of the present invention further comprise at least one sparingly soluble salt such as an earth-alkaline phosphate such as tribasic calcium phosphate in a molar ratio of 1/100 to 2.00 of the molar amount of the above polymers in nitrite-form and hydroxide-form or acetate-form based on these functional groups of said polymers. Preferred is a molar ratio of 1/10 to 0.9, for earth-alkaline phosphates more preferred is a molar ratio of 0.1-0.5 and most preferred is a molar ratio of 0.1-0.25 based on the functional groups of the above polymers and a ratio of 1/(m z) is optimum for an anion Y^{z-} of a sparingly soluble salt Me_nY_m. Values lower than 0.01 would reduce corrosion-inhibiting action against rain water that comprises few anions while higher molar rations than 0.5 would offer little or no advantage.

[0094] Preferred copolymers with anion-exchange groups are copolymers (or terpolymers) of vinylbenzyltrimethylammonium chloride and methacrylates, acrylates and styrene, copolymers of diallyldimethylammonium chloride with acrylates, methacrylates or styrene or substituted or unsubstituted 1-vinyl-3-alkyl-imidazolium with acrylates, methacrylates or styrene with a glass transition temperature T_g between 30°C and 100°C. More preferred are copolymers with T_g between 40°C and 80°C. Also preferred are copolymers (or terpolymers) of acrylamidopropyltrimethylammonium chloride (and analogous esters comprising a quaternary ammonium-group, see Fig. 6) comprising a quaternary ammonium-group bound via a bridge (BR in Fig. 6) with acrylates, methacrylates or styrene.

[0095] According to an embodiment of the present invention t-butylesters of acrylic acid (t-butylacrylate, d.h. R_5 = t-butyl, $R_3 = H$) or methacrylic acid (t-butylmethacrylate, i.e. R_5 = t-butyl, $R_3 = CH_3$) and styrene are most preferred as monomers for alkali-resistant copolymers as these copolymers do not react with alkaline solutions up to pH<12. Those copolymers offer good resistance against alkaline solutions and alkaline hydroxides as corrosion products of metals so lacquer based on these copolymers is not attacked by such alkaline solutions. Also preferred as monomers is methylmethacrylate (MMA) for solutions of pH<11.

[0096] According to a further embodiment of the present invention anion-exchange polymers (or copolymers or terpolymers) comprising imidazolium-groups, pyridinium-groups, pyrrolium-groups or quaternary phosphonium-groups are preferred although other positively charged quaternary groups of heterocyclic compounds and trimethyldiamine (DABCO) or quinuclidinge or sulfonium-groups, benzimidazolium-groups or triazolium-groups may be suitable, too.

[0097] A molar fraction of monomers with positively charged functional groups such as quaternary ammonium-groups, imidazolium-groups or phosphonium-groups of all monomers (including monomers without charged groups) for manufacture of anion-exchanging polymers according to the present invention between 0.01 mole-% and 30 mole-% is preferred. A molar fraction between 1 mole-% and 20 mole-% is more preferred. A molar fraction of functionalized monomers between 5 mole-% and 10 mole-% is most preferred. Polymers with a molar fraction below 0.01 mole-% offer little corrosion-inhibiting action while polymers with a molar fraction above 30 mole-% would be water-soluble and would be removed by any water and rain.

[0098] According to a further embodiment of the present invention said corrosion-inhibiting compositions comprising said functional polymers may be further comprising inert polymers such as polystyrene or poly(t-butylacrylate).

[0099] Although the formation of nitrosamines from quaternary ammoniumions and nitrite in sufficiently alkaline solution is nearly ruled out even in ppt-traces n-alkyl-imidazolium-groups, pyridinium-groups, pyrrolium-groups or quaternary phosphonium-groups offer the advantage that even after oxidative cleavage of one or more n-alkyl-groups (or P-alkyl-groups) in acidic solutions do not form nitrosamines. Most preferred are alkali-resistant 1-alkyl-2-alkyl-3-alkyl-imidazolium-groups such as 1-alkyl-2-isopropyl-3-alkylimidazolium-groups or 1-alkyl-2-methyl-3-alkyl-imidazolium-groups, tris(2,4,6-trialkoxyphenyl)benzylphosphonium-groups such as tris(2,4,6-trimethoxyphenyl)benzylphosphonium-groups (see Fig. 4, R = CH_3O-), tetrabenzylphosphonium-groups, which do not form nitrosamines although other alkali-resistant quaternary phosphonium-groups with substituents that are resistant against oxidizing substances may be suitable, too.

[0100] More preferred are imidazolium-derivatives as positively charged anion-exchange groups that are alkylated on both heterocyclic nitrogen-atoms (see Fig. 2) with an alkyl-group or benzyl-group although other substituents may be suitable, too. These groups do not form stable nitrosamines after oxidative cleavage of an N-alkyl-group if the substituents are properly chosen. Moreover the educts are inexpensive and available in large amounts for industrial production.

[0101] Most preferred are rather alkali-resistant imidazolium-groups obtainable from 2-alkylimidazole such as 2-isopropyl-1-methyl-3-benzylimidazolium-groups. As alkyl-substituents are isopropyl-groups or methyl-groups preferred although other alkyl-groups such as t-butyl-groups or trifluormethyl-groups may be suitable, too. Less preferred are phenyl-, benzyl- and cyclohexyl-substituents in the 2-position of imidazole as stable N-nitrosamines are known to be formed in acidic solutions comprising nitrous acid from these imidazole-derivatives. The corresponding imidazoles may be formed by reaction of copolymers of vinylbenzylchloride (obtained for example by emulsion polymerisation) with imidazole-derivatives that are finally alkylated to form the desired imidazolium-groups. Alternatively similar copolymers may be obtainable by copolymerization of vinylimidazoles, allylimidazoles or imidazolyl-derivatives (e.g. 2-(1H-imidazol-1-yl)ethyl esters) of acrylic acid or methacrylic acid such as 2-(1H-imidazol-1-yl)ethylmethacrylate with the other monomers.

[0102] According to a further embodiment of the present invention anion-exchanging groups of quaternary nitrogenium type may be bound to the main polymer chain by oxdation-resistant bridges such as difluoromethyl-bridges. Such difluoromethyl-bridges may be introduced by chlorodifluoromethylation of aromatic rings of the polymer using chlorodifluoroacetic anhydride. Such bridges offer the advantage that nitrosamines that might be formed in trace amounts are bound in the polymer until the decay of the nitrosamines (e.g. by UV-radiation).

[0103] In order to avoid an oxidative cleavage of N-Alkyl-groups that might form undesired free tertiary or secondary amines according to a further embodiment of the invention oxidation-resistant substituents on the nitrogen of the quaternary ammonium-group may be used. As oxidation-resistant substituents of the quaternary ammonium group perfluoroalkyl-groups such as trifluoromethylgroups are preferred that may be introduced by electrophilic trifluoromethylation. Oxidation-resistant perfluoroalkyl-groups may be also used in 2-position of the above imidazoles in order to improve the alkali-resistance of the imidazolium-groups. Alternatively similar compolymers may be a obtainable from copolymerization of vinylimidazoles with the other monomers.

[0104] Also preferred are polymers with pyridinium-groups (see Fig. 3) because pyridine also does not form stable nitrosamines according to the literature. Polymers comprising pyridinium-groups should not form nitrosamines by oxidative cleavage of the pyridine-ring. Alternatively similar copolymers are obtainable from copolymerization of vinylpyridines with other monomers.

[0105] According to a further embodiment of the present invention also preferred are polymers comprising a quaternary ammonium-group wherein the nitrogen is part of a bicyclic system such as n-alkylated 1,2,4,5-tetrahydropyrrolo[3,2,1-hi]indole or more preferred n-alkylated julolidine (2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline) that are bound by a suitable bridge via one of the carbon-atoms to the polymer chain (see Fig. 5). Such groups only form amines by oxidative cleavage of two alkyl-groups that are still bound to the polymer because of the three bridges to the polymer-chain. So no nitrosamines can be released even after cleavage of two bonds. Alternatively alkylated quinuclidine may be bound in an analog way to the polymer chain in order to reach this aim or the quaternary nitrogen may be bound by two alky-bridges.

[0106] Most preferred are copolymers that are available by copolymerization of t-butylacrylate or t-butylmethacrylate or alkylmethacrylates such as methylmethacrylate or styrene with the synthons vinylbenzyltrimethylammonium hydroxide or a vinylbenzyltrimethylammonium carboxylate, especially vinylbenzyltrimethylammonium acetate and vinylbenzyltrimethylammonium nitrate. Most preferred are also copolymers that are available by copolymerisation of t-butylacrylate or t-butylmethacrylate or alkylmethacrylates such as methylmethacrylate or styrene with 1-vinylbenzyl-2-alkyl-3-alkylimidazolium hydroxide (i.e. 3-(4-ethenylbenzyl)-1-alkyl-2-alkyl-1H-imidazol-3-ium hydroxide) or 1-vinylbenzyl-2-alkyl-3-alkylimidazolium carboxylate, especially 1-vinylbenzyl-2-alkyl-3-alkylimidazolium acetate, and at least one monomer selected from the group consisting of 1-vinylbenzyl-2-alkyl-3-alkylimidazolium nitrate or 1-vinylbenzyl-2-alkyl-3-alkylimidazolium nitrite.

[0107] According to a further embodiment of the present invention instead of polymers with such functional groups ionic liquids that are soluble in the corrosion-inhibiting composition may be added to the corrosion-inhibiting composition. For example ionic liquids such as 1-butyl-3-methylimidazolium acetate (bmim-acetate) and 1-butyl-3-methylimidazolium nitrite (bmim nitrite) may be added. More preferred are ionic liquids with large organic cations such as ionic liquids with long chained alkyl-groups such as 1-hexyl-3-methylimidazolium acetate (or nitrite) or 1-methyl-3-

octylimidazolium acetate (or nitrite). Also preferred are ionic liquids based on pyridinium salts. Also preferred are ionic liquids comprising cations with trimethoxysilyl-groups. Ionic liquids may be also combined with functional polymers according to the present invention.

[0108] According to a further embodiment of the present invention ionic liquids are adsorbed on a support such as silicium dioxide, glass- or silicate-particles or cyclodextrines as corrosion-inhibitors. Preferred are ionic liquids with cations comprising trimethoxysilyl-groups or with anions such as bis(trifluoromethane)sulfonimide-ions depending on the support material.

[0109] Preferred anions bound in the above anion-exchange polymers or ionic liquids are basic anions such as hydroxide-anions, acetate-ions, benzoate-ions and other carboxylate-ions and nitrite-ions or molybdate-ions, tungstate-ions or vanadate-ions although other anions such as chromate-anions may be suitable, too.

[0110] More preferred are anion-exchange polymers that are supplied in the form of a basic anion such as hydroxide-form or acetate-form that are partially converted into the nitrite form.

[0111] Preferred sparingly-soluble salts of the corrosion-inhibiting-compositions (e.g. lacquers) according to the present invention comprising anion-exchanging polymers in the form of basic anions and nitrite-form (or ionic liquids with basic anions and nitrite-anions) are sparingly-soluble earth-alkaline phosphates, lithium phosphate and phosphates of transition metals such as zinc phosphate although other sparingly water-soluble salts that do not increase the corrosion rate may be suitable, too. More preferred are calcium phosphate and strontium phosphate. Most preferred is a composition comprising at least two different earth-alkaline phosphates with different solubilities in water.

[0112] According to a further embodiment of the present invention anion-exchanging copolymers (or terpolymers) in the form of a basic anion or in nitrite-form are preferred that are soluble in an organic solvent that can form a conventional physically drying lacquer with corrosion-inhibiting properties in the presence of sparingly soluble salts with corrosion inhibiting anions such as earth-alkaline phosphates that eluate the basic anions and the nitrite anions of those polymers.

Such copolymers for conventional lacquers typically have longer polymer chains than low VOC-lacquers as it is known in the art.

[0113] According to a further embodiment of the present invention short-chained copolymers are preferred for low VOC-lacquers that are soluble in organic solvents in higher concentration.

[0114] According to a further embodiment of the present invention lacquers comprising said corrosion-inhibiting composition may be also water-based dispersions. By adding small amounts of a hydrophobe solvent such as ethers the corrosion-protecting reaction between the copolymer and the sparingly-soluble salt may be delayed or inhibited.

[0115] Corrosion-inhibiting compositions comprising anion-exchange-polymers and a sparingly soluble corrosion protecting salt (e.g. a phosphate) according to the present invention may be used with polymers comprising epoxy-groups and anion-exchange copolymers according to the present invention may comprise epoxy-groups that may be cured by epoxy-curing reactions, too.

[0116] Preferred curing agents for these polymers comprising epoxy-groups are carboxylic anhydrides such as phthalic anhydride or pyromellitic dianhydride. According to an embodiment of the present invention tertiary amines such as triethylenediamine (DABCO) and imidazole as catalyst are preferred curing agents.

[0117] According to a further embodiment of the present invention corrosion-inhibiting compositions according to the present invention are used for powder-coating of metal parts. Anion-exchange polymers comprising epoxy-groups may be used for this purpose.

[0118] According to a further embodiment of the present invention corrosion-inhibiting compositions according to the present invention may be used for electrophoretic deposition lacquers called KTL-lacquer. For cathodic deposition additional functional groups such as tertiary amines in protonated form (preferred from the carboxylic acid corresponding to the basic anion) are required in order to convert the polymers into a water-soluble form. Moreover additional reactive groups such as epoxy-groups for later curing of the deposited lacquer are required.

[0119] The preferred process of manufacture of anion-exchanging polymers according to the present invention comprises the step of polymerization of aromatic or aliphatic monomers comprising a double bond and a leaving group such as vinylbenzylchloride that can react by nucleophilic substituation with tertiary amines or heterocyclic compounds comprising nitrogen (such as imidazole) with acrylates, methacrylates or styrene. This preferred process also comprises the subsequent step of reaction with a tertiary amine such as trimethylamine, triethylamine or other trialkylamines or heterocyclic compounds comprising nitrogen such as imidazole, more preferred 2,3-dimethylimidazol, 2-isopropyl-3-methylimidazol, 2-methyl-3-butylimidazol, 2-isopropyl-3-butylimidazol although other imidazole or benzimidazole derivates may be suitable, too.

[0120] A more preferred process of manufacture comprises the step of copolymerization of 1-vinylimidazole or more preferred 1-vinyl-2-methylimidazol, 1-vinyl-2-isopropylimidazole with acrylates such as t-butylmethacrylate, methacrylates such as t-butylmethacrylate or methylmethacrylate such as t-butylmethacrylate oder methylmethacrylate. In a subsequent step the resulting polymer is alkylated by methyl iodide, 1-bromobutane in order to convert them into charged imidazolium-groups. In a more preferred embodiment of the invention this subsequent alkylation step is performed by the use of alkyl carbonates as alkylating agents.

[0121] Instead of these processes that polymerize non-ionic monomers that are functionalized in a subsequent step a process of direct copolymerization of vinylbenzyltrimethylammonium halides or 1-vinylimidazolium salts with methacrylates, acrylates or styrene in a suitable solvent is also preferred according to another embodiment of the present invention.

[0122] Product of all above production processes are typically anion-exchange polymers in a halide-form although other polymers in the form of other anions may be produced by the use of different alkylation agents. These products in halide-form may be converted into the hydroxide-form by ion-exchange processes such as the action of sodium hydroxide solution on the polymer. The products in halide-form may be also converted to the acetate-form by immersion in sodium acetate solution for several hours. Products in the hydroxide-form or acetate-form may be completely or partially converted into the nitrite-form by immersion in sodium nitrite solution.

[0123] A partially conversion of the hydroxide-form or acetate-form into the nitrite-form is more preferred in order to keep the polymer in a basic medium permanently.

[0124] According to another embodiment of the present invention the alkylation step of polymers is performed by alkyl carbonates as alkylation agents that may be converted into the acetate-form by reaction of the carbonate-form with acetic acid as Bronsted-acid in order to yield products free from corrosive halogenid-ions such as chloride-ions.

[0125] Although free-radical polymerisation is the most preferred production process for functional polymers according to the present invention polymers obtained by anionic or cationic polymerisation may be suitable, too. Instead of polymers obtained by polymerisation polymers obtained by polycondensation or polyaddition may be used for corrosion-inhibiting compositions, too, if they are compatible to alkaline ions and nitrite- or nitrate-ions. Functional polymers obtained by graft-reactions are suitable, too.

[0126] According to another embodiment of the present invention polymers comprising anion-exchanging groups according to the present invention in nitrite-form may be also used for corrosion-protection of non-iron metals such as aluminium alloys. Corrosion-inhibiting compositions for aluminium may be also comprising a sparingly-watersoluble salt such as an alkaline-earth phosphate. The compositions may be further comprising an additional corrosion-inhibitor such as a benzothiazole or a benzotriazole.

[0127] According to another embodiment of the invention epoxy-resins, curing-agents for epoxy-resins or other reactive components such as reactive thinners bearing the above functional groups according to the present invention may be also used as corrosion inhibiting prime-coating.

[0128] As epoxy-resins according to the present invention bisphenol-A-based epoxy-resins such as bisphenol-A-diglycidylether (BADGE, Fig. 12A), other bisphenol-A-epichlorohydrine-resin of a higher molecular weight (see Fig. 12B) with n=0.1 to n=26, bisphenol-F-epichlorohydrine-resin bearing functional groups according to the present invention such as imidazolium-groups, ammonium-groups or phosphonium-groups in nitrate-form or nitrite-form and in form of weakly basic anions such as carboxylate-form such as acetate-form, maleate-form, borate-form, hydrogenphosphate-form, dicyanamide-form, silikate-form, hydrogencarbonate-Form, phosphate-form or carbonate-form may be used.

[0129] Preferred are epoxy-resins such as bisphenol-A-diglycidylether (BADGE) bearing functional groups according to the present invention or lower molecular bisphenol-A-epichlorohydrine-resins that are liquid at temperatures <80°C with n=0.1 to n=1.1 bearing functional groups according to the present invention.

[0130] Also preferred are t-butyl acrylate-copolymers with glycidyl methacrylate as epoxy resins.

[0131] Those epoxy-resins bearing functional groups according to the present invention may be cured with amines, carboxylic anhydrides or thioles as curing agents although other curing agents such as phenols may be suitable, too. However epoxy-resins bearing functional groups in nitrite form must not be used to cure amines in order to avoid formation of nitrosamines.

[0132] According to a further embodiment of the present invention mercaptanes, especially mercaptanes with 2 to 4 thiol-groups per molecule such as pentaerythrite tetra(3-mercaptopropionate) (commonly sold under the trademark “THIOCURE PETMP” (RTM) by Bruno Bock Chemische Fabrik GmbH & Co. KG, 21436 Marschacht, Germany) are preferred curing agents for epoxy resins. According to a further embodiment of the present invention such mercaptanes may also comprise quaternary ammonium-, phosphonium- or imidazolium groups in the Form of corrosion-inhibiting anions as counter-ions according to the invention.

[0133] As curing-agents all known curing-agents for epoxy-resins may be used if they are compatible to the corrosion-inhibiting anions used and yield alkali-resistant polymers, especially polysulfides, polyamidee, imidazolines, adducts of amines with epoxides, Mannich-bases, ketimine, acrylonitrile-adducts with ethyleneamines, dialkylaminopropylamine, hexamethylenediamine and other long chain diamines, polyetheramines, polymeric amines, aromatic-aliphatic amines such as meta-xylenediamine (MXDA), cyclic aliphatic amines, dicyandiamide, melamine, guanamine, aromatic amine, phenol-novolac-resins, resol-resins, amino-formaldehyde resins (such as urea-formaldehyde- or melamine-formaldehyde-resins) although other curing-agents such as carboxylic hydrazides and hydrazine might be also usable, too. According to an embodiment of the present invention such curing agents may comprise corrosion-inhibiting functionel groups according to the invention, too.

[0134] Preferred are epoxy-resins with functional groups according to the present invention in nitrate-form and in form of a weakly-basic anion and an amine curing-agent such as ethylene diamine, dipropylene triamine, 4,4'-diamino-3,3'-dimethyldicyclohexylmethane, 4,4'-diaminodiphenylmethane, ketimine, polyamidamine from dicarboxylic acid and ethylene diamine, and unmodified or substituted dicyandiamide.

[0135] According to a further embodiment of the present invention curing-agents comprising >=2 thiole groups are also preferred for curing of epoxy-resins according to the present invention.

[0136] According to a further embodiment of the present invention curing-agents may be used that comprise corrosion-inhibiting functional groups according to the present invention as shown in Fig. 13. Such functionalized curing-agents may be used for curing conventional epoxy-resins in order to obtain a corrosion-protecting coating.

[0137] According to a further embodiment of the present invention reactive thinners comprising corrosing-inhibiting groups according to the present invention according to Fig. 14 are preferred that are added to the epoxy-resin. Those reactive thinners are ionic liquids in nitrate-form, nitrite-form and in form of weakly basic anions further comprising an epoxy-group.

[0138] Preferred reactive thinners according to the present invention are 1-glycidyl-3-alkylimidazolium nitrate with C_1-C_{12} -alkyl-groups such as 1-glycidyl-3-butylimidazolium nitrate and 1-glycidyl-3-alkylimidazolium acetate (with C_1-C_{12}-alkyl-groups) such as 1-glycidyl-3-butylimidazolium acetate (see Fig. 14). Also preferred are 1,3-diglycidyl imidazolium nitrate and 1,3-diglycidyl imidazolium acetate (see Fig. 14) or similar compounds comprising at least two glycidyl-groups and an imidazolium-group. Also preferred are glycidyltrimethylammonium nitrate and glycidyltrimethylammonium acetate. A mixture of several reactive thinners may be used, too.

[0139] More preferred are 1-glycidyl-2-alkyl-3-butylimidazolium nitrate or 1-glycidyl-2-alkyl-3-butylimidazolium acetate as well as other 1-glycidyl-2-alkyl-3-alkylimidazolium nitrates or acetates with branched or unbranched C_{3-} C_{10}-alkyl-groups and 1,3-diglycidyl-2-alkylimidazolium nitrate or acetate with alkyl groups such as methyl-groups (see Fig. 14). Isopropyl-groups are more preferred alkyl-groups as substituents in 2-position of the imidazole-ring.

[0140] Also preferred are 1-(1,2-epoxyethyl)-3-alkylimidazolium nitrate/acetate with C_1-C_{12}-alkyl groups such as 1-(1,2-epoxyethyl)-3-methylimidazolium nitrate/acetate, 1-(1,2-epoxyethyl)-3-ethylimidazolium nitrate/acetate, 1-(1,2-epoxyethyl)-3-n-propylimidazolium nitrate/acetate, 1-(1,2-epoxyethyl)-3-isopropylimidazolium nitrate/acetate , 1-(1,2-epoxyethyl)-3-butylimidazolium nitrate/acetate , 1-(1,2-epoxyethyl)-3-pentylimidazolium nitrate/acetate, 1-(1,2-epoxyethyl)-3-hexylimidazolium nitrate/acetate. More preferred are 1-(1,2-epoxyethyl)-2-$(\text{alkyl})_{II}$-3-$(\text{alkyl})_{I}$-imidazolium nitrate/acetate with C_1-C_{12}-alkyl groups in 3-position and methyl-, ethyl-, isopropyl-, n-butyl- und tert.-butyl-groups in 2-position.

[0141] An equimolar amount of resins, curing-agents or reactive thinners bearing corrosion-inhibiting functional groups (i.e. epoxy-resins, curing agents or reactive thinners with ammonium-, imidazolium- or phosphonium-groups) in nitrate form (or nitrite-form) and resins, curing-agents or reactive thinners bearing those functional-groups in form of basic anions (such as in acetate-form) of 1 mol nitrate-form to 1 mol acetate-form is preferred.

[0142] A molar ratio of sparingly-soluble salts (such as alkaline earth-phosphates) to the above funtionalized components between 0.1:1 and 1:1 based on the anions of the salts is preferred.
A molar ratio between 0.25:1 and 0.9:1 is more preferred. A molar ratio between 0.5:1 and 0.75:1 is most preferred. A molar ratio of 0.67:1 is optimum for alkaline earth phosphates.

[0143] Preferred is an ion-exchange capacity of resulting epoxy-coatings according to the present invention as calculated from the content of anion-exchange-groups between 0.01 meq/g to 7 meq/g. An ion-exchange capacity between 0.1 meq/g to 2 meq/g is more preferred. An ion-exchange capacity between 0.25 meq/g to 1.2 meq/g is most preferred.

[0144] According to a further embodiment of the present invention the corrosion-inhibiting epoxy-resins or reactive thinners according to the present invention are used in a prime-coating.

[0145] Such prime-coatings may be further comprising inhibitors in form of basic anions and in form of nitrate-anions. Moreover these epoxy-resins are amine-based curing agents itself may be further comprising quaternary ammonium-, imidazolium-, or pyridinium-groups in nitrate-form or in form of basic anions.

[0146] According to a further embodiment of the present invention instead of epoxy-resins comprising corrosion-inhibiting functional groups according to the invention (i.e. quaternary ammonium-, imidazolium-, or pyridinium- oder phosphonium-groups with said corrosion-inhibiting anions) isocyanates are also preferred. Preferred curing-agents for isocyanates according to this embodiment of the present invention are alcohols.

[0147] Said alcohols may be also comprising corrosion-inhibiting functional-groups, especially quaternary ammonium-, imidazolium-, pyridinium- or phosphonium-groups in nitrate-form and acetate-form according to a further embodiment of the present invention.

[0148] According to a further embodiment of the present invention blocked isocyanates are preferred for curing with hydroxyl-groups. As blocking-agents commonly used blocking agents for isocyanates such as diethylmalonate, 3,5-dimethyl-1,2-pyrazole or ethylacetoacetate may be used, although methylethylketoxime, 1,2,4-triazole, epsilon-caprolactame oder phenols may be useable, too. Preferred are blocked isocyanates, comprising corrosions-inhibiting funktional groups according to the present invention.

[0149] According to an embodiment of the present invention aminoalcohol-modified epoxy-resins are preferred as curing-agents with hydroxy-groups for isocyanates. More preferred are curing-agents in the form of water-soluble KTL-lacquer for the electrophoretic deposition of lacquer. The modified epoxy-resin may be further comprising corrosion-inhibiting functional groups according to the present invention instead of the blocked isocyanate. Alternatively both components may be comprising said corrosion-inhibiting functional groups.

[0150] According to a further embodiment of the present invention alkyd-resins comprising corrosion-inhibiting functional groups according to the present invention, especially alkyd-resins comprising a quaternary ammonium-, imidazolium-, pyridinium- or phosphonium-groups in nitrate and acetate-form may be used instead of epoxy-resins (or isocyanates) comprising corrosion-inhibiting functional groups.

[0151] Preferred are alkyd-resins such as polyesters of phthalic acid with pentarythrite and long chained unsaturated carboxylic acids, while carboxylic acid is comprising corrosion-inhibiting functional groups comprising a quaternary nitrogen (or phosphorus). As carboxylic acids more preferred is a substituted benzoic acid of benzoic acid-modifizied alkyd-resins, wherein parts of the 9,12-linoleic acid in said ester with pentaerythrite is replaced by benzoic acid. Alternatively a substituted phthalic acid with corrosion-inhibiting functional groups may be used in said alkyd-resins.

[0152] For curing said alkyd-resins in this embodiment of the present invention als Alkydharz catalysts such as cobalt- or manganese-compounds are preferred.

[0153] According to a further embodiment of the present invention an amino-resin, e.g. a melamine-resin such as hexamethoxymethyl-melamine resin, is also preferred as curing agent for alkyd-resins. The amino-resin that is used as such a curing-agent may comprise corrosion-inhibiting functional groups.

[0154] According to a further embodiment of the present invention acrylic resins or saturated polyester resins may be also used as reaction partners with corrosions-inhibiting funktional groups for amino-resins for stove-enamels according to a present invention.

BEST MODE OF CARRYING OUT THE INVENTION

[0155] The following examples illustrate the best mode of carrying out the embodiments of the invention. Example 1 illustrates the use of milled anion exchange polymers, examples 2-4 and example 7 the use of corrosion-protecting compositions comprising milled anion exchange resin beads in hydroxide- and nitrite-form. Examples 5 gives a test result for an inert paint, example 6 gives the test result for a partial coating using a corrosion-protecting paint comprising zinc phosphate as corrosion-inhibitor in the same test.

EXAMPLES

Example 1

Preparation of tribasic Strontium phosphate

[0156] 0.2162 g Strontium nitrate (analytical grade, procured from Fluka, Taufkirchen, Germany) are dissolved in 21.6892 ml of deionized water (ion chromatography grade with <1 μg/kg anions was used for all solutions and washing). 4.3508 g of dibasic potassium phosphate K_2HPO_4 (Biochemica ultra grade procured from Fluka, Taufkirchen, Germany) in 4.0844 g deionized water and 3.7462 g of a solution of 0.3016 g Potassium hydroxide (86% KOH, analytical grade, procured from Fluka, Taufkirchen, Germany) in 3.8167 g deionized water was added. All solutions were cooled to +10°C. The strontium nitrate solution was added dropwise to the stirred solution of dibasic potassium phosphate and potassium hydroxide. The resulting suspension of $Sr_3(PO_4)_2 \cdot 4\ H_2O$ is filtered using vacuum and a glass filter (porosity 4 with a filter paper procured from Schleicher& Schuell, Germany, No. 595), washed with deionized water, absolute ethanol (procured from Riedel de Haen, Taufkirchen, Germany), absolute ether (procured from Fluka AG, Buchs, Switzerland and dried for several hours in a vacuum exsiccator using silicagel. Then the product is converted to $Sr_3(PO_4)_2$ in an oven at 250°C for 45 minutes and at temperatures of up to 500°C by heating in a quartz crucible.

Example 2

Manufacture of anion exchange resin in nitrite-form

[0157] 3.3934 g anion exchange resin DOWEX 550A UPW(RTM) are suspended in 9.1 g demineralized water (ion chromatography grade; <1 μg/kg anions). A solution of 2.5966 g sodium nitrite in 9.4 g demineralized water is added and the suspension is stirred for 12 hours using a magnetic stirrer. Finally the ionen exchange beads are filtered using a glass filter and vacuum and washed several times with demineralized water.

Example 3

Demonstration of the corrosion-inhibiting action

[0158] Samples of a size of 50 mm x 50 mm are cut from an 250 mm x 500 mm steel sheet of thickness 0.825 mm (EAN 4001116381041, Alfer Aluminium GmbH, 79793 Wutöschingen, http://products.alfer.com/en/Products/Hardware/combitech-system-Sheets-and-accessories/Sheetssteel/Sheet-raw-steel.html) and cleaned with acetone (Fluka, Taufkirchen). 0.2449 g anion exchange resin DOWEX 550A UPW(RTM) in hydroxide-form and 0.3160 g anionen-exchange resin in nitrite-form from example 2 are placed on the metal sheet. 1 ml of a solution of 0.5260 sodium phosphat-dodekahydrate ($Na_3(PO_4) . 12 H_2O$, Fluka, Taufkirchen) in 10.5119 g demineralized water are added to the metal sheet with the above ion-exchange resins. A piece of analytical filter paper (Whatman S&S, No. 595) is placed on the steel sheet and wetted and kept wet using demineralized water. The sample doesn't show any corrosion after periods of testing of 4 days.

Example 4

Demonstration of the corrosion-inhibiting composition using a sparingly soluble salt

[0159] As in example 3 a sheet of steel is partially coated with corrosion-inhibiting polymers. As sparingly soluble phosphate calcium phosphate or strontium phosphate from example 1 are added. The samples are tested as in example 2. The samples don't show any corrosion after periods of 4 days.

Example 5

Comparative example

[0160] 2.82 g Poly(vinylidenefluoride-co-hexafluoropropene) (PVDF-HFP, Sigma-Aldrich, Taufkirchen) are dissolved in 22.14 g Acetone. In order to get a homogenous dispersion the solution is untrasonicated in an ultrasonic cleaner (40 W power, manufactured by EMAG AG, Moerfelden, Germany) for one hour. As in example 3 a steel sheet is coated with the resulting dispersion of PVDF-HFP in acetone. The steel sheet shows corrosion on all defects of the coating within a few hours exposure to demineralized water in a test as in examples 2 and 3.

Example 6

Comparative example

[0161] As in example 5 a steel sheet is coated with a commercial corrosion-protecting paint comprising zinc phosphate as corrosion inhibitor. A 2 cm x 2 cm field in the center of each sheet is not coated. The steel sheet shows corrosion in all uncoated areas even next to the paint within a few hours exposure to demineralized water in a test as in examples 2 and 3.

Prospective Example 7

Preparation of a corrosion protecting paint with milled anion exchange particles

[0162] 1.1 gram beads of DOWEX 550A UPW(RTM) (procured from Sigma-Aldrich, Taufkirchen, Germany) anion exchanger are crushed in a ball mill using porcelain milling balls. The resulting particles and 0.15 g of tribasic Strontium phosphate $Sr_3(PO_4)_2$ (obtained in example 1) are dispersed in a solution of 1 grams of Poly(vinylidene fluoride-co-hexafluoropropene (PVDF-HFP) copolymer (procured from Sigma Aldrich, Taufkirchen, Germany) in 20.6 g N-methylpyrrolidinone (NMP). The solution is applied as a paint on an iron sheet.

[0163] Examples 8-12 demonstrate the manufacture of copolymers according to the present invention for the use as corrosion inhibitors with imidazolium-groups, example 13 the manufacture of a copolymer with ammonium-groups.

EXAMPLES

Example 8

Copolymerisation of t-butyl acrylate with vinylbenzyl chloride

[0164] 23.44 g t-butyl acrylate (98%, Sigma-Aldrich, Taufkirchen, Germany) und 3.45 g vinylbenzyl chloride (97%, mixture 3- und 4-isomers, Sigma-Aldrich, Taufkirchen, Germany) are extracted with 0.5% sodium hydroxide solution in a separatory funnel in order to remove the stabilizers. 23.10 g of said t-butyla crylate and 2.86 g of the vinylbenzyl chloride are placed in a round bottom flask. 25.26 g distilled water and 153.7 mg sodiumlauryl sulfate (Sigma-Aldrich, Taufkirchen, Germany) in 1.2613 g deionized water and a solution of 145.5 mg sodium hydrogencarbonate in 3.4148 g deionized water are added. Then 0.45 g ammonium peroxodisulfate (p.a., Fluka AG, Buchs, Switzerland) and 0.37g sodium peroxodisulfate (Bayer AG, Leverkusen) are added and the flask is purged for 20 minutes with argon. Finally polymerisation was accomplished by heating the stirred suspension with a magnetic stirrer up to 70°C under reflux for 3 hours. The reaction yields 13.6 g of an agglomerate of solid polymer and 49.7 g of a polymer-latex.

Example 9

Reaction of the copolymer with 1,2-Dimethylimidazole

[0165] 0.4 g of the agglomerate from example 8 are mixed with 7.0 g 1,2-dimethylimidazole (Sigma-Aldrich, Taufkirchen, Germany) and stirred for 28 hours at ambient temperature using a magnetic stirrer. A foaming dispersion of the desired polymer with imidazolium-groups in chloride-form in dimethylimidazole is formed.

Example 10

Drying of the Imidazolium-Copolymer

[0166] 1 ml of the dispersion of the copolymer with imidazolium-groups from example 9 are placed on a glass plate and dried at 80°C on the hot plate of a magnetic stirrer for at least 3 hours. Solvent (i.e. dimethylimidazole) is removed from the remaining dispersion by destillation in vacuum at about 80°C.

Example 11

Conversion of the polymer into the acetate-form

[0167] The glass plate with the dried copolymer film in chloride form from example 10 is placed for 24 hours in 80 ml 1 M potassium hydroxide-solution (KOH purissimum p.a., Fluka, Taufkirchen). A film of the Copolymeren with imidazolium-groups in hydroxide-form is formed which can be converted by a second subsequent ion-exchange with 1M acetic acid, sodium acetate-solution or sodium nitrite solution or potassium nitrate solution or nitric acid for 24 hours into the acetate or nitrite or nitrate form.

Example 12

Manufacture of a dispersion of the Copolymer in acetate-form

[0168] The polymer in acetate-form obtained in Example 11 is dissolved in 20 ml tetrahydrofurane (dried over molecular sieve, Fluka, Taufkirchen, Germany) by heating at boil under reflux.

Example 13

Manufacture of a copolymer with quaternary ammonium-groups

[0169] 13.8 g of the latex from example 8 are mixed with 5.8 g triethylamine (Fluka AG, Buchs) in a round bottom flask and stirred for 5 days at 40°C using a magnetic stirrer. The resulting dispersion of a polymer with quaternary ammonium-groups is processed as in examples 9-12.

[0170] Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. For example it is possible to use paints according to the present invention on alloys of other metals.

Claims:

What is claimed is:

1. A corrosion-inhibiting paint, comprising
a) at least one first polymer or prepolymer comprising anion-exchanging groups wherein said anion-exchanging groups are in the form of basic anions; and
b) at least one second polymer or prepolymer comprising anion-exchanging-groups as a second anion exchange resin wherein said anion-exchanging groups are at least partially in the form of nitrite or nitrate ions,
wherein said first polymer, first prepolymer, second polymer and second prepolymer have sufficient hydrolytic stability in basic solutions.

2. A corrosion-inhibiting paint according to claim 1, wherein the anion-exchanging groups of said first polymer are in hydroxide form.

3. A corrosion-inhibiting paint according to claim 1, comprising at least one polymer comprising anion-exchanging-groups wherein said anion-exchanging-groups of said first polymer comprise the form of weakly basic anions.

4. A corrosion-inhibiting paint according to claim 1 or claim 3, wherein said weakly basic anions are anions of an acid with a $pK_s>4.0$.

5. A corrosion-inhibiting paint according to claim 1 or claim 3, wherein said weakly basic anions are anions of an acid with a $pK_s>4.7$.

6. A corrosion-inhibiting paint according to claim 1 or claim 3 to 5, wherein carboxylic-anions are used as weakly-basic anions.

7. A corrosion-inhibiting paint according to claim 1 or claim 3 to 6, comprising anion-exchange polymers in acetate-form as first polymer.

8. A corrosion-inhibiting paint according to claim 1 or claim 3 to 6, comprising at least one first anion-exchange polymer selected from the group consisting of anion-exchange-polymers in benzoate-form, anion-exchange-polymers in propionate-form, and anion-exchange polymers in valeriate-form.

9. A corrosion-inhibiting paint according to claim 1 or claim 3 to 6, comprising at least one first anion-exchange polymer selected from the group comprising anion-exchange polymers in maleate-form, anion-exchange polymers in fumarate-form, anion-exchange polymers in azelate-form, and anion-exchange polymers in tartrate-form.

10. A corrosion-inhibiting paint according to claim 1 or claim 3 to claim 6, comprising first anion-exchange polymers selected from the group consisting of anion-exchange polymers in phthalate form, and anion-exchange-polymers in cinnamate-form.

02 08 21

11. A corrosion-inhibiting paint according to claim 1 or claim 3, comprising first anion-exchange polymers selected from the group consisting of anion-exchange polymers in hydrogencarbonate-form, anion-exchange polymers in borate-form, anion-exchange polymers in hydrogenphosphate-form, anion-exchange polymers in silicate-form, anion-exchange polymers in carbonate-form, anion-exchange polymers in alkylcarbonate-form, and anion-exchange polymers in dicyanamide-form.

12. A corrosion-inhibiting paint according to claim 1 to claim 11, wherein said second anion-exchange-polymers comprise imidazolium-groups.

13. A corrosion-inhibiting paint according to claim 1 to claim 12, wherein said first anion-exchange-polymers comprise imidazolium-groups.

14. A corrosion-inhibiting paint according to claim 1 to claim 11, wherein said second anion-exchange-polymers comprise pyridinium-groups.

15. A corrosion-inhibiting paint according to claim 1 to claim 12 or claim 14, wherein said

first anion-exchange-polymers comprise pyridinium-groups.

16. A corrosion-inhibiting paint according to claim 1 to claim 11, wherein said second anion-exchange-polymers comprise phosphonium-groups.

17. A corrosion-inhibiting paint according to claim 1 to claim 12, claim 14 or claim 16, wherein said first anion-exchange-polymers comprise phosphonium-groups.

18. A corrosion-inhibiting paint according to claim 1 to claim 11, wherein at least said second anion-exchange-polymers comprise a quatemary nitrogen that is bound via three alkyl-bridges to the polymer-chain.

19. A corrosion-inhibiting paint according to claim 1 to claim 18, wherein said first and second anion-exchange polymers are soluble in an organic solvent.

20. A corrosion-inhibiting paint according to claim 1 to claim 19, wherein said first and second anion-exchange polymers are insoluble in water.

21. A corrosion-inhibiting paint according to claim 1 to claim 20, wherein said first anion-exchange-polymers are alkali-resistant copolymers or terpolymers with acrylates or methacrylates.

22. A corrosion-inhibiting paint according to claim 1 to claim 21, wherein said second anion-exchange-polymers are alkali-resistant copolymers or terpolymers with acrylates or methacrylates.

23. A corrosion-inhibiting paint according to claim 1 to claim 22, wherein said first anion-exchange-polymers are alkali-resistant copolymers or terpolymers with tert.-butylacrylate or tert.-butylmethacrylate.

24. A corrosion-inhibiting paint according to claim 1 to claim 23, wherein said second anion-exchange-polymers are alkali-resistant copolymers or terpolymers with tert.-butylacrylate oder tert.-butylmethacrylate.

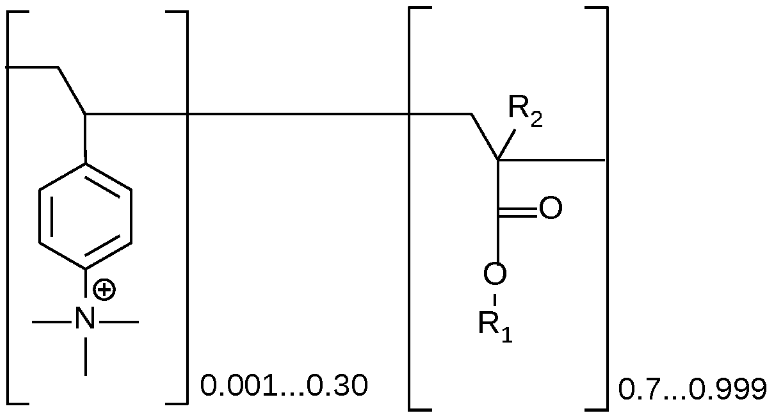
25. A corrosion-protecting paint comprising a corrosion inhibiting composition according to claim 1 to claim 24, further comprising a sparingly water-soluble salt.

26. A corrosion-protecting paint comprising a corrosion inhibiting composition according to claim 25, wherein said sparingly water-soluble salt is selected from the group consisting of calcium phosphate, strontium phosphate, barium phosphate, and lithium phosphate.

27. A corrosion-protecting paint comprising a corrosion inhibiting composition according to claim 1 to claim 26, further comprising 0.35 mmol of tribasic strontium phosphate per gram of said first and second anion exchange resins, wherein the weight capacity of said first and second anion exchange resin is 1.1 meq/g.

28. A corrosion-protecting paint according to claim 1 to claim 26 comprising a copolymer of vinylbenzyldimethylammonium hydroxide and an alkene and 0.25 mmol of tribasic strontium phosphate per gram of said copolymer. wherein the weight capacity of said copolymer is 0.5 meq/g.

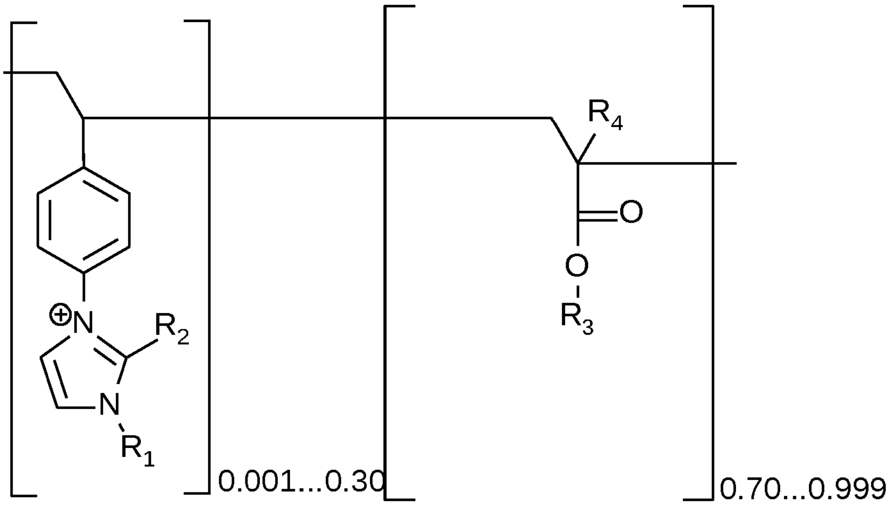
29. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



,

wherein R_2 is hydrogen or a methyl-group and R_1 is a methyl-, ethyl-, n-propyl-, iso-propyl, n-butyl-, tert.-butyl-, pentyl-, hexyl-, heptyl- or octyl-group and wherein said polymer is in carboxylate or nitrate form.

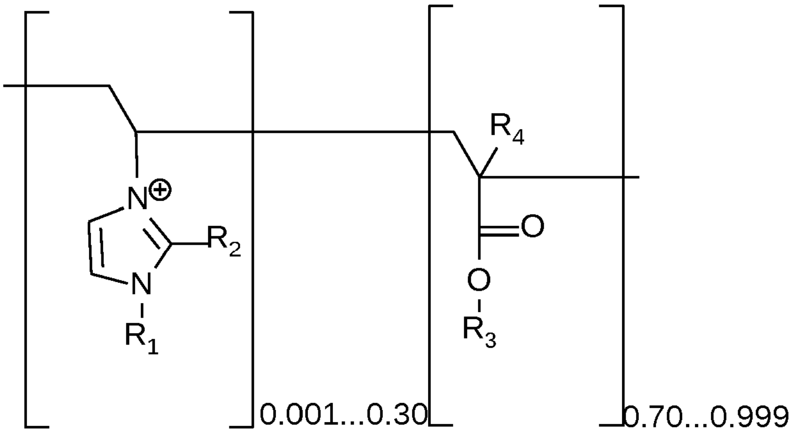
30. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



,

wherein R_1 and R_2 are C_1-C_{22} alkyl-groups, R_4 is hydrogen or a methyl-group and R_3 is a methyl-, ethyl-, n-propyl-, iso-propyl, n-butyl-, tert.-butyl-, pentyl-, hexyl-, heptyl-, octyl-, 2-ethylhexyl- or dodecyl-group and wherein said polymer is in carboxylate, nitrite or nitrate form.

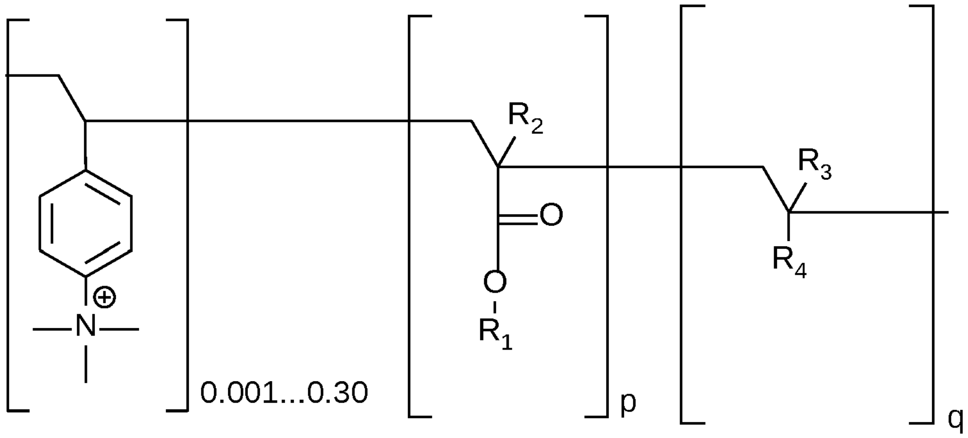
31. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



,

wherein R_1 and R_2 are C_1-C_{22} alkyl-groups, R_4 is hydrogen or a methyl-group and R_3 is a methyl-, ethyl-, n-propyl-, iso-propyl, n-butyl-, tert.-butyl-, pentyl-, hexyl-, heptyl-, octyl-, 2-ethylhexyl- or dodecyl-group and wherein said polymer is in carboxylate, nitrite or nitrate form.

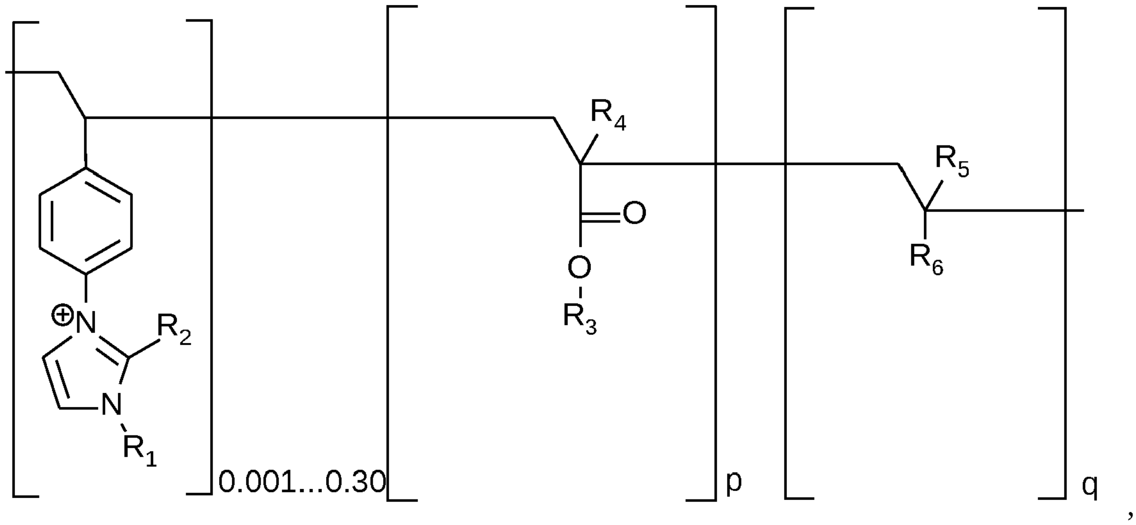
32. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



,

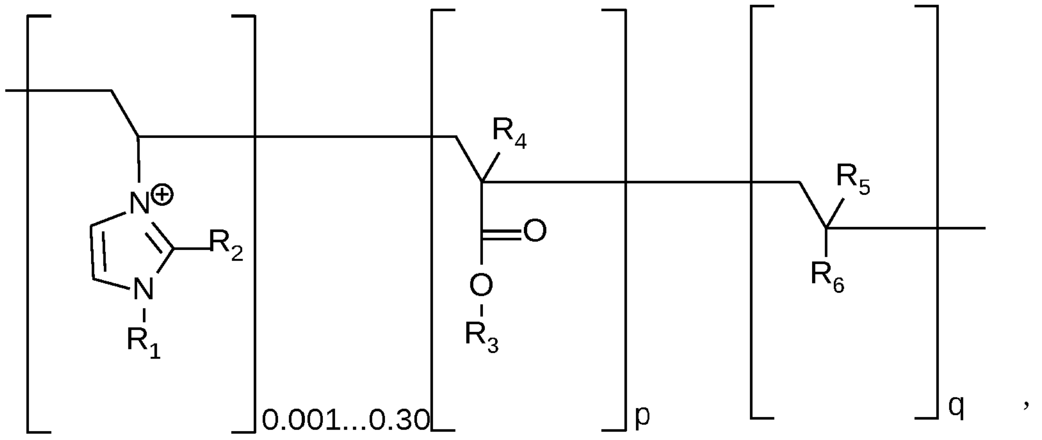
wherein p+q are chosen within the interval $0,70 \leq p+q \leq 0,999$, R_2 and R_3 are Hydrogen or a methyl-group, R_1 is a methyl-, ethyl-, n-propyl-, iso-propyl, n-butyl-, tert.-butyl-, pentyl-, hexyl-, heptyl-, octyl-, 2-ethylhexyl- or dodecyl-group and R_4 is a benzene-group or a carboxy-group and wherein said polymer is in carboxylate, nitrite or nitrate form.

33. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



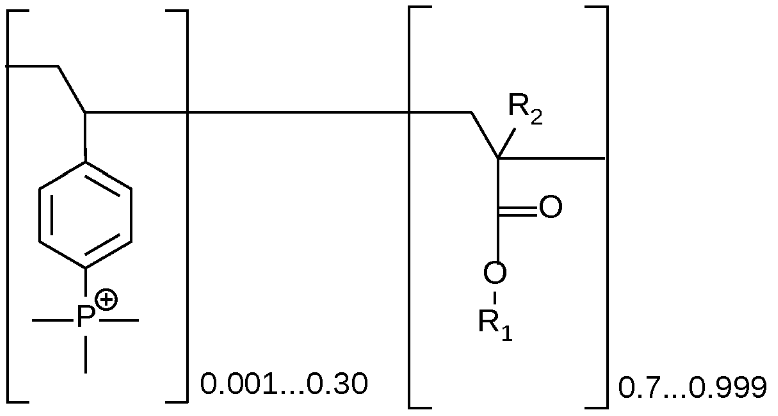
wherein p+q are chosen within the interval $0,70 \leq p+q \leq 0,999$, R_1 is a C_1-C_{22} alkyl-group, R_2 is hydrogen or a C_1-C_{22} alkyl-group, R_4 and R_5 are Hydrogen or a methyl-group, R_3 is a methyl-, ethyl-, n-propyl-, iso-propyl, n-butyl-, tert.-butyl-, pentyl-, hexyl-, heptyl-, octyl-, 2-ethylhexyl- or dodecyl-group and R_6 is a benzene-group or a carboxy-group and wherein said polymer is in carboxylate, nitrite or nitrate form.

34. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



wherein p+q are chosen within the interval $0,70 \leq p+q \leq 0,999$, R_1 is a C_1-C_{22} alkyl-group, R_2 is hydrogen or a C_1-C_{22} alkyl-group, R_4 and R_5 are hydrogen or a methyl-group and R_3 is a methyl-, ethyl-, n-propyl-, iso-propyl, n-butyl-, tert.-butyl-, pentyl-, hexyl-, heptyl-, octyl-, 2-ethylhexyl- or dodecyl-group and R_6 is a benzene-group or carboxylic group and wherein said polymer is in carboxylate, nitrite or nitrate form.

35. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



,

wherein R_2 is hydrogen or a methyl-group and R_1 is a methyl-, ethyl-, n-propyl-, iso-propyl, n-butyl-, tert.-butyl-, pentyl-, hexyl-, heptyl- or octyl-group and wherein said polymer is in carboxylate, nitrite-form or nitrate form.

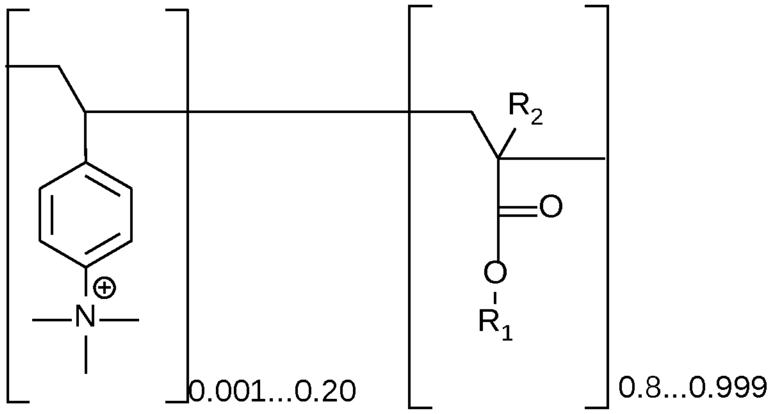
02 08 21

36. A corrosion-inhibiting paint according to claim 29 to 35, wherein said carboxylates are acetates.

37. A corrosion-inhibiting paint according to claim 29, 32 or 35, wherein said alkyl group R_1 is a tert.-butyl-group.

38. A corrosion-inhibiting paint according to claim 30, 31, 33 or 34, wherein said alkyl group R_3 is a tert.-butyl-group.

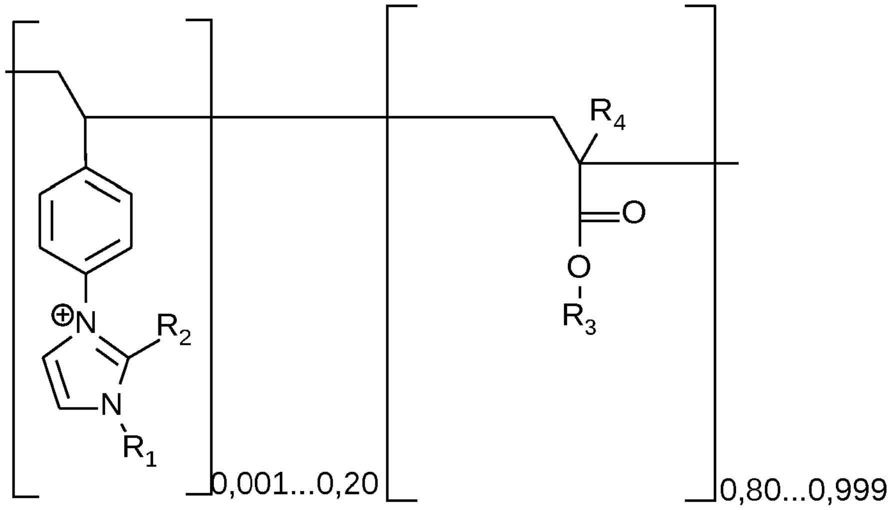
39. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



,

wherein R_2 is hydrogen or a methyl-group and R_1 is a methyl-, n-butyl- or tert.-butyl-group and wherein said polymer is in carboxylate or nitrate form.

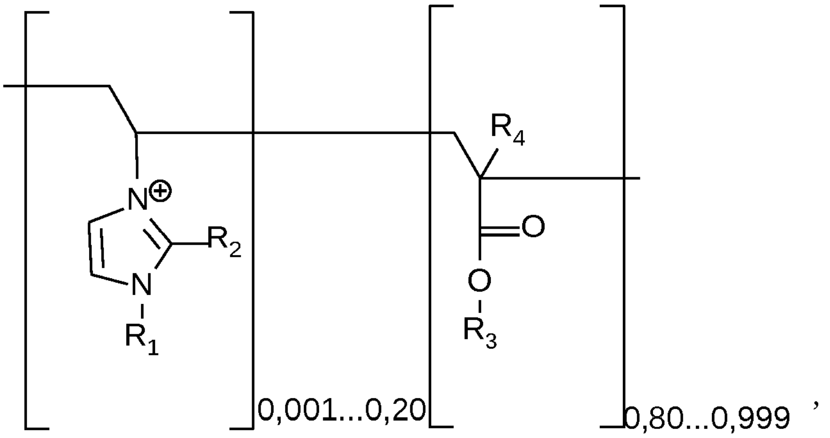
40. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



,

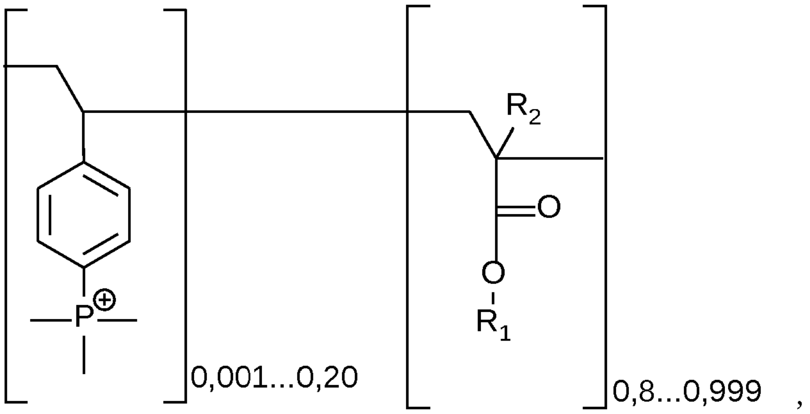
wherein R_1 is a C_1-C_{22} alkyl-group, R_2 is hydrogen or a C_1-C_{22} alkyl-group, R_4 is hydrogen or a methyl-group and R_3 is a methyl-, n-butyl- or tert.-butyl-group and wherein said polymer is in carboxylate, nitrite or nitrate form.

41. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



wherein R_1 is a methyl- or butyl-group, R_2 is hydrogen or a methyl-group, R_4 is hydrogen or a methyl-group and R_3 is a methyl-, n-butyl- or tert.-butyl-group and wherein said polymer is in carboxylate, nitrite or nitrate form.

42. A corrosion-inhibiting paint according to claim 1 to claim 28 comprising a first or second polymer of the following structure



wherein R_2 is hydrogen or a methyl-group and R_1 is a methyl-, n-butyl- or tert.-butyl-group and wherein said polymer is in carboxylate, nitrite-form or nitrate form.

43. A corrosion-inhibiting paint according to claim 1 to claim 17 or claim 25 to claim 28, wherein said corrosion-inhibiting paint is an epoxy-resin paint comprising at least one reactive thinner as said first or second prepolymer comprising:

(a) an epoxy-group; and

(b) at least one cationic group selected from the group consisting of trialkylammonium group, benzyldialkylammonium group, phosphonium-group, sulfonium-group, imidazolium-group, pyridinium-group in the form of a carboxylate or a nitrate or nitrite.

44. A corrosion-inhibiting paint according to claim 43, comprising at least one 1 -glycidyl-3-alkylimidazolium nitrate or 1-glycidyl-3-alkylimidazolium acetate as a reactive thinner.

45. A corrosion-inhibiting paint according to claim 44, wherein the alkyl-substituent of said 1-glycidyl-3-alkylimidazolium nitrates or 1-glycidyl-3-alkylimidazolium acetates is a C_1- to C_{12}-alkyl group.

46. A corrosion-inhibiting paint according to claim 44 to claim 45, wherein the alkyl-substituent of said 1-glycidyl-3-alkylimidazolium nitrates or 1-glycidyl-3-alkylimidazolium acetates are C_3-to C_{12}-alkyl groups.

47. A corrosion-inhibiting paint according to claim 44 to claim 46, wherein the alkyl-substituent of said 1-glycidyl-3-alkylimidazolium nitrates or 1-glycidyl-3-alkylimidazolium acetates are selected from the group consisting of isopropyl-, tert.-butyl-, isobutyl-, and 2-ethylhexyl-groups.

48. A corrosion-inhibiting paint according to claim 44, comprising 1-glycidyl-2-alkyl-3-alkylimidazolium nitrate or 1-glycidyl-2-alkyl-3-alkylimidazolium acetate as said reactive thinner.

49. A corrosion-inhibiting paint according to claim 48, wherein the alkyl-substituent of said 1-glycidyl-2-alkyl-3-alkylimidazolium nitrates or 1-glycidyl-2-alkyl-3-alkylimidazolium acetates in 3-position are C_1- to C_{12}-alkyl groups and the alkyl-substituent in 2-position is selected from the group consisting of methyl-groups, ethyl-groups, propyl-groups, isopropyl-groups, n-butyl-groups,

isobutyl-groups, and tert.-butyl-groups.

50. A corrosion-inhibiting paint according to claim 48 to claim 49, wherein the alkyl-substituent of said 1-glycidyl-2-alkyl-3-alkylimidazolium nitrates or 1-glycidyl-2-alkyl-3-alkylimidazolium acetates in 3-position are C_3- to C_{12}-alkyl groups and the alkyl-substituent in 2-position is selected from the group consisting of a methyl group, an ethyl-group, an n-propyl-groups, an isopropyl-group, an n-butyl-group, an isobutyl-group,and and a tert.-butyl-group.

51. A corrosion-inhibiting paint according to claim 48 to claim 49, wherein the alkyl-substituent of said l-glycidyl-2-alkyl-3-alkylimidazolium nitrates or 1-glycidyl-2-alkyl-3-alkylimidazolium acetates in the 3-position are selected from the group consisting of an isopropyl-group, a tert.-butyl-group, an isobutyl-group, and a 2-ethylhexyl-group and the alkyl-substituent in 2-position is selected from the group consisting of a methyl-group, an ethyl-group, and an isopropyl-group.

52. A corrosion-inhibiting paint according to claim 43, comprising 1,3-diglycidyl imidazolium nitrate or 1,3-diglycidyl imidazolium acetate as said reactive thinner.

53. A corrosion-inhibiting paint according to claim 43, comprising 1,3-diglycidyl-2-alkylimidazolium nitrate or 1,3-diglycidyl-2-alkyl imidazolium acetate as reactive thinner.

54. A corrosion-inhibiting paint, according to claim 53, wherein said alkyl-group is selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an isopropyl-group, an n-butyl group, an isobutyl group, and a tert.-butyl group.

55. A corrosion-inhibiting paint, according to claim 53, wherein said alkyl-group is selected from the group consisting of a methyl group, an ethyl group, and an isopropyl group.

56. A corrosion-inhibiting paint according to claim 43 comprising:

reactive thinners comprising ionic liquids or salts with cations selected from the group consisting of 1-(1,2-epoxyethyl)-3-alkylimidazolium-cations with branched or unbranched C_1-to C_{12}-alkyl groups, 1 -(1,2-epoxyethyl-2-alkyl-3-alkylimidazolium-cations with branched or unbranched C_1- to C_{12}-alkyl groups in 3-position and methyl-, ethyl, n-propyl-, isopropyl-, n-butyl-, isobutyl- or tert.-butyl-groups as alkyl groups in 2-position, 1-(1,2-epoxyethyl)-3-glycidylimidazolium-cations, 1-(1,2-epoxyethyl)-2-alkyl-3-glycidylimidazolium-cations with methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl- or tert.-butyl-groups as alkyl- groups in 2-position, 1,3-bis(1,2-epoxyethyl)-imidazolium cations, 1,3-bis(1,2-epoxyethyl)-2-alkylimidazolium cations with methyl-, ethyl-, n-propyl-, iopropyl-, n-butyl-, isobutyl-or tert.-butyl groups as alkyl groups in 2-position, N-glycidylpyridinium-cations, glycidyltrialkylammonium-cations with branched or unbranched C_1- to C_{12}-alkyl groups, and glycidyltrialkylphosphonium-cations with branched or unbranched C_1- to C_{12}-alkyl groups.

57. A corrosion-inhibiting paint according to claim 1 to claim 17 or claim 25 to claim 28, comprising an epoxy-resin as said first prepolymer or second prepolymer which comprises_an epoxy-group and at least one cationic group selected from the group consisting of trialkylammonium groups, benzyldialkylammonium groups, phosphonium-groups, sulfonium-groups, imidazolium-groups, pyridinium-groups in carboxylate-form, nitrate-form or nitrite-form.

58. A corrosion-inhibiting paint according to claim 1 to 17 or claim 25 to claim 28, which comprises at least one curing agent as said first prepolymer or second prepolymer which comprises:
    (a) a plurality of reactive groups selected from the group consisting of amine-groups, thiol-groups, and carboxylic anhydride-groups; and
    (b) at least one cationic group selected from the group consisting of trialkylammonium groups, benzyltrialkylammonium groups, phosphonium-groups, sulfonium-groups, imidazolium-groups, pyridinium-groups in the form of a basic anion or in nitrate-form or nitrite-form.

59. A curing composition according to claim 58, wherein the anion of said basic salt is a carboxylate anion.

60. A curing composition according to claim 59, wherein said basic anion is an acetate ion.

61. A corrosion-inhibiting paint according to claim 58 comprising a curing agent, wherein said basic anion is selected from the group consisting of hydrogencarbonate anions, borate anions, hydrogenphosphate anions, silicate anions, carbonate anions, alkylcarbonate-anions, and dicyanamide anions.

62. A corrosion-inhibiting paint according to claims 57 to 58, wherein said imidazolium group is a 1,3-disubstituted imidazolium groups and wherein one substituent is a C_1- to C_{12}-alkyl group.

63. A corrosion-inhibiting paint according to claim 62, wherein said alkyl-group of said 1,3-disubstituted imidazolium groups is a C_3- to C_{12}-alkyl group.

64. A corrosion-inhibiting paint according to claim 62 to claim 63, wherein said alkyl-group of said 1,3-disubstituted imidazolium groups is selected from the group consisting of isopropyl-, butyl-, isobutyl-, and 2-ethylhexyl-groups.

65. A corrosion-inhibiting paint according to claim 57 to claim 58, wherein said imidazolium group is a 1,2,3-trisubstituted imidazolium group wherein the substituents in 3-position are C_1- to C_{12}-alkyl groups and the alkyl-substituent in 2-position is selected from the group consisting of methyl-groups, ethyl-groups, propyl-groups, isopropyl-groups, n-butyl-groups, isobutyl-groups, and tert.-butyl-groups.

66. A corrosion-inhibiting paint according to claim 43 to claim 65, further comprising at least one sparingly water-soluble salt with non-corrosive anions with a charge of $n \geq 2$.

67. A corrosion-inhibiting paint according to claim 66, wherein said sparingly water-soluble salt is a tribasic alkaline earth phosphate.

68. A corrosion-inhibiting paint according to claim 67, wherein said sparingly water-soluble salt is selected from the group consisting of tribasic calcium phosphate, tribasic strontium phosphate, and tribasic barium phosphate.

69. A kit for a corrosion-inhibiting paint comprising a reactive thinner according to claims 43 to 56 or an epoxy resin according or a curing agent according to claims 57 to 68 further comprising packaging materials therefor.

70. An article of metal that is coated with one of the corrosion-protecting paints according to claim 1 to claim 68.