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(71) **Applicant**: **AKZO NOBEL COATINGS INTERNATIONAL B.V.** [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).

(72) **Inventors**: **CRAUN, Gary, Pierce**; 409 Crescent Drive, Berea, Ohio 44017 (US). **RADEMACHER, Jude, Thomas**; 714 Hearthstone Circle, Akron, Ohio 44320 (US). **GEELEN, Patricia**; Heulsstraat 12B, NL-6413 EJ Heerlen (NL).

(74) **Agent**: **AKZO NOBEL IP DEPARTMENT**; Association No. 485, Velperweg 76, NL-6824 BM Arnhem (NL).

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(54) **Title**: AQUEOUS COATING COMPOSITIONS OF IMPROVED ADHESION

(57) **Abstract**: An aqueous coating composition comprising a. a binder polymer b. a substituted succinimide compound having sufficient acid groups such that the acid value of the substituted succinimide compound is at least 30mg KOH/g of the substituted succinimide compound wherein the succinimide compound is the reaction product of i. an unsaturated oil comprising at least one non-aromatic unsaturated carbon-carbon bond, a polymer derived from the unsaturated oil or a mixture thereof, ii. maleic anhydride and iii. primary amine.

Aqueous Coating Compositions of Improved Adhesion

This invention relates to aqueous coating compositions, especially protective coatings comprising substituted succinimide compounds, methods of preparing the coating compositions and substrates coated with the coating compositions. The coating compositions exhibit improved adhesion and corrosion resistance when applied to metallic substrates, especially aluminium, bare steel and corroded steel.

Many metals corrode when exposed to oxygen, forming a metal oxide crust in the process. We are all familiar with the rust that forms on ferrous metals. Not only is the rust disfiguring and unsightly, but it also weakens any structure constructed from the metal.

Special coatings, known as metal primers, have been formulated to be applied direct to the metal in order to prevent such corrosion. The coatings typically contain very high levels of anti-corrosion pigments such as zinc phosphate and are typically grey in colour. Such primers must be further coated with a topcoat layer to provide the desired aesthetic look of a coated article.

We have now discovered that incorporating small amounts of a particular group of compounds into aqueous coating compositions allows coatings to be made which have excellent adhesion to and corrosion resistance on bare metals. Surprisingly, the compositions also exhibit excellent corrosion resistance over rusted steel, even when the composition is free of anti-corrosion pigments.

Accordingly, there is provided an aqueous coating composition comprising

a. binder polymer
b. a substituted succinimide compound having sufficient acid groups such that the acid value of the substituted succinimide compound is at least 30 mg KOH/g of the substituted succinimide compound wherein

the substituted succinimide compound is the reaction product of

i. an unsaturated oil comprising at least one non-aromatic unsaturated carbon-carbon bond, a polymer derived from the unsaturated oil, or a mixture thereof
ii. maleic anhydride and
iii. primary amine

Preferably the substituted succinimide compound comprises from 0.5 to 5wt% of the liquid coating composition. Above 5wt% can cause the adhesion to deteriorate and below 0.5wt% there is no improvement in corrosion performance.

The aqueous coatings of the present invention is especially useful for coating bare metal substrates where they provide improved adhesion of the dried coating to bare steel, rusted steel, galvanised steel, electrocoated tin plate steel and aluminium and can also improve corrosion resistance.

The substituted succinimide compound contains the molecular fragment O=C–N(R)–C=O where R is an alkyl or aryl group. Preferably, the alkyl or aryl group contains up to 30 carbon atoms.

The unsaturated carbon-carbon bond of the unsaturated oil is preferably a double bond. In practice, commercially useful compounds contain double bonds and they may be singly-unsaturated – containing only one double bond; or multiply-unsaturated – containing more than one double bond. Multi-unsaturated compounds may contain conjugated or non-conjugated double bonds. Conjugated double bonds are separated by only one single carbon-carbon bond whereas non-conjugated double bonds are separated by more than one single carbon-carbon bond.

The reaction of maleic anhydride with such unsaturated bonds is by the Diels-Alder reaction or the Alder-ene reaction.

The unsaturated oil and the polymer derived from the oil may be prepared by esterification of one or more polyols, polycarboxylic acids, fatty acids, and mixtures thereof. At least part of the unsaturated oil and the polymer derived from the unsaturated oil may be oxidatively drying as a result of the incorporation of unsaturated aliphatic compounds, such as unsaturated fatty acids. Suitable examples of unsaturated fatty acids include myristoleic acid, palmitoleic acid, oleic acid, gadoleic acid, erucic acid, ricinoleic acid, oleic acid, linoleic acid, linolenic acid, tall oil fatty acid, sunflower fatty acid, safflower fatty acid, soybean oil fatty acid, and the like. Examples of fatty acids containing conjugated double bonds include dehydrated castor oil fatty acid and wood oil fatty acid. Monocarboxylic acids suitable for use include tetrahydrobenzoic acid and hydrogenated or non-hydrogenated abietic acid or its isomer. If so desired, the monocarboxylic acids may be used wholly or in part as triglyceride, for example as a vegetable oil, in the preparation of the unsaturated oil and the polymer derived from the unsaturated oil. If so desired, mixtures of two or more of such monocarboxylic acids or triglycerides may be employed, optionally in the presence of one or more saturated, (cyclo)aliphatic or aromatic monocarboxylic acids, for example, pivalic acid, 2-ethylhexanoic acid, lauric acid, palmitic acid, stearic acid, 4-tert-butyl-benzoic acid, cyclopentane carboxylic acid, naphthenic acid, cyclohexane carboxylic acid, 2,4-dimethyl benzoic acid, 2-methyl benzoic acid, and benzoic acid.

Polycarboxylic acids may also be incorporated into the unsaturated oil and the polymer derived from the unsaturated oil, such as phthalic acid, isophthalic acid, terephthalic acid, 5-tert-butyl isophthalic acid, trimellitic acid, pyromellitic acid, succinic acid, adipic acid, 2,2,4-trimethyl adipic acid, azelaic acid, sebacic acid, dimerized fatty acids, cyclopentane-1,2-dicarboxylic acid, cyclohexane-1,2-dicarboxylic acid, 4-methylcyclohexane-1,2-dicarboxylic acid, tetrahydrophthalic acid, butane-1,2,3,4-tetracarboxylic acid, endoisopropylidene-cyclohexane-1,2-dicarboxylic acid, cyclohexane- 1,2,4,5-tetracarboxylic acid, and butane-1,2,3,4-tetracarboxylic acid. If so desired, the carboxylic acids may be used as an anhydride or in the form of an ester, for example, an ester of an alcohol having 1-4 carbon atoms.

The unsaturated oil and the polymer derived from the unsaturated oil may further comprise polyol building blocks. Examples of suitable polyols include ethylene glycol, 1,3-propane diol, 1,6-hexane diol, 1,12-dodecane diol, 3-methyl-1,5-pentane diol, 2,2,4-trimethyl-1,6-hexane diol, 2,2-dimethyl-1,3-propane diol, and 2-methyl-2-cyclohexyl-1,3-propane diol. Examples of suitable triols include glycerol, trimethylol ethane, and trimethylol propane. Suitable polyols having more than three hydroxyl groups include pentaerythritol, sorbitol, and etherification products, such as ditrimethylol propane and di-, tri-, and tetrapentaerythritol.

The unsaturated oil and the polymer derived from the unsaturated oil can be obtained by direct esterification of the constituent components, with the option of a portion of these components having been pre-converted into ester diols or polyester diols. In some embodiments, the unsaturated oil and the polymer derived from the unsaturated oil can be added in the form of a drying oil, such as linseed oil, fish oil, or dehydrated castor oil. The unsaturated oil and the polymer derived from the unsaturated oil may be produced by transesterification with other acids and polyols at a temperature in the range of about 200 to about 250 C, optionally in the presence of solvents such as toluene and/or xylene.

Preferably, the unsaturated oil comprises or consists of vegetable oil or fish oil or a mixture of the two. Vegetable oils are preferred as they are readily available in many grades and are more cost effective than other oils, such as fish oils. By vegetable oil and fish oil is meant oil extracted from vegetable and fish matter respectively.

Vegetable oils comprise triglycerides, being tri-esters of glycerol and fatty acids. The triglycerides making up unsaturated vegetable oils comprise at least one unsaturated fatty acid. The fatty acids preferably have chain length of from 12 to 24 carbon atoms and the triglyceride can comprise the same or different fatty acids, including saturated fatty acids.

Suitable unsaturated vegetable oils include soy bean oil, linseed oil, tall oil; sunflower oil, corn oil, hempseed oil, perilla oil, poppyseed oil and canola oil. Preferably, soy bean oil is used.

Suitable examples of polymers derived from unsaturated oil include alkyd resins. Such resins can be considered as polyesters modified with unsaturated fatty acids directly or by unsaturated oils comprising unsaturated fatty acids.

The number average molecular weight of polymers derived from the unsaturated oil should be at least 1000 Daltons, preferably from 1000 to 75000 Daltons and more preferably from 2000 to 50000 Daltons.

Primary amines have the general formula RNH_2 where R can be an alkyl or aryl group preferably with from 2 to 30 carbon atoms, more preferably from 3 to 12 carbon atoms.

Examples of suitable primary amines include the alkylamines such as 2-ethyl hexylamine, hexylamine and benzylamine. R may be substituted with an acid group such as carboxyl, phosphoric. Where the acid group is carboxyl, R is an amino acid. Examples of suitable amino acids include glycine, β-alanine, arginine, asparagine, cysteine, leucine and glutamine. Preferably, β-alanine is used. Preferably, the acid and the amine group of the amino acid are separated by more than one carbon atom as such amino acids are more reactive than when the groups are separated by only one carbon atom.

The acid value of the substituted succinimide compound is preferably sufficiently high to enable the substituted succinimide to be dispersible, preferably soluble, in water or aqueous media when neutralized. The solubility of the substituted succinimide compound will depend partly on the hydrophobicity of the substituted succinimide compound itself and also the nature of the aqueous medium in which it is to be dissolved or dispersed.

Preferably the acid value is from 30 to 300 mg KOH/g substituted succinimide compound, more preferably from 50 to 150mg KOH/g. Preferably the acid value of the substituted succinimide compound is provided by carboxyl groups.

Preferably, the number average molecular weight of the substituted succinimide compound is from 400 to 10000 Daltons, more preferably from 1000 to 10000 as measured by gel permeation chromatography.

By aqueous is meant that the continuous phase of the composition comprises at least 50% water, preferably at least 65%, more preferably, 80%, even more preferably, 90% and most preferably, 100% water. The remainder of the continuous phase may comprise organic solvents. These may be water soluble, partly water soluble or water insoluble. Preferably, they are partly water soluble and most preferably they are water soluble. The solubility is assessed at 23ºC.

Suitable solvents include n-butanol and ethylene glycol monobutyl ether.

The acid groups of the substituted succinimide compound may be partially or fully neutralised prior to addition to the coating composition to facilitate dissolution or dispersion in the continuous phase of the aqueous coating composition. Alternatively, an aqueous emulsion of the substituted succinimide compound may be pre-formed by adding a neutralising agent to the substituted succinimide compound and diluting with water whilst stirring. Such emulsions are often more convenient to incorporate into aqueous compositions.

Suitable neutralising agents include ammonia, amines, alkali metal bases and mixtures thereof.

Suitable amines include dimethyl amino ethanol, triethylamine, amino-2-methyl propanol, dimethyl amino propanol, dimethyl amino-2-methyl propanol.

Suitable alkali metal bases include, potassium hydroxide, sodium hydroxide.

Figure 1 shows the steps in a suggested reaction scheme where the primary amine is an amino acid, β-alanine.

Step 1 is the reaction of an unsaturated oil and/or a polymer derived from an unsaturated oil, in this case having one double bond, with the maleic anhydride to form a substituted succinic anhydride intermediate (I).

Step 2 shows the reaction of the substituted succinic anhydride intermediate (I) with the primary amine to form an amic acid (II) which goes on to lose water in step 3 to form the substituted succinimide compound (III).

Preferably the coating composition has a gloss of at least 80 gloss units when measured at 60 degrees.

The composition is preferably free of anti-corrosion pigments as the presence of such pigments can reduce the gloss to unacceptably low levels. It is not clear why anti-corrosive pigments should decrease the gloss.

Anti-corrosion pigments are well known and used extensively in the coatings industry to provide paints which prevent metal substrates to which they are applied from corroding. Surprisingly, coatings of the present invention which are free of such anti-corrosion pigments, may be applied directly to bare metal, in particular steel, and yet protect the metal from corrosion.

Surprisingly, the adhesion of the dried coating to bare steel is also substantially improved.

Examples of anti-corrosion pigments that preferably are avoided include potassium silicate; hydrogen phosphates such as $CaHPO_4$, $MgHPO_4$ and $SrHPO_4$; orthophosphates such as co-precipitated zinc orthophosphate, zinc orthophosphate hydrate, zinc aluminium orthophosphate and organically modified basic; polyphosphates such as strontium aluminium polyphosphate hydrate, zinc aluminium polyphosphate hydrate, magnesium aluminium polyphosphate, zinc aluminium triphosphate and magnesium aluminium triphosphate; phosphosilicates such as calcium strontium phosphosilicates and strontium zinc phosphosilicate; other phosphates such as zinc phosphate and strontium borophosphate; hybrid pigments using mixtures of inorganic and organic inhibitors such as zinc phosphate and zinc oxide and zinc (2,5-dimercapto-1,3,4-thiadazole)$_2$ also known as (DMTD)$_2$; metal oxides such as oxides of zinc, magnesium, aluminium, lithium, molybdenum, strontium, cerium and mixtures thereof; metals like metallic zinc, metallic magnesium and magnesium alloys; and ion exchange pigments such as calcium, magnesium.

Such pigments are insoluble in the paint and thus exist in the paint in particulate form.

Anti-corrosion pigments differ from non-pigment corrosion inhibitors. Such non-pigment corrosion inhibitors are materials which are soluble in organic or aqueous media, at least up to about 5wt% based on the liquid coating formulation. Examples of such corrosion inhibitors include azoles such as imidazoles, thiazoles, tetrazoles and triazoles and 2-mercaptobenzothiazole; amines like N-phenyl-1,4- phenylenediamine and Schiff bases like N,N'-o-phenylen-bis(3methoxysalicylidenimine); amino acids like tryptophan thiol compounds like DMTD or 1-phenyl-2, 5-dithiohydrazodicarbonamide; phthalazin derivatives including 2-

[(7-anilino-5-[1,2,4]triazolo [3,4-b][1,3,4]thiadiazin-3-yl)methyl]phthalazin-1(2H)-one; tannins and substituted uracils; phosphonic acid group containing materials including styrenephosphonic acid; succinic acid; 2-(1,3 benzothiazol-2ylthio)succinic acid.

Such non-pigment corrosion inhibitors may be used in the present invention at levels from 0 to 5.0wt%, preferably from 0.5 to 3.0wt%, more preferably from 0.5 to 2.0wt%, yet more preferably from 0.5 to 1.0wt%. However, most preferably the coating is free of any such non-pigment corrosion inhibitors.

Like many waterborne compositions applied to bare steel, the compositions of the present inventions preferably contain flash rust inhibitors to prevent corrosion occurring during or soon after the application process. The rust appears as a stain immediately after or within hours of the coating being applied to the metal substrate. Such flash rust inhibitors are used in very small amounts, preferably at least 0.1 to 0.6 % by weight based on the 100% liquid formulation, more preferably from 0.1 to 0.5, even more preferably from 0.15 to 0.45, yet more preferably from 0.2 to 0.4 and most preferably from 0.25 to 0.35%.

Flash rust inhibitors fall into two groups namely, nitrite containing and nitrite-free. Suitable nitrite containing inhibitors include sodium nitrite. Suitable nitrite-free inhibitors include alkanolamine borate; amino carboxylates such as Halox 510; phosphate salts such as neutralised form of phosphate co-ester of aliphatic alcohols; specially formulated film forming inhibitor based on an organic zinc complex and a nitrogen compound (such as Nalzin FA 379); high ratio copolymerised calcium sulphonate (such as Termarust TR2010R1).

Suitable flash rusting inhibitors include the nitrite-free range available from Halox, such as Halox 510, 515 and 570; Flash-X 330, 350D; Wayneflash 115; Nubirox FR20; WorleeADD 358; Nalzin 3358, 379, 579; Raybo 90 NoRust NF; Termarust TR2010R; Rodine Flash Rust Inhibitor; Heucorin FR; Vancor 081; Nacorr 1352, 1652, 1754, 4426, XR; Synthro Cor C 08B, C660B, CA50B; Strodex MOK-70 potassium salt.

Also available are the nitrite containing flash rust inhibitors such as Flash X 150; Wayneflash 110, 111; Nubirox FR10; Nalzin 179; Cortec M-111, M-240, M-435, 380; Synthro cor EV B;

Vancor 073; Worlee Add 357; Drew2gard 794 SA, 795A; Additive EDA, ETE, IDA, TA-40, TA-41.

Nitrite free flash rust inhibitors are preferred.

The coating composition of the invention may further contain pigments which are not anti-corrosion pigments such as coloured pigments. Such non-anti-corrosion pigments may be organic or inorganic, including carbon black titanium dioxide, phthalocyanine blue, iron oxide; metal flake pigments such as iron, aluminium and bronze.

Suitable binder polymers for use in the invention include acrylic polymers, styrene-acrylic polymers, polyurethane polymers, alkyd polymers, epoxy ester polymers and mixtures and/or hybrids thereof. Preferably acrylic polymers or styrene-acrylic polymers are used and most preferably acrylic polymers are used.

By acrylic polymer is meant that the polymer is derived only from monomers selected from the esters of acrylic acid and methacrylic acid and the acids themselves. A styrene-acrylic polymer further comprises styrene or a derivative of styrene such as α-methyl styrene or vinyl toluene.

The binder polymer preferably forms a coherent film at ambient temperatures of from 0 to 40°C, preferably from 5 to 30°C and most preferably from 5 to 25°C.

The binder can comprise an aqueous dispersion of particles formed directly using known emulsion polymerization processes. Such dispersions are often referred to as latex. Alternatively, an emulsion of a polymer can be made by emulsifying the polymer itself or the polymer dissolved in solvent, in aqueous medium using high shear mixing and optionally in the presence of surfactants.

Where the polymer is in the form of a dispersion of polymer particles such dispersion are conveniently and preferably made using emulsion polymerisation methods, including mini-emulsion polymerization or microsuspension polymerization.

Suitable monomers to prepare the binder polymer includestyrene, alpha-methyl styrene, alkyl esters of acrylic or methacrylic acid such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, n-octyl acrylate, lauryl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, nonyl acrylate,decyl acrylate, benzyl methacrylate, isobutyl methacrylate, isobornyl methacrylate the hydroxyalkyl esters of the same acids such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, glycidyl acrylate and glycidyl methacrylate, acrylic acid and methacrylic acid.

A method of protecting a metal substrate including the steps of applying a coating composition of the invention and causing it to form a solid coating.

In another aspect of the invention there is provided a metal substrate coated with a coating composition of the invention.

In another aspect of the invention there is provided a method of providing corrosion resistance to a metal substrate including the steps of applying a coating composition of the invention to the metal substrate and causing it to form a solid coating.

In another aspect of the invention there is provided a method of preparing the aqueous composition of the invention comprising the steps

i. reacting an unsaturated oil comprising at least one non-aromatic unsaturated carbon-carbon bond or a polymer derived from the oil or a mixture thereof, with maleic anhydride to form a substituted succinic anhydride intermediate
ii. reacting the substituted succinic anhydride intermediate with a primary amine to form an amic acid mixture
iii. evolving water from the mixture to form a substituted succinimide compound
iv. neutralising the substituted succinimide compound in the presence of water to form an aqueous dispersion

and mixing the aqueous dispersion with a binder polymer to form an aqueous dispersion to form an aqueous coating formation.For example, soybean oil can be heated in the presence of maleic anhydride to about 225 °C to attach the anhydride to the soybean oil by an Alder-Ene reaction to form a substituted succinic anhydride soybean oil intermediate. β-alanine can be added to the mixture at about 140 °C to form an amic acid intermediate. As the mixture is gradually heated to about 170 °C, water is evolved to yield the soybean oil substituted succinimide compound. After cooling to about 100 °C, a neutralizing base such as a tertiary amine or ammonia can be added with water to form an aqueous dispersion of the soybean oil substituted succinimide compound. Thereafter, the aqueous dispersion of the soy bean oil substituted succinimide compound is mixed with a binder polymer to form a coating composition of the invention.

The coating composition of the invention may further contain conventional additives for coatings. Suitable such additives include thickeners, defoamers, anti-foam agent, flow aids, anti-crater agents, wetting agents and cure agents.

The coating compositions may be applied to a substrate using known methods including brush, roller, blade, pad, spray and dip

The invention will now be illustrated by the following examples.

Ingredients

The following ingredients were used in the examples.

Soy bean oil available from Sigma Aldrich

Gum Rosin available from Sigma Aldrich

Texanol is an ester alcohol solvent available from Eastman.

Nalzin FA179 is flash rust inhibitor available from Elementis Specialties

Setal 276 XX-98 is an alkyd resin available from Nuplex Resins BV

Tests

The acid value was measured using the following procedure.

About 0.1g of sample is dissolved in a 1:1 mixture of xylene and isopropanol and one drop of phenolphthalein in ethanol is added to the resulting mixture. The mixture is then titrated to a light pink end point using 0.1 normal potassium hydroxide solution.

Example 1a

Preparation of a substituted succinimide compound from an unsaturated vegetable oil

The following ingredients were reacted according to the method described below.

	g	mol
Soy bean oil	150.0	0.17
Xylene	3.0	
Maleic anhydride	50.0	0.51
β-alanine	45.5	0.51

Step 1

Preparation of the substituted succinic anhydride :

The soybean oil, xylene and maleic anhydride were added (under a nitrogen blanket) to a 1 litre flask (equipped with stirrer and condenser) whilst stirring. The temperature was raised to 180ºC and then further increased to 220 ºC over 45 minutes. This temperature was held for 1.5 hours after which time the mixture was cooled to 100ºC. Note: the xylene washes down subliming maleic anhydride and thus gives better conversion and a cleaner reaction. It distilled off in step 2 with the water.

Steps 2 and 3

Conversion of the substituted succinic anhydride to a substituted succinimide compound:

The reflux condenser was removed from the flask and replaced with a Dean and Stark condenser allowing vapors to be removed and collected from the flask. The β-alanine was added and the temperature increased to 170ºC over 1 hour. Care is required to control the resulting exotherm and foaming from the reaction of the anhydride and the amine. As foaming subsides at 170ºC a vacuum is applied to drive the reaction forward. About 7g water was collected over about 2 hours at 170ºC as the substituted succinimide compound was formed.

Example 1b

Formation of an emulsion:

The substituted succinimide was cooled to about 90ºC, and 35g of dimethylethanol amine dissolved in 100g water was added over about 2 minutes. A further 408g of water was added over about 15 minutes with good agitation (400 rpm, 3 inch flat blade) as the emulsion was formed and cooled. The measured solids content of the emulsion was 20.4%.

Example 2

Formation of a substituted succinimide compound from rosin

The same procedure was followed as in example 1 but using the following ingredients.

	g	mol
Gum Rosin	135.0	0.40
Xylene	3.0	
Maleic anhydride	45.0	0.46
β-alanine	41.0	0.46

Formation of an emulsion

The same procedure was followed as in example 1 except that 33g of dimethyl amino ethanol was used and a total of 602g of water.

Example 3

Preparation of a substituted succinimide from a polymer derived from an alkyd resin

The following ingredients were reacted according to the method described below.

	g	mol
[1]Setal 276 XX-98	200.0	0.10
Xylene	3.0	
Maleic anhydride	50.0	0.51
β-alanine	45.5	0.51

[1] Long oil alkyd

Step 1

Preparation of the substituted succinic anhydride:

The Setal 276 XX-98, xylene and maleic anhydride were added (under a nitrogen blanket) to a 1 litre flask (equipped with stirrer and condenser) whilst stirring. The temperature was raised to 180°C and then further increased to 220 °C over 45 minutes. This temperature was held for 1.5 hours after which time the mixture was cooled to 100°C and a vacuum applied to remove xylene and unreactd maleic anhydride if present.

Step 2

Conversion of maleinised oil intermediate to succinimide:

The reflux condenser was removed from the flask and replaced with a Dean and Stark condenser allowing vapors to be removed and collected from the flask. The β-alanine was added and the temperature increased to 150°C over 1 hour. Care is required to control the resulting exotherm and foaming from the reaction of the anhydride and the amine.

Example 3b

Formation of an emulsion:

The substituted succinimide was cooled to about 90°C, and 35g of dimethylethanol amine dissolved in 100g water was added over about 2 minutes. A further 408g of water was added over about 15 minutes with good agitation (400 rpm, 3 inch flat blade) as the emulsion was formed and cooled.

Example 4 (Paint)

Preparation of a paint containing the aqueous substituted succinimide emulsion of example 1b.

The ingredients listed below were added to a 100 cm^3 container in the order indicated under using mild stirring conditions.

g

[3] Acrylic latex	40.00
[1] Texanol	0.80
[2] Nalzin FA179	0.12
Black colorant (22wt% carbon black)	1.20
Emulsion of Example 1b	2.00

[1] Cosolvent – 2,2,4-trimethyl-1,3 pentanediol-monoisobutyrate

[2] Comprises sodium nitrite, zinc salts of C6-C19 fatty acids, morpholine benzoate and undisclosed proprietary material.

[3] Primal AC 337, 45.5% solids content of MFFT 12-16ºC

Once the additions were complete, stirring continued for a further 10 minutes and the mixture left to stand overnight.

Comparative Example A (Paint)

The same ingredients and process was used as in example 4 other than that Example 1b was omitted from the paint.

Preparation of panels I and II

Example 4 and Comparative Example A were applied to steel panels using the method described below.

Two 10 x 20 cm cold rolled steel panels were cleaned of the protective oil layer by wiping with a solvent mixture (xylene and acetone at a ratio of 35:65) and allowed to dry. When dry, the panel was dry sanded using sandpaper. The panels were then wiped with absorbent paper. A 135 micron wet layer of paint was drawn down using a roll bar to give a dry paint film thickness of about 55 microns.

Testing

Adhesion

Following application of the paint to the cleaned bare steel panels according to the method described above, the panels were allowed to dry at room temperature (20-25°C) for 24 hours. They were then cross-hatched with a sharp knife using a template, the distance between the lines being 1mm, following which adhesive tape (Scotch filament tape 8981) was firmly applied over the cross-hatched area. The tape was then removed in one swift, sharp action and the percentage of the cross-hatched area removed assessed.

Corrosion

The paint was applied to the cleaned bare steel panels as described above to give a 50μm dry paint layer and then allowed to dry for 24 hours. The panels were scribed with a cross using a knife (Erichsen type 463). The scribed panels were then exposed to an accelerated cyclical salt spray corrosion test in accordance with ASTM G85-A5.

Any blisters are evaluated according the ASTM D714-02 where the size and density are estimated. Blister size 8 is the smallest blister size with 6, 4 and 2 representing progressively larger blister. The density is self-explanatory.

Results

Panel	Steel Panel painted with	Adhesion/% removed	Corrosion
I	Example 4	0	Body: No corrosion or blisters. Scribed cut: Blisters 8, very few/few
II	Comparative Example A	100	Body: No corrosion. Blisters 4, few. Scribed cut: Blisters 6, dense.

Example 5 (Paint) using a different binder polymer

Preparation of a paint containing the aqueous succinimide emulsion of example 1b.

The ingredients listed below were added to a 100 cm^3 container in the order indicated under using mild stirring conditions.

	g
[3] Acrylic latex	45.13
[1]Ethyl diglycol	1.35
[2]Dowanol DPM	1.35
Texanol	0.68
Nalzin FA179	0.14
Black colorant (22wt% carbon black)	1.35
Emulsion of Example 1b	2.5

[1] CAS number – 111-90-0

[2] Dipropopylene glycol methyl ethyl ether

[3] monomer composition: methylmethacrylate, styrene, 2-ethylhexylacrylate, 2-ethylhexylmethacrylate and cyclohexylmethacrylate. 47% solids content of MFFT 10-30°C

Once the additions were complete, stirring continued for a further 10 minutes and the mixture left to stand overnight.

Comparative Example B (Paint)

Comparative Paint B was prepared using the same ingredients and process as used to make Example 5 other than that the substituted succinimide emulsion, Example 1b, was omitted from the paint.

Preparation of Panels III and IV

Example 5 and Comparative Example B were applied to steel panels using the method described below.

Clean steel panels were prepared using the same method as described for panels I and II.

Two rusted 10 x 20 cm cold rolled steel panels were prepared using the following method; the panels were cleaned of the protective oil layer by wiping with a solvent mixture (xylene and acetone at a ratio of 35:65) and allowed to dry. When dry, the panel was dry sanded using sandpaper. The panels were then wiped with absorbent paper. These were then exposed to outside weathering conditions to create corroded steel panels. The panels were wiped with wire wool to remove loose rust on the panel. A 135 micron wet layer of paint was drawn down using a roll bar to give a dry paint film thickness of about 55 microns.

Testing

Adhesion to rusted steel

Following application of the paint to the rusted steel panels according to the method described above, the panels were allowed to dry at room temperature (20-25°C) for 7 days. They were then cross-hatched with a sharp knife using a template, the distance between the lines being 1mm, following which adhesive tape (Scotch filament tape 8981) was firmly applied over the cross-hatched area. The tape was then removed in one swift, sharp action and the percentage of the cross-hatched area removed assessed.

Corrosion

The paint was applied to the cleaned bare steel panels as described above to give a 50μm dry paint layer and then allowed to dry for 24 hours. The panels were scribed with a cross using a knife (Erichsen type 463). The scribed panels were then exposed to an accelerated cyclical salt spray corrosion test in accordance with ASTM G85-A5.

Any blisters are evaluated according the ASTM D714-02 where the size and density are estimated. Blister size 8 is the smallest blister size with 6, 4 and 2 representing progressively larger blister. The density is self-explanatory.

Rusting was evaluated according to ASTM D610-01, where the percentage of rust is estimated, and 3 types of rust are distinguished: spot rusting, general rusting or pinpoint rusting.

Results

Panel	Painted with	Adhesion on rusted steel/% removed	Corrosion
III	Example 5	10	Body: 0.03-0.1% pinpoint rusting, no blisters. Scribed cut: Blisters 8, very few/few
IV	Comparative Example B	50	Body: 1-3% pinpoint rusting, Blisters 8, few Scribed cut: Blisters 6, dense.

Claims

1. An aqueous coating composition comprising
    a. a binder polymer
    b. a substituted succinimide compound having sufficient acid groups such that the acid value of the substituted succinimide compound is at least 30mg KOH/g of the substituted succinimide compound wherein the substituted succinimide compound is the reaction product of
    i. an unsaturated oil comprising at least one non-aromatic unsaturated carbon-carbon bond, a polymer derived from the unsaturated oil, or a mixture thereof,
    ii. maleic anhydride and
    iii. primary amine.
2. The aqueous coating composition of claim 1 wherein the number average molecular weight of the substituted succinimide compound is from 400 to 10000 Daltons.
3. A coating composition according to claim 1 or claim 2 wherein the unsaturated oil is a vegetable oil.
4. A coating composition according to any one of the preceding claims wherein the unsaturated oil and/or the primary amine comprise acid groups.
5. A coating composition according to any one of the preceding claims wherein the unsaturated oil is selected from the group comprising or consisting of linseed oil, perilla oil, tall oil, soy bean oil,safflower oil and combinations thereof.
6. A coating composition according to any one of the preceding claims wherein the primary amine is β-alanine.
7. A coating composition according to any one of the preceding claims and further comprising sufficient neutralising agent to at least partially neutralise the acid groups of the substituted succinimide compound .
8. A coating composition according to any one of the preceding claims wherein the composition is free of anti-corrosion pigments.
9. A coating composition according to any one of the preceding claims wherein the composition comprises from 0.5 to 5wt% substituted succinimide compound based on the liquid coating composition.

10. A coating composition according to any one of the preceding claims and further containing from 0.1 to 0.6% by weight of flash rust inhibitor calculated on the liquid coating composition.
11. A coating composition according to any one of the preceding claims which is free of non-pigment corrosion inhibitor.
12. A coating composition according to any one of the preceding claims comprising non-anti-corrosion pigments.
13. A method of preparing the coating composition of any one of the previous claims comprising the steps of
    i. reacting the unsaturated oil comprising at least one non-aromatic unsaturated carbon-carbon bond or a polymer derived from the oil or a mixture thereof, with maleic anhydride to form a substituted succinic anhydride intermediate
    ii. reacting the substituted succinic anhydride intermediate with a primary amine to form an amic acid mixture
    iii. evolving water from the mixture to form a substituted succinimide compound
    iv. neutralising the substituted succinimide compound in the presence of water to form an aqueous dispersion and
    v. mixing the aqueous dispersion with a binder polymer to form an aqueous dispersion to form an aqueous coating composition.
14. A method of protecting a metal substrate including the steps of applying a coating composition according to any one of claims 1 to 12 and causing it to form a solid coating.
15. A metal substrate coated with a coating according to any one of claims 1 to 12.

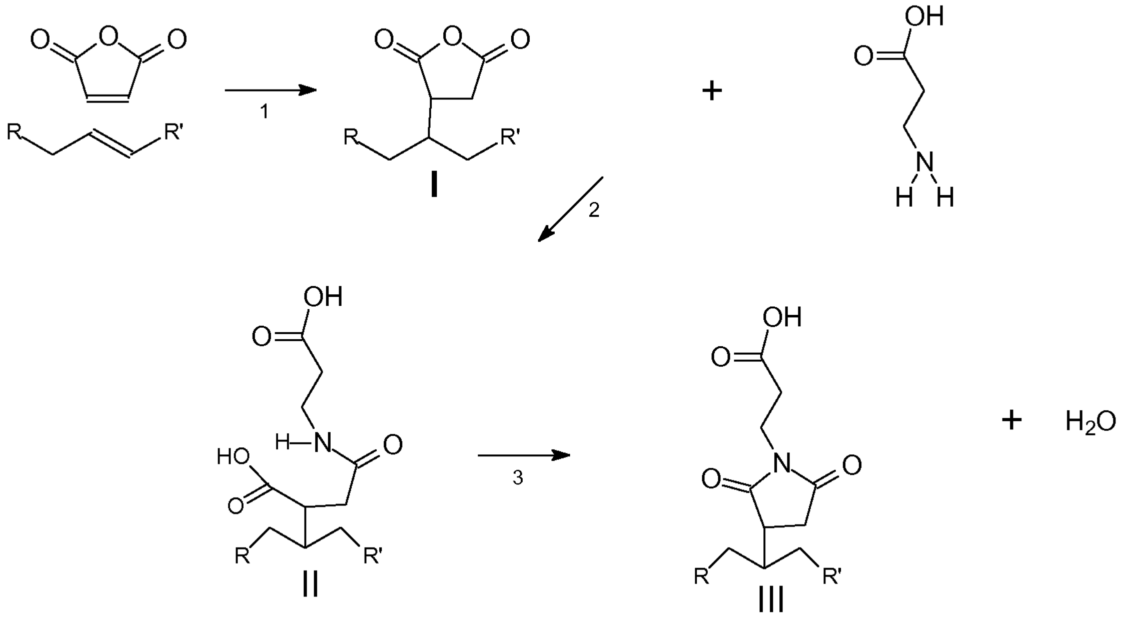

Fig 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/069424

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D4/06 C09D5/00 C09D5/08 C09D7/12 C09F7/00
C08K5/353 C23F11/14 B65D23/02
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D C09F C08K C23F B65D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/029155 A1 (GOETHLICH ALEXANDER [DE] ET AL) 29 January 2009 (2009-01-29) claims 1, 2, 6, 10-14 paragraphs [0087] - [0105], [0111], [0122] -----	1-15
Y	US 3 293 201 A (SHAHADE FRED S ET AL) 20 December 1966 (1966-12-20) claims 1-4 column 1, line 56 - column 4, line 45 examples F, H, V ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Mayer, Anne

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/069424

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2009/006527 A1 (GEORGIA PACIFIC CHEMICALS LLC [US]; JOHNSON ROGER SCOTT [US]; HURD PHI) 8 January 2009 (2009-01-08) paragraphs [0010] - [0013], [0016] - [0018], [0021], [0024] paragraphs [0029] - [0047], [0053] - [0058], [0062], [0063] paragraphs [0089] - [0091], [0099], [0100], [0118] - [0120], [0132] - [0135] -----	1-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/069424

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