OXIDATIVELY CURABLE COATING COMPOSITION

COMPOSITION  DE  REVÊTEMENT DURCISSABLE OXYDATIF

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Description

FIELD

The present invention relates to an oxidatively curable coating formulation comprising an oxidatively curable alkyd-based resin and a bis-triazacyclononane-based chelant, which chelant may optionally be complexed with a suitable transition metal ion. The formulations may be paints or other oxidatively curable coating compositions. The invention also provides methods for making such formulations and compositions resultant from the curing of such formulations.

BACKGROUND

Alkyd resins are a well understood and dominant binder in many oxidatively curable paints and other solvent-based coatings. Alkyd emulsion paints, in which the continuous phase is aqueous, are also widely available commercially. Alkyd resins are produced by the reaction of polyols with carboxylic acids or anhydrides. To make them susceptible to what is commonly referred to as a drying process, some alkyd resins are reacted with unsaturated triglycerides or other source of unsaturation. Plant and vegetable oils, such as linseed oil, are frequently used as the source of triglycerides. In these drying processes, unsaturated groups, in particular carbon-carbon double bonds, can react with oxygen from the air, causing the oils to crosslink, forming a three-dimensional network, and harden. This oxidative curing process, although not drying, gives the appearance of drying and is often and herein referred to as such. The length of time required for drying depends on a variety of factors, including the constituents of the alkyd resin formulation and the amount and nature of the liquid continuous phase (e.g. solvent) in which the alkyd resin is formulated.

Film formation results from the antioxidation and polymerisation chemistries that occur during the drying of alkyd-based resins. It will proceed in the absence of catalysis. However, it is customary to include in formulations of curable resins small, i.e. catalytic, quantities of optionally organic metal salts, often referred to as metal driers, which catalyse the polymerisation of unsaturated material so as to form the three-dimensional network.

Driers used for solvent-based coatings typically include alkyl carboxylates, typically C₆-C₁₈ carboxylates, of metals such as cobalt, manganese, lead, zirconium, zinc, vanadium, strontium, calcium and iron. Such metal carboxylates are often referred to as metal soaps. Redox-active metals, such as manganese, iron, cobalt, vanadium and copper enhance radical formation, and thus the oxidative curing process, whilst so-called secondary driers (sometimes referred to as auxiliary driers), such as complexes based on strontium, zirconium and calcium, enhance the action of the redox-active metals. Often these soaps are based on medium-chain alkyl carboxylates such as 2-ethyl-hexanoate. The lipophilic units in such soaps enhance the solubility of the drier in solvent-based paints and other oxidatively curable coating compositions.

As well as metal driers, a variety of metal driers that are redox metal complexes containing organic ligands can be used as driers, for example manganese complexes comprising 2,2'-bipyridine.

The formation of a skin or lumpy matter is a problem observed in many oil-based (i.e. organic solvent-based) formulations, and in particular in organic solvent-based alkyd resins, as a consequence of oxidation during storage or transportation. Oxidative polymerisation reactions can thus lead to the skin formation before application, as well as the intended drying after application. As alluded to above, these polymerisation reactions can be triggered by radicals generated by the action of metal-based driers, for example cobalt-, manganese- or iron-containing driers. In other words, the cause of the skin formation is often associated with the presence of metal driers.

Skin formation during manufacture and storage of air-drying paints and other coatings, in particular of alkyd-based resins, is clearly undesirable. Skin formation can lead to material losses and usage problems, such as surface irregularity after application owing to skin particles remaining in the paint.

Addition of compounds that quench the radicals formed during the storage or transportation processes reduce the skin-forming tendencies of such formulations. Many antiskinning agents are therefore antioxidants. However, addition of such antiskinning antioxidants can also slow the drying desired after application, by reducing the activity of the metal driers.

Oximes, and in particular methylethylketoxime (MEKO), are known to reduce skin formation considerably, particularly with cobalt-based driers. It is understood that the oxime binds to the metal ion during storage of the resin, thereby preventing the metal drier from reacting with oxygen and the substrate for radical formation that otherwise leads to polymerisation and skin formation. Upon application of the paint or other coating as a thin layer on a surface, the MEKO can evaporate. In this way, skinning can be prevented or ameliorated, but the cobalt soap can function, after application, as a polymerisation catalyst (see J H Bieleman in Additives in Plastics and Paints, Chimia, 56, 184 (2002)).

Antiskinning agents, or ways to address the problem of skinning, other than those involving the use of oximes such as MEKO, have been described. For example, WO 00/11090 A1 (Akzo Nobel N.V.) describes the use of 1,3-diketones, pyrazoles and imidazoles to reduce the skinning properties; WO 2007/024592 A1 (Arkema Inc.) describes the use of isoascorbate as an antiskinning agent and a co-promoter of metal-based driers; and WO 2008/127739 A1...
(Rockwood Pigments NA, Inc.) describes the use of hydroxylamine as an antiskinning agent. Whilst such additives reduce the tendency towards skinning, they can lead to decreased performance of the metal drier if their degree of incorporation is too great and they do not evaporate sufficiently during the coating (e.g. paint) application.

[0011] Whilst cobalt driers have been employed for many years as paint driers, there is a desire to develop alternatives, not least since cobalt soaps may need to be registered as carcinogenic materials. Iron- and manganese-based paint driers in particular have received considerable attention in recent years in the academic and patent literature as alternatives to cobalt-based driers. For some recent scientific publications addressing this topic in detail see publications by J H Bieleman (in Additives in Plastics and Paints, Chimia, infra)); J H Bieleman (Marcomol. Symp., 187, 811 (2002)); and R E van Gorkum and E Bouwman (Coord. Chem. Rev., 249, 1709 (2005)).

[0012] WO 03/093384 A1 (Ato B.V.) describes the use of reducing biomolecules in combination with transition-metal salts or complexes based on pyrazoles, aliphatic and aromatic amines, 2,2’-bipyridine, 1,10’-phenanthroline and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me3TACN).

[0013] WO 03/029371 A1 (Akzo Nobel N.V.) describes the use of complexes comprising Schiff base compounds to enhance the drying of coatings, in which complexes at least one solubilising group is covalently bound to the organic ligand.


[0015] WO 2008/003652 A1 (Unilever PLC et al.) describes the use of tetradaentate, pentadentate or hexadentate nitrogen ligands bound to manganese and iron as siccative for curing alkyd-based resins.


[0017] WO 2012/092034 A2 (Dura Chemicals, Inc.) describes the use of a transition metal and a porphyrin based ligand as a siccative for resin compositions.

[0018] The use of mixtures of metal salts and ligands to enhance drying of paint formulations is known. For example, W H Canty, G K Wheeler and R R Myers (Ind. Eng. Chem., 52, 67 (1960)) describe the drying capability of a mixture of 1,10-phenanthroline (phen) and Mn soap, which is similar to that of prepared Mn-phen complexes. Mixtures of 2,2’-bipyridine (bpy) and manganese soaps show a better drying performance than manganese soaps without bpy (see P K Weissenborn and A Motiejauskaite, Prog. Org. Coat., 40, 253 (2000)). Also, R van Gorkum et al. (Inorg. Chem., 43, 2456 (2004)), describe that the addition of bpy to Mn(acetylacetone)₃ gives an acceleration in the drying performance, and attribute this to the formation of manganese-bipyridine complexes. The use of manganese complexes with acetylacetone and bidentate nitrogen donor ligands in paint drying has also been described in EP 1382648 A1 (Universiteit Leiden).

[0019] In WO 2012/093250 A1 (OMG Additives Limited) it is described that, by contacting an aqueous solution of transition metal ions and polydentate ligands with alkyd-based formulations, the resultant formulation shows reduced skinning tendency as compared with the introduction of metal ions and polydentate ligands in nonaqueous media.

[0020] It may be inferred from the recent literature, including patent literature, published in the field of oxidatively curable formulations, for example from WO 2008/003652 A1, WO 2011/098583 A1, WO 2011/098584 A1, WO 2011/098587 A1 and WO 2012/092034 A2, that advantageous curing rates of oxidatively curable resins, for example alkyd-based resins, results from the use of metal driers comprising ligands that give rise to relatively stable transition metal-ligand complexes. In general, when using polydentate ligands, i.e. ligands that bind a metal ion through more than one donor site, improved stability of the resultant metal complexes in different redox states can be observed as compared to the corresponding complexes were monodentate ligands are used.

[0021] Nevertheless, there remains a need in the art of oxidatively curable formulations for the provision of further curable formulations, which need not comprise cobalt-based driers, but which nevertheless exhibit acceptable rates of curing. Also, there remains a need in the field of oxidatively curable alkyd-based formulations to be able to provide a formulation which, on the one hand, ameliorates the problem of skinning upon storage of such formulations that comprise metal-based driers, and on the other hand requires less modification by the manufacturers of oxidatively curable coating compositions suitable for application than existing oxidatively curable alkyd-based formulations that are essentially absent metal-based driers. The present invention is intended to address these needs.

SUMMARY

[0022] We have found that transition metal complexes, for example manganese complexes, comprising bis-triazacyclononane-based ligands, are effective for accelerating curing of oxidatively curable coating formulations.

[0023] Viewed from a first aspect, therefore, the invention provides a formulation comprising an oxidatively curable alkyd-based curable resin and a complex of a chelant of the formula (I):
As summarised above, the present invention is based, in part, on the recognition that transition metal complexes, for example, of manganese, comprising bis-triazacyclononane-based ligands, or chelants, of formula (I) catalyse faster curing of oxidatively curable alkyd-based resin formulations than would have been expected from the prior art.

The oxidatively curable resin of the formulation is alkyd-based. As noted above, alkyd resins are a well-understood binder class used in film-forming coating compositions. The term coating composition is to be interpreted broadly and embraces, for example, varnishes, primary coats, filling pastes and glazes. Coating compositions may be solvent-based or water based, e.g. emulsions. Typical coating compositions comprise solvent-based air-drying coatings and/or paints for domestic use. According to particular embodiments of the present invention, the formulations of the invention (including the fully formulated oxidatively curable coating compositions described herein) are paints. The formulations of the invention (including the fully formulated oxidatively curable coating compositions described herein) may comprise inks, for example a metal plate ink, lithographic ink, relief printing ink, screen ink or offset overprinting ink.

By oxidatively curable alkyd-based resin formulations is meant herein liquids that form a continuous solid coating as a consequence of the course of oxidative reactions (curing) and, generally, evaporation of a liquid continuous phase (generally solvent).

Typically, curing results in formation of cross-linkages and other bond formations through reactions involving unsaturated components within alkyd-based resin formulations.

In alkyd-based resin formulations, also referred to herein as alkyd-based formulations, the major binder present is an alkyd. By binder is meant in the art and herein the film-forming (curable) component within curable compositions, i.e. the component within the compositions that forms the desired three-dimensional network upon curing.
Typically the curable component of an oxidatively curable composition (e.g. a formulation of the invention) will comprise between about 1 and about 98 % by weight, for example between about 1 and about 90% by weight of the total weight of the composition, e.g. between about 20 and about 70% by weight of the total weight of the composition. At least 50% by weight of the oxidatively curable portion (i.e. of the binder) in an oxidatively curable alkyd-based resin, i.e. from about 50% by weight to about 100% by weight, is curable alkyd resin. Typically, at least 75% by weight of the binder in an oxidatively curable alkyd-based resin, i.e. from about 75% by weight to about 100% by weight (e.g. from about 90% by weight to about 100% by weight), is curable alkyd resin. According to particular embodiments, about 100% by weight of the binder in an oxidatively curable alkyd-based resin is curable alkyd resin. The balance, if any, of the curable (i.e. binder) component may be, for example, curable acrylate, urethane, polybutadiene and epoxy ester resins.

The skilled person is aware that introducing quantities of curable binders other than curable alkyds allows the distinct properties of such binders to be introduced to a controllable degree into the ultimate coating resultant from application of a composition, such as an oxidatively curable composition, which may be made from the formulation of the invention.

As described above, oxidatively curable alkyd resins are a well-understood and indeed dominant binder in many oxidatively curable paints (both for commercial and domestic use) and other coating compositions. They are employed, in particular, in solvent-based coating compositions.

Alkyds (used synonymously herein with alkyd resins) are produced by the condensation, typically polycondensation, of polyols with carboxylic acids or anhydrides. To make them susceptible to the so-called drying process, some alkyd resins (i.e. those that are oxidatively curable, present in the formulation of the invention) are reacted with unsaturated triglycerides or other source of unsaturation. Plant and vegetable oils, such as linseed oil, are frequently used as the source of triglycerides. The term oxidatively curable alkyd resin thus generally refers to the art, and herein, to polyesters modified with fatty acids. As is known in the art, alkyd resins are generally prepared via condensation polymerisation reactions between three types of monomers: (i) one or more polyols (also known as polyols), (ii) one or more polybasic acids (also known as polyacids); and (iii) long chain unsaturated fatty acids or triglyceride oils, which confer upon the alkyds the susceptibility towards curing.

Owing to its presence in naturally occurring oils, glycerol is a widely used polyol in the preparation of alkyds. Other examples of suitable polyhydric alcohols include: pentaerythritol, dipentaerythritol, ethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, trimethylol propane, trimethylol ethane, di-trimethylol propane and 1,6-hexane diol.

Polycarboxylic acids and the corresponding anhydrides, used to synthesise alkyds, comprise aromatic, aliphatic and cycloaliphatic components, which are generally derived from petrochemical feedstocks. Typical examples of such polyacids include: phthalic acid and its regioisomeric analogues, trimellitic acid, pyromellitic acid, pimelic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid and tetrahydrophthalic acid.

Suitable so-called drying and semi-drying fatty acids or mixture thereof, useful herein, are typically ethylenically unsaturated conjugated or non-conjugated C<sub>2</sub>–C<sub>24</sub> carboxylic acids, such as oleic, ricinoleic, linoleic, linolenic, cicanic acid and oleoestearic acids or mixture thereof, typically used in the forms of mixtures of fatty acids derived from natural or synthetic oils.

By semi-drying and drying fatty acids is meant fatty acids that have the same fatty acid composition as the oils (i.e. the esters) from which they are derived. The classification of the oils is based on the iodine number: for a drying oil the iodine number is >140; for a semi-drying oil the iodine number is ranging between 125 and 140, and for a non-drying oil the iodine number is <125 (see "Surface Coatings", part 1, Chapman & Hall, London, page 55, 1993).

Typically, oxidatively curable alkyd-based formulations, both generally and according to the first aspect of the invention, are liquids. More typically still, such formulations are solvent-based, that is to say they comprise an organic solvent (which may be a mixture of solvents) for the binder and, in accordance with the first aspect of the invention, the chelant.

In other words, "solvent-based" implies to the skilled person in this context formulations that are based on organic (i.e. non-aqueous) solvents, i.e. comprising an organic solvent as a liquid continuous phase. Examples of suitable solvents include aliphatic (including alicyclic and branched) hydrocarbons, such as hexane, heptane, octane, cyclohexane, cycloheptane and isoparaffins; aromatic hydrocarbons such as toluene and xylene; ketones, e.g. methyl ethyl ketone and methyl isobutyl ketone; alcohols, such as secondary butanol, isopropyl alcohol, n-butyl alcohol and n-propyl alcohol, glycols such as propylene glycol; alcohol ethers and esters, glycol monoethers, such as the monoethers of ethylene glycol and diethylene glycol; monoether glycol acetates, such as 2-ethoxyethyl acetate; N-methylpyrrolidone; as well as mixtures thereof. Isomeric variants are included. Thus, for example, the term hexane embraces mixtures of hexanes. According to particular embodiments of the invention, the solvent is a hydrocarbonyl (i.e. hydrocarbon) solvent, e.g. an aliphatic hydrocarbonyl solvent, e.g. solvents comprising mixtures of hydrocarbons. Examples include white spirit and solvents available under the trademarks Shellsol, from Shell Chemicals and Solvesso and Exxon, from Exxon.
liquid phase). Accordingly, compositions and formulations described herein may be of alkyd-based resin formulations in the form of emulsions, and may thus comprise a suitable emulsifier, as is well known in the art.

When an alkyd-based formulation or composition is referred to herein as "oxidatively curable", it is to be understood that this term is being used to describe a composition susceptible to the reactions that occur between unsaturated groups (e.g. carbon-carbon double bonds) and oxygen from the air, which reactions constitute oxidative curing and are manifested in hardening and formation of solid coatings obtainable from such compositions or formulations. Thus, an oxidatively curable alkyd-based resin formulation is a formulation capable of oxidative curing, but which has not yet been allowed to cure. In contrast, the composition of the third aspect of the invention is directed towards formulations after curing, i.e. when cured. The formation of the desired coating resultant from curing may be accelerated through the use of catalytic drying, for example by transition metal-based driers, in particular transition metal-based driers comprising chelants of formula (I).

A characteristic feature of the various aspects of the present invention is the use of chelants of formula (I). Complexes comprising these chelants and one or more suitable transition metal ions accelerate the curing of the oxidatively curable formulation of the invention, which acceleration is absent in the absence of suitable transition metal ions.

The nature of the chelants of formula (I) will now be described. It will be understood that more than one such chelant may be used in accordance with the various aspects of the invention. Typically, however, only one kind of chelant will be used. The chelant is of formula (I):

wherein:

- each R is independently selected from hydrogen, C₁-C₂₄ alkyl, CH₃CH₂OH, CH₃COOH and pyridin-2-ylmethyl;
- Q is a C₂-C₆ alkylene bridge, a C₆-C₁₀ arylene bridge or a bridge comprising one or two C₁-C₃ alkylene units and one C₆-C₁₀ arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁-C₂₄ alkyl groups; and
- each R₁, R₂, R₃, and R₄ is independently selected from hydrogen, C₁-C₄ alkyl and C₁-C₄ alkyl hydroxy.

The chelants of formula (I) are bridged dimers of triazacyclononane-based ligands, in which one nitrogen atom in each of the two triazacyclononane-based ligands is attached to the same (and thus the bridging) linker (Q).

Q may be a C₂-C₆ alkylene bridge. Such alkylene bridges are typically although not necessarily straight chain alkylene bridges as discussed below. They may, however, be cyclic alkylene groups (e.g. the bridge may be cyclohexylene). Where Q is a C₆-C₁₀ arylene bridge, this may be, for example, phenylene or the corresponding arylene formed by abstraction of two hydrogen atoms from naphthalene. Where Q comprises one or two C₁-C₃ alkylene units and one C₆-C₁₀ arylene unit, such bridges may be, for example, -CH₂C₆H₄CH₂- or -CH₂C₆H₄-. It will be understood that each of these bridges may be optionally substituted one or more times, for example once, with independently selected C₁-C₂₄ alkyl (e.g. C₁-C₁₈ alkyl) groups.

In these chelants of formula (I), Q is typically a C₂-C₆ alkylene bridge. Where this is so, Q is typically a straight chain alkylene, e.g. is ethylene, n-propylene, n-butylene, n-pentylene or n-hexylene. According to particular embodiments, the C₂-C₆ alkylene bridge is ethylene or n-propylene. According to still more particular embodiments, the C₂-C₆ alkylene bridge is ethylene. Hereinafter, references to propylene are intended to refer to n-propylene (i.e. -CH₂CH₂CH₂-).

In particular embodiments:

- each R is independently selected from: hydrogen, CH₃, C₂H₅, CH₃CH₂OH and CH₃COOH; and/or
- Q is selected from ethylene and propylene.

In still more particular embodiments, each R, R₁, R₂, R₃, and R₄ is independently selected from H and Me and Q is ethylene.
A manufacturer of an alkyd-based resin formulation suitable for oxidative curing can thus include a chelant of formula (I) in an amount appropriate for a given oxidatively curable alkyd-based resin formulation. Each type of oxidatively curable alkyd-based resin can, and typically does, have different sensitivity towards radical curing and may thus require a particular concentration of a metal drier for optimal curing. However, to determine the appropriate concentration in practice is not straightforward, since a metal drier, for example a manganese-based catalyst, can initiate radical curing before the coating composition (e.g. paint) comprising an oxidatively curable alkyd-based resin formulation (and other components) can be applied, leading to undesirable degradation and/or hardening of the resin formulation. In contrast, a manufacturer of an oxidatively curable alkyd-based resin formulation, as opposed to the manufacture of a fully formulated oxidatively curable coating composition comprising such an oxidatively curable alkyd-based resin formulation, can determine the optimum amount of metal drier for a given alkyd-based resin formulation and add to batches of it a suitable amount of chelant of formula (I) (but not the transition metal ions that allow formation of a catalytically active drier, which are often, but not necessarily, manganese, iron, cobalt, vanadium or copper ions). An appropriate quantity of transition metal ions can then be added to the resultant formulation by, for example, a manufacturer of a fully formulated coating composition, along with other components to make a fully formulated oxidatively curable coating composition.

Mixing of appropriate chelants of formula (I) with alkyd-based resin formulations in the essential absence of at least manganese, iron, cobalt, vanadium and copper ions which, if present, render these chelants catalytically active as metal driers, affords formulations at least less susceptible to skinning or instability without the requirement to add antiskinning agents and/or to take other specific measures to avoid skinning.

Moreover, we have found that mixing of appropriate chelants of formula (I) with alkyd-based resin formulations in the essential absence of at least manganese, iron, cobalt, vanadium and copper ions is advantageous other than because doing so affords formulations at least less susceptible to skinning or instability without the requirement to add antiskinning agents and/or to take other specific measures to avoid skinning. In particular, we have found that, when formulations are prepared by contacting a chelant of formula (I) with an alkyd-based resin formulation in the essential absence of at least manganese, iron, cobalt, vanadium and copper ions, the resultant formulations, after they have been contacted with a suitable source of transition metal ions (typically selected from the group consisting of manganese, iron, cobalt, vanadium and copper ions, e.g. manganese ions whereby to provide formulations of the first aspect of the invention, cure more quickly than similar formulations (not of the invention) that are prepared by contacting a composition comprising an alkyd-based resin with a composition comprising a well-defined complex comprising the same chelant of formula (I).

By well-defined complex is meant herein (as the term is used customarily in the art) a complex that has been isolated such that it is susceptible to characterisation (i.e. definition) and analysis (e.g. to determine its structure and degree of purity). In contrast, a complex that is not well-defined is one that is prepared without isolation from the medium (e.g. reaction medium) in which it is prepared. That formulations according to the first aspect of the invention prepared other than from well-defined complexes cure more quickly is particularly surprising. Such formulations are described in further detail below, in connection with the method of the second aspect of the invention.

Where formulations that comprise an oxidatively curable alkyd-based resin and a chelant of formula (I) are essentially absent at least manganese, iron, cobalt, vanadium and copper ions, this means that they comprise less than 0.001 % by weight of at least ions of each of manganese, iron, cobalt, vanadium and copper. By this is meant that such formulations are absent 0.001% by weight manganese ions, absent 0.001% by weight iron ions, absent 0.001% by weight cobalt ions, absent 0.001% by weight vanadium ions and absent 0.001% by weight copper ions. An appropriate quantity of suitable transition metal cations (e.g. ions of one or more of manganese, iron, cobalt, vanadium and copper) can be added after preparation of such a formulation, for example when introducing optional additional components to
form an oxidatively curable coating composition.

[0061] Particular formulations that comprise an oxidatively curable alkyd-based resin and a chelant of formula (I) can if desired comprise less than 0.0001% by weight of each of at least manganese, iron, cobalt, vanadium and copper ions. Still other such formulations comprise less than 0.001% by weight of each of manganese, iron, cobalt, vanadium, copper, titanium, molybdenum, tungsten, cerium and zirconium. Still other such embodiments of formulations of the invention comprise less than 0.0001% by weight of each of manganese, iron, cobalt, vanadium, copper, titanium, molybdenum, tungsten, cerium and zirconium.

[0062] Ideally, formulations not of the invention of the invention with concentrations of specific transition metal ions of less than 0.001 wt% or 0.0001 wt% are absent any of the transition metal ions specified. Obviously, however, this is in practice impossible to achieve. Accordingly, these formulations are preferably absent of the transition metal ions specified to the greatest extent practicable.

[0063] In order to make, in accordance with a method of the second aspect of the invention, a formulation according to the first aspect of the invention, a composition comprising an oxidatively curable alkyd-based resin is contacted with a composition comprising a chelant of formula (I). The composition comprising the chelant of formula (I) that is contacted with the composition comprising the alkyd-based resin may, in some embodiments, comprise a transition metal ion-containing complex comprising the chelant. This is a complex that is not well-defined. Further, a mixture of well-defined complex and a non-complexed chelant of formula (I) may be employed in the composition comprising the alkyd-based resin. In other embodiments, the composition comprising the chelant of formula (I) is not part of a transition metal ion-containing complex, in which case a source of transition metal ions may, if wished, be added afterwards (or indeed have been formulated together with the alkyd-based resin before addition of the chelant of formula (I)) so as to form a complex comprising the chelant of formula (I) in situ (i.e. within the alkyd-based resin formulation). It will be understood that such a complex may be regarded as not well-defined. Both of these different types of embodiments are described below.

[0064] The typical molar ratio between any transition metal ions and the chelant is between about 0.1:1 and about 10:1, often between about 0.3:1 and about 3:1. Often, the molar ratio between chelant and transition metal ions will be approximately between 1:2 and 1:1. However, this need not necessarily be the case. Without being bound to theory, an excess of transition metal ions may be beneficial to allow some adsorption on solid particles without losing too much siccative activity. On the other hand, a stoichiometric excess of chelant may be beneficial to improve regeneration of catalytically active species during curing, which can lead to improved drying (i.e. curing) performance despite using a lower quantity of transition metal ions. Using a stoichiometric excess of chelant can also be advantageous by reducing the intensity of coloured metal complexes. The skilled person will be able to take into account these considerations when preparing oxidatively curable coating compositions, for example formulations of the invention.

[0065] The contacting of the method of the second aspect of the invention may be during formulation of fully formulated oxidatively curable alkyd-based resin coating compositions (described below), particularly if it is part of a complex comprising a suitable transition metal ion.

[0066] If the chelant of formula (I) is introduced as a transition metal ion-containing complex, the complex may, for example, be prepared by contacting a chelant of formula (I) with a suitable transition metal salt in a suitable solvent, by which is meant that either or both of the chelant and transition metal salt may be in a suitable solvent prior to contact with each other. The salt can be a soap. The resultant complexes-containing mixture may then be contacted with a composition comprising an oxidatively curable alkyd-based resin, which is typically dissolved in an organic solvent described above when describing solvent-based alkyd-based formulations (or emulsified in a water-based formulation) such as those described above when describing water-based alkyd-based formulations.

[0067] It will be understood from the discussion above concerning the formulations of the first aspect of the invention that, where a complex that is not well-defined is contacted with a composition comprising an alkyd-based resin, in accordance with a method of the second aspect of the invention, such embodiments are noteworthy in relation to both the first and second aspect of the invention. According to such embodiments, there is provided a formulation according to the first aspect of the invention that is obtainable by carrying out a method of the second aspect of the invention in which the chelant is not part of a well-defined complex comprising a suitable transition metal ion (e.g. an ion selected from the group consisting of ions of manganese, iron, cobalt, vanadium and copper, e.g. a manganese ion). Alternatively, such formulations may be regarded as being obtainable by a method of the second aspect of the invention, the method further comprising providing the chelant of formula (I) as a complex that is obtained, or obtainable, by contacting a chelant of formula (I) with a suitable transition metal salt (which may be a soap) in a suitable solvent. Typically, the resultant mixture is contacted, as is (i.e. without further manipulation, including purification), with the composition comprising the alkyd-based resin. In other words, particular embodiments of the second aspect of the invention comprise contacting the composition comprising the alkyd-based resin with a mixture of a chelant of formula (I) and a suitable transition metal ion-containing salt, typically of a manganese, iron, vanadium, cobalt or copper ion.

[0068] Often, the metal salt used will be a manganese salt, typically of a divalent or trivalent redox state. Upon contacting the manganese (or other transition metal) salt with the chelant, formation of manganese-chelant complexes (or other transition metal-chelant complexes) takes place.
The transition metal salt used can be a solid, a suspension, or as a solution in a variety of solvents. Typically the salt comprises a manganese (II) or manganese (III) ion although other salts, e.g. manganese (IV) salts may also be used. Such manganese (or other metal ion) salts can be added as solids, suspensions, or as solutions in a variety of solvents. The invention contemplates use of a mixture of metal salts although a single salt is typically used.

Adding the chelant as a solution can be advantageous in permitting improved and/or easier mixing with the (solution of) binder(s). It may be beneficial to dilute chelant in a suitable solvent before adding to the binder if it is wished to introduce a very small amount of chelant, so greater accuracy of dosing can be achieved. Depending on the properties of the chelant and the desired resin-chelant formulation, suitable solvents include aliphatic hydrocarbons, such as heptanes, water, alcohols, such as ethanol or propylene glycol, or mixtures thereof. The skilled person will be able to easily formulate such solutions, generally using solvent such as those described above.

It will be understood that there is no particular limitation as to the source of the transition metal ions. Typically, however, salts are selected from the group consisting of optionally hydrated MnCl₂, FeCl₂, FeCl₃, MnBr₂, Mn(NO₃)₂, Fe(NO₃)₃, MnSO₄, FeSO₄, (Fe₂SO₄)₃, Mn(acetylacetonate)₂, Fe(acetylacetonate)₂, Mn(acetylacetonate)₃, Fe(acetyl- lacetonate)₃, Mn(R₅COO)₃ (including Mn(acetate)₃), Fe(R₅COO)₃, Mn(R₅COO)₂ and Fe(R₅COO)₂, wherein R₅ is selected from a C₁₋₂₄ alkyl. According to particular embodiments, the above-mentioned salts are based on manganese. Where the salt comprises two R₅ groups, these can be the same or different. The alkyl moieties, by which is meant saturated hydrocarbon radicals, may be straight-chain or branched and/or cyclic portions. Indeed, throughout the specification, where reference is made to alkyl, unless the context dictates to the contrary, this means a C₁₋₂₄ alkyl, which may be straight-chain or branched and perhaps cycloalkyl or comprise a cyclic portion (e.g. alkyl may be cyclohexylmethyl), for example C₁₋₁₀ alkyl or C₁₋₆ alkyl, e.g. methyl.

Often, the manganese salt is selected from Mn(R₅COO)₂, particularly with R₅=COO⁻ being selected from acetate, octanoate, 2-ethylhexanoate, neodecanoate (3,3,5,5-tetramethylhexanoate), and naphthenate. Particularly often, a manganese salt is used, which, for example is selected from manganese(octanoate)₂, manganese(naphthenate)₂, manganese(2-ethylhexanoate)₂ and manganese (neodecanoate)₂. The invention also contemplates use of a mixture of different redox states of the manganese ions with the same counterion, for example a mixture of manganese(2-ethylhexanoate)₂ and manganese(2-ethylhexanoate)₃.

The term optionally hydrated is well known in the art. Metal salts often contain water molecules within a crystal lattice, which will remain present unless the hydrated metals salts are subjected to specific drying steps by heating or drying under reduced pressure. However, partially or fully dehydrated metal salts can also be used. For example, manganese (II) acetate, and manganese (II) chloride can be bought as tetrahydrate salts or as dehydrated salts. Commercial manganese sulfate is available in both tetrahydrate and monohydrate forms.

Often these transition metal salts are commercially available as solutions, particularly if they are of the formulae Mn(R₅COO)₂ described above, for example in hydrocarbon solutions to facilitate dissolution in the solvent-based curable compositions such as paint formulations. However, other solvents may also be used, including alcohols and water (or aqueous solutions), especially for chloride, sulfate and acetate salts of manganese and iron ions.

Formulations that comprise an oxidatively curable alkyd-based resin and a chelant of formula (I), and which comprise less than 0.001 % (or 0.0001 %) by weight of ions of each of at least manganese, iron, cobalt, vanadium and copper may be prepared by contacting chelant of formula (I) with (e.g. adding it to) an oxidatively curable alkyd-based binder, typically dissolved in an organic solvent described above (or emulsified in a water-based liquid), as described above. The chelant may be added as a pure material to the resin(s), or as a solution. Adding the chelant as a solution can be advantageous in permitting improved and/or easier mixing with the (solution of) binder(s). It may be beneficial to dilute chelant in a suitable solvent before adding to the binder if it is wished to introduce a very small amount of chelant, so greater accuracy of dosing can be achieved. Depending on the properties of the chelant and the desired resin-chelant formulation, suitable solvents include aliphatic hydrocarbons, such as heptanes, water, alcohols, such as ethanol or propylene glycol, or mixtures thereof. The skilled person will be able to easily formulate such solutions, generally using a solvent such as those described above.

Thus, as described herein, formulations of the invention, which comprise transition metal ion-containing complexes of the chelant of formula (I), can be prepared, either by contacting an alkyl-based resin composition with such a complex directly, or by contacting an alkyl-based resin composition with chelant that is not part of such a complex and then adding to the resultant formulation a source of transition metal ions. As a still further embodiment of the method of the second aspect of the invention, an alkyl-based resin composition comprising suitable transition metal ions may be contacted with the chelant of formula (I). Generally, formulations of the invention comprise a concentration of between about 0.0003 wt% and about 0.07 wt%, for example about 0.0005 wt% and about 0.05 wt%, e.g. between about 0.005 wt% and about 0.05 wt%, of the suitable transition metal ion, such as those described immediately below.

Transition metal ions to which the chelants of formula (I) may coordinate, to provide metal driers (transition metal ion-containing complexes that can accelerate curing of the oxidatively curable alkyd-based resin in the formulation of the invention) may be, for example manganese, iron, cobalt, vanadium and copper ions, still more typically manganese ions, or mixtures of any of these metal ions. The valency of the metal ions may range from +1 to +6, often from +2 to +5.
Examples include metal ions selected from the group consisting of Mn(II), Mn(III), Mn(IV), Mn(V), Cu(I), Cu(II), Cu(III), Fe(II), Fe(III), Fe(IV), Fe(V), Co(I), Co(II), Co(III), V(II), V(III), V(IV), and V(V), for example metal ions selected from the group consisting of Mn(II), Mn(III), and Mn(IV).

[0078] In complexes comprising the chelant of formula (I), the number of metal ions per chelant molecule may be either 1 or 2. Since a chelant of formula (I) contains two cyclic nitrogen donor moieties, each of these rings may bind to one metal ion. Thus one may obtain a molar ratio of the chelant of formula (I) to metal ion of 1:2. Also one may obtain complexes or species whereby one chelant of formula (I) binds to only one metal ion, for example if a molar excess of chelant of formula (I) is employed. In this way, there is provided a molar ratio of the chelant of formula (I) to metal ion of 1:1.

[0079] A formulation of the invention can, and generally will, be used in the manufacture of a fully formulated oxidatively curable coating composition. By the term "fully formulated oxidatively curable coating composition" is implied, as is known to those of skill in the art, oxidatively curable formulstions that comprise additional components over and above the binder (the oxidatively curable material, which is predominantly oxidatively curable alkyd resin according to the present invention), an aqueous or non-aqueous solvent/liquid continuous phase and any metal driers intended to accelerate the curing process. Such additional components are generally included so as to confer desirable properties upon the coating composition, such as colour or other visual characteristics such as glossiness or mattness), physical, chemical and even biological stability (enhanced biological stability being conferred upon coating compositions by the use of biocides by example), or modified texture, plasticity, adhesion and viscosity.

[0080] For example, such optional additional components may be selected from solvents, antioxidants (sometimes referred to as antiskinning agents), additional siccatives (i.e. not comprising chelants of formula (I)), auxiliary driers, colourants (including inks and coloured pigments), fillers, plasticisers, viscosity modifiers, UV light absorbers, stabilisers, antistatic agents, flame retardants, lubricants, emulsifiers (in particular where an oxidatively curable coating composition or formulation of the invention is aqueous-based), anti-foaming agents, viscosity modifiers, antifoaming agents, biocides (e.g. bactericides, fungicides, algacides and insecticides), anticorrosion agents, antireflective agents, anti-freezing agents, waxes and thickeners. Typically, formulations prepared in accordance with embodiments of the method of the second aspect of the invention will comprise at least an organic solvent, selected from the list of solvents described above and a filler, and generally an antiskinning agent, in addition to the alkyd and optionally other binders and chelant present in the formulation of the invention. The skilled person is familiar with the incorporation of these and other components into oxidatively curable coating composition so as to optimise such compositions' properties.

[0081] It will be appreciated that some of these optional additional components possess more than one functional property. For example, some fillers may also function as colourants. The nature of any additional components and the amounts used may be determined in accordance with the knowledge of those of skill in the art and will depend on the application for which the curable coating compositions intended. Examples are provided below but these are intended to be illustrative, not limiting.

[0082] When producing a fully formulated oxidatively curable coating composition that is, for example, a paint, one or more antioxidants (customarily referred to in the art as antiskinning agents) are often included to avoid premature curing of the oxidatively curable coating composition prior to its use. Such premature curing may be manifested by, for example, the formation of a skin on or lumpy matter in the oxidatively curable coating composition as a result of curing during storage, for example hardening of the surface of a paint layer in a can, owing to the activity of the siccative with oxygen on the oxidatively curable binder. Antiskinning agents are understood to reduce skinning by quenching radicals formed and/or by inactivation of drier catalysts by binding to one or more of the coordination sites. Examples include, but are not limited to, methylethylketoxime, acetonoxime, butyaldoxime, methyl-isobutylketoxime, 2-cyclohexylphenol, 4-cyclohexylnaphthalene, t-butyl-hydroquinone, dialkylhydroxylamine, acetylacetone, ammonia, vitamin E (tocopherol), hydroxylamine, triethylamine, dimethylethanolamine, 2-t-butyl-4-methylphenol, and 2-[(1-methylpropyl)amino]ethanol. According to particular embodiments, the antiskinning agent is selected from the group consisting of methylethylketoxime, acetonoxime, butyaldoxime, dialkylhydroxylamine, ammonia, hydroxylamine, triethylamine, dimethylethanolamine, o-cyclohexylphenol, p-cyclohexylphenol and 2-t-butyl-4-methylphenol.

[0083] The quantity of antiskinning agent present in an oxidatively curable coating composition is typically between about 0.001 and about 2.5 wt%. The antioxidant or antiskinning agent may be added to an alkyd-based resin formulation, e.g. of the invention, together with (or separately from) the chelant prior to or during the preparation of a fully formulated oxidatively curable coating composition (for example a paint or other coating composition).

[0084] Colourants include pigments and inks. Titanium dioxide is a pigment commonly included in many coating compositions, in particular paints.

[0085] Fillers may be added to an oxidatively curable coating composition for a number of reasons, for example to bulk out the coating composition and to compare particular properties on the cured composition. Typically, fillers will be inorganic solids that are generally introduced in particulate (finely divided) form. Examples include silica, silicates or clays (for example mica, talc, kaolin), carbonate or other minerals and metal salts or oxides (such as marble, quartzite). Other suitable fillers will be evident to the skilled person.

[0086] It may be advantageous if an alkyd resin manufacturer has determined a particular concentration of metal drier
that is appropriate for a particular alkyd-based resin formulation for the manufacturer to recommend to users of the formulation an appropriate source of transition metal ions that may be added in order to generate a desired metal drier in situ.

Moreover, according to the fourth aspect of the invention, there is provided a kit comprising an oxidatively curable alkyd-based resin and a chelant of formula (I), defined in accordance with the first aspect of the invention, comprising less than 0.001% by weight of ions of each of at least manganese, iron, cobalt, vanadium and copper and, separately, a composition comprising a source of suitable transition metal ions, typically ions selected from the group consisting of manganese, iron, cobalt, vanadium and copper ions, more typically manganese ions, often in the form of a salt such as those described above, for admixture to the formulation. The kit may optionally comprise instructions or other guidance as to methods according to which the formulation and the transition metal ions may be contacted. In this way, the manufacture of a formulation of the invention can, after optimising the nature of the source of transition metal ions, for example by the preparation of a particular solution of a particular transition metal ions salt, optimise the manner in which formulations containing transition metal complexes can be prepared. The preparation of an oxidatively curable alkyd-based coating composition may be by the manufacturer of such compositions (e.g. a paint manufacturer) or by an end consumer of oxidatively curable alkyd-based coating compositions, who can contact a source of transition metal ions with an otherwise fully formulated oxidatively curable alkyd-based coating composition.

It is also within the scope of the current invention that a paint manufacturer, for example, would add commercial metal-soap/chelant mixtures, such as the non-limiting example of Borchers® Dry 0410 (a mixture of bpy with Mn(neodecanoate)₂ commercially available from OMG), as a mixture of bpy with Mn(neodecanoate)₂. The additional chelant present in the alkyd resin will improve the drying behaviour without causing excessive yellowing which may be occurring if more of the Mn-soap/ligand mixture is added to the paint formulation.

Additionally, one or more auxiliary driers may be added to the fully formulated oxidatively curable coating composition. Such auxiliary driers may be optional additional components within, but are often not present in, the formulation of the invention. Such auxiliary driers include fatty acid soaps of zirconium, bismuth, barium, cerium, calcium, lithium, strontium, and zinc. Typically, fatty acid soaps are optionally substituted octanoates, hexanoates and naphthenates. Without being bound by theory, auxiliary driers (sometimes referred to as through driers) are generally understood to diminish the effect of adsorption of the main drier on solid particles often present in an oxidatively curable coating composition. Other non-metal based auxiliary driers may also be present if desired. These may include, for example, thiol compounds, as described in US 2001/0008932 A1 (Bakkeren et al.) or biomolecules as described in US 2005/0245639 A1 (Oostveen et al.). Concentrations of auxiliary driers within oxidatively curable coating compositions (or formulations of the invention) are typically between about 0.01 wt% and 2.5 wt% as is known in the art.

The formulations of the invention (including the fully formulated oxidatively curable coating compositions described herein) may be used as a decorative coating, e.g. applied to wood substrates, such as door or window frames, or for other substrates such as those made of synthetic materials (such as plastics including elastomeric materials), concrete, leather, textile, glass, ceramic or metal, in accordance with the fifth aspect of the invention. The thus-applied composition may then be allowed to cure. In this respect, the third aspect of the invention is directed towards a formulation according to the first aspect, or obtainable according to the second aspect, when cured.

Each and every patent and non-patent reference referred to herein is hereby incorporated by reference in its entirety, as if the entire contents of each reference were set forth herein in its entirety.

The invention may be further understood with reference to the following non-limiting clauses:

1. A formulation comprising an oxidatively curable alkyd-based curable resin and a complex of a chelant of the formula (I):

\[
\begin{align*}
\text{R}_2\text{R}_1\text{C} & \text{N} \text{CR}_3\text{R}_4 \\
\text{R}_4\text{R}_3\text{C} & \text{N} \text{CR}_1\text{R}_2 \\
\text{R}_3\text{R}_2\text{C} & \text{N} \text{CR}_4\text{R}_1 \\
\text{R}_2\text{R}_1\text{N} & \text{C} \text{CR}_3\text{R}_4 \\
\text{R}_4\text{R}_3\text{C} & \text{N} \text{CR}_1\text{R}_2 \\
\end{align*}
\]

(wherein:}
each R is independently selected from hydrogen, C1-C24 alkyl, CH2CH2OH, CH2COOH and pyridin-2-ylmethyl; Q is a C2-C6 alkylene bridge, a C6-C10 arylene bridge or a bridge comprising one or two C1-C3 alkylene units and one C6-C10 arylene unit, which bridge may be optionally substituted one or more times with independently selected C1-C24 alkyl groups; and each R1, R2, R3, and R4 is independently selected from H, C1-C4 alkyl and C1-C4 alkyl hydroxy)

and a transition metal ion selected from the group consisting of ions of manganese, iron, cobalt, vanadium and copper, wherein the complex is not well-defined.

2. The formulation of clause 1, wherein each R is independently selected from hydrogen, CH3, C2H5, CH2CH2OH and CH2COOH and Q is selected from ethylene and n-propylene.

3. The formulation of clause 2, wherein each of R, R1, R2, R3, and R4 is independently selected from hydrogen and methyl and Q is ethylene.

4. The formulation of clause 1, wherein the chelant is 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane.

5. The formulation of any one of clauses 1 to 4, wherein the chelant is present in the formulation at a concentration of between about 0.00005 and about 0.5 wt% with respect to curable resin.

6. The formulation of any one of clauses 1 to 4, wherein the chelant is present in the formulation at a concentration of between about 0.001 and about 0.1 wt% with respect to curable resin.

7. The formulation of any one of clauses 1 to 6, which is a solvent-based formulation.

8. The formulation of any one of clauses 1 to 7, further comprising an antiskinning agent.

9. The formulation of clause 8, wherein the antiskinning agent is selected from the group consisting of methylethylketone-oxime, acetonoxime, butyraldoxime, diethylhydroxylamine, ammonia, hydroxylamine, triethylamine, dimethylethanolamine, p-cyclohexylphenol, o-cyclohexylphenol and 2-t-butyl-4-methylphenol.

10. The method of preparing a formulation as defined in any one of clauses 1 to 10, the method comprising contacting a composition comprising an alkyd-based resin with a composition comprising a chelant of formula (I).

11. The method of clause 11 wherein the transition metal ions are manganese ions.

12. The method of clause 11 wherein the method comprises contacting a formulation comprising an oxidatively curable alkyd-based curable resin and chelant of formula (I), as defined in clause 1, which formulation comprises less than 0.001 % by weight of ions of each of manganese, iron, cobalt, vanadium and copper, with a source of manganese, iron, cobalt, vanadium or copper ions.

13. The method of clause 12, wherein the transition metal ions are manganese ions.

14. The method of clause 12 or clause 13 wherein a solution of transition metal ions is contacted with the formulation.

15. The method of any one of clauses 12 to 14, wherein the formulation is contacted with an optionally hydrated salt selected from the group consisting of MnCl2, FeCl2, FeCl3, MnBr2, Mn(NO3)2, Fe(NO3)3, MnSO4, FeSO4, (Fe)2(SO4)3, Mn(acetylacetonate)2, Fe(acetylacetonate)2, Mn(acetylacetonate)3, Fe(acetylacetonate)3, Mn(R5COO)3, Fe(R5COO)3, Mn(R5COO)2 and Fe(R5COO)2, wherein each R5 is independently a C1-C24 alkyl.

16. The method of clause 15, wherein the formulation is contacted with an optionally hydrated salt selected from the group consisting of MnSO4, MnCl2, MnBr2, Mn(NO3)2, Mn(CH3COO)3, Mn(CH3COO)2, Mn(acetylacetonate)2, Mn(acetylacetonate)3, Mn(octanolate)2, Mn(2-ethylhexanoate)2, Mn(naphthenate)2 and Mn(neodecanoate)2.

17. The method of clause 11, wherein the composition comprising the chelant of formula (I) comprises a complex as defined in clause 1.

18. The method of clause 17, wherein the composition comprising the complex comprises a mixture of the chelant
of formula (I) and a salt of the transition metal ion.

19. The method of clause 18, wherein the salt is as defined in clause 15 or clause 16.

20. The formulation of any one of clauses 1 to 10, which is obtainable by a method as defined in any one of clauses 12 to 19.

21. A composition resultant from curing of a formulation as defined in any one of clauses 1 to 10 and 20.

22. A kit comprising a formulation comprising an oxidatively curable alkyd-based resin and a chelant of formula (I) defined in clause 1, which formulation comprises less than 0.001 % by weight of ions of each of manganese, iron, cobalt, vanadium and copper, and, separately, a composition comprising transition metal ions selected from the group consisting of manganese, iron, cobalt, vanadium and copper ions.

23. The kit of clause 22, wherein the transition metal ions are manganese ions.

24. The kit of clause 23, wherein the ions are provided as a salt as defined in clause 15 or clause 16.

25. A method comprising applying to a substrate a formulation as defined in any one of clauses 1 to 10 and 20.

The non-limiting examples below more fully illustrate the embodiments of this invention.

**EXPERIMENTAL**

**[0094]** The ligand 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane (Me4-DTNE) (purity level of 92.4% w/w) was obtained as disclosed in WO 2012/003712 (Unilever PLC et al.). [Mn2(μ-O)(μ-CH3COO)(Me4-DTNE)]Cl2 (purity level of 87% w/w) was obtained as disclosed in WO 2011/106906 Unilever PLC et al.) Alkyd resin (catalogue number A/1552/15; an alkyd resin solution of 70 wt% in white spirits) was obtained from Acros Organics. Manganese(II) 2-ethylhexanoate (abbreviated as Mn(2-EH)2 below; catalogue number 93-2532; 40% solution in mineral spirits, 6wt% Mn) was obtained from Strem Chemicals. Manganese(II) acetate tetrahydrate and Manganese(III) acetate dihydrate were obtained from Aldrich. Manganese chloride tetrahydrate was obtained from Fluka.

**Experiment 1a**

To 5 g of alkyd resin was added 16.8 mg Me4-DTNE dissolved in 0.10 mL ethanol. This mixture was stirred manually for ca. 1 minute and was stored in a closed vial overnight at room temperature. Then, 41.67 mg of Mn(2-EH)2 was added and the mixture was stirred manually for ca. 1 minute. This led to a Mn level of 0.05 wt% with respect to resin solution (or 0.07 wt% with respect to solid resin) and a 1:1 molar ratio Mn : Me4-DTNE. The next day, 150 mg of this mixture was spread evenly on 10 cm2 of a glass plate. Dryness of the film was determined every 30 minutes by running a needle through the film. 'Dry' was defined when the needle could no longer run through the film, but gave wrinkling of the film's surface. A drying time of 1.2 h was measured.

**Experiment 1b**

[0096] Experiment 1a was repeated, except that manganese(II) acetate tetrahydrate was used instead of Mn(2-EH)2: 11.2 mg of manganese(II) acetate tetrahydrate dissolved in 0.3 mL ethanol was added to the resin. A drying time of 1.2 h was measured.

**Experiment 1c**

[0097] Experiment 1a was repeated, except that manganese(III) acetate dihydrate was used instead of Mn(2-EH)2: 12.2 mg of manganese(III) acetate dihydrate dissolved in 0.3 mL ethanol was added to the resin. A drying time of 1.1 h was measured.

**Experiment 1d**

[0098] Experiment 1a was repeated, except that manganese chloride tetrahydrate was used instead of Mn(2-EH)2; to the resin now 9.0 mg of manganese(II) chloride tetrahydrate dissolved in 0.3 mL ethanol was added to the resin. A
Experiment 2

[0099] To 5 g of alkyd resin was added 8.4 mg Me₄-DTNE dissolved in 0.10 mL ethanol. This mixture was stirred manually for ca. 1 minute and was stored in a closed vial overnight at room temperature. Then, 41.67 mg of Mn(2-EH)₂ was added and the mixture was stirred manually for ca. 1 minute. This led to a Mn level of 0.05 wt% with respect to resin solution (or 0.07 wt% with respect to solid resin) and a 2:1 molar ratio Mn : Me₄-DTNE. The next day, 150 mg of this mixture was spread evenly on 10 cm² of a glass plate. Dryness of the film was determined every 30 minutes by running a needle through the film. 'Dry' was defined when the needle could no longer run through the film, but gave wrinkling of the film's surface. A drying time of 1.1 h was measured.

Experiment 3a

[0100] To 5 g of alkyd resin was added 3.4 mg Me₄-DTNE dissolved in 0.04 mL ethanol. This mixture was stirred manually for ca. 1 minute and was stored in a closed vial overnight at room temperature. Then, 8.3 mg of Mn(2-EH)₂ was added and the mixture was stirred manually for ca. 1 minute. This led to a Mn level of 0.01 wt% with respect to resin solution (or 0.014 wt% with respect to solid resin) and a 1:1 molar ratio Mn : Me₄-DTNE. The next day, 150 mg of this mixture was spread evenly on 10 cm² of a glass plate. Dryness of the film was determined every 30 minutes by running a needle through the film. 'Dry' was defined when the needle could no longer run through the film, but gave wrinkling of the film's surface. A drying time of 3.0 h was measured.

Experiment 3b

[0101] Experiment 3a was repeated, except that manganese(II) acetate tetrahydrate was used instead of Mn(2-EH)₂; 2.23 mg of manganese(II) acetate tetrahydrate dissolved in 0.3 mL ethanol was added to the resin. A drying time of 2.8 h was measured.

Experiment 3c

[0102] Experiment 3a was repeated, except that manganese(III) acetate dihydrate was used instead of Mn(2-EH)₂; 2.44 mg of manganese(III) acetate dihydrate dissolved in 0.3 mL ethanol was added to the resin. A drying time of 2.7 h was measured.

Experiment 3d

[0103] Experiment 3a was repeated, except that manganese chloride tetrahydrate was used instead of Mn(2-EH)₂; to the resin now 1.80 mg of manganese(II) chloride tetrahydrate dissolved in 0.3 mL ethanol was added to the resin. A drying time of 3.0 h was measured.

Experiment 4

[0104] To 5 g of alkyd resin was added 1.7 mg Me₄-DTNE dissolved in 0.02 mL ethanol. This mixture was stirred manually for ca. 1 minute and was stored in a closed vial overnight at room temperature. Then, 8.3 mg of Mn(2-EH)₂ was added and the mixture was stirred manually for ca. 1 minute. This led to a Mn level of 0.01 wt% with respect to resin solution (or 0.014 wt% with respect to solid resin) and a 2:1 molar ratio Mn : Me₄-DTNE. The next day, 150 mg of this mixture was spread evenly on 10 cm² of a glass plate. Dryness of the film was determined every 30 minutes by running a needle through the film. 'Dry' was defined when the needle could no longer run through the film, but gave wrinkling of the film's surface. A drying time of 3.7 h was measured.

Experiment 5

[0105] To 5 g of alkyd resin was added 16.0 mg [Mn2(µ-O)2(µ-CH₃COO)(Me₄-DTNE)]Cl₂ dissolved in 0.2 mL ethanol. This led to a Mn level of 0.05 wt% with respect to resin solution (or 0.07 wt% with respect to solid resin). This mixture was stirred manually for ca. 1 minute and was stored in a closed vial overnight at room temperature. The next day, 150 mg of this mixture was spread evenly on 10 cm² of a glass plate. Dryness of the film was determined every 30 minutes by running a needle through the film. 'Dry' was defined when the needle could no longer run through the film, but gave wrinkling of the film's surface. A drying time of 4.8 h was measured.
Comparative Experiment 6 - alkyd resin with manganese(II) 2-ethylhexanoate

To 5 g of alkyd resin was added 41.67 mg of Mn(2-EH)2. This led to a Mn level of 0.05 wt% with respect to resin solution (or 0.07 wt% with respect to solid resin). This mixture was stirred manually for ca. 1 minute and was then stored in a closed vial overnight. The next day, 150 mg of this mixture was spread evenly on 10 cm² of a glass plate. Dryness of the film was determined every 30 minutes by running a needle through the film. ‘Dry’ was defined when the needle could no longer run through the film, but gave wrinkling of the film’s surface. No drying was observed within 8 h.

Comparative Experiment 7

To 5 g of alkyd resin was added 16.8 mg Me4-DTNE dissolved in 0.1 mL ethanol. This mixture was stirred manually for ca. 1 minute and was stored in a closed vial overnight at room temperature. The next day, 150 mg of this mixture was spread evenly on 10 cm² of a glass plate. Dryness of the film was determined every 30 minutes by running a needle through the film. ‘Dry’ was defined when the needle could no longer run through the film, but gave wrinkling of the film’s surface. No drying was observed within 8 h.

The results of Experiment 1a, 2, 3a, 4, and 5 and Comparative Experiment 6 show that the presence of Me4dtne either dosed together with Mn(2-EH)2 (experiments 1a, 2, 3a, and 4) or as a well-defined dinuclear complex (experiment 5) yield a significantly improved paint drying activity as compared to Mn(2-EH)2 only. Further comparing the results of experiments 1a, 2, 3a, and 4 (mixing Me4dtne ligand with Mn(2-EH)2) with experiment 5 (using the well-defined preformed complex with Me4dtne) shows that the drying time of the Me4dtne ligand/ Mn(2-EH)2 mixture is significantly faster than that found for the well-defined complex. For example experiment 2 and 5 (both having 0.05% Mn in the formulation) gave in experiment 2 a drying time of 1.9 h and in experiment 5 of 4.8 h. Even reducing the amount of Mn in experiment by a factor of 5 (to 0.01% Mn) yielded a better drying time (3.7h) than found for the well-defined complex at a Mn level of 0.05%.

Further, experiments 1a-1d and 3a-3d show that in combination with the Me4dtne ligand, a similar drying time of the alkyd resin is obtained irrespective of the Mn salt used (being Mn(2-EH)2, Mn(acetate)2, Mn(acetate)3, or MnCl2).

Finally, comparative experiment 7 shows that no alkyd resin is obtained when using the Me4dtne ligand without manganese salt or soap.

Claims

1. A formulation comprising an oxidatively curable alkyd-based curable resin and a complex of a chelant of the formula (I):

   (wherein:
   each R is independently selected from hydrogen, C1-C24 alkyl, CH2CH2OH, CH2COOH and pyridin-2-ylmethyl;
   Q is a C2-C9 alkylene bridge, a C6-C10 arylene bridge or a bridge comprising one or two C1-C3 alkylene units and one C6-C10 arylene unit, which bridge may be optionally substituted one or more times with independently selected C1-C24 alkyl groups; and
   each R1, R2, R3, and R4 is independently selected from H, C1-C2 alkyl and C1-C2 alkylhydroxy)

   and a transition metal ion selected from the group consisting of ions of manganese, iron, cobalt, vanadium and copper, wherein the complex is not well-defined.
2. The formulation of claim 1, wherein Q is ethylene, n-propylene, n-butylene, n-pentylene or n-hexylene.

3. The formulation of claim 1, wherein the chelant is 1,2-bis-(4,7-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane.

4. A method of preparing a formulation as defined in any one of claims 1 to 3, the method comprising contacting a composition comprising an alkyd-based resin with a composition comprising a chelant of formula (I).

5. The method of claim 4 wherein the method comprises contacting a formulation comprising an oxidatively curable alkyd-based curable resin and a chelant of the formula (I), as defined in claim 1, which formulation comprises less than 0.001 % by weight of ions of each of manganese, iron, cobalt, vanadium and copper, with a source of manganese, iron, cobalt, vanadium or copper ions.

6. The method of claim 5, wherein the formulation is contacted with an optionally hydrated salt selected from the group consisting of MnSO₄, MnCl₂, MnBr₂, Mn(NO₃)₂, Mn(CH₃COO)₃, Mn(CH₃COO)₂, Mn(acetylacetonate)₂, Mn(acetylacetonate)₃, Mn(octanate)₂, Mn(2-ethylhexanoate)₂, Mn(naphthenate)₂ and Mn(neodecanoate)₂.

7. The method of claim 4, wherein the composition comprising the chelant of formula (I) comprises a complex as defined in any one of claims 1 to 3.

8. The method of claim 7, wherein the composition comprising the complex comprises a mixture of the chelant of formula (I) and a salt of the transition metal ion.

9. The formulation of any one of claims 1 to 3, which is obtainable by a method as defined in any one of claims 5 to 8.

10. A composition resultant from curing of a formulation as defined in any one of claims 1 to 3 and 9.

11. A method comprising applying to a substrate a formulation as defined in any one of claims 1 to 3 and 9.

12. A kit comprising a formulation comprising an oxidatively curable alkyd-based curable resin and a chelant of the formula (I), as defined in claim 1, which formulation comprises less than 0.001 % by weight of ions of each of manganese, iron, cobalt, vanadium and copper, and, separately, a composition comprising transition metal ions selected from the group consisting of manganese, iron, cobalt, vanadium and copper ions.

13. The kit of claim 12 wherein Q is ethylene, n-propylene, n-butylene, n-pentylene or n-hexylene or the chelant is 1,2-bis-(4,7-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane.

Patentansprüche

1. Formulierung, umfassend ein oxidativ härtares, auf Alkyd basierendes härtares Harz und einen Komplex eines Chelatbildners der Formel (I):

![Chemical structure](image)

(worin:

- jedes R unabhängig ausgewählt ist aus Wasserstoff, C₁₋C₂₄-Alkyl, CH₂CH₂OH, CH₂COOH und Pyridin-2-ylmethyl;
- Q eine C₂₋C₆-Alkylen-Brücke, eine C₆₋C₁₀-Arylen-Brücke oder eine Brücke ist, die ein oder zwei C₁₋C₃-Alkylen-
Einheiten und eine C₆-C₁₀-Arylen-Einheit aufweist, wobei die Brücke wahlweise einmal oder mehrmals mit unabhängig ausgewählten C₁-C₂₄-Alkyl-Gruppen substituiert sein kann; und jedes R₁, R₂, R₃ und R₄ unabhängig ausgewählt ist aus H, C₁-C₄-Alkyl und C₁-C₄-Alkylhydroxy) und ein Übergangsmetall-Ion, wobei das ausgewählt ist aus der Gruppe bestehend aus Ionen von Mangan, Eisen, Cobalt, Vanadium und Kupfer, wobei der Komplex nicht klar abgegrenzt ist.

2. Formulierung nach Anspruch 1, wobei Q Ethylen, n-Propylen, n-Butylen, n-Pentylen oder n-Hexylen ist.

3. Formulierung nach Anspruch 1, wobei der Chelatbildner 1,2-Bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethan ist.

4. Verfahren zur Herstellung einer Formulierung nach einem der Ansprüche 1 bis 3, wobei das Verfahren das Inkontaktbringen einer Zusammensetzung, die ein Harz auf Alkyd-Basis umfasst, mit einer Zusammensetzung umfasst, die einen Chelatbildner der Formel (I) aufweist.

5. Verfahren nach Anspruch 4, wobei das Verfahren das Inkontaktbringen einer Formulierung, die ein oxidativ härtabares, auf Alkyd basierendes härtabares Harz umfasst, und eines Chelatbildners der Formel (I), wie in Anspruch 1 festgelegt ist, wobei die Formulierung weniger als 0,001 Gew.-% Ionen von jeweils Mangan, Eisen, Cobalt, Vanadium und Kupfer aufweist, mit einer Quelle von Ionen von Mangan, Eisen, Cobalt, Vanadium und Kupfer umfasst.

6. Verfahren nach Anspruch 5, wobei die Formulierung in Kontakt gebracht wird mit einem wahlweise hydratisierten Salz, das ausgewählt ist aus der Gruppe bestehend aus MnSO₄, MnCl₂, MnBr₂, Mn(NO₃)₂, Mn(CH₃COO)₃, Mn(CH₃COO)₂, Mn(Acetylacetonat)₂, Mn(Octanonat)₂, Mn(2-Ethylhexanoat)₂, Mn(Naphthenat)₂ und Mn(Neodecanoat)₂.

7. Verfahren nach Anspruch 4, wobei die den Chelatbildner umfassende Zusammensetzung der Formel (I) einen Komplex umfasst, wie er in einem der Ansprüche 1 bis 3 festgelegt ist.

8. Verfahren nach Anspruch 7, wobei die den Komplex umfassende Zusammensetzung eine Mischung aus dem Chelatbildner der Formel (I) und einem Salz des Übergangsmetall-Ions umfasst.

9. Formulierung nach einem der Ansprüche 1 bis 3, die mit Hilfe eines Verfahrens nach einem der Ansprüche 5 bis 8 erhalten wird.


11. Verfahren, umfassend das Aufbringen einer Formulierung nach einem der Ansprüche 1 bis 3 und 9 auf ein Substrat.

12. Kit, umfassend eine Formulierung, die ein oxidativ härtabares, auf Alkyd basierendes härtabares Harz und einen Chelatbildner der Formel (I), wie in Anspruch 1 definiert, wobei die Formulierung weniger als 0,001 Gew.-% Ionen von jeweils Mangan, Eisen, Cobalt, Vanadium und Kupfer aufweist, und separat eine Zusammensetzung aufweist, umfassend Übergangsmetall-Ionen, die ausgewählt sind aus der Gruppe bestehend aus Ionen von Mangan, Eisen, Cobalt, Vanadium und Kupfer.

13. Kit nach Anspruch 12, wobei Q Ethylen, n-Propylen, n-Butylen, n-Pentylen oder n-Hexylen ist oder der Chelatbildner 1,2-Bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethan ist.

Regvendications

1. Formulation comprenant une résine durcissable à base d’alkyde durcissable par oxydation et un complexe d’un chélateur de la formule (I):
(où:
chaque $R$ est sélectionné indépendamment parmi hydrogène, alkyle $C_1-C_{24}$, $\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_2\text{COOH}$ et pyridin-2-ylméthyle;

$Q$ est un pont alkyle $C_2-C_6$, un pont aryle $C_6-C_{10}$ ou un pont comprenant une ou deux unités d’alkyle
$C_1-C_3$ et une unité d’arylène $C_6-C_{10}$, lequel pont peut être optionnellement substitué une ou plusieurs fois par
des groupes alkyles $C_1-C_{24}$ sélectionnés indépendamment; et

chaque $R_1$, $R_2$, $R_3$ et $R_4$ est sélectionné indépendamment parmi H, alkyle $C_1-C_4$ et alkylhydroxy $C_1-C_4$)
ed d’un ion de métal de transition sélectionné parmi le groupe consistant en ions de manganèse, de fer, de
cobalt, de vanadium et de cuivre, où le complexe n’est pas bien défini.

2. Formulation selon la revendication 1, dans laquelle $Q$ est un éthylène, un n-propylène, n-butylène, n-pentylène ou
n-hexylène.

3. Formulation selon la revendication 1, dans laquelle le chélateur est du 1,2-bis-(4,7-diméthyl-1,4,7,-triazacyclonon-
1 -yl)-éthane.

4. Procédé de préparation d’une formulation selon l’une quelconque des revendications 1 à 3, le procédé comprenant
mettre une composition comprenant une résine à base d’alkyde en contact avec une composition comprenant un
chélateur de la formule (I).

5. Procédé selon la revendication 4, où le procédé comprend mettre en contact une formulation comprenant une résine
durcissable à base d’alkyde durcissable par oxydation et un chélateur de la formule (I), selon la revendication 1,
laquelle formulation comprend moins de 0,001 % en poids d’ions de chacun d’entre manganèse, fer, cobalt, vanadium
e cuivre, avec une source d’ions de manganèse, de fer, de cobalt de vanadium ou de cuivre.

6. Procédé selon la revendication 5, dans lequel la formulation est mise en contact avec un sel optionnellement hydraté
sélectionné parmi le groupe consistant en $\text{MnSO}_4$, $\text{MnCl}_2$, $\text{MnBr}_2$, $\text{Mn(NO}_3\text{)}_2$, $\text{Mn(\text{CH}_3\text{COO})}_3$, $\text{Mn(\text{CH}_3\text{COO})}_2$
$\text{Mn(\text{acétylacétonate})}_2$, $\text{Mn(\text{acétylacétonate})}_3$, $\text{Mn(octanonate)}_2$, $\text{Mn(2-éthylhexanoate)}_2$, $\text{Mn(naphténate)}_2$ et
$\text{Mn(neodécanoate)}_2$.

7. Procédé selon la revendication 4, dans lequel la composition comprenant le chélateur de la formule (I) comprend
un complexe selon l’une quelconque des revendications 1 à 3.

8. Procédé selon la revendication 7, dans lequel la composition comprenant le complexe comprend un mélange du
chélateur de la formule (I) et d’un sel de l’ion de métal de transition.

9. Formulation selon l’une quelconque des revendications 1 à 3, qui peut être obtenue par un procédé selon l’une
quelconque des revendications 5 à 8.


11. Procédé comprenant appliquer à un substrat une formulation selon l’une quelconque des revendications 1 à 3 et 9.

12. Kit comprenant une formulation comprenant une résine durcissable à base d’alkyde durcissable par oxydation et
un chélateur de la formule (I), selon la revendication 1, laquelle formulation comprend moins de 0,001 % en poids
d’ions de chacun d’entre manganèse, fer, cobalt, vanadium et cuivre et, séparément, une composition comprenant
des ions de métal de transition sélectionnés parmi le groupe consistant en ions de manganèse, de fer, de cobalt, de vanadium et de cuivre.

13. Kit selon la revendication 12, dans lequel Q est un éthylène, un n-propylène, n-butylène, n-pentylène ou n-hexylène ou bien le chélateur est du 1,2-bis-(4,7-diméthyl-1,4,7,-triazacyclonon-1-yl)-éthane.
REFERENCES CITED IN THE DESCRIPTION

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