Sprayable coating composition

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Applicant(s)
Akzo Nobel N.V.

Inventor(s)
Van Beelen, Jan Cornelis; Klinkenberg, Huig

Agent / Attorney
Griffith Hack, 509 St Kilda Road, Melbourne, VIC, 3004

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Title: SPRAYABLE COATING COMPOSITION

Abstract: The present invention relates to a sprayable coating composition comprising (a) at least one isocyanate reactive compound comprising at least one thiol group, (b) at least one polyisocyanate-functional compound, and (c) a catalyst comprising at least one organic metal compound where the metal is a metal of Groups 3 to 13 of the Periodic Table. The invention also relates to use of the sprayable coating composition as a clear coat, its use as a clear coat, its use as a clear coat in a multi-layer lacquer coating, and its use in the refinish industry and in finishing large transportation vehicles.
SPRAYABLE COATING COMPOSITION

The invention relates to the use of a sprayable coating composition, its use as a clear coat, its use as a clear coat in a multi-layer lacquer coating, and its use in the refinish industry and in finishing large transportation vehicles.

Coatings used for painting motor vehicles and repairing the original paint are required to have good physical properties such as hardness, mechanical strength, and resistance to water, acids, and solvents. The coatings are also required to have good appearance properties, which means that films must be smooth and have a high gloss and a high distinctness of image. It is also desirable that all properties are retained under prolonged outdoor weathering.

For environmental reasons, it is required to use a coating composition which can be applied easily using spray application at a low volatile organic content (VOC). Coatings with a lower organic solvent content emit lower levels of solvent when they are used, and so the atmosphere becomes less polluted.

US 4,788,083 discloses a sprayable coating composition comprising a hydroxyl compound, an isocyanate, a metal catalyst selected from tin and bismuth, and a molar excess of a complexing agent such as a mercapto compound. Although tin and bismuth catalysts are known metal catalysts for the hydroxyl isocyanate reaction, it has been found that these metal catalysts do not catalyse the thiol isocyanate reaction. Furthermore, the mercapto compound in US 4,788,083 is used to complex and thus deactivate the metal catalyst. The activation of the metal catalyst is effectuated by heat or the addition of a tertiary amine activator. So, the reaction of hydroxyl isocyanate only starts when the metal catalyst is activated.

The present invention relates to the use of a sprayable coating composition comprising
a) at least one isocyanate reactive compound comprising at least one thiol group,
b) at least one polyisocyanate-functional compound, and
c) a catalyst comprising at least one organic metal compound where the metal is a metal of Groups 3 to 13 of the Periodic Table.

It has surprisingly been found that sprayable coating composition can be provided where the thiol isocyanate reaction can be catalysed in the presence of an organic metal compound, the metal being a metal of Groups 3 to 13 of the Periodic Table, both at room temperature and at higher temperatures such as 60°C. At all temperatures, an excellent pot life - drying balance is shown. An additional advantage is the fact that there is no necessity to add a tertiary amine activator to the coating composition. This addition would have a negative effect on the pot life of the coating composition. Furthermore, the sprayable coating composition provides excellent properties such as were mentioned above to be necessary for its use in the refinish industry and in finishing large transportation vehicles.

Although we do not want to be bound by any theory, it is suggested that the capacity of the organic metal compound to hydrolyse plays a significant role in the reaction mechanism of the thiol isocyanate reaction. Therefore, the reaction of thiol and isocyanate compounds performs quite differently from the reaction of hydroxyl and isocyanate compounds in the presence of metal catalysts.

US 5,849,864 discloses a sprayable coating composition comprising a polymercapto resin, a polyisocyanate, and a tin catalyst complex. The tin catalyst is complexed with sulphonic acid. Upon exposure to an amine, the catalyst complex becomes activated. It has been found that tin catalyst complexes do not catalyse the thiol isocyanate reaction. Furthermore, as mentioned above, it is a disadvantage to use amine in coating compositions.
WO 98/15585 discloses a sprayable coating composition comprising a hydroxyl compound, an isocyanate, and a catalyst which is the reaction product of a titanium, zirconium, hafnium or aluminium ortho ester, a beta-diketone or beta-ketoester, and a complexing agent such as a mercapto compound. The catalyst as such can be used in the range of 0.005 to 0.5 per cent by weight with respect to the weight of the reaction mixture. Although a mercapto compound is present in the coating composition, this is in such small quantities that WO 98/15585 does not disclose the coating composition of the present invention.

JP-A-04-063823 discloses an architectural sealant comprising a compound having two or more thiol groups per molecule, a polyisocyanate compound, and a metallic soap. It is not disclosed or suggested how to prepare a sprayable coating composition thereof, nor is its use in a clear coat with the above-mentioned properties described.

US 5,064,871 discloses a composition comprising an isocyanate reactive compound, a polyisocyanate, and a catalyst comprising a bismuth and a zirconium carboxylate. Although the use of polymercaptan as an isocyanate reactive compound is mentioned in the description, only polyol resins are exemplified. Furthermore, the composition is used in particular as an adhesive. It is not disclosed or suggested how to prepare a sprayable coating composition thereof, nor is its use in a clear coat with the above-mentioned properties described.

US 4,312,971 discloses a composition comprising an organic compound comprising at least two active hydrogen atoms, a polyisocyanate, and a catalyst comprising an organo zirconium and an organo mercury compound. Although the use of aliphatic thiols as an organic compound comprising at least two active hydrogen atoms is mentioned in the description, only polyol resins are exemplified. Furthermore, the composition is used in particular as non-cellular polyurethanes, and cellular rigid and flexible polyurethane foams. It is not
disclosed or suggested how to prepare a sprayable coating composition thereof, nor is its use in a clear coat with the above-mentioned properties described.

JP-A-10182786 discloses a sealant comprising a polymer having two or more thiol groups per molecule, a polyisocyanate compound, and an organic metal. Although it is mentioned in the description that organic mercury compounds and organic lead compounds can be used, only organic tin compounds are exemplified. As already mentioned before, tin does not catalyse the reaction of thiol and isocyanate. Furthermore, in JP-A-10182876 it is not disclosed or suggested how to prepare a sprayable coating composition thereof, nor is its use in a clear coat with the above-mentioned properties described.

The use of organic metal compounds, such as zirconium, hafnium, and aluminium complexes, in the hydroxyl isocyanate reaction is disclosed in Florio J., *Paint & Coatings Industry*, October 1997, pp. 110-120, and in US 5,846,897. However, it is not disclosed or suggested that these complexes may be used in the thiol isocyanate reaction.

The catalyst comprises at least one organic metal compound where the metal is a metal of Groups 3 to 13 of the Periodic Table. Preferably, the metal is a transition metal. More preferably, the metal is a metal of Group 4 of the Periodic Table.

The organic metal compounds comprise metal salts and/or complexes of organic compounds. The organic compounds are groups having 2 to 40 carbon atoms, optionally comprising atoms such as O, N, and S. The metal salts comprise anions selected from the groups of carboxylates. Examples thereof include propionate, butyrate, pentanoate, 2-ethyl hexanoate, naphthenate, oxalate, malonate, succinate, glutamate, and adipate. The metal complexes comprise ligands selected from the group of beta-diketones, alkyl acetoacetates, alcoholates, and combinations thereof. Examples thereof include acetyl acetone (2,4-pentanedione), 2,4-heptanedione, 6-methyl-2,4-heptadione,
2,4-octanedione, propoxide, isopropoxide, and butoxide. Preferably, the organic metal compound is a metal complex.

Examples of metals include aluminium, titanium, zirconium, and hafnium.

Examples of metal complexes include aluminium complexed with 2,4-pentanediocne (K-KAT® XC5218 ex King Industries), aluminium triacetyl acetonate, zirconium tetraacetyl acetonate, zirconium tetrabutoxide (Tyzor® NBZ ex Dupont), titanium tetrabutoxide (Tyzor® TBT ex Dupont), zirconium complexed with 6-methyl-2,4-heptadione, K-KAT® XC6212 ex King Industries, aluminium trisopropoxide, and titanium diisopropoxide bis-2,4(pentadiionate) (Tyzor® AA ex DuPont). These catalysts may be used in an amount of 0.01 to 10 wt.% on solid curable material, preferably 0.1 to 5 wt. %.

Examples of the isocyanate reactive compound comprising at least one thiol group include a thiol-functional compound comprising at least two thiol-functional groups and a compound comprising at least one thiol-functional group and one hydroxyl-functional group. Also mixtures of these compounds may be used in the compositions of the present invention.

Suitable thiol group-containing compounds are generally prepared by reacting hydroxyl group-containing compounds with thiol group-containing acids, such as 3-mercapto propionic acid, 2-mercapto propionic acid, thio-salicylic acid, mercapto succinic acid, mercapto acetic acid, or cysteine. Examples of suitable hydroxyl group-containing compounds are diols, triols, and tetraols, such as 1,4-butane diol, 1,6-hexane diol, 2,2-dimethyl-1,3-propane diol, 2-ethyl-2-propyl-1,3-propane diol, 1,2-, 1,3-, and 1,4-cyclohexane diols, and the corresponding cyclohexane dimethanol, 1,1,1-trimethylol propane, 1,2,3-trimethylol propane, and pentaerythritol. Examples of compounds prepared according to such a method include pentaerythritol tetrakis (3-mercapto propionate), pentaerythritol tetrakis (2-mercapto acetate), trimethylol propane tris (3-mercapto propionate), trimethylol propane tris (2-mercapto propionate), and trimethylol propane tris (2-mercapto acetate). Good results have been obtained with trimethylol propane
tris (3-mercapto propionate) and pentaerythritol tetrakis (3-mercapto propionate).

A further example of a compound prepared according to such a method consists of a hyperbranched polyl core based on a starter polyl, e.g., trimethylol propane, and dimethylol propionic acid. This polyl is subsequently esterified with 3-mercaptopropionic acid and isononanoic acid. These methods are described in European patent application EP-A 0 448 224 and International patent application WO 93/17060.

Other syntheses to prepare compounds comprising at least two thiol-functional groups involve:
- the reaction of an aryl or alkyl halide with NaHS to introduce a pendent thiol group into the alkyl and aryl compounds, respectively;
- the reaction of a Grignard reagent with sulphur to introduce a pendent thiol group into the structure;
- the reaction of a polymercaptan with a polyolefin according to a Michael addition reaction, a nucleophilic reaction, an electrophilic reaction or a radical reaction;
- the reaction of a polyisocyanate with a thiol-functional alcohol, and
- the reduction of disulphides.

The compound comprising at least one thiol-functional group and one hydroxyl-functional group may for example have a structure according to the following formula: T[(C₃H₆O)nCH₂CHOHCH₂SH]₃, with T being a triol such as trimethylol propane or glycerol. An example of such a compound is commercially available from Henkel under the trademark Henkel Capcure® 3/800.

Alternatively, the isocyanate reactive compound comprising at least one thiol group is a resin having as a backbone a polyester resin, polyurethane resin, polyacrylate resin, and polyether resin. These isocyanate reactive compounds may then also comprise hydroxyl groups.
The isocyanate reactive compound comprising at least one thiol group may be a polyester prepared from (a) at least one polycarboxylic acid or reactive derivatives thereof, (b) at least one polyol, and (c) at least one thiol-functional carboxylic acid. The polyesters preferably possess a branched structure. Branched polyesters are conventionally obtained through condensation of polycarboxylic acids or reactive derivatives thereof, such as the corresponding anhydrides or lower alkyl esters, with polyalcohols, when at least one of the reactants has a functionality of at least 3.

Examples of suitable polycarboxylic acids or reactive derivatives thereof are tetrahydrophthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic acid, hexahydrophthalic anhydride, methyl hexahydrophthalic acid, methyl hexahydrophthalic anhydride, dimethycyclohexane dicarboxylate, 1,4-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid, phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, 5-tert. butyl isophthalic acid, trimellitic anhydride, maleic acid, maleic anhydride, fumaric acid, succinic acid, succinic anhydride, dodecenyl succinic anhydride, dimethyl succinate, glutaric acid, adipic acid, dimethyl adipate, azelaic acid, and mixtures thereof.

Examples of suitable polyols include trimethylol propane, trimethylol ethane, glycerol, 1,2,6-hexanetriol, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 2-methylpropane-1,3-diol, neopentyl glycol, 2-butyl-2-ethyl-1,3-propane diol, cyclohexane-1,4-dimethylol, the monoester of neopentyl glycol and hydroxypivalic acid, hydrogenated Bisphenol A, 1,5-pentane diol, 3-methylpentane diol, 1,6-hexane diol, 2,2,4-trimethyl pentane-1,3-diol, dimethylol propionic acid, pentaerythritol, di-trimethylol propane, dipentaerythritol, and mixtures thereof.

Examples of suitable thiol-functional organic acids include 3-mercaptopropionic acid, 2-mercaptobenzonic acid, thio-salicylic acid, mercaptosuccinic acid, mercaptoacetic acid, cysteine, and mixtures thereof.
Optionally, monocarboxylic acids and monoalcohols may be used in the preparation of the polyesters. Preferably, C₄-C₁₈ monocarboxylic acids and C₆-C₁₈ monoalcohols are used. Examples of the C₄-C₁₈ monocarboxylic acids include pivalic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, 2-ethylhexanoic acid, isononanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, isostearic acid, stearic acid, hydroxystearic acid, benzoic acid, 4-tert. butyl benzoic acid, and mixtures thereof. Examples of the C₆-C₁₈ monoalcohols include cyclohexanol, 2-ethylhexanol, stearyl alcohol, and 4-tert. butyl cyclohexanol.

Good results may also be obtained with an aqueous thiol-functional polyurethane dispersion which is obtainable by first preparing an isocyanate-functional polyurethane from diols, diisocyanates, and building blocks containing groups which facilitate the stabilisation of the resin in an aqueous dispersion, followed by reaction of the isocyanate-functional polyurethane with a polyfunctional thiol in a base-catalysed addition reaction, followed by dispersion in water.

The isocyanate reactive compound comprising at least one thiol group may be a thiol-functional polyacrylate. Such a polyacrylate is derived from hydroxy-functional acrylic monomers, such as hydroxy ethyl (meth)acrylate, hydroxy propyl (meth)acrylate, hydroxy butyl (meth)acrylate, other acrylic monomers such as (meth)acrylic acid, methyl (meth)acrylate, butyl (meth)acrylate, optionally in combination with a vinyl derivative such as styrene, and the like, or mixtures thereof, wherein the terms (meth)acrylate and (meth)acrylic acid refer to both methacrylate and acrylate, as well as methacrylic acid and acrylic acid, respectively. The thiol group is introduced by the reaction product of dimethylm-isopropenyl benzyl isocyanate and mercapto ethanol. Alternatively, glycidyl methacrylate is introduced into the polymer to prepare an epoxy-functional polyacrylate. The epoxy groups are then reacted with suitable thiol-functional organic acids such as mentioned above. The polyacrylate is prepared by
conventional methods, for instance, by the slow addition of appropriate monomers to a solution of an appropriate polymerisation initiator, such as an azo or peroxo initiator.

Also included in the coating compositions may be di-, tri-, or higher thiol-functional diluents such as ethane dithiol or bis-beta-mercapto-ethyl sulphide. Preference is given to the use of higher-molecular weight thiol-functional compounds, which may be obtained by reaction of a polythiol-functional compound with a polyisocyanate.

Preferably, the isocyanate reactive compound comprising at least one thiol group is derived from a polyester compound. Examples thereof include the above-mentioned reaction product of hydroxyl group-containing compounds with thiol group-containing acids and the above-mentioned polyester prepared from (a) at least one polycarboxylic acid or reactive derivatives thereof, (b) at least one polyol, and (c) at least one thiol-functional carboxylic acid. The most preferred thiol-functional compound is pentaerythritol tetrakis (3-mercapto propionate).

The organic polyisocyanate includes polyfunctional, preferably free polyisocyanates, with an average NCO functionality of 2.5 to 5, and may be (cyclo)aliphatic, araliphatic or aromatic in nature. The polyisocyanate may include biuret, urethane, uretdione, and isocyanurate derivatives. Examples of these organic polyisocyanates include 1,6-diisocyanatohexane, isophorone diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, diphenyl methane-diisocyanate, 4,4'-bis(isocyanato-cyclohexyl) methane, 1,4-diisocyanatobutane, 1,5-diisocyanato-2,2-dimethyl pentane, 2,2,4-trimethyl-1,6-diisocyanatohexane, 1,10-diisocyanatodecane, 4,4-diisocyanato-cyclohexane, 2,4-hexahydrotoluene diisocyanate, 2,6-hexahydrotoluene diisocyanate, norbornane diisocyanate, 1,3-xylene diisocyanate, 1,4-xylene diisocyanate, 1-isocyanato-3-(isocyanato methyl)-1-methyl cyclohexane, m-α,α'-α'-tetramethyl xylylene diisocyanate, the above-mentioned derivatives thereof, and
mixtures thereof. Normally, these products are liquid at ambient temperature and commercially available in a wide range. Particularly preferred isocyanate curing agents are trisocyanates and adducts. Examples thereof are 1,8-diisocyanato-4-(isocyanatomethyl) octane, the adduct of 3 moles of toluene diisocyanate to 1 mole of trimethylol propane, the isocyanurate trimer of 1,6-diisocyanatohexane, the isocyanurate trimer of isophorone diisocyanate, the uretdione dimer of 1,6-diisocyanatohexane, the biuret trimer of 1,6-diisocyanatohexane, the adduct of 3 moles of m-\(\alpha,\alpha',\alpha''\)-tetramethyl xylene diisocyanate to 1 mole of trimethylol propane, and mixtures thereof. Preferred are cyclic trimers (isocyanurates) and uretdiones of 1,5-hexane diisocyanate and isophorone diisocyanate. Usually these compounds contain small quantities of their higher homologues.

Optionally, a water borne coating composition according to the present invention may also comprise an organic hydrophilic polyisocyanate compound substituted with non-ionic groups, such as C\(_1\)-C\(_4\) alkoxy polyalkylene oxide groups. Preferably, 30 wt.% of non-ionic groups will be present on the total solid polyisocyanate compound, more preferably 20 wt.%, most preferably 15 wt.%. Preferred are the isocyanurates of 1,6-hexane diisocyanate and isophorone diisocyanate substituted with methoxy polyethylene glycol.

Optionally, a hydroxyl-functional compound comprising at least two hydroxyl-functional groups may be present in the curable material. The hydroxyl-functional compound comprising at least two hydroxyl-functional groups may be selected from polyester polyols, polyether polyols, polyacrylate polyols, polyurethane polyols, cellulose acetobutyrate, hydroxyl-functional epoxy resins, alkyds, and dendrimeric polyols such as described in WO 93/17050. Also, hydroxyl-functional oligomers and monomers, such as castor oil and trimethylol propane, may be included. A preferred polyl is an acrylate polyl. More preferred is an acrylate polyl available from Akzo Nobel Resins having the trade name Setalux\textsuperscript{®} 1157.
The polyisocyanate and the compound comprising isocyanate reactive groups should be mixed such that the ratio of isocyanate groups to isocyanate reactive groups is in the range of 0.5-3:1, preferably 0.75-2.5:1, and more preferably 1-2:1. It is preferred that at least 10% of the isocyanate reactive groups are thiol groups, more preferred at least 25%, most preferred at least 50%.

If hydroxyl-functional compounds are present in the coating composition, catalysts for the cross-linking of isocyanate groups with hydroxyl groups may be present. Examples thereof include Sn-based catalysts, such as dibutyl tin dilaurate and dibutyl tin diacetate.

The polyisocyanate may be mixed with the isocyanate reactive compound by any suitable technique. However, simply stirring usually is sufficient. Sometimes it may be useful to dilute the polyisocyanate somewhat with an organic solvent like ethyl acetate or 1-methoxy-2-propyl acetate to reduce its viscosity.

Optionally, a ketone based chelating agent may be added to the coating composition. Examples of these chelating agent include beta-dicarbonyls, alpha-hydroxyl ketones, fused aromatic beta-hydroxy ketones, dialkyl malonates, aceto acetic esters, alkyl lactates, and alkyl pyruvates. Preferably, beta-dicarbonyls such as acetyl acetone are used. The ketone based chelating agent may be used in an amount up to 10 wt.% on solids, preferably up to 5 wt.%.

The composition may be a water borne composition, a solvent borne composition or a solvent-free composition. Since the composition may be composed of liquid oligomers, it is especially suitable for use as a high solids composition or a solvent-free composition. Alternatively, the coating composition of the present invention may be an aqueous powder coating dispersion wherein the isocyanate reactive compound comprising at least one thiol group has a Tg above 20°C. The coating composition may as well be used in powder coating compositions and hot melt coatings.
compositions. Preferably, the theoretical volatile organic content (VOC) in the composition is less than about 450 g/l, more preferably less than about 350 g/l, most preferably less than about 250 g/l.

The coating compositions may further comprise other ingredients, additives or auxiliaries, such as pigments, dyes, emulsifiers (surfactants), pigment dispersion aids, levelling agents, anti-cratering agents, antifoaming agents, wetting agents, antisagging agents, heat stabilisers, UV absorbers, antioxidants, and fillers.

The coating composition may be applied to any substrate. The substrate may be, for example, metal, plastic, wood, glass, ceramic, or some other coating layer. The other coating layer may be comprised of the coating composition or it may be a different coating composition. The coating compositions show particular utility as clear coats, base coats, pigmented top coats, primers, and fillers. Preferably, the coating composition may be used according to the present invention as clear coat or as primer.

The coating compositions can be applied by conventional means such as by spray gun, brush, or roller, spraying being preferred. Curing temperatures preferably are between 0 and 100°C and more preferably between 20 and 60°C. The compositions are particularly suitable in the preparation of coated metal substrates, such as in the refinish industry, in particular the body shop, to repair automobiles and transportation vehicles, and in finishing large transportation vehicles such as trains, trucks, buses, and aeroplanes.

The composition is also suitable for application by an external mixing apparatus, one where a liquid composition comprising at least one isocyanate-functional compound and at least one isocyanate reactive compound is sprayed via a spray nozzle, with a small amount of catalyst. Such an apparatus is described, for example, in WO 98/41316. Due to the very effective use of the catalysts, the compositions have very short curing times, which makes this method
specifically suitable for these compositions.

In the case of the coating composition being a clear coat, the base coat may be a conventional base coat known in the coating art. Examples are solvent borne base coats, e.g., Autobase® ex Akzo Nobel Coatings BV, based on cellulose acetobutyrate, acrylic resins, and melamine resins, and water borne base coats, e.g., Autowave® ex Akzo Nobel Coatings BV, based on an acrylic resin dispersion and polyester resin. Furthermore, the base coat may comprise pigments (colour pigments, metallics and/or pearls), wax, solvents, flow additives, neutralising agent, and defoamers. Also high solids base coats can be used. These are, for instance, based on polyols, imines, and isocyanates.

The clear coat composition is applied to the surface of a base coat and then cured. An intermediate curing step for the base coat may be introduced.

The invention will be illustrated with reference to the following examples. Of course these examples are submitted for a better understanding of the invention only; they are not to be construed as limiting in any manner the scope thereof.
Examples

List of abbreviations:
Penta(SH)₄: pentaerythritol tetrakis (3-mercaptop propionate)

Other compounds used:
- Tolonate® HDT-LV ex Rhodia: isocyanurate of hexamethylene diisocyanate
- Byk® 306 ex Byk Chemie: levelling agent
- Tyzor® NBZ ex Dupont: zirconium tetrabutoxide (80 wt.% in n-butanol)
- Tyzor® TBT ex Dupont: titanium tetrabutoxide
- K-KAT® XC5218 ex King Industries: aluminium complexed with 2,4-pentanedione
- K-KAT® XC6212 ex King Industries: zirconium complex
- K-KAT® 348 ex King Industries: bismuth carboxylate 2-ethyl hexanoic acid

Methods

A coating is cured when the mark from firm pushing with the thumb does not leave any imprint.

The gelling time was determined visually and is the time after which the composition is no longer influenced by gravity.
Examples 1 to 11 and Comparative Examples A and B

A formulation was prepared comprising the following compounds:

| Penta(SH)$_4$ | 50 |
| Tolonate® HDT LV | 90 |
| Byk 306(10 wt.% in butyl acetate) | 7,0 |

To this formulation were added several organic metal compounds, optionally in combination with acetyl acetone (acac). A 50 µm thick film was drawn out onto tin plated metal. The drying time was evaluated at room temperature (RT) and at 60°C.

<table>
<thead>
<tr>
<th>Wt.% catalyst on solid binders</th>
<th>Wt.% acac added on catalyst</th>
<th>Gel time</th>
<th>drying RT</th>
<th>drying 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1% K-KAT® XC5218</td>
<td>-</td>
<td>&gt; 1 day</td>
<td>1 hr</td>
<td>18 min.</td>
</tr>
<tr>
<td>2 3% K-KAT® XC5212</td>
<td>-</td>
<td>&gt; 1 day</td>
<td>45 min.</td>
<td>15 min.</td>
</tr>
<tr>
<td>3 0.5% Tyzor® NBZ</td>
<td>-</td>
<td>20 min.</td>
<td>15 min.</td>
<td>2 min.</td>
</tr>
<tr>
<td>4 0.5% Tyzor® NBZ</td>
<td>500%</td>
<td>&gt; 1 day</td>
<td>25 min.</td>
<td>5 min.</td>
</tr>
<tr>
<td>5 0.5% Tyzor® NBZ</td>
<td>900%</td>
<td>&gt; 1 day</td>
<td>35 min.</td>
<td>7 min.</td>
</tr>
<tr>
<td>6 0.5% Zr(acac)$_4$*</td>
<td>-</td>
<td>10 min.</td>
<td>6 min.</td>
<td>3 min.</td>
</tr>
<tr>
<td>7 0.5% Zr(acac)$_4$</td>
<td>100%</td>
<td>1 day</td>
<td>10 min.</td>
<td>4 min.</td>
</tr>
<tr>
<td>8 1.5% Tyzor® TBT</td>
<td>-</td>
<td>35 min.</td>
<td>20 min.</td>
<td>4 min.</td>
</tr>
<tr>
<td>9 0.5% Tyzor® TBT</td>
<td>100%</td>
<td>&gt; 1 day</td>
<td>75 min.</td>
<td>20 min</td>
</tr>
<tr>
<td>10 0.5% Al(iPrO)$_3$**</td>
<td>-</td>
<td>6 min.</td>
<td>11 min.</td>
<td>4 min</td>
</tr>
<tr>
<td>11 0.5% Al(acac)$_3$***</td>
<td>-</td>
<td>&gt; 1 day</td>
<td>210 min.</td>
<td>25 min</td>
</tr>
<tr>
<td>A 1% K-KAT® 348</td>
<td>-</td>
<td>&gt;&gt; 1 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 1% dibutyl tin dilaurate</td>
<td>-</td>
<td>&gt;&gt; 1 h</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* zirconium tetraacetyl acetonate  
** aluminium triisopropoxide  
*** aluminium triacetyl acetonate
These examples show that organic metal compounds where the metal is a metal of Groups 3 to 13 of the Periodic Table, such as zirconium, aluminium, and titanium compounds, are very active catalysts in the reaction between thiol and isocyanate. Their results, optionally in combination with acetyl acetone, show an excellent pot life / drying balance. Well-known catalysts for the reaction between hydroxyl and isocyanate like dibutyl tin dilaurate or bismuth carboxylate 2-ethyl hexanoic acid show no activity at all.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Use of a sprayable coating composition comprising
   a) at least one isocyanate reactive compound
   comprising at least one thiol group,
   b) at least one polyisocyanate-functional compound, and
   c) a catalyst comprising at least one organic metal compound where the metal is a metal of Groups 3 to 13 of the Periodic Table.
in the refinish industry and in finishing large transportation vehicles.

2. Use according to claim 1, characterised in that the metal is a transition metal.

3. Use according to claim 2, characterised in that the metal is a metal of Group 4 of the Periodic Table.

4. Use according to claim 1, characterised in that the metal is selected from the group of aluminium, titanium, zirconium, and hafnium compounds.

5. Use according to any one of the preceding claims, characterised in that the organic metal compound is a metal complex.

6. Use according to claim 5, characterised in that the metal complexes comprise ligands selected from the group of beta-diketones, alkyl acetoacetates, alcoholates, and combinations thereof.

7. Use according to any one of the preceding claims, characterised in that a ketone based chelating agent is added to the coating composition.

8. Use according to any one of the preceding claims, characterised in that at least 50% of the isocyanate reactive groups are thiol groups.
9. Use according to any one of the preceding claims, characterised in that the isocyanate reactive compound comprising at least one thiol group is derived from a polyester compound.

10. Use of a coating composition according to any one of the preceding claims, comprising applying the composition as a clear coat.

11. Use of a coating composition according to claim 10, comprising applying the composition as a clear coat in a multi-layer lacquer coating.

12. Use of a sprayable coating composition substantially as herein described with reference to the accompanying examples (excluding comparative examples).

Dated this 14th day of February 2005
AKZO NOBEL N.V.
By their Patent Attorneys
GRIFFITH HACK
Fellows Institute of Patent and Trade Mark Attorneys of Australia