

The translation of the title is:

**Mono-noble metal dithiolates and their use for the production
of decoration containing noble metals on storable substrates**

**Mono-noble metal dithiolates, preparations containing them
and use thereof**

5 Specification

This invention relates to mono-noble metal dithiolates, in particular water-soluble monogold(I) dithiolates, to the production and to the use thereof for the production of
10 decoration containing noble metal, in particular high gloss decoration consisting of a continuous noble metal film, on storable substrates. The present invention also provides preparations containing noble metals as well as transfers both of which contain at least one mono-noble metal
15 dithiolate according to the invention for the decoration of storable substrates.

So-called noble metal preparations, for example bright gold and burnished gold preparations, have long been used to
20 produce noble metal decoration, in particular decoration substantially consisting of gold and/or silver in the form of a high gloss metal film, including conductor strips, in particular of gold, on integrated circuits, on a storable substrate. Such preparations generally contain one or more
25 organosulphur noble metal compounds, so-called noble metal thiolates in a purely organic or organic/aqueous carrier medium, wherein, in the case of Ag and Au, the noble metal is present in the monovalent oxidation state. Apart from the noble metal compound, the solvent and one or more
30 organic polymeric binders, the stated preparations additionally contain one or more fluxes, such as so-called resins and/or simple salts oxides or coordination compounds of the elements boron, silicon, vanadium, chromium, indium, zinc, antimony, bismuth and rhodium,
35 together with further auxiliary substances to establish

processing and service characteristics. The noble metal preparations are applied to the surfaces to be coated by means of customary direct or indirect printing processes, spraying or brushing or using transfer techniques.

5 Evaporation of the solvent is followed by a stoving operation at a temperature adjusted to the substrate and the gold preparation - the maximum stoving temperature is generally between 400 and 900°C, but higher temperatures are also possible in special cases. A noble metal film is
10 formed by the stoving operation and fixed onto the surface of the substrate. It is well known among experts that, in order to obtain high-gloss noble metal films, the noble metal thiolate used, the binder system and the solvent system have to be carefully coordinated with one another in
15 order to produce bright decorative films which adhere firmly to the substrate, decorative films also being taken to include conductor strips for electrical/electronic purposes.

20 The organosulphur gold compounds for the stated decorative preparations have long been almost exclusively so-called gold sulphoresinates obtained from a gold salt and a sulphurised terpene, in particular a naturally occurring terpene. Synthetically produced noble metal thiolates, in
25 particular gold(I) thiolates of the general formula Au-S-R have recently become more significant; R denotes in this formula an alkyl, cycloalkyl, aryl or aralkyl group or a bicyclic hydrocarbon residue. The stated gold(I) thiolates generally require the use of a purely organic solvent
30 system - reference is, for example, made to EP-B 0 491 143.

For reasons of occupational hygiene, safety and environmental protection, industry has been making efforts to discover noble metal preparations for decorating
35 storable substrate in which at least a proportion of the

organic solvent in the solvent system is replaced with water. DE-OS 32 17 049 thus describes a paint for applying an overglaze decoration on porcelain, which contains 15 to 40 wt.% of polyvinylpyrrolidone or a mixture of
5 polyvinylpyrrolidone and aqueous polyethylene oxide, 45 to 85 wt.% of ethylene glycol and/or propylene glycol and possibly water. Oxides, gold and organic gold compounds are stated as the colouring materials in this document, but without any teaching being provided as to the structure of
10 the gold compounds.

A burnished gold preparation containing polyvinylpyrrolidone and water and, additionally, an aqueous acrylate resin dispersion as binder and gold powder
15 and/or a sparingly soluble gold compound as colouring component is known from GB-A 22 16 536. As may be seen from the examples, alcoholic solvents are always present in these preparations too. The example preparations additionally contain a quantity of 5 or 6 wt.% of a non-
20 ionic wetting agent. This document contains no indication of using a water-soluble gold compound nor of dispensing with the presence of glycols and alcohols. As has been found in practice, noble metal preparations based on the above-stated documents often give rise to decoration which
25 exhibits inadequate gloss.

Homogeneous compositions, preferably solutions, are known from EP-A 0 514 073, which form a glossy metallic noble metal film on stoving. The compositions contain 3 to
30 22 wt.% of a noble metal thiolate, a polymeric resin and, as the solvent system, a mixture of water and an organic solvent (cosolvent), which preferably comprises water-miscible alcohols, ethers or esters. Both the noble metal thiolate and the binder should be soluble in the
35 water/cosolvent mixture. The preferably used gold(I)

thiolates are those of the general formulae Au-S-R-H or Au-S-R-X , wherein X denotes a nitro group or $-\text{COOH}$, $-\text{SO}_2\text{OH}$, $-\text{OH}$, $-\text{CONH}_2$, $-\text{NH}_2$ or $-\text{O-P(O)(OH)}_2$, wherein the H atoms may optionally be substituted, or salts thereof and R denotes a
5 divalent organic residue. It is clear from many examples and comparative examples in the stated document that only very specific gold(I) thiolates in such gold preparations containing water and cosolvent give rise to decoration with good gloss and good adhesion to the decorated substrate. On
10 the basis of the comparative examples described in this document, it was only possible to obtain decoration of a dull appearance with some of the gold(I) thiolates of the above formulae, including for example gold(I) mercaptosuccinic acid.

15 The object of the present invention is accordingly to provide another group of noble metal thiolates which are suitable for the production of high gloss noble metal decoration on storable substrates. The novel noble metal
20 thiolates should perform properly in bright noble metal preparations with an aqueous/organic and in particular a purely aqueous solvent system. The novel noble metal thiolates should be reliable in use and give rise to aesthetically high-quality decoration, in particular high
25 gloss, pore- and spot-free decoration having good adhesion on storable substrates.

It has surprisingly been found that the introduction of a second sulphydryl group into the organic compound on which
30 the noble metal thiolate is based considerably improves the suitability of the noble metal thiolate as a constituent of decorative noble metal preparations for the production of high gloss decoration.

The present invention accordingly provides mono-noble metal dithiolates of the general formula (A)

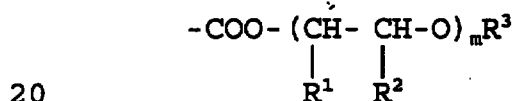


in which

Em: means a noble metal from the series Au(I), Ag(I) or an equivalent of Pd(II) or Pt(II) or Rh(III)

Q: means a tetravalent organic residue with 2 to 10 C atoms

Y: means a hydrophilic group from the series -COOH, -COO⁻cat⁺, wherein cat⁺ denotes Li⁺, Na⁺, K⁺, NH₄⁺, (C₁ to C₃ alkyl)_nN⁺H_{4-n} or (hydroxy(C₁ to C₃ alkyl)_nN⁺H_{4-n} and n denotes an integer between 1 and 4, or



where R¹, R² and R³ are identical or different and mean H or methyl and m equals an integer from 1 to 12,

Z: equals Y or H or a group from the series -OR', -SR', -SO₃R', -NR'₂, -NR'₃X⁻, wherein X⁻ denotes a mineral acid or carboxylic acid anion and R' denotes hydrogen or the group -(CH₂-CH-O)_mH



and R¹ and m have the above-stated meaning.

Preferred mono-noble metal dithiolates contain gold or silver, in particular gold, as the noble metal.

The tetravalent organic residue Q and the substituents Z and Y are preferably selected such that the resultant mono-noble metal dithiolate has elevated solubility in water. Good water solubility is in particular achieved when Y and/or Z mean(s) COO⁻cat⁺.

Where Y and/or Z in the mono-noble metal dithiolates according to the invention mean(s) $-\text{COO}^-\text{cat}^+$, the stated ammonium cations are preferred over the alkali metal cations. In the case of alkylammonium cations, alkyl may
5 mean methyl, ethyl, n-propyl or i-propyl; the alkylammonium cations may be mono-, di-, tri- or tetraalkylammonium with the above-stated alkyl groups, which may also be mixed. In the mono-, di-, tri- or tetra-hydroxyalkylammonium cations, the hydroxyalkyl group denotes hydroxymethyl, hydroxyethyl,
10 2-hydroxypropyl or 3-hydroxypropyl. If Y and/or Z equal(s) carboxyl, the stated salts may readily be produced by a conventional neutralisation reaction using the corresponding amine or ammonium hydroxide.

15 Where Y denotes the group $-\text{COO}(\text{CHR}^1-\text{CHR}^2-\text{O})_m\text{R}^3$, m preferably means in integer between 3 and 7. Mono-noble metal dithiolates in which Z means hydrogen intrinsically have a lower water solubility and are thus less suitable for noble metal preparations containing water than compounds in which
20 Z is itself a hydrophilic group.

The organic residue Q contains between 2 and 10 C atoms; the residue may additionally contain oxygen, nitrogen or sulphur atoms, for example in the form of hydroxyl,
25 carboxyl, alkoxy, amino, alkylamino, mercapto or alkylmercapto groups. The organic residue Q is particularly preferably a C_2 , C_3 or C_4 alkanetetrayl residue. According to another embodiment, the organic residue Q is a 5- or 6-membered cycloaliphatic tetrayl residue, wherein one C
30 ring member may be replaced by oxygen ($-\text{O}-$) or an imino group ($-\text{NH}-$ or $-\text{NR}-$); the cyclic residues Q are consequently cyclohexanetetrayl, cyclopentanetetrayl, tetrahydrofuranetetrayl, pyrrolidinetetrayl, piperidine-tetrayl or tetrahydropyranetetrayl.

In the mono-noble metal dithiolates according to the invention, the SH group and SEm group may be attached to adjacent carbon atoms or to carbon atoms separated by one or more members. Compounds in which the SH and SEm group are borne on adjacent carbon atoms are particularly preferred. Consequently, mono-noble metal dithiolates, in particular monogold(I) and monosilver dithiolates, of dimercaptosuccinic acid, 2,3-dimercaptoglutaric acid and 2,3- or 3,4- or 2,5-dimercaptoadipic acid, together with the salts thereof with the cation cat^+ , are particularly preferred. It is particularly convenient to form a salt from the mono-noble metal dimercaptosuccinic acid with a mono-, di- or tri-(C_1 to C_3)-alkylamine or mono-, di- or tri-(hydroxy-(C_1 to C_3)-alkylamine. An amine from the series mono-, di- or triethanolamine, together with triethyl-, tri-n- or tri-iso-propylamine in a quantity sufficient to neutralise the carboxyl groups present is particularly suitable for salt formation. The stated amines are also suitable for salt formation with other mono-noble metal dithiolates according to the invention.

Mono-noble metal dithiolates of the above-stated structure have hitherto never been described and have thus also never been suggested for use in the production of metallic decoration containing noble metal on storable substrates. On the basis of a comparison of the properties of decoration produced on the one hand with mono-noble metal dithiolates according to the invention and on the other hand with known, structurally similar noble metal thiolates which have no additional SH group, it is assumed that the mono-noble metal thiolates according to the invention are stabilised by the additional SH group in such a manner that a continuous, firmly adhering, high-gloss noble metal film may be formed during stoving of the noble metal compound

applied onto a storable substrate, such as glass, porcelain and ceramic.

The mono-noble metal dithiolates of the general formula

5 (A')



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in which Q, Y and Z have the above-stated meaning are produced in essentially the same manner as known noble metal thiolates, c.f. the documents cited above. In the case of mono-gold(I) dithiolates, a gold(I) complex of the formula $\text{AuCl}(\text{R}''\text{SR}''')$ is formed from tetrachloroauric acid after addition of twice the equivalent quantity of a thioether $\text{R}''\text{SR}'''$; the stated complex is then reacted in the presence of a solvent with a substantially equivalent molar quantity of a dithiol (dimercapto compound) of the general formula (B)

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wherein Q, Y and Z again have the same meaning as in the formula (A'). Methionine is a particularly convenient thioether for the formation of the gold(I) complex.

30 The dithiol compound (B) is produced using conventional process stages: for example, dimercaptoalkane dicarboxylic acids may be obtained by reacting the corresponding alkyne dicarboxylic acid with thioacetic acid; another possible method for obtaining aliphatic and cyclic dimercapto compounds of the general structure (B) is to react the corresponding dihalogen compound $(\text{Z-Q}(\text{hal})_2\text{-Y})$ with an alkali metal sulphide. Ag compounds according to the invention may readily be obtained by reacting a soluble Ag

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salt with a dithiol (B). Pd and Pt compounds according to the invention may similarly be obtained from a Pd(II) or Pt(II) salt and the dithiol, in this case at a molar ratio of approximately 1:2.

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The mono-noble metal dithiolates according to the invention may conveniently be used in the form of preparations containing noble metal for decorating storable substrates, in particular glass, porcelain and ceramic. Such
10 preparations contain at least one mono-noble metal dithiolate according to the invention, one or more polymeric organic binders together with solvents, preferably an aqueous/organic or particularly preferably a purely aqueous solvent system in order to dissolve the
15 organic polymers and the mono-noble metal dithiolate or otherwise to ensure a homogeneous distribution. If necessary, the preparations containing noble metal additionally contain auxiliary substances in order to establish desired processing characteristics, such as a
20 screen-printable viscosity and an elevated drying speed of the preparation and certain optical properties (colour hues) and service properties, such as adhesion to the substrate.

25 Substantially purely aqueous noble metal preparations may be produced using selected mono-noble metal dithiolates according to the invention. Such preparations are characterised in that they contain water and less than 2 wt.%, relative to the preparation, of organic solvent as
30 the solvent, that the binder is water soluble, the mono-noble metal dithiolate has at least one functional group capable of salt formation and is present in the form of a water soluble salt and an effective quantity of a surfactant is additionally present. The preparations
35 particularly preferably contain a salt prepared from a

mono-noble metal dithiolate containing one or more carboxyl groups and a primary, secondary or tertiary amine or an N-heterocyclic base. The proportion of organic solvents is preferably less than 1 wt.%, in particular 0 wt.%, relative to the preparation. The stated residual content of organic solvents may arise, for example, from the use of auxiliary substances if these are commercially available in the form of organic solutions and are used in this form.

- 10 The mono-noble metal dithiolates which may be used in aqueous/organic and purely aqueous preparations according to the invention have structural elements, namely at least one acidic or basic group capable of salt formation, which imparts sufficient water solubility to them. The
- 15 preparations generally contain 2 to 25 wt.%, preferably 5 to 15 wt.% of noble metal in the form of one or more thiolates. Accordingly, at an elevated noble metal content, the water solubility of the thiolate must be higher than at a low content. Efforts are made to obtain an organic
- 20 decoration with the smallest possible quantity of gold.

- Aqueous preparations according to the invention contain such polymeric binders as are soluble in water or form a clear dispersion therein. Convenient binders are
- 25 polyacrylic acid, polymethacrylic acid, polyvinylpyrrolidone, cellulose ethers, in particular carboxyalkyl and hydroxyalkyl cellulose, polyalkylene glycol, polyvinyl acetate, polyvinyl alcohol, polyamines, alkyd resins and polyurethane resins. The binders may be used in the form of
- 30 homopolymers or copolymers or block polymers, in each case alone or as a mixture. Polyvinylpyrrolidone homo- or copolymers, polymethacrylic acid homo- or copolymers together with cellulose ether based resins are particularly preferred for purely aqueous preparations and those with an
- 35 elevated water content.

The proportion of polymeric binders in the organic/aqueous and substantially purely aqueous preparations is conventionally in the range between 3 and 45 wt.%, preferably between 3 and 20 wt.% and in particular 4 to 10 wt.%. The weight ratio of binder to noble metal in the preparations is conveniently in the range between 0.1 and 2, preferably between 0.3 and 1.2 and in particular between 0.5 and 1.0. The water content of aqueous/organic preparations is generally between 10 and 80 wt.%, preferably between 30 and 60 wt.%, and the content of organic solvents between 10 and 40 wt.%, in each case relative to the preparation. The water content of substantially purely aqueous preparations is generally between 10 and 90 wt.%, preferably from 40 to 80 wt.%, in each case relative to the preparation.

Preparations with an aqueous/organic solvent system contain one or more water soluble organic solvents, in particular water soluble alcohols, ethers and esters, as the solvent. Particularly preferably used solvents are glycols with 2 to 4 C atoms together with oligo- and poly-(C₂ to C₄)glycols or mono(C₁ to C₄)alkyl ethers of the stated glycols or oligoglycols, together with (C₂ to C₅) hydroxycarboxylic acids or lower alkyl esters thereof, such as in particular C₁ to C₃ alkyl lactate.

A constituent of the substantially purely aqueous preparations which is essential to the invention is an effective quantity of a surfactant compatible with the thiolate salt selected from the range of anionic, non-ionic, zwitterionic and cationic surfactants. The person skilled in the art will verify the compatibility and efficacy of a selected surfactant by means of investigatory tests, as interactions with the other constituents of the preparations may also occur. A good effect is

conventionally achieved with a quantity of surfactant of between 0.1 and 2 wt.%, relative to the preparation; larger or smaller quantities are, however, also possible in individual cases. The surfactant content is preferably
5 between 0.2 and 1 wt.%.

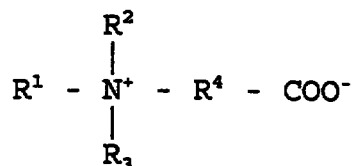
Each molecule of the surfactants contains a hydrophobic residue with 8 to 26 and in particular 10 to 18 C atoms or another hydrophobic group, such as, for example, a group
10 based on polydimethylsiloxane, and at least one anionic, zwitterionic, non-ionic or cationic water solubilising group.

Examples of suitable anionic surfactants which may be cited
15 are: linear or branched alkylbenzene sulphonates, in particular those with a linear C₈ to C₁₆ alkyl group, aliphatic and olefinic (C₈ to C₁₈) sulphonates, hydroxyalkane sulphonates, fatty acid esters of oxyethanesulphonic acid; fatty alcohol sulphates, sulphated
20 fatty acid alkylolamides and fatty acid monoglycerides together with sulphated alkoxylation products of fatty alcohols, alkylphenols, fatty acid amides; saturated and unsaturated fatty acid salts, alkyl and alkenyl ether carboxylic acid salts containing a (C₁₀ to C₂₀) alkyl or
25 alkenyl group and a polyethylene glycol group comprising 1 to 8 units; α -sulpho fatty acids; amide-type condensation products of fatty acids or sulphonic acids with aminocarboxylic acids, such as glycine, sarcosine, protein hydrolysates. Particularly suitable anionic surfactants are
30 alkylbenzene sulphonates with 8 to 14 C atoms, in particular in the form of a salt with an amine in a quantity of 0.1 to 2 wt.%, preferably 0.2 to 1 wt.%, relative to the preparation.

Non-ionic surfactants owe their water-solubility to the presence of polyether groups, as well as amine oxide, sulphoxide, phosphine oxide and alkylolamide groups. Alkoxylation products are of particular interest,
5 especially ethoxylation products of fatty alcohols, alkylphenols, fatty amines, alkanolamines, fatty acids, fatty acid amides and sulphonic acid amides.

Another group of non-ionic surfactants which are
10 particularly effective in the substantially purely aqueous preparations according to the invention are water soluble polyether-modified polysiloxanes - these are polyether-polysiloxane copolymers, wherein linear or branched block copolymer structures may be present. The quantity used of
15 this class is preferably between 0.1 and 2.0 wt.%, in particular between 0.2 and 1.0 wt.%, relative to the preparation. The polyether segments are polyoxyethylene, polyoxypropylene or poly(oxyethylene-oxypropylene) segments, wherein polyoxyethylene segments and in
20 particular those with 4 to 20 oxyethylene units are preferred. The polysiloxane segments are preferably based on dimethylsiloxane. The polyether and polysiloxane segments may be attached to each other by Si-O-C- or Si-C-bonds. Reference is, for example, made to *Ullmann's*
25 *Encyclopedia of Industrial Chemistry*, 5th edition, volume A 24, p. 83-84 (1993) and *Ind. Eng. Chem. Proc. Res., Dev.* 6 (1967), p. 88-92.

Zwitterionic surfactants contain both an acidic group, such
30 as a carboxyl, sulphonic acid, sulphuric acid semiester or phosphoric acid partial ester group, and a basic hydrophilic group, such as a primary, secondary, tertiary, quaternary ammonium group. Such surfactants include betaines, such as those of the type

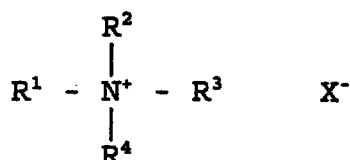


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where R^1 is alkyl, alkenyl, hydroxyalkyl with 8 to 24 C atoms, R^2 and R^3 are identical or different alkyl or hydroxyalkyl with 1 to 4 C atoms, R^4 is alkylene or hydroxyalkylene with 1 to 6 C atoms.

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The cationic surfactants are mainly substances of the formula



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where R^1 is alkyl or alkenyl with 8 to 24 C atoms, R^2 to R^4 are alkyl or hydroxyalkyl with 1 to 5 C atoms and X^- is a
20 halogen atom.

Gilding preparations, in particular bright gold preparations and burnished gold preparations, contain in order to influence colour a small quantity of one or more
25 different noble metal compounds substantially soluble in the system in the form of resinsates or sulphoresinsates or in the form of simple noble metal salts or complexes. The preparations additionally conventionally contain fluxes in the form of compounds, for example resinsates, salts, oxides
30 or coordination compounds, of one or more of the elements boron, silicon, vanadium, chromium, indium, tin, antimony, bismuth and rhodium. The quantity of flux used is conventionally within the range between 0.01 and 2 wt.%, relative to the preparation.

35

Further auxiliary substances in the preparations according to the invention may include conventional substances to modify the rheological properties of the preparation,

surface-active agents, adhesion-promoting auxiliaries together with drying accelerators if a UV-curable resin is used. It has in many cases proved convenient additionally to use an aqueous polysulphide solution, especially in
5 preparations containing polyvinylpyrrolidone. So-called burnished gold preparations generally also contain gold powder and/or finely divided insoluble gold compounds. Depending upon the desired effect, burnished gold preparations may additionally contain glass frits and/or
10 organosilicon compounds.

The aqueous preparations are produced by directly using a water soluble salt of a mono-noble metal dithiolate or the salt is formed *in situ* in water at room temperature or
15 elevated temperature, preferably at 30 to 80°C, from a mono-noble metal dithiolate containing at least one acidic functional group and a base, such as an alkali metal hydroxide solution, ammonia or an amine or from a mono-noble metal dithiolate containing an amino group and
20 an acid, such as a lower carboxylic acid.

The quantity of base used for each mol of thiolate is generally the quantity necessary to neutralise the acid groups; complete dissolution is sometimes achieved even
25 with a deficit of base. An excess of base is possible, but not generally necessary. The fluxes are added to the resultant solution and dissolved. The binder is then directly added to the solution and dissolved therein. Alternatively, the binder or binder mixture, optionally
30 with the addition of further auxiliary substances, such as for example a polysulphide solution, may be dissolved in water and this solution combined with the solution containing noble metal. The surfactant is added to one of the solutions during production of the preparation or to
35 the preparation itself on completion of production.

The preparations containing mono-noble metal dithiolates according to the invention may be applied directly onto the surface to be decorated using conventional decoration processes, such as spraying, brushing or known printing
5 processes, in particular screen printing and, once the solvent constituents have evaporated, the decoration is stoved at a temperature generally of between 400 and 900°C. Alternatively, the noble metal preparation according to the invention may be transferred onto the article to be
10 decorated using a transfer. The transfer is produced in a manner known to the person skilled in the art, wherein the monogold(I) dithiolate according to the invention is located in the decorative layer of the transfer: a decorative layer is applied onto a water-soluble release
15 layer or a thermal release layer applied to a support using a preparation containing noble metal as described above, the solvent constituents being allowed to evaporate and the binder optionally being crosslinked; the decorative layer is conventionally provided with a film coating.

20 The invention makes a novel class of substances available, which are outstandingly well suited to the production of film-type decoration containing noble metal. The decoration is of surprisingly elevated brightness and adheres
25 excellently to the substrate surface since a continuous film is formed. The mono-noble metal dithiolates according to the invention provide the expert with a novel class of substances, which may be used not only in conventional noble metal preparations substantially containing only
30 organic solvents as their solvent component, but also in noble metal preparations which contain an aqueous/organic solvent system or substantially only water as the solvent. The production of novel noble metal compounds and their outstanding suitability in water-containing and purely
35 aqueous preparations for decorating storable substrates are

described in the examples. The comparative examples show that when structurally similar compounds which do not contain a second mercapto group are used, it is not possible to produce noble metal decoration, or only a less
5 satisfactory decoration.

The decoration is of surprisingly elevated brightness and adheres excellently to the substrate surface since a continuous film is formed. It is additionally possible to
10 produce spot- and pore-free films which fulfil aesthetic requirements.

With regard to the prior art, it was not predictable that it would be possible to provide noble metal preparations
15 for the production of noble metal decoration, in particular bright gold decoration, in which it is possible to dispense with the use of organic solvents. It is possible, as is shown by the following examples, by means of the combination according to the invention of specific
20 thiolates, water-soluble polymers and a surfactant, to obtain purely aqueous preparations and to use them to produce high-quality decoration on storable substrates.

Example 1

Production of monogold dimercaptosuccinic acid

- 5 a) 0.035 mol = 18.49 g of HAuCl_4 (37.29% Au) is added dropwise with stirring to a suspension of 0.07 mol of methionine in 70 ml of H_2O . The temperature is maintained at 0 to 5°C by external cooling. On completion of the reaction, the gold(I) complex is added dropwise within one hour to a suspension of
- 10 0.035 mol = 6.38 g of meso-2,3-dimercapto-succinic acid in 150 ml of dichloromethane. The precipitate is suction filtered, washed several times with water and vacuum dried in a desiccator over blue gel. The yield of monogold dimercaptosuccinic acid is 96.5% relative
- 15 to the gold used.

Analysis:	Au	C	H	S
calculated:	52.09%	12.70%	1.33%	16.96%
found:	50.81%	12.05%	1.52%	15.62%

Beginning of decomposition: 195°C

- 20 ^{13}C -NMR in D_2O + trimethylamine δ/ppm 52.58 (CH), 60.95 (CH), 180.64 (CO_2^-) and 182.51 (CO_2^-)

- 25 b) Example 1a was repeated, but using water instead of dichloromethane. In this case too, monogold(I) dimercaptosuccinic acid was obtained in elevated yield and purity.

Comparative example 1

- 30 In a similar manner to comparative example 7 in EP-A 0 514 073, the following constituents are mixed:

		Parts by weight
5	Polymethacrylate resin (Versicol K11 from Allied Colloids)	11
	Gold mercaptosuccinic acid	18
	1,3-propanediol	15
	Water	40
	Isopropanol	15
10	Rhodium complex	0.04
	Chromium trioxide	0.05

The preparation is applied by brush onto porcelain and heated for 10 minutes at 820°C, wherein the heating-up time is 1 hour. A matt film is obtained. Gloss measurements produced the following results:

15	Angle	Gloss units	Standard deviation
	20°	58.3	5.4
	60°	54.2	4.1

Gloss measurements were performed with a ByK Gardner "haze-gloss" reflectometer. The preparation was applied with a brush onto a 4 cm x 4 cm porcelain plate and measured at various points. The values stated are the mean of the individual measurements and the associated standard deviation as indicated by the measuring instrument, and the angle at which the measurements were performed.

25

Comparative example 2

The following composition was prepared in a similar manner to comparative example 1:

		Parts by weight
	Polyvinylpyrrolidone (PVP K25 from Fluka)	8.1
	Gold mercaptosuccinic acid	17.2
5	1,2-propanediol	8.1
	Water	39.9
	Ethyl lactate	16.2
	Rhodium complex	0.15
	Chromium sulphate	0.04
10	Ammonium bismuth citrate	0.44
	Triethylamine	5.3
	Ammonium polysulphide solution (15% in water)	1.9
	Silver mercaptopropionyl glycine	2.6

15

The preparation is applied by brush onto porcelain and heated for 10 minutes at 820°C, wherein the heating-up time is 1 hour. A matt film is obtained. Gloss measurements produced the following results:

20	Angle	Gloss units	Standard deviation
	20°	20.1	4.6
	60°	38.2	2.1

Example 2

25

In contrast to comparative example 2, the gold compound of example 1 according to the invention was used in the following composition:

Parts by weight		
	PVP K25	8.1
	Monogold dimercaptosuccinic acid	18.8
	1,2-propanediol	8.1
5	Water	38.3
	Ethyl lactate	16.2
	Rhodium complex	0.15
	Chromium sulphate	0.04
	Ammonium bismuth citrate	0.44
10	Triethylamine	5.3
	Ammonium polysulphide solution (15%)	1.9
	Silver mercaptopropionyl glycine	2.6
15	The preparation is applied by brush onto porcelain and heated for 10 minutes at 820°C, wherein the heating-up time is 1 hour. A glossy, firmly adhering film is obtained. Gloss measurements produced the following results:	
	Angle	Gloss units Standard deviation
20	20°	741 42.4
	60°	503 6.4

Example 3

25 The following constituents were mixed:

		Parts by weight
	PVP K25	8.6
	Monogold dimercaptosuccinic acid	19.5
	1,2-propanediol	8.6
5	Water	34.3
	Ethyl lactate	17.3
	Rhodium complex	0.16
	Chromium sulphate	0.07
	Ammonium bismuth citrate	0.53
10	Triethylamine	5.7
	Ammonium polysulphide solution (15%)	2.6
	Monosilver dimercaptosuccinic acid	2.6

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The preparation is applied by brush onto porcelain and heated for 2 minutes at 880°C, wherein the heating-up time is 30 minutes. A glossy, firmly adhering film is obtained.

20 **Example 4 to 8**

In a similar manner to the method stated in example 1, further monogold dimercapto compounds were produced by reacting the gold(I) methionine complex with further
25 dimercapto compounds in a 1:1 molar ratio:

Example 4: Reaction with 1,4-dimercapto-2,3-butanediol:
the Au content of the isolated product was
67.01% (theoretical 56.24).

30

Example 5: Reaction with 2,3-dimercapto-1-propane-sulphonic acid sodium salt: Au content 57.45% (theoretical 46.43%). The resultant product, substantially consisting of the monogold compound and, evidently, also of the digold compound of the stated sulphonic acid, dissolved smoothly in water. The product is suitable for the production of noble metal decoration, especially such decoration which has a silk-like sheen after burnishing.

Example 6: Reaction with 6,8-dimercaptooctanoic acid: Au content 57.47% (theoretical 48.72%). The compound is suitable as a gold preparation in organic decorative preparations but not in aqueous preparations due to its low water solubility.

Example 7: Reaction with N-(3'-mercapto-2'-methyl-propionyl)-2-amino-4-mercaptobutanoic acid: Au content 51.22% (theoretical 45.46%). The resultant monogold dimercapto compound is suitable as an Au compound in organic and aqueous decorative preparations which stove attractively and produce a glossy and light coloured decoration.

Example 8: Reaction with α,α' -dimercaptoadipic acid: Au content 49.07% (theoretical 48.48%). In decorative preparations, the Au compound is initially somewhat dull after stoving, but produces a very attractive light gloss after gentle burnishing. The Au compound is thus particularly suitable in burnished gold

preparations with a low percentage content of Au. The low Au content is an advantage in comparison with conventional burnished gold preparations.

5

Example 9

Bright gold preparation

10 An aqueous solution containing monogold(I) dimercapto-
succinic acid was prepared in accordance with a general
work instruction. Triethylamine was used as the base.
Rhodium chloride, chromium sulphate and ammonium bismuth
citrate were then added as fluxes. An aqueous polyvinyl-
pyrrolidone solution, which additionally contained ammonium
15 polysulphide, was added to the resultant solution, together
with a polyether-modified polydimethylsiloxane (ByK®346) as
the surfactant. The preparation contained only
approximately 0.5 wt.% of an organic solvent contained in
the conventional commercial surfactant solution and was
20 otherwise purely aqueous.

The noble metal and flux contents, calculated as stated,
and the content of binder, surfactant and auxiliary
substances in the preparation may be found in the table.

Constituents	wt.% in preparation
Au content	9.35
Rh content	0.06
Cr ₂ O ₃ content	0.13
5 Bi ₂ O ₃	0.21
Polyvinylpyrrolidone (PVP K25 from Fluka)	5.2
Surfactant solution (ByK®346; surfactant content 46%)	1.0
10 N(C ₂ H ₅) ₃ (for salt formation)	4.8
(NH ₄) ₂ Sx	0.15

Examples 10 and 11

15

Substantially purely aqueous bright gold preparations were produced in a similar manner to example 9, wherein the product from example 1 was used as the Au thiolate and silver 2-mercaptopropionyl glycine was additionally used as
20 the silver thiolate. The binder used was a hydroxyethyl cellulose (Natrassol from Aqualon Ltd., UK); a polysulphide was not used. ByK®346 was again used as the surfactant in the preparation according to the invention of example 10; the preparation of example 11, which was not according to
25 the invention, contained no surfactant. The contents of the constituents may be found in the table.

	Example 10	Example 11
	(wt.% in preparation)	
Au content	9.62	9.71
Ag content	1.08	1.10
5 Rh content	0.07	0.07
Cr ₂ O ₃ content	0.01	0.01
Bi ₂ O ₃ content	0.30	0.30
Hydroxyethyl cellulose	5.3	5.3
Surfactant solution (ByK®346;	1.0	-
10 surfactant content 46%)		
N(C ₂ H ₅) ₃ (for salt formation)	5.3	5.3

Example 12

15 Decoration of porcelain

Application of preparations of examples 9, 10 and 11 by screen printing (example 12/9, 12/10, 12/11).

20 Stoving conditions: heating to 820°C in 1 h, holding time at 820°C 10 minutes.

Glossy and spot-free decorative films with good adhesion were obtained using the preparations according to the invention of examples 9 and 10. Only spotty decoration was
25 obtained using the surfactant-free preparation of example 11, which was not according to the invention.



Patent Claims

1. Mono-noble metal dithiolate of the general formula (A)



in which

Em: means a noble metal from the series Au(I) or Ag(I) or an equivalent of Pd(II) or Pt(II) or Rh(III)

Q: means a tetravalent organic residue with 2 to 10 C atoms

Y: means a hydrophilic group from the series -COOH, -COO⁻cat⁺, wherein cat⁺ denotes Li⁺, Na⁺, K⁺, NH₄⁺, (C₁ to C₃ alkyl)_nN⁺H_{4-n} or (hydroxy(C₁ to C₃ alkyl)_nN⁺H_{4-n} and n denotes an integer between 1 and 4, or -COO-(CH-CH-O)_mR³

$$\begin{array}{cc} | & | \\ \text{R}^1 & \text{R}^2 \end{array}$$

where R¹, R² and R³ are identical or different and mean H or methyl and m equals an integer from 1 to 12,

Z: equals Y or H or a group from the series -OR', -SR', -SO₃R', -NR'₂, -NR'₃X⁻, wherein X⁻ denotes a mineral acid or carboxylic acid anion and R' denotes hydrogen or the group -(CH₂-CH-O)_mH

$$\begin{array}{c} | \\ \text{R}^1 \end{array}$$

and R¹ and m have the above-stated meaning.

2. Mono-noble metal dithiolate according to claim 1, characterised in that Em denotes gold or silver, in each case in oxidation state (I).

3. Mono-noble metal dithiolate according to claim 1 or 2, characterised in that it is water soluble and Y and/or



Z mean(s) COO^-cat^+ or Y is a carboxyl group and Z an amino group of the formula $-\text{NR}'_2$ capable of internal salt formation with the carboxyl group, wherein cat^+ and R' have the above-stated meaning.

- 5
4. Mono-noble metal dithiolate according to one of claims 1 to 3, characterised in that the organic residue Q is an aliphatic C_2 to C_4 alkanetetrayl residue or a 5- or 6-membered cycloaliphatic tetrayl residue, optionally containing an oxygen or imine ring member.
- 10
5. Mono-noble metal dithiolate according to one of claims 1 to 4, characterised in that it is monogold(I) or monosilver dimercaptosuccinic acid or a salt thereof with the cation cat^+ having the above-stated meaning.
- 15
6. Process for the production of mono-noble metal dithiolates of the general formula (A')



25

in which Q, Y and Z have the meaning according to claim 1 by reacting an Au(I) complex of the formula $\text{AuCl} \cdot \text{R}''\text{SR}'''$, wherein $\text{R}''\text{SR}'''$ is a thioether, preferably methionine, with a substantially equivalent molar quantity of a thiol in the presence of a solvent, characterised in that the thiol used is of

30

the general formula (B)



wherein Q, Y and Z have the same meaning as in the formula (A').



7. Process for the production of mono-noble metal dithiolates of the formula A according to claim 1, wherein Em denotes Ag(I) or an equivalent of Pd(II) or Pt(II), by reacting a soluble salt of Ag(I), Pd(II) or Pt(II) with a thiol compound, characterised in that the thiol compound used is a dithiol compound of the formula B according to claim 6.
8. Preparation containing noble metal for decorating storable substrates, in particular glass, porcelain and ceramic, for the production of a noble metal decoration, in particular a high gloss noble metal decoration, containing one or more noble metal thiolates, one or more polymeric organic binders, together with solvents for the noble metal thiolate(s) and the binder(s) and, if necessary, auxiliary substances to establish the processing characteristics of the preparation and the optical and service properties of the decoration containing noble metal to be produced therewith, characterised in that the preparation contains at least one mono-noble metal dithiolate of claims 1 to 5 as the noble metal thiolate.
9. Preparation according to claim 8, characterised in that it contains a polar organic solvent, in particular from the series of C₂ to C₄ glycols, oligo-(C₂ to C₄)glycols, C₁ to C₄ monoethers of the stated glycols and oligoglycols, (C₂ to C₃) hydroxycarboxylic acids and (C₁ to C₃)alkyl esters thereof, and water as solvent.
10. Preparation containing noble metal according to claim 8, characterised in that it contains water and less than 2 wt.%, relative to the preparation, of organic



5 solvents as the solvent, the binder is water soluble,
the mono-noble metal dithiolate has at least one
functional group capable of salt formation and is
present in the form of a water soluble salt and an
effective quantity of a surfactant is additionally
present.

10 11. Preparation according to one of claims 8 to 10,
characterised in that the polymeric organic binder is
selected from the series of polyvinylpyrrolidone homo-
or copolymers, polyacrylic acid homo- or copolymers,
polymethacrylic acid homo- or copolymers and water
soluble cellulose ethers, together with mixtures of
the stated binders.

15 12. Preparation according to claim 10 or 11, characterised
in that it contains a water soluble salt prepared from
a mono-noble metal dithiolate containing one or more
carboxyl groups and a primary, secondary or tertiary
20 amine or an N-heterocyclic base.

25 13. Preparation according to one of claims 10 to 12,
characterised in that the mono-noble metal dithiolate
is present in the form of a salt with tri-(C₁ to
C₃)alkylamine or mono-, di- or triethanolamine and the
preparation additionally contains conventional
auxiliary substances to establish optical and service
properties of the decoration to be produced and/or the
processing characteristics of the preparation.

30 14. Preparation according to one of claims 8 to 13,
characterised in that it contains a water soluble salt
of monogold(I) dimercaptosuccinic acid.



15. Preparation according to one of claims 10 to 14,
characterised in that it contains 0.1 to 2.0 wt.%,
preferably 0.2 to 1.0 wt.%, of a polyoxyethylene-
polydimethylsiloxane as surfactant.
- 5
16. Preparation according to one of claims 10 to 15,
characterised in that it contains a quantity of 0.1 to
2 wt.%, preferably of 0.2 to 1 wt.%, of an
alkylbenzene sulphonate with 8 to 14 C atoms in the
10 alkyl group in the form of a salt with an amine as
surfactant.
17. Transfer for the production of decoration containing
noble metal on storable substrates, in particular
15 glass, porcelain or ceramic, containing in a
decorative layer one or more noble metal thiolates,
one or more polymeric organic binders and, if
necessary, auxiliary substances from the production of
the transfer and to influence optical and service
20 properties of the decoration containing noble metal to
be produced, characterised in that a mono-noble metal
dithiolate according to one of claims 1 to 5 is
present in a homogeneous distribution as the noble
metal thiolate.
- 25
18. Process for decorating storable substrates, in
particular glass, porcelain or ceramic by applying a
preparation containing noble metal or a transfer
containing such a preparation in the dry state onto
30 the substrate and stoving at 400 to 900°C,
characterised in that a preparation containing noble
metal according to one of claims 8 to 16 or a transfer
according to claim 17 is applied.