(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 December 2017 (28.12.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/220790 A1

(51) International Patent Classification:
C23F 11/12 (2006.01) *C23F 11/16* (2006.01)
C23F 11/14 (2006.01) *C11D 3/20* (2006.01)

(21) International Application Number:
PCT/EP2017/065564

(22) International Filing Date:
23 June 2017 (23.06.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
16175905.5 23 June 2016 (23.06.2016) EP

(71) Applicant: **ATOTECH DEUTSCHLAND GMBH** [DE/DE]; Erasmusstraße 20, 10553 Berlin (DE).

(72) Inventors: **ARAI, Chiho**; c/o Atotech Deutschland GmbH, Patent Management, Erasmusstraße 20, 10553 Berlin (DE). **LAGORCE-BROC, Florence**; c/o Atotech Deutschland GmbH, Patent Management, Erasmusstraße 20, 10553 Berlin (DE). **RÜTHER, Dr. Robert**; c/o Atotech Deutschland GmbH, Patent Management, Erasmusstraße 20, 10553 Berlin (DE). **KURTZ, Olaf**; c/o Atotech Deutschland GmbH, Patent Management, Erasmusstraße 20, 10553 Berlin (DE).

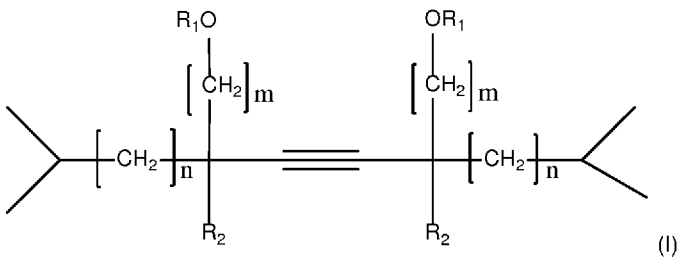
(74) Agent: **SCHULZ, Hendrik**; c/o Atotech Deutschland GmbH, Patent Management, Erasmusstraße 20, 10553 Berlin (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) Title: A WATER-BASED COMPOSITION FOR POST-TREATMENT OF METAL SURFACES



(57) Abstract: A water-based composition for post-treatment of metal surfaces, preferably a silver or silver alloy surface, comprising an alkanethiol an anionic, cationic, non-ionic, amphoteric or zwitterionic surfactant with a HLB value of 12 to 18, a compound of the general formula (I) wherein R_1 is -H, $-CH_3$, $-C_2H_5$, $-(C_2H_4O)_p-H$, $-(C_2H_4O)_p-CH_3$, $-(C_2H_4O)_p-CH(CH_3)_2$, $-(C_2H_4O)_p-C(CH_3)_3$, wherein p is 1 to 20, R_2 is H, or CH_3 n is an integer in the range of 0 to 3, m is an integer in the range of 0 to 2.

WO 2017/220790 A1

A water-based composition for post-treatment of metal surfaces

Description of the Invention

Field of the Invention

The present invention relates to a water-based composition for post-treatment of metal surfaces, the use thereof and to a method for post-treatment of metal surfaces.

Background of the Invention

Silver and silver alloys are used in electronic devices but it is inevitable that finished articles will require further cleaning and polishing to temporarily remove undesired tarnish products. It is well-known that with exposure to everyday atmospheric conditions, silver and silver alloys develop a lustre-destroying dark film known as tarnish. Prevention of tarnishing of metals and metal alloys is a challenging problem in numerous industries. The tarnishing of metal and metal alloys has been especially problematic in the electronic materials industry where tarnishing may lead to faulty electrical contact between components in electronic devices.

US20070277906A1 discloses for use in treating a metal, e.g. silver or an alloy of silver, a water-based composition comprising a treatment agent selected from an alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide and at least one of an amphoteric, nonionic or cationic surfactant in a concentration that is effective to solubilise the treatment agent. Preferably the composition comprises at least a non-ionic relatively hydrophobic surfactant e.g. cocamide DEA. The composition is particularly suitable for the treatment of Ag-Cu-Ge alloys.

Objectives of the Invention

The objective of the present invention was to provide a composition for effective post-treatment of metal surfaces, particularly silver or silver alloys, in order to prevent tarnishing of such surfaces.

Summary and Detailed Description of the Invention

The invention provides with a water-based composition for post-treatment of metal surfaces, preferably a silver or silver alloy surface, the use thereof and a method. Preferred embodiments are described within the dependent claims.

The metal surfaces are especially surfaces in the field of technical and decorative surfaces either on metal substrates or plastic materials, e.g. on connectors or IC / leadframe applications as well as surfaces on automotive, aerospace, construction, communication, furniture, sanitary and consumer goods.

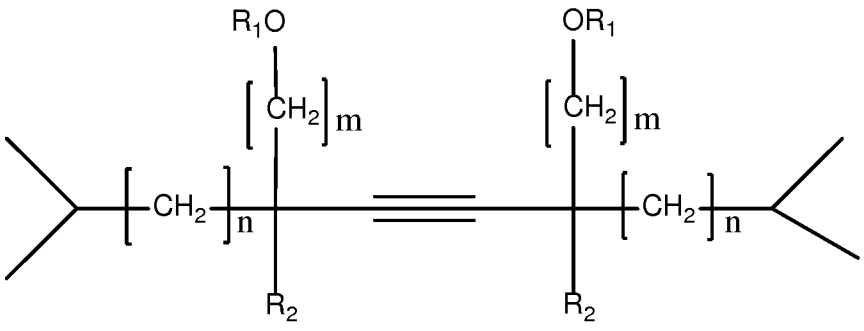
The invention in particularly provides with a water-based composition for post-treatment of metal surfaces, preferably a silver or silver alloy surface comprising:

an alkanethiol,

an anionic, cationic, non-ionic, amphoteric or zwitterionic surfactant with a HLB value of 12 to 18, preferably 15,

wherein the water-based composition further contains

a compound of the general formula I:



(I)

wherein

R_1 is -H, $-CH_3$, $-C_2H_5$, $-(C_2H_4O)_p-H$, $-(C_2H_4O)_p-CH_3$, $-(C_2H_4O)_p-CH(CH_3)_2$, $-(C_2H_4O)_p-C(CH_3)_3$, wherein p is an integer in the range of 1 to 20, preferably 1 to 10, more preferably 2 to 6,

R_2 is H or CH_3, preferably CH_3,

n is an integer in the range of 0 to 3, preferably 1 to 3, even more preferably 1 or 2,

m is an integer in the range of 0, 1 or 2, preferably 0.

HLB values were determined according to the method of W.C. Griffin.

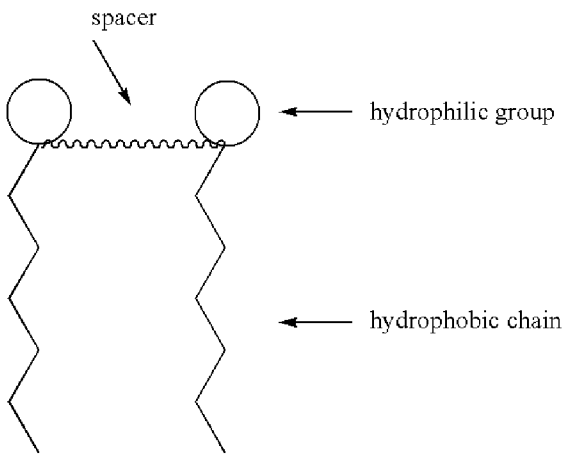
With the present invention, in general or one of the following further embodiments, one or more of the following benefits are obtained:

- enhancing of anti-tarnish properties (particularly proven by K_2S test)
- transparent protective coating provides a highly hydrophobic surface property
- repelling oxidation agents
- transparent composition, prevention of negative effects on appearance of a surface treated with the composition
- enhanced formation of a self-assembled thiol monolayer onto immersed silver surfaces, thereby providing with a non-polar film
- improved rinsing capability of hydrophobic alkanethiol rests after silver surfaces treatment, effective elimination of oily residues

The composition can be an emulsion.

The alkanethiol forms a self-assembled thiol monolayer onto immersed silver surfaces which prevents or retards tarnishing.

The compound of formula I is also called a „gemini surfactant“ which has the more general, following structure:



Gemini surfactants are composed of two polar heads (hydrophilic groups) flanked by a spacer to which hydrophobic tails are linked; the spacer can be rigid or flexible, polar or apolar. The invention also discloses using such general surfactants in a composition for post-treatment of metal surfaces. It has been shown that by addition of a surfactant with above structure, particularly by addition of a component of formula I, improved anti tarnishing properties of the composition can be reached.

In a preferred embodiment of the compound of formula I is m = 0, n in the range of 0 to 3, preferably n in the range of 1 to 3, more preferably n is 1 or 2, and R_1 is independently selected from the group consisting of R_1 is -H, $-CH_3$, $-C_2H_5$ and $-(C_2H_4O)_p$-H with p in the range 2 to 6.

More preferred the compound of formula I is selected from the group consisting of 2,3,6,7-tetramethyl-4-octyne-3,6-diol, 2,5,8,11-tetramethyl-6-dodecyn-5,8-diol ethoxylate, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 2,2'-[(2,4,7,9-tetramethyl-5-decyne-4,7-diyl) bis(oxy)] diethanol, and 2,4,7,9-tetramethyl-5-decyne-4,7-diolbispolyoxyethylene-ether.

The anionic, cationic, non-ionic, amphoteric or zwitterionic surfactant may have a hydrophobic tail that may linear or branched.

The anionic, cationic, non-ionic, amphoteric or zwitterionic surfactant may be an ethoxylated or propoxylated alkyl, ethoxylated or propoxylated amine, ethoxylated or propoxylated amide, ethoxylated or propoxylated alcohol, or a mixture thereof. A beneficial surfactant is 3-ethoxy-2-methylnonane.

The surfactant may have the general formula II:

$R_3O(CH_2CH_2O)_xH$ formula II

wherein
R_3 is a linear or branched alkyl group, having 6 – 15 carbon atoms, preferably 8-12 carbon atoms,
x is an integer in the range of 3 – 15, preferably 7 – 11.

Preferably the surfactant is a polyethylene glycol, more preferably PEG-11 C10-11 Oxo alcohol ethoxylate (CAS Nr: 78330-20-8).

The water-based composition may comprise a co-emulgator, which can also be called a "second surfactant".

The co-emulgator may have the general formula III

$R_4O(CH_2CH_2O)_yH$ formula III

wherein
R_4 is a linear or branched alkyl group, having 16 – 20 carbon atoms, preferably 16-18 carbon atoms,
y is an integer in the range of 2 – 10, preferably 3 – 6.

The co-emulgator is preferably polyalkylene glycol ether. Preferably the co-emulgator is an Alcohol C16-18 ethoxylated propoxylated, (CAS Nr. 68002-96-0).

The alkanethiol is preferably a branched or unbranched C_{10}- to C_{20}-alkanethiol, more preferred unbranched C_{10}- to C_{20}-alkanethiol, e.g. decanthiol, undecanthiol, dodecanthiol, hexadecanthiol, heptadecanthiol, octadecanthiol, nonadecanthiol, eicosanthiol, most preferably heptadecanthiol, octadecanthiol, nonadecanthiol, eicosanthiol. In one preferred embodiment alkanethiol is octadecanthiol.

In a preferred embodiment, the water-based composition is free of chromate and/or free of organic solvent.

The water-based composition may have a pH in the range of 1 to 6, preferably 2 to 4. The pH may be adjusted by a buffer system. Suitable buffer systems are citric acid / citrate, acetic acid / acetate, tartaric acid / tartrate, phosphoric acid / phosphate or any suitable acid and salts combinations.

The water-based composition may comprise the mentioned constituents in following amounts:

alkanethiol:	0.1 - 5 g/L, preferably 0.5 – 4 g/L
surfactant:	2 - 30 g/L, preferably 5 – 20 g/L
compound of formula I:	1 - 10 g/L, preferably 1 – 5 g/L; and
optionally Co-emulgator:	0.1 – 5 g/L, preferably 0.5 – 2 g/L

In another aspect, the invention is directed to the use of the water-based composition above for post-treatment of metal surface, particularly a silver or silver alloy surface, to avoid tarnishing after metal deposition, particularly after silver or silver alloy deposition.

In still another aspect, the invention is directed to a method for post-treatment of a metal surface, particularly a silver or silver alloy surface comprising, in this order, the steps:

a. providing a metal surface, particularly a silver or silver alloy surface,
b. contacting the metal surface, particularly the silver or silver alloy surface, with the water-based composition as described before. Any of the water-based compositions that were described before can be employed.

Contacting can be done by any suitable method. The contacting in step b. may particularly be done by immersing into the water-based composition and/or by spraying with the water-based-composition onto the surface.

Contacting in step b. may be done additionally under electroless conditions, i.e. without supplying a current between the metal surface and an electrode.

In another embodiment, contacting in step b. takes place under applying an electrical current between the metal surface, particularly the silver or silver alloy surface, and at least one electrode when the metal surface is immersed into the water-based composition. The metal

surface can act as cathode and the other electrode (which is the counter electrode) can act as anode, or vice versa. Preferably the metal surface is cathodic.

The present invention works preferably with a composition temperature in a range of room temperature (22±2°C) or higher, more preferably 30 °C or higher, most preferably in a range of 35 – 65 °C.

EXAMPLES

Hereinafter, the invention is illustrated by working examples.

Inventive Example 1:

Water-based compositions were provided, wherein the concentrations of c.) compound of the general formula I (compound c1)), vary while the concentrations of other components are fixed, respectively.

The water-based composition was made by dissolving the following components in water:

a. alkanethiol: octadecanthiol. (CAS Nr. 2885-00-9)
   amount: 2,5 g/L
b. surfactant: *PEG-11 C10-11 Oxo alcohol ethoxylates* (CAS Nr: 78330-20-8)
   amount: 17,5 g/l
c. compound of the general formula I: c1) *2,5,8,11-Tetramethyl-6-dodecyn-5,8-diol ethoxylate*, (CAS Nr. 169117-72-0) in an amount: 2, 3 or 4 g/l
d. co-emulgator: Alcohol C16-18 polyalkylene glycol ether, (CAS Nr. 68002-96-0)
   amount: 2,5 g/L.

Inventive Example 2:

Water-based composition was provided wherein the following compound c2) 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate (CAS Nr. 9014-85-1) and c3) 2,4,7,9-tetramethyl-5-decyne-4,7-diol (CAS Nr. 126-86-3) of c.) compound of the general formula I were separately used at same concentrations:

The water-based composition was made by dissolving the following components in water:

a. alkanethiol: octadecanthiol. (CAS Nr. 2885-00-9)
   amount: 2,5 g/L
b. surfactant: *PEG-11 C10-11 Oxo alcohol ethoxylates* (CAS Nr: 78330-20-8)
   amount: 17,5 g/l

c. compound of the general formula I (c2 or c3): amount: 2 g/l
d. co-emulgator: Alcohol C16-18 polyalkylene glycol ether, (CAS Nr. 68002-96-0) amount: 2,5 g/L.

Comparative Example:

Comparative water-based compositions were provided, comprising a., b. and d. wherein the concentrations of compound of the general formula I (c1-c3) was zero and the other concentrations were as stated above.

1. Methods

The post-treatment was performed on silver plated copper panels. These panels, having a copper surface, may be provided from the following steps:

- Providing copper panels
    1. Degrease Uniclean™ 260 (electrophoretic alkaline cleaner) cathodic 7V / 45°C / 30 sec
    2. Activate: Uniclean™ 675 (mild acidic activator)immersion / RT / 30 sec
    3. Pre-silver Pre-silver (low silver concentrated solution) cathodic 3V / RT / 15 sec
    4. Silver Silverlume Plus (bright silver deposition solution) cathodic 1 ASD / RT / 5 min
       or AgO-56 (technical silver deposition solution) cathodic 1 ASD / RT / 5 min
       or Argalux™ NC mod. (cyanid-free bright silver deposition solution) cathodic 0.8 ASD / RT / 5 min

wherein RT is room temperature between 22±2°C; DI water is deionized water; ASD is Ampere per square decimeter A/dm² and V is volt/voltage.

In the sense of this invention the post-treatment composition may work also with otherwise obtained silver plated surfaces in the field of use of technical or decorative (with or without cyanide) silver deposition solutions for silver plating to avoid tarnishing after this silver plating.

The inventive water-based compositions according to the invention for post-treatment and the comparative water-based compositions were used under various conditions (see tests below).

After post-treatment in the water-based composition all samples were rinsed with:
- Hot DI water rinse,
- Cold DI water rinse and
- dried with compressed air.

- Optical evaluation after post-treatment with the inventive and comparative composition and subsequent sulphide test due to:

  - Residues immediately after post-treatment and rinse
  - Colorations and tarnishing after sulphide test

  The observations have been carried out without any instruments by skilled person.

- Sulphide test
  - Material: Glass beaker
  - Chemicals: Potassium Sulphide 44% K_2S, 2% w/w in water
  - Temperature: 22 ± 2°C
  - Dipping time: 5 – 10 min
  - Evaluation by the skilled person
  - according to colour intensity

2. Results

2.1 Rinsing capability test

The inventive water-based compositions showed improved rinsing capability in comparison with the comparative water-based compositions and eliminate oily residues issues completely. The treatment of Silverlume Plus, AgO-56 and Argalux™ NC mod. plated silver surfaces with the comparative water-based compositions the surfaces showed poor rinsing capability, whereas the inventive water-based compositions show very good rinsing capability.

2.2 Anti tarnishing tests

The inventive water-based compositions showed improved anti-tarnish protection in comparison with the comparative water-based compositions without the compound of the general formula I (c1-c3). The not-treated silver surfaces obtained from silver plating solutions as Silverlume Plus, AgO-56 and Argalux™ NC mod. exhibit very poor anti-tarnish protection. These plated silver surfaces treated with the comparative water-based compositions showed less discoloration after sulphide test, whereas the surfaces treated with the inventive water-based compositions show few to no discoloration.

Test material: bright silver plated surface (Silverlume Plus)
Water-based composition conditions: pH 2.5 – Temperature 55°C – agitation 200 RPM – immersion process for 1 min, rinse & dry.

Test material: bright decorative silver layer (Silverlume Plus)				
Compound of formula I	0 g/L (comparative example)	2 g/L (c1-c3)	3 g/L (c1)	4 g/L (c1)
Residues	Very poor (many residues)	Excellent (none)	Excellent (none)	Excellent (none)
Anti-tarnish (after 5 min into K_2S 2%)	Very poor (dark discoloration)	Improved (yellow discoloration)	Strongly improved (Yellow to no discoloration)	Excellent (no discoloration)

Test material: bright silver plated surface (Argalux NC ™ mod), cyanide free
Water-based composition conditions: pH 2.5 – Temperature 55°C – Agitation 200 RPM – 1 min immersion process, rinse & dry.

Test material: bright silver cyanide free (Argalux NC ™ mod.)			
Compound (c1) of formula I	0 g/L (comparative example)	3 g/L	4 g/L
Residues	Poor (many)	Excellent (none)	Excellent (none)
Anti-tarnish (after 5 min into K_2S 2%)	Very poor (dark colored)	Strongly improved (yellow colored)	Excellent (no discoloration)

Test material: technical silver plated surface (AgO-56 ™)

Water-based composition conditions: pH 2.5 – Temperature 55°C – agitation 200 RPM – immersion process for 1 min, rinse & dry.

Test material: technical silver (AgO-56 ™)			
Compound (c1) of formula I	0 g/L (comparative example)	3 g/L	4 g/L
Residues	Poor (many)	Excellent (none)	Excellent (none)
Anti-tarnish (after 5 min into K_2S 2%)	Very poor (dark colored)	Strongly improved (yellow to no discoloration)	Excellent (no discoloration)

2.3 Cathodic use

Test material: technical silver plated surface (AgO-56 ™)

Water-based composition conditions: pH 2.5 – Temperature 55°C – Agitation 200 RPM – immersion for 1 min or cathodic 0.5 A/dm² for 1 min, rinse & dry

Test material: *technical silver (AgO-56 ™)*				
Compound (c1) of formula I	*0 g/L* (comparative example)		*3 g/L*	
Process	*Immersion*	*Cathodic*	*Immersion*	*Cathodic*
Residues	*Poor (many)*	*Poor (many)*	*Excellent (none)*	*Excellent (none)*
Anti-tarnish (dipping time into K_2S 2%)	*5 min*	*10 min*	*5 min*	*10 min*
	Very poor (dark colored)	*Strongly improved*	*Good (yellow to no discoloration)*	*Excellent (no discoloration)*

3. Conclusions

- The inventive water-based compositions do improve:
  - The wettability of immersed metal surfaces, especially silver.
  - The formation of a self-assembled thiol monolayer onto immersed silver surfaces, making a non-polar film and enhancing anti-tarnish properties.
  - The rinsing of hydrophobic alkanethiol rests after silver surfaces treatment with water based solution of the invention.
- Immersion and electrophoretic uses are suitable in avoiding tarnishing of the metal plated surfaces after metal plating.

Claims

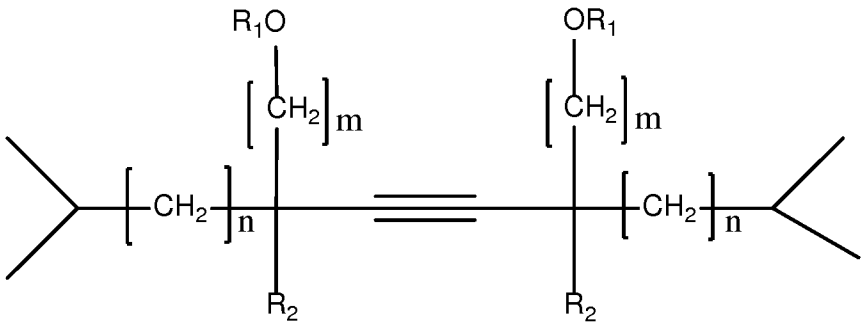
1. A water-based composition for post-treatment of metal surfaces, preferably a silver or silver alloy surface, comprising

   an alkanethiol,

   an anionic, cationic, non-ionic, amphoteric or zwitterionic surfactant with a HLB value of 12 to 18,

   characterized in that the water-based composition further contains

   a compound of the general formula I:



(I)

   wherein

   R_1 is -H, $-CH_3$, $-C_2H_5$, $-(C_2H_4O)_p$-H, $-(C_2H_4O)_p-CH_3$, $-(C_2H_4O)_p-CH(CH_3)_2$, $-(C_2H_4O)_p-C(CH_3)_3$, wherein p is an integer in the range of 1 to 20,

   R_2 is H or CH_3,

   n is an integer in the range of 0 to 3,

   m is an integer in the range of 0, 1 or 2.

2. The water-based composition according to claim 1, wherein in the compound of formula I is m = 0, n in the range of 0 to 3 and R_1 is independently selected from the group consisting of -H, $-CH_3$, $-C_2H_5$ and $-(C_2H_4O)_p$-H wherein p in the range 2 to 6.

3. The water-based composition according to claim 1, wherein the compound of formula I is selected from the group consisting of 2,3,6,7-tetramethyl-4-octyne-3,6-diol, 2,5,8,11-tetramethyl-6-dodecyn-5,8-diol ethoxylate, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate, 2,4,7,9-tetramethyl-5-decyne-4,7-diol-bispolyoxyethyleneether, and 2,4,7,9-tetramethyl-5-decyne-4,7-diol.

4. The water-based composition according to any of the foregoing claims, wherein the surfactant is an ethoxylated or propoxylated alkyl, ethoxylated or propoxylated amine, ethoxylated or propoxylated amide, ethoxylated or propoxylated alcohol, or a mixture thereof.

5. The water-based composition according to any of the foregoing claims, wherein the surfactant has the general formula II

   $R_3O(CH_2CH_2O)_xH$ (II)

   wherein
   R_3 is a linear or branched alkyl group, having 6 – 15 carbon atoms, preferably 8-12 carbon atoms,
   x is an integer in the range of 3 – 15, preferably 7 – 11.

6. The water-based composition according to any of the foregoing claims, wherein the alkanethiol is a C_{10}- to C_{20}-alkanethiol.

7. The water-based composition according to any of the foregoing claims, wherein the composition comprises a co-emulgator

8. The water-based composition according to claim 7, wherein the co-emulgator has the general formula III

   $R_4O(CH_2CH_2O)_yH$ (III)

   wherein

R4 is a linear or branched alkyl group, having 16 – 20 carbon atoms, preferably 16-18 carbon atoms,
y is an integer in the range of 2 – 10, preferably 3 – 6.

9. The water-based composition according to claim 7 or 8, wherein the co-emulgator is a polyalkylene glycol ether.

10. The water-based composition according to any of the foregoing claims, wherein the composition is free of chromate and/or free of organic solvent.

11. The water-based composition according to any of the foregoing claims, having a pH in the range of 1 to 10.

12. The use of the water-based composition according to one of the foregoing claims 1 – 10 for post-treatment of metal surface, particularly a silver or silver alloy surface, to avoid metal tarnishing.

13. A method for post-treatment of a metal surface, particularly a silver or silver alloy surface comprising, in this order, the steps

    a. providing a metal surface, particularly a silver or silver alloy surface,

    b. contacting the metal surface, particularly the silver or silver alloy surface, with a water-based composition according to any of claims 1 – 11.

14. The method according to claim 13, wherein the contacting in step b. is applied as immersing and/or per spraying and/or per any other suitable method allowing the contact between the metal and the claim solution.

15. The method according to claim 13 or 14, wherein the contacting in step b. takes place under applying an electrical current between the metal surface, particularly the silver or silver alloy surface, and at least one electrode when the metal is immersed into the claim solution.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/065564

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23F11/12 C23F11/14 C23F11/16 C11D3/20
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23F C11D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/277906 A1 (JOHNS PETER G [GB] ET AL) 6 December 2007 (2007-12-06) cited in the application the whole document	1-15
A	EP 0 725 165 A1 (ENTHONE OMI INC [US]) 7 August 1996 (1996-08-07) page 1, paragraph 1; example II	1-15
A	EP 2 535 380 A1 (FUJIFILM CORP [JP]) 19 December 2012 (2012-12-19) page 52 paragraphs [0001], [0096] - [0097]	1-15
A	US 2007/111903 A1 (ENGEL DAVID B [US] ET AL) 17 May 2007 (2007-05-17) claims 1,3	1-15

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 July 2017	02/08/2017

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

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/065564

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007277906 A1	06-12-2007	AU 2005229275 A1	13-10-2005
		CA 2559989 A1	13-10-2005
		CN 1946878 A	11-04-2007
		EA 200601805 A1	27-02-2007
		EP 1730325 A1	13-12-2006
		GB 2412666 A	05-10-2005
		JP 2007537354 A	20-12-2007
		US 2007277906 A1	06-12-2007
		WO 2005095675 A1	13-10-2005
EP 0725165 A1	07-08-1996	CA 2166503 A1	02-08-1996
		CN 1138637 A	25-12-1996
		EP 0725165 A1	07-08-1996
		JP 3340611 B2	05-11-2002
		JP H08283983 A	29-10-1996
		US 5525206 A	11-06-1996
EP 2535380 A1	19-12-2012	CN 102827511 A	19-12-2012
		EP 2535380 A1	19-12-2012
		JP 5599762 B2	01-10-2014
		JP 2013018951 A	31-01-2013
		US 2012320124 A1	20-12-2012
US 2007111903 A1	17-05-2007	BR PI0620498 A2	16-11-2011
		CA 2628148 A1	31-05-2007
		CA 2811048 A1	31-05-2007
		US 2007111903 A1	17-05-2007
		WO 2007061722 A2	31-05-2007