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(54) Titre : UTILISATION DE TENSIOACTIFS NON IONIQUES DANS L'EXTRACTION DE METAL PAR ELECTROLYSE
(54) Title: USE OF NONIONIC SURFACTANTS IN METAL EXTRACTION BY ELECTROLYSIS

(57) **Abrégé/Abstract:**

A process for the electrolytic treatment of metal-containing solutions, wherein at least one nonionic surfactant is used in the electrolyte solution, the surfactant reducing the surface tension of the electrolyte solution at a surfactant concentration of 0.2% by weight and a temperature of 24°C in an aqueous solution with 190 g/l of sulfuric acid and 157 g/l of copper sulfate, which is diluted with water in a ratio of 1: 10, by from 20 to 60%, is useful for working up ores or the purification of metals, like copper, chromium, nickel, zinc, gold and silver.

Abstract

A process for the electrolytic treatment of metal-containing solutions, wherein at least one nonionic surfactant is used in the electrolyte solution, the surfactant reducing the surface tension of the electrolyte solution at a surfactant concentration of 0.2% by weight and a temperature of 24°C in an aqueous solution with 190 g/l of sulfuric acid and 157 g/l of copper sulfate, which is diluted with water in a ratio of 1 : 10, by from 20 to 60%, is useful for working up ores or the purification of metals, like copper, chromium, nickel, zinc, gold and silver.

Use of nonionic surfactants in metal extraction by electrolysis

5 Description

The present invention relates to processes for the electrolytic working-up of metals and the use of nonionic surfactants in these processes.

10 Apart from the noble metals, pure metals occur only very rarely in nature. They are extracted predominantly from their ores, which comprise metal oxides or metal sulfides as main components. There are two different processes for extracting the pure metals from ores. The method used for the extraction depends on the composition of the ores and their chemical properties.

15 Firstly, the oxygen can be abstracted from the metal oxides by heating with carbon. Elemental metal and carbon dioxide form thereby.

20 Secondly, the ores of some metals, if they are not already present as oxides, can be oxidized by roasting and then converted into their salts with acids. The pure metals are then obtained from these salt solutions by means of electrolysis. Furthermore, in the case of certain ores, the metals can be extracted directly from the ore by leaching processes, for example by means of acidic or basic aqueous solutions, worked up and then obtained by means of electrolytic methods.

25 Metals, for example copper, which occur in elemental form together with other metals are likewise purified by electrolysis.

30 The electrolytic treatment for the extraction of metals or for the purification thereof is an important process step.

35 The disadvantage of electrolysis is that the electrolyses frequently take place in acidic media, where not only the formation of the desired pure metal, but in addition the chemical redox processes with formation of, for example, oxygen, hydrogen or chlorine, occur at the electrodes. The resulting gas bubbles rise through the electrolyte solution and bubble out of said solution. The electrolyte solution thus forms a mist. This mist is usually highly corrosive and toxic. Particular measures, for example for protection of persons, are therefore frequently required in electrolytic plants.

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The literature recommends the use of surfactants in the electrolyte solutions for reducing the mist formation.

5 Thus, for example, US 4,484,990 and WO 95/30783 describe the use of fluorine-containing surfactants for suppressing acidic mists in copper extraction. In addition, it is stated that at the same time the copper quality is improved with the use of these surfactants.

10 *Hydrometallurgy* 70, 2003, pages 1 to 8, describes a method for assessing foam blankets in the electrolytic extraction of copper. The foam blankets building up on the electrolyte solutions due to addition of surfactants influence the mist formation. The surfactant Pluronic® F68 is used for this purpose in *Hydrometallurgy* and the influence thereof on the formation of foam blankets is investigated.

15 US 2004/149589 describes the use of saponins, a natural extract from the *Quillaja saponaria* tree, for the formation of foam blankets, by means of which the mist formation in copper electrolysis can be avoided.

20 In *Canadian Metallurgical Quarterly* 43, 2004, 4, pages 449 to 460, the influence of different surfactant systems in the electrolytic extraction of copper is described.

The surfactant systems known for metal electrolysis do not always have a positive effect on the purity and density of the metal deposited. Furthermore, it is not possible in
25 the case of all known surfactant systems for the electrolyte solution obtained after electrolysis is complete to be reused without working-up. Moreover, not all surfactant systems known to date for electrolytic processes are stable under the respective process conditions.

30 It is therefore the object of the present invention to provide surfactant systems which, preferably when used in concentrations which are as low as possible, substantially avoid the mist formation in the electrolysis of acidic solutions and preferably simultaneously lead to an improvement in the property profile of the metal deposited, in particular with respect to purity and density. In addition, the surfactant systems should
35 be capable of being reused after electrolysis is complete, preferably without working-up thereof.

For achieving this object, the present invention starts from a process for the electrolytic treatment of metal-containing solutions.

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In the process according to the invention, at least one nonionic surfactant is used in the electrolyte solution, the surfactant reducing the surface tension of the electrolyte solution at a surfactant concentration of 0.2% by weight and a temperature of 24°C in an aqueous solution comprising 190 g/l of sulfuric acid and 157 g/l of copper sulfate, which is diluted with water in a ratio of 1:10, by from 20 to 60%, particularly preferably from 25 to 55%, in particular from 30 to 50%.

Moreover, in the process according to the invention, the nonionic surfactant preferably has a foam volume of at least 10ml, particularly preferably 25 ml, especially preferably at least 40 ml, in a solution comprising 50 g of an aqueous solution with 190 g/l of sulfuric acid and 157 g/l of copper sulfate with 0.5% by weight of the surfactant, based on the solution, after shaking twenty times in the course of 5 seconds.

According to the invention, it was found that surfactant systems having the abovementioned property spectrum, when used in very low concentrations, positively influence the mist formation and the quality, in particular the purity and density, of the metal deposited in the electrolysis of metal salts. As a result of their use, the surface tension of the electrolysis solutions is reduced and hence the escape of the gases forming, for example of hydrogen, oxygen or chlorine, is facilitated and mist formation by the electrolyte solution when the gases escape is prevented. In addition, if appropriate the formation of a foam blanket on the surface, which likewise prevents mist formation by the electrolyte, can be achieved by using the surfactant or surfactant systems described.

A measure of the ability to form a foam blanket on the surface of an electrolyte solution is the ability to form a foam volume under the conditions defined above. The method determining the foam volume yields reproducible results, the same foam values being obtained in a 0.05% strength solution of the surfactant in an overhead mixer from Gerhardt (Bonn, Germany), type RA 20, if the apparatus is operated at level 7 with 60 revolutions (test time: about 2 minutes).

Both measuring methods for determining the foam volume are preferably carried out in a shaking cylinder having a diameter of, particularly preferably, about 30 mm, in particular a diameter of 30 mm.

In a preferred embodiment, the process according to the invention starts from aqueous solutions of the metal, the process according to the invention being suitable for all electrolysis processes known to the person skilled in the art. In particular, the process according to the invention is suitable for separating substances, for example in

chloroalkali electrolysis, for working up ores, for example for working up copper, chromium, nickel and/or zinc, and for purifying metals, for example for purifying gold, silver, nickel or copper.

- 5 The electrolytic treatment according to the invention is particularly suitable as a process step in the process for extracting metals with the aid of solvent extraction / electrowinning, which are known to the person skilled in the art by the designation "SX-EW":
- 10 There, the metal is obtained starting from aqueous solutions which are prepared by leaching the metal from a metal-containing starting material, the leaching being effected by means of acid or alkalis and a metal-containing mother liquor being obtained. In general, the metal-containing mother liquor thus obtained is first treated with an organic phase, the metal being transferred to the organic phase. The organic
- 15 phase is then treated with an acidic aqueous solution, the metal being transferred to the acidic aqueous solution. Starting from this acidic aqueous solution, the process according to the invention for the electrolytic treatment is carried out. In a preferred embodiment, the preparation of the acidic aqueous solution of the metal therefore comprises the following process steps:
- 20
- (a) leaching of the metal from a metal-containing starting material by a treatment thereof with acids or alkalis, a metal-containing mother liquor being obtained;
 - 25 (b) treatment of the metal-containing mother liquor with an organic phase which comprises an extracting agent (complexing agent) suitable for the metal to be extracted, the metal being transferred to the organic phase;
 - (c) treatment of the organic phase with an acidic aqueous solution, the metal
 - 30 being transferred to the acidic aqueous solution.

In this respect, the surfactants provided according to the invention have the advantage that they have no substantial emulsifying effect so that phase separation is still possible. At the same time, they result in an advantageous reduction of the surface

35 tension.

The "SX/EW" process is described in US 4,484,990, the disclosure of which in this context is hereby incorporated by reference in the present invention.

In the present invention, the use of electrolyte solutions comprising sulfuric acid is particularly preferred.

5 In a particular embodiment of the present invention, these are chromium-, nickel- or copper-containing solutions comprising sulfuric acid.

The concentration of the nonionic surfactant in the electrolyte solution is preferably chosen so that the surface tension of the resulting electrolyte solution is in the abovementioned range and a substantially cohesive foam blanket results on the electrolyte surface. In a preferred embodiment, the concentration of the nonionic
10 surfactant and the electrolyte solution is preferably from 0.001 to 0.5% by weight, particularly preferably from 0.005 to 0.2% by weight, based in each case on the electrolyte solution.

The addition of the nonionic surfactant to the electrolyte solution can be effected either
15 during the electrolytic treatment or in one of the optionally upstream treatment steps, for example the transfer of the metal from the organic phase to the acidic aqueous solution. Surfactants which do not interfere with the phase separation between organic and aqueous acidic phase are preferred.

20 The addition of the nonionic surfactant can be effected continuously or batchwise.

If the use of a solid nonionic surfactant is intended, the solid nonionic surfactant may be dissolved beforehand. For example, the acidic aqueous solution is suitable for this purpose. Alternatively, however, it is also possible to add the solid surfactant to the
25 electrolyte solution.

Nonionic surfactants suitable for the present invention should preferably be stable under the acidic conditions of the sulfuric acid in an aqueous solution and moreover should preferably be biodegradable, particularly preferably readily biodegradable.
30 Within the context of the present invention, the term "acid-stable" is understood as meaning that the nonionic surfactant in a 20% strength H_2SO_4 solution achieves a reduction of the surface tension of preferably at least 85%, particularly preferably at least 90%, especially preferably at least 95%, of the initially determined values after one week.

35 In a preferred embodiment of the present invention, the nonionic surfactants are selected from the group consisting of alkoxylated C_4 - C_{22} -alcohols, alkylpolyglucosides, N-alkylpolyglucosides, N-alkylglucamides, fatty acid alkoxylates, fatty acid polyglycol esters, fatty acid amine alkoxylates, fatty acid amide alkoxylates, fatty acid
40 alkanolamide alkoxylates, N-alkoxypolyhydroxy-fatty acid amides, N-aryloxypolyhydroxy-fatty acid amides, polyisobutene alkoxylates, polyisobutene/maleic

anhydride derivatives, fatty acid glycerides, sorbitan esters, polyhydroxy-fatty acid derivatives, polyalkoxy-fatty acid derivatives and bisglycerides.

Particularly suitable nonionic surfactants are:

5

- alkoxyated C₄-C₂₂-alcohols, such as fatty alcohol alkoxyates or oxo alcohol alkoxyates. These may be alkoxyated with ethylene oxide, propylene oxide and/or butylene oxide. Surfactants which may be used here are all alkoxyated alcohols which comprise at least two added molecules of one of the abovementioned alkylene oxides. Block polymers of ethylene oxide, propylene oxide and/or butylene oxide or adducts which comprise alkylene oxides in random distribution are suitable here. The nonionic surfactants generally comprise from 2 to 50, preferably from 3 to 20, mol of at least one alkylene oxide per mole of alcohol. These preferably comprise ethylene oxide as the alkylene oxide. The alcohols preferably have from 10 to 18 carbon atoms. Depending on the type of alkoxylation catalyst used in the preparation, and the type of preparation process and on the method of working up, the alkoxyates have a broad or narrow alkylene oxide homolog distribution;
- alkylpolyglucosides having 6 to 22, preferably 8 to 18, carbon atoms in the alkyl chain and in general 1 to 20, preferably 1.1 to 5, glucoside units sorbitan alkanates, including in alkoxyated form;
- N-alkylglucamides, fatty acid alkoxyates, fatty acid amine alkoxyates, fatty acid amide alkoxyates, fatty acid alkanolamide alkoxyates, polyisobutene ethoxyates, polyisobutene/maleic anhydride derivatives, optionally alkoxyated monoglycerides, glyceryl monostearates, sorbitan esters and bisglycerides.

Particularly suitable nonionic surfactants are alkyl alkoxyates or mixtures of alkyl alkoxyates, as described, for example, in DE-A 102 43 363, DE-A 102 43 361, DE-A 102 43 360, DE-A 102 43 365, DE-A 102 43 366, DE-A 102 43 362 or DE-A 43 25 237. These are alkoxylation products which were obtained by reaction of alkanols with alkylene oxides in the presence of alkoxylation catalysts or are mixtures of alkoxylation products. Particularly suitable initiator alcohols are the so-called Guerbet alcohols, in particular ethylhexanol, propylhexanol and butyloctanol. Propylheptanol is particularly preferred. Preferred alkylene oxides are propylene oxide and ethylene oxide, alkyl alkoxyates having a direct link of a preferably short polypropylene oxide block to the initiator molecule, as described, for example, in DE-A 102 43 365, being preferred in particular because of their low residual alcohol content and their good biodegradability.

In an embodiment of the present invention, the alkoxylates are C₁₂₋₁₈-fatty alcohol ethoxylates which have been reacted with from 2 to 80 ethylene oxide units. C₁₆₋₁₈-Fatty alcohol ethoxylates having from 10 to 80, in particular from 15 to 50, especially 25, ethylene oxide units are preferred in this respect.

5

In addition, the fatty alcohol used in these alkoxylates is preferably a primary alcohol.

In an embodiment of the present invention, alcohol alkoxylates of the general formula (I)

10



where

15

R¹ is at least singly branched C₄₋₂₂-alkyl or -alkylphenol,

R² is C₃₋₄-alkyl,

R⁵ is C₁₋₄-alkyl,

R⁶ is methyl or ethyl,

n has a mean value of from 1 to 50,

20

m has a mean value of from 0 to 20, preferably from 0.5 to 20,

r has a mean value of from 0 to 50, and

s has a mean value of from 0 to 50,

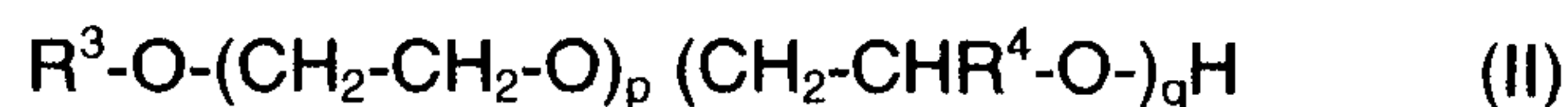
m being at least 0.5 if R⁵ is methyl or ethyl or r has the value 0.

25

A mixture of from 20 to 95% by weight, preferably from 30 to 95% by weight, of at least one of the above alcohol alkoxylates and from 5 to 80% by weight, preferably from 5 to 70% by weight, of a corresponding alcohol alkoxylate, but in which R¹ is a straight-chain alkyl radical having an even number of carbon atoms, is furthermore possible.

30

It may furthermore be alcohol alkoxylates of the general formula (II)



where

35

R³ is branched or straight-chain C₄₋₂₂-alkyl or -alkylphenol,

R⁴ is C₃₋₄-alkyl,

p has a mean value of from 1 to 50, preferably from 4 to 15, and

q has a mean value of from 0.5 to 20, preferably from 0.5 to 4, more preferably

40

from 0.5 to 2.

A mixture from 5 to 95% by weight of at least one branched alcohol alkoxylate (II), as described directly above, and from 5 to 95% by weight of a corresponding alcohol alkoxylate in which, however, a straight-chain alkyl radical is present instead of a branched alkyl radical is furthermore possible.

In the alcohol alkoxylates of the general formula (I), R^2 is preferably propyl, in particular n-propyl.

In the alcohol alkoxylates of the general formula (I), n preferably has a mean value of from 4 to 15, particularly preferably from 6 to 12, in particular from 7 to 10.

m preferably has a mean value of from 0.5 to 4, particularly preferably from 0.5 to 2, in particular from 1 to 2. The expression "mean value" relates to industrial products in which different numbers of alkylene oxide units may be present in the individual molecules. It describes the proportion of the corresponding alkylene oxide units present on average in industrial products. A value of 0.5 therefore means that on average every second molecule carries a corresponding unit. According to a preferred embodiment of the invention, the lower limit 1 is present instead of the lower limit of 0.5 for the indices n, m, p and q.

r is preferably 0. s is preferably 0.

The radical R^1 is preferably a C_{8-15} -alkyl, particularly preferably C_{8-13} -alkyl, in particular C_{8-12} -alkyl radical which is at least singly branched. A plurality of branches may also be present.

R^5 is preferably methyl or ethyl, in particular methyl.

R^6 is preferably ethyl.

In the mixtures, compounds having straight-chain and having branched alcohol radicals R^1 are present. This is the case, for example, in oxo alcohols which have a proportion of linear alcohol chains and a proportion of branched alcohol chains. For example, a $C_{13/15}$ -oxo alcohol frequently has about 60% by weight of completely linear alcohol chains, but also about 40% by weight of α -methyl-branched and C_{22} -branched alcohol chains.

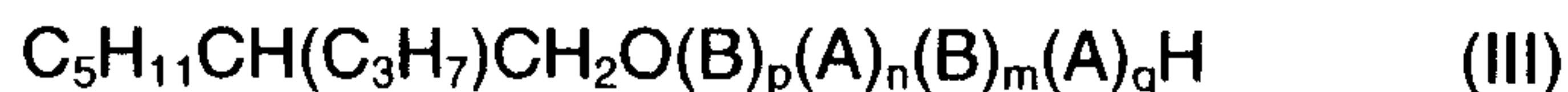
In the alcohol alkoxylates of the general formula (II), R^3 is preferably a branched or straight-chain C_{8-15} -alkyl radical, particularly preferably a branched or straight-chain C_{8-13} -alkyl radical and in particular a branched or straight-chain C_{8-12} -alkyl radical. R^4 is preferably propyl, in particular n-propyl. p preferably has a mean value of from 4 to 15, particularly preferably a mean value of from 6 to 12 and in particular a mean value of from 7 to 10. q preferably has a mean value of from 0.5 to 4, particularly preferably from 0.5 to 2, in particular from 1 to 2.

Depending on the alcohol alkoxylates of the general formula (I), the alcohol alkoxylates of the general formula (II) may also be present as mixtures having straight-chain and branched alcohol radicals.

Suitable alcohol components on which the alcohol alkoxylates are based are not only pure alkanols but also homologous mixtures having a range of carbon atoms. Examples are $C_{8/10}$ -alkanols, $C_{10/12}$ -alkanols, $C_{13/15}$ -alkanols and $C_{12/15}$ -alkanols. Mixtures of a plurality of alkanols are also possible.

The above alkanol alkoxylates according to the invention or mixtures are preferably prepared by reacting alcohols of the general formula R^1 -OH or R^3 -OH or mixtures of corresponding branched and straight-chain alcohols, if appropriate first with C_{3-6} -alkylene oxide, then with ethylene oxide and subsequently, if appropriate, with C_{3-4} -alkylene oxide and then with a corresponding C_{5-6} -alkylene oxide. The alkoxylation is preferably carried out in the presence of alkoxylation catalysts. In particular, basic catalysts, such as potassium hydroxide, are used. By means of special alkoxylation catalysts, such as modified bentonites or hydrotalcites, as described, for example, in WO 95/04024, the random distribution of the amounts of the incorporated alkylene oxide can be greatly so that narrow-range alkoxylates are obtained.

A further particular embodiment of the present invention employs alkoxylate mixtures comprising alkoxylates of the general formula (III)



where

A is ethyleneoxy,

B in each case independently, is C_{3-10} -alkyleneoxy, preferably propyleneoxy, butyleneoxy, pentyleneoxy or mixtures thereof,

groups A and B being present in the form of blocks in the stated sequence, and

p is a number from 0 to 10,

n is a number from greater than 0 to 20,

5 m is a number from greater than 0 to 20,

q is a number from greater than 0 to 10, and

10 p + n + m + q is at least 1,

from 70 to 99% by weight of alkoxyates A1 in which C_5H_{11} has the meaning n- C_5H_{11} and

15 from 1 to 30% by weight of alkoxyates A2 in which C_5H_{11} has the meaning $C_2H_5CH(CH_3)CH_2$ and/or $CH_3CH(CH_3)CH_2CH_2$

being present in the mixture.

20 In the general formula (III), p is a number from 0 to 10, preferably from 0 to 5, in particular from 0 to 3. If blocks $(B)_p$ are present, p is preferably a number from 0.1 to 10, particularly preferably from 0.5 to 5, in particular from 1 to 3.

25 In the general formula (III), n is preferably a number in the range from 0.25 to 10, in particular from 0.5 to 7, and m is preferably a number in the range from 2 to 10, in particular from 3 to 6. B is preferably propyleneoxy and/or butyleneoxy, especially propyleneoxy in both positions.

30 q is preferably a number in the range from 1 to 5, particularly preferably in the range from 2 to 3.

The sum p + n + m + q is at least 1, preferably from 3 to 25, particularly preferably from 5 to 15, in particular from 7 to 13.

35 In the alkoxyates preferably 3 or 4 alkylene oxide blocks are present. According to one embodiment, adjacent to the alcohol radical are firstly ethyleneoxy units, adjacent thereto propylene oxide units and adjacent thereto ethyleneoxy units. According to a further embodiment, propyleneoxy units are initially adjacent to the alcohol radical, then ethyleneoxy units, then propyleneoxy units and finally ethyleneoxy units. Instead of the propyleneoxy units, the other alkyleneoxy units stated may also be present.

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p, n, m and q denote a mean value which results as the average for the alkoxylates. p, n, m and q may therefore also deviate from integral values. In the alkoxylation of alkanols, a distribution of the degree of alkoxylation is generally obtained, which distribution can be adjusted to a certain extent by using different alkoxylation catalysts. Through the choice of suitable amounts of groups A and B, the property spectrum of the alkoxylate mixtures according to the invention can be adapted according to practical requirements.

The alkoxylate mixtures are obtained by alkoxylation of the parent alcohols $C_5H_{11}CH(C_3H_7)CH_2OH$. The starting alcohols can be mixed from the individual components so that the ratio according to the invention results. They can be prepared by aldol condensation of valeraldehyde and subsequent hydrogenation. The preparation of valeraldehyde and the corresponding isomers is effected by hydroformylation of butene, as described, for example, in US 4,287,370; Beilstein E IV 1, 32 68, Ullmanns Encyclopedia of Industrial Chemistry, 5th Edition, Volume A1, pages 323 and 328 et seq. The subsequent aldol condensation is described, for example, in US 5,434,313 and Römpp, Chemie Lexikon, 9th Edition, key word "Aldol-Addition" page 91. The hydrogenation of the aldol condensate conforms to general hydrogenation conditions.

Furthermore, 2-propylheptanol can be prepared by condensation of 1-pentanol (as a mixture of the corresponding methylbutan-1-ols) in the presence of KOH at elevated temperatures, cf. for example Marcel Guerbet, C.R. Acad Sci Paris 128, 511, 1002 (1899). Furthermore, reference may be made to Römpp, Chemie Lexikon, 9th Edition, Georg Thieme Verlag Stuttgart, and the citations mentioned there, and Tetrahedron, Vol. 23, pages 1723 to 1733.

In the general formula (III), the radical C_5H_{11} may have the meaning $n-C_5H_{11}$, $C_2H_5CH(CH_3)CH_2$ or $CH_3CH(CH_3)CH_2CH_2$. The alkoxylates are mixtures which comprise

from 70 to 99% by weight, preferably from 85 to 96% by weight, of alkoxylates A1 in which C_5H_{11} has the meaning $n-C_5H_{11}$ and

from 1 to 30% by weight, preferably from 4 to 15% by weight, of alkoxylates A2 in which C_5H_{11} has the meaning $C_2H_5CH(CH_3)CH_2$ and/or $CH_3CH(CH_3)CH_2CH_2$.

The radical C_3H_7 preferably has the meaning $n-C_3H_7$.

The alkoxlation is preferably catalyzed by strong bases, which are expediently added in the form of an alkali metal alcoholate, alkali metal hydroxide or alkaline earth metal hydroxide, as a rule in an amount of from 0.1 to 1% by weight, based on the amount of the alkanol R^2-OH (cf. G. Gee et al., J. Chem. Soc. (1961), page 1345; B. Wojtech, Makromol. Chem. 66, (1966), page 180).

Acidic catalysis of the addition reaction is also possible. In addition to Bronsted acids, Lewis acids, such as, for example, $AlCl_3$ or BF_3 dietherate, BF_3 , $BF_3 \cdot H_3PO_4$, $SbCl_4 \cdot 2 H_2O$ or hydrotalcite, are also suitable (cf. P.H. Plesch, The Chemistry of Cationic Polymerization, Pergamon Press, New York (1963)). Double metal cyanide (DMC) compounds are also suitable as the catalyst.

In principle, all suitable compounds known to the person skilled in the art can be used as the DMC compounds.

DMC compounds suitable as the catalyst are described, for example, in WO 99/16775 and DE-A-101 17 273. In particular, double metal cyanide compounds of the general formula (IV) are suitable as the catalyst for the alkoxylation:



where

- 25 - M^1 is at least one metal ion selected from the group consisting of Zn^{2+} , Fe^{2+} , Fe^{3+} , Co^{3+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Sn^{2+} , Pb^{2+} , Mo^{4+} , Mo^{6+} , Al^{3+} , V^{4+} , V^{5+} , Sr^{2+} , W^{4+} , W^{6+} , Cr^{2+} , Cr^{3+} , Cd^{2+} , Hg^{2+} , Pd^{2+} , Pt^{2+} , V^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cu^{2+} , La^{3+} , Ce^{3+} , Ce^{4+} , Eu^{3+} , Ti^{3+} , Ti^{4+} , Ag^+ , Rh^{2+} , Rh^{3+} , Ru^{2+} and Ru^{3+} ,
- 30 - M^2 is at least one metal ion selected from the group consisting of Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} , Mn^{2+} , Mn^{3+} , V^{4+} , V^{5+} , Cr^{2+} , Cr^{3+} , Rh^{3+} , Ru^{2+} and Ir^{3+} ,
- 35 - A and X, independently of one another, are an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate, nitrate, nitrosyl, hydrogen sulfate, phosphate, dihydrogen phosphate, hydrogen phosphate and bicarbonate,
- 40 - L is a water-miscible ligand selected from the group consisting of alcohols, aldehydes, ketones, ethers, polyethers, esters, polyesters, polycarbonate, ureas, amides, primary, secondary and tertiary amines,

- 13 -

ligands having pyridinenitrogen, nitriles, sulfides, phosphides, phosphites, phosphanes, phosphonates and phosphates,

- 5 - k is a fraction or integer greater than or equal to zero,
- P is an organic additive,
- a, b, c, d, g and n are selected so that the electroneutrality of the compound (I) is ensured, it being possible for c to be 0,
- 10 - e, the number of ligand molecules, is a fraction or integer greater than 0 or is 0, and
- f and h, independently of one another, are a fraction or integer which is
- 15 greater than 0 or is 0.

The following may be mentioned as organic additives P: polyether, polyester, polycarbonates, polyalkylene glycol sorbitan ester, polyalkylene glycol glycidyl ether, polyacrylamide, poly(acrylamide-co-acrylic acid), polyacrylic acid, poly(acrylamide-co-

20 maleic acid), polyacrylonitrile, polyalkyl acrylates, polyalkyl methacrylates, polyvinyl methyl ether, polyvinyl ethyl ether, polyvinyl acetate, polyvinyl alcohol, poly-N-vinylpyrrolidone, poly(N-vinylpyrrolidone-co-acrylic acid), polyvinyl methyl ketone, poly(4-vinylphenol), poly(acrylic acid-co-styrene), oxazoline polymers, polyalkylenimines, maleic acid and maleic anhydride copolymers,

25 hydroxyethylcellulose, polyacetates, ionic surface-active and interface-active compounds, gallic acid or salts, esters or amides thereof, carboxylic esters of polyhydric alcohols and glycosides.

30 These catalysts may be crystalline or amorphous. If k is zero, crystalline double metal cyanide compounds are preferred. If k is greater than zero, crystalline, semicrystalline and substantially amorphous catalysts are preferred.

35 There are various preferred embodiments among the modified catalysts. A preferred embodiment comprises catalysts of the formula (IV) in which k is greater than zero. The preferred catalyst then comprises at least one double metal cyanide compound, at least one organic ligand and at least one organic additive P.

40 In another preferred embodiment, k is zero, optionally e is also zero and X is exclusively a carboxylate, preferably formate, acetate and propionate. Such catalysts are described in WO 99/16775. In this embodiment, crystalline double metal cyanide

catalysts are preferred. Double metal cyanide catalysts as described in WO 00/74845, which are crystalline and lamellar, are furthermore preferred.

5 The preparation of the modified catalysts is effected by combining a metal salt solution with a cyanometallate solution which may optionally comprise both an organic ligand L and an organic additive P. The organic ligand and optionally the organic additive are then added. In a preferred embodiment of the catalyst preparation, first an inactive double metal cyanide phase is prepared and this is then converted into an active double metal cyanide phase by recrystallization, as described in PCT/EP01/01893.

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In another preferred embodiment of the catalysts, f, e and k are not zero. These are double metal cyanide catalysts which comprise a water-miscible organic ligand (in general in amounts of from 0.5 to 30% by weight) and an organic additive (in general in amounts of from 5 to 80% by weight), as described in WO 98/06312. The catalysts can be prepared either with vigorous stirring (24 000 rpm with Turrax) or with stirring, as described in US 5,158,922.

15

Double metal cyanide compounds which comprise zinc, cobalt or iron or two thereof are particularly suitable as a catalyst for the alkoxylation. For example, Prussian Blue is particularly suitable.

20

Crystalline DMC compounds are preferably used. In a preferred embodiment, a crystalline DMC compound of the Zn-Co type which comprises zinc acetate as a further metal salt component is used as the catalyst. Such compounds crystallize with a monoclinic structure and have a lamellar habit. Such compounds are described, for example, in WO 00/74845 or PCT/EP01/01893.

25

DMC compounds suitable as a catalyst can be prepared in principle by all methods known to the person skilled in the art. For example, the DMC compounds can be prepared by direct precipitation or the incipient wetness method or by preparation of a precursor phase and subsequent recrystallization.

30

The DMC compounds can be used as powder, paste or suspension or can be molded to give a molding, introduced into moldings, foams or the like or applied to moldings, foams or the like.

35

The catalyst concentration used for the alkoxylation is typically less than 2000 ppm (i.e. mg of catalyst per kg of product), preferably less than 1000 ppm, in particular less than 500 ppm, particularly preferably less than 100 ppm, for example less than 50 ppm or 35 ppm, particularly preferably less than 25 ppm, based on the final quantity range.

40

The addition reaction is carried out at temperatures from 90 to 240°C, preferably from 120 to 180°C, in a closed vessel. The alkylene oxide or the mixture of different alkylene oxides is fed to the mixture comprising alkanol mixture according to the invention and alkali under the vapor pressure of the alkylene oxide mixture which prevails at the
5 chosen reaction temperature. If desired, the alkylene oxide can be diluted with up to about 30 to 60% of an inert gas. This provides additional safety with regard to explosive polyaddition of the alkylene oxide.

If an alkylene oxide mixture is used, polyether chains in which the various alkylene
10 oxide building blocks are virtually randomly distributed are formed. Variations in the distribution of the building blocks along the polyether chain are the result of different reaction rates of the components and can also be achieved arbitrarily by continuous feeding of an alkylene oxide mixture having a program-controlled composition. If the various alkylene oxides are reacted in succession, polyether chains having a block-like
15 distribution in the alkylene oxide building blocks are obtained.

The length of the polyether chains varies randomly within the reaction product about a mean value, the stoichiometric value resulting substantially from the amount added.

20 Preferred alkoxyate mixtures of the general formula (III) can be obtained by reacting alcohols of the general formula $C_5H_{11}CH(C_3H_7)CH_2OH$ with propylene oxide/ethylene oxide in the abovementioned sequence under alkoxylation conditions. Suitable alkoxylation conditions are described above and in Nikolaus Schönfeldt, Grenzflächenaktive Äthylenoxid-Addukte, Wissenschaftliche Verlagsgesellschaft mbH
25 Stuttgart 1984. As a rule, the alkoxylation is carried out in the presence of basic catalysts, such as KOH, in the absence of a solvent. The alkoxylation can, however, also be carried out with concomitant use of a solvent. Polymerization of the alkylene oxide is initiated which inevitably results in a random distribution of homologs, the mean value of which is indicated here by p, n, m and q.

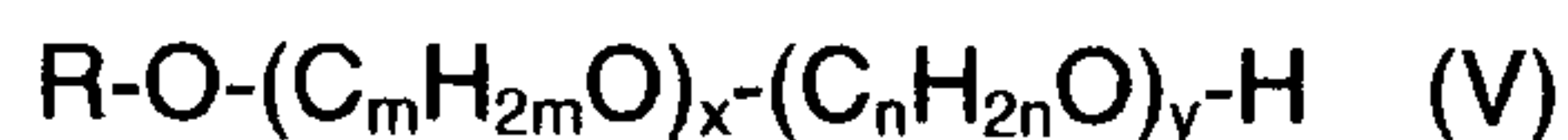
30 In a preferably initially carried out propoxylation and only subsequently effected ethoxylation, the content of residual alcohol in the alkoxyates can be reduced since propylene oxide undergoes an addition reaction uniformly with the alcohol component. In contrast, ethylene oxide reacts preferentially with ethoxyates, so that, if ethylene
35 oxide is used initially for reaction with the alkanols, a broader homolog distribution may result. The alcohol mixtures used according to the invention have as a rule a natural odor, which can be very substantially suppressed by complete alkoxylation.

The alkoxyate mixtures according to the invention require only one propylene oxide
40 (PO) block of very short length, preferably bonded directly to the alcohol, for reducing the residual alcohol content. This is particularly advantageous in particular because the

biodegradability of the product decreases on lengthening the PO block. Such alkoxyate mixtures therefore permit maximum degrees of freedom in the choice of the length of the PO block, the lower limit of the length being determined by the increasing residual alcohol content and the upper limit by the deterioration in the biodegradability.

5

They may furthermore be block-like isotridecanol alkoxyates of the general formula (V)



where

10 R is an isotridecyl radical,

m is the number 2 and at the same time n is the number 3 or 4 or

m is the number 3 or 4 and at the same time n is the number 2 and

x and y, independently of one another, are numbers from 1 to 20,

the variables x being greater than or equal to y when $m = 2/n = 3$ or 4.

15

These block-like isotridecanol alkoxyates are described, for example, in DE 196 21 843 A1, the entire disclosure of which in this context is hereby incorporated by reference in the present invention.

20 The isotridecanol (isotridecyl alcohol) present as the parent alcohol component is of synthetic origin and is prepared by oligomerization of suitable low olefin building blocks and subsequent oxo synthesis (hydroformylation). Thus, isobutylene, 1-butylene, 2-butylene or mixtures thereof can be catalytically trimerized, propylene can be catalytically tetramerized or 2-methyl-1-pentene can be catalytically dimerized. The
25 C_{12} -olefins thus obtainable are then converted into the homologous C_{13} -alcohol, for example by means of CO and H_2 over a suitable catalyst.

The main amount of the isotridecanol comprises primary C_{13} -alkanols having at least 3, in particular 4, branches (alkyl side chains). As a rule, they are tetramethylnonanols,
30 e.g. 2,4,6,8-tetramethyl-1-nonanol or 3,4,6,8-tetramethyl-1-nonanol. Ethyldimethylnonanols, such as 5-ethyl-4,7-dimethyl-1-nonanol may also be present.

However, a suitable parent alcohol component is not only pure isotridecanol but also homolog mixtures of branched C_{11} - C_{14} -alkanols which comprise isotridecanol as the
35 main component. Such homolog mixtures form under certain conditions in the above-described oligomerization of lower olefin building blocks and subsequent oxo synthesis. A typical composition of such a mixture is the following:

- 40 - branched C_{11} -alcohol (isoundecanol) 2-15% by weight,
- branched C_{12} -alcohol (isododecanol) 15-35% by weight,

- 17 -

- isotridecanol 55-75% by weight and
 - branched C₁₄-alkanol (isotetradecanol) 1-10% by weight.
- 5 The "C₁₃/C₁₅-oxo alcohols", which are mixtures of corresponding linear olefins, i.e. α -dodecene and α -tetradecene, which have been hydroformylated, are to be differentiated from the isotridecanol used in the present invention. The C₁₃- and C₁₅-alkanols obtained are linear and have not more than one branch.
- 10 The degrees of alkoxylation x and y, which as a rule are average values since random distribution of the alkylene oxide units with a frequency maximum is generally present, are preferably, independently of one another, numbers from 1.5 to 12. By means of special alkoxylation catalysts, for example modified bentonites or hydrocalcites, as described in WO-A 95/04024, the random distribution can be greatly restricted so that
- 15 narrow-range alkoxyates are obtained.

The block-like isotridecanol alkoxyates (V) described are either ethylene oxide/propylene oxide or butylene oxide adducts of the formula (Va)



where n = 3 or 4 (Va) or propylene oxide or butylene oxide/ethylene oxide adducts of the formula (Vb)



where m = 3 or 4 (Vb).

If m or n is the number 3 or 4, the number 3 (propylene oxide block) is preferred.

30 The ratio of the variables x and y, which is one of the decisive factors with regard to the balance between hydrophilic and hydrophobic parts of the molecule, is greater than or equal to 1 in the case of the adducts (Va); preferably, the ratio of x to y is from 1 : 1 to 4 : 1, in particular from 1.5 : 1 to 3 : 1.

35 The ratio of the variables x and y in the case of the adducts (Vb) is somewhat less critical and is as a rule from 1 : 3 to 3 : 1, preferably from 1 : 1.5 to 3 : 1.

40 Another suitable class of nonionic surfactants comprises endcapped alcohol alkoxyates, in particular of abovementioned alcohol alkoxyates. In a particular embodiment, these are the corresponding endcapped alcohol alkoxyates of the alcohol

alkoxylates of the general formulae (I), (II), (III) and (V). The endcapping can be effected, for example, with dialkyl sulfate, C₁₋₁₀-alkyl halides, C₃₋₈-cycloalkyl halides, phenyl halides, preferably chlorides or bromides, particularly preferably cyclohexyl chloride, cyclohexyl bromide, phenyl chloride or phenyl bromide.

5

Examples of endcapped alkoxylates are also described in DE-A 37 26 121, the entire disclosure which in this context is hereby incorporated by reference in the present invention. In a preferred embodiment, these alcohol alkoxylates have the general structure (VI)

10



where

- 15 R^I is hydrogen or C₁-C₂₀-alkyl,
 R^{II} and R^{III} are identical or different and, in each case independently of one another, are hydrogen, methyl or ethyl,
 R^{IV} is C₁-C₁₀-alkyl, preferably C₁-C₄-alkyl, or cyclohexyl or phenyl,
 m' and n' are identical or different and are greater than or equal to 0,
 20 with the proviso that the sum of the m' and n' is from 3 to 300.

These compounds are prepared by reacting polyoxyalkylene compounds of the formula (VII)

25



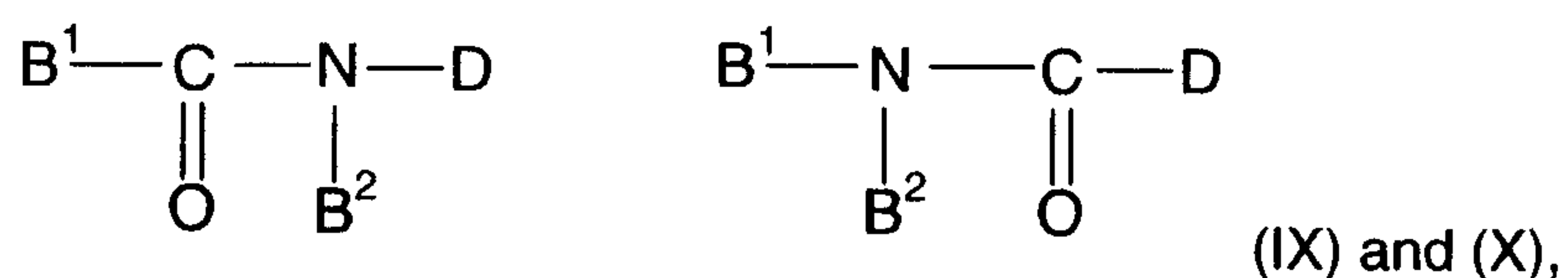
where R^V is hydrogen or C₁-C₂₀-alkyl and R^{II} , R^{III} , m' and n' each have the abovementioned meaning, with a dialkyl sulfate of the formula (VIII)

- 30 $(R^{IV}O)_2SO_2$ (VIII) or a C₁-C₁₀-alkyl halide, in particular C₁-C₄-alkyl halide, preferably chloride or bromide, cyclohexyl or phenyl halide, preferably chloride or bromide,

where R^{IV} has the abovementioned meaning, in the presence of alkali metal hydroxide. The reaction is carried out at a temperature of from 20 to 60°C in the presence of an aqueous solution of an alkali metal hydroxide, the concentration of alkali metal hydroxide not being permitted to be less than 35% by weight, based on the aqueous phase, during the entire duration of the reaction, and at least 1 mole of dialkyl sulfate of the formula (VIII) and at least one mole of alkali metal hydroxide being used per mole equivalent of organic hydroxyl groups. All alkyl groups occurring in the abovementioned formulae (VI), (VII) and (VIII) may be either straight-chain or branched. R^I , R^{IV} and R^V are, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl or sec-butyl.

40

- R^I and R^V are furthermore, for example, pentyl, isopentyl, sec-pentyl, tert-pentyl, hexyl, 2-methylpentyl, heptyl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, 3,5,5,7-tetramethylnonyl, isotridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl or eicosyl (the designations isooctyl, isononyl, isodecyl and isotridecyl are trivial names and originate from the alcohols obtained in the oxo synthesis – cf. in this context Ullmann, Enzyklopädie der Technischen Chemie, 4th Edition, Volume 7, pages 215 to 217, and Volume 11, pages 435 and 436).
- Preferably used starting materials are polyoxyalkylene derivatives of the formula (VI), where R^V is hydrogen or C₈-C₁₆-alkyl.
- Other preferred polyoxyalkylene derivatives of the formula (VII) are those in which the sum of m' and n' is from 3 to 10 or from 50 to 100.
- A preferred alkylating agent is a dialkyl sulfate of the formula (VIII), where R^{IV} is ethyl or in particular methyl.
- If such polyoxyalkylene derivatives of the formula (VII), where R^V is hydrogen, are used as starting materials, a dietherification takes place. In this case, etherified polyoxyalkylene derivatives of the formula (VI), where R^I is identical to R^{IV}, are obtained.
- Another class of nonionic surfactants comprises alkylpolyglucosides having, preferably, from 6 to 22, particularly preferably from 8 to 18, carbon atoms in the alkyl chain. These compounds generally comprise from 1 to 20, preferably from 1.1 to 5, glucoside units.
- Another class of nonionic surfactants comprises N-alkylglucamides of the general structures (IX) and (X)



- where B¹ is a C₆- to C₂₂-alkyl, B² is hydrogen or C₁- to C₄-alkyl and D is a polyhydroxyalkyl radical having from 5 to 12 carbon atoms and at least 3 hydroxyl groups. Preferably, B¹ is C₁₀- to C₁₈-alkyl, B² is CH₃ and D is a C₅- or C₆-radical. For

example, such compounds are obtained by acylation of reductively aminated sugars with acid chlorides of C₁₀- to C₁₈-carboxylic acids.

Further suitable nonionic surfactants are the endcapped fatty acid amide alkoxylates disclosed in WO-A 95/11225 and of the general formula (XI)



where

10

R¹ is a C₅- to C₂₁-alkyl or alkenyl radical,

R² is a C₁- to C₄-alkyl group,

A¹ is C₂- to C₄-alkylene,

y is the number 2 or 3 and

15 x has a value of from 1 to 6.

Examples of such compounds are the reaction products of n-butyltriglycolamine of the formula H₂N-(CH₂-CH₂-O)₃-C₄H₉ with methyl dodecanoate or the reaction products of ethyltetraglycolamine of the formula H₂N-(CH₂-CH₂-O)₄-C₂H₅ with a commercial mixture of saturated C₈- to C₁₈-fatty acid methyl esters.

Other suitable nonionic surfactants are polyhydroxy- or polyalkoxy-fatty acid derivatives, such as polyhydroxy fatty acid amides, N-alkoxy- or N-aryloxypolyhydroxy-fatty acid amides, fatty acid amide ethoxylates, in particular endcapped ones, and fatty acid alkanolamide alkoxylates.

In addition to these abovementioned nonionic surfactants, the following surfactants may also be used, if appropriate in combination with the abovementioned surfactants:

30 - In this context, the block copolymers of ethylene oxide and propylene oxide may first be mentioned, polypropylene glycol preferably forming the central molecular moiety.

35 - Also suitable are block copolymers of ethylene oxide, propylene oxide and butylene oxide. In a preferred embodiment, these are three-block copolymers comprising polypropylene/polyethylene/polypropylene blocks and having a molecular weight of from 4000 to 16 000, the amount by weight of the polyethylene blocks being from 55 to 90%, based on the three-block copolymer. Three-block copolymers having a molecular weight of more than 8000 and a polyethylene content of from 60 to 85% by weight, based on the three-block copolymer, are particularly preferred.

40

- In addition, block copolymers of ethylene oxide, propylene oxide and/or butylene oxide which are blocked at one or both ends may also preferably be used. Blocking at one end is achieved, for example, by using an alcohol, in particular a C₁₋₂₂-alkyl alcohol, for example methanol, as a starting compound for the reaction with an alkylene oxide. In addition, for example, the second endcapping can be effected by reacting the free block copolymer with dialkyl sulfate, C₁₋₁₀-alkyl halides, C₃-C₈-cycloalkyl halides, phenyl halides, preferably chlorides or bromides, particularly preferably cyclohexyl chloride, cyclohexyl bromide, phenyl chloride or phenyl bromide.
- Furthermore, the natural extracts from the *Quillaja saponaria* tree, the compounds referred to as saponins, which are commercially available under the name Mistop[®], may be mentioned.

Individual nonionic surfactants or a combination of different nonionic surfactants may additionally be used. It is possible to use nonionic surfactants from only one class, in particular only alkoxyated C₄-C₂₂-alcohols. Alternatively, however, surfactant mixtures from different classes may also be used.

In a further embodiment of the present invention, an anionic surfactant may additionally be introduced into the electrolyte solution.

If an anionic surfactant is used in the composition according to the invention, it can preferably be selected from the group consisting of fatty alcohol sulfates, sulfated alkoxyated alcohols, alkanesulfonates, N-acyl sarcosinates, alkylbenzenesulfonates, olefin sulfonates and olefin disulfonates, alkyl ester sulfonates, sulfonated polycarboxylic acids, alkylglyceryl sulfonates, fatty acid glyceryl ester sulfonates, alkylphenol polyglycol ether sulfates, paraffinsulfonates, alkyl phosphates, acyl isothionates, acyl taurates, acyl methyl taurates, alkylsuccinic acids, alkenylsuccinic acids or the monoesters or monoamides thereof, alkylsulfosuccinic acids or the amides thereof, mono- and diesters of sulfosuccinic acids, sulfated alkylpolyglycosides, alkylpolyglycol carboxylates and hydroxyalkyl sarcosinates.

Suitable anionic surfactants are fatty alcohol sulfates of fatty alcohols having, for example, 8 to 22, preferably 10 to 18, carbon atoms, C₁₂-C₁₈-alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate.

Further suitable anionic surfactants are sulfated ethoxyated C₈-C₂₂-alcohols (alkyl ether sulfates) or the soluble salts thereof. Compounds of this type are prepared, for

example, by first alkoxyating a C₈-C₂₂-alcohol, preferably a C₁₀-C₁₈-alcohol, e.g. a fatty alcohol, and then sulfating the alkoxylation product. Ethylene oxide is preferably used for the alkoxylation, from 1 to 50, preferably from 1 to 20, mol of ethylene oxide being used per mole of alcohol. The alkoxylation of the alcohols can, however, also be
5 carried out with propylene oxide alone and, if appropriate, butylene oxide. Those alkoxyated C₈-C₂₂-alcohols which comprise ethylene oxide and propylene oxide or ethylene oxide and butylene oxide or ethylene oxide and propylene oxide and butylene oxide are also suitable. The alkoxyated C₈-C₂₂-alcohols may comprise the ethylene oxide, propylene oxide and butylene oxide units in the form of blocks or in random
10 distribution. Depending on the type of alkoxylation catalysts, alkyl ether sulfates having a broad or narrow alkylene oxide homolog distribution can be obtained.

Further suitable anionic surfactants are alkanesulfonates, such as C₈-C₂₄-alkanesulfonates, preferably C₁₀-C₁₈-alkanesulfonates, and soaps, such as, for
15 example, the sodium and potassium salts of saturated and/or unsaturated C₈- to C₂₄-carboxylic acids.

Further suitable anionic surfactants are linear C₈-C₂₀-alkylbenzenesulfonates ("LAS"), preferably linear C₉-C₁₃-alkylbenzenesulfonates and C₉-C₁₃-alkyltoluenesulfonates.
20

Other suitable anionic surfactants are C₈-C₂₄-olefin sulfonates and disulfonates, which may also be mixtures of alkene- and hydroxyalkanesulfonates or -disulfonates, alkyl ester sulfonates, sulfonated polycarboxylic acids, alkylglyceryl sulfonates, fatty acid glyceryl ester sulfonates, alkylphenol polyglycol ether sulfonates, paraffin sulfonates
25 having about 20 to about 50 carbon atoms (based on paraffin or paraffin mixtures obtained from natural sources), alkyl phosphates, acyl isothionates, acyl taurates, acyl methyl taurates, alkylsuccinic acids, alkenylsuccinic acids or the monoesters or monoamides thereof, alkylsulfosuccinic acids or the amides thereof, mono- and diesters of sulfosuccinic acids, acyl sarcosinates, sulfated alkylpolyglucosides, alkylpolyglycol
30 carboxylates and hydroxyalkyl sarcosinates.

The anionic surfactants are added to the composition according to the invention, preferably in the form of salts. Suitable cations in these salts are alkali metal ions, such as sodium, potassium and lithium, and ammonium salts, such as, for example,
35 hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium salts.

Individual anionic surfactants or a combination of different anionic surfactants may be used. It is possible to use anionic surfactants from only one class, for example only
40 fatty alcohol sulfates or only alkylbenzenesulfonates, but it is also possible to use

surfactant mixtures from different classes, for example a mixture of fatty alcohol sulfates and alkylbenzenesulfonates.

In a further embodiment of the present invention, a cationic surfactant may additionally
5 be introduced into the electrolyte solution.

If a cationic surfactant is used in the process according to the invention, this is preferably selected from the group consisting of tetraalkylammonium salts, imidazolinium salts and amine oxides.

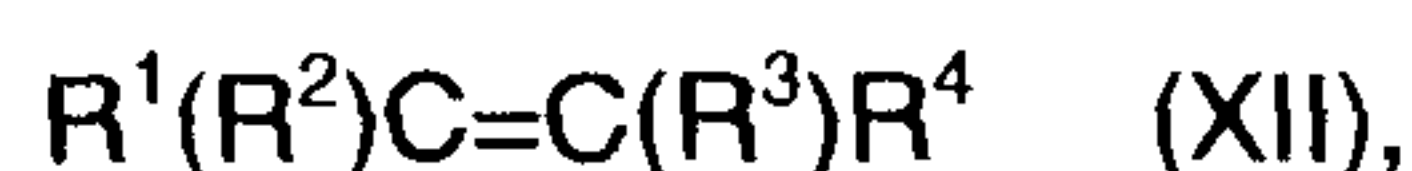
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It is furthermore possible to use cationic surfactants, as described in WO 99/19435. Examples are C₈-C₁₆-dialkyldimethylammonium salts, dialkoxymethylammonium salts or imidazolinium salts having a long-chain alkyl radical.

15 It is possible to use individual cationic surfactants or a combination of different cationic surfactants. It is possible to use cationic surfactants from only one class, but it is also possible to use surfactant mixtures from different classes.

In a further embodiment of the present invention, an amphoteric surfactant may
20 additionally be introduced into the electrolyte solution.

If an amphoteric surfactant is used in the process according to the invention, this can be selected from the group consisting of the surfactants comprising carboxylic acids, preferably ethylenically unsaturated carboxylic acids, and furthermore comprises at
25 least one ethylenically unsaturated monomer unit of the general formula (XII)



where R¹ to R⁴, independently of one another, are -H, -CH₃, a straight-chain or
30 branched saturated alkyl radical having 2 to 12 carbon atoms, a straight-chain or branched, mono- or polyunsaturated alkenyl radical having 2 to 12 carbon atoms, alkyl or alkenyl radicals as defined above which are substituted by -NH₂, -OH or -COOH, a hetero atomic group having at least one positively charged group, a quaternized nitrogen atom or at least one amino group having a positive charge in the pH range
35 from 2 to 11, or are -COOH or -COOR⁵, where R⁵ is a saturated or unsaturated, straight-chain or branched hydrocarbon radical having 1 to 12 carbon atoms.

Examples of the abovementioned monomer units of the formula (XII) are diallylamine, methyldiallylamine, tetramethylammonium salts, acrylamidopropyl(trimethyl)ammonium
40 salts (R¹, R² and R³ = H, R⁴ = C(O)NH(CH₂)₂N⁺(CH₃)₃X⁻) or

methacrylamidopropyl(trimethyl)ammonium salts (R^1 and $R^2 = H$, $R^3 = CH_3$, H , $R^4 = C(O)NH(CH_2)_2N^+(CH_3)_3X^-$).

5 Particularly preferred amphoteric surfactants comprise, as monomer units, derivatives of diallylamine, in particular dimethyldiallylammonium salt and/or methacrylamidopropyl(trimethyl)ammonium salt, preferably in the form of the chloride, of the bromide, of the iodide, of the hydroxide, of the phosphate, of the sulfate, of the hydrogen sulfate, of the ethylsulfate, of the methylsulfate, of the mesylate, of the tosylate, of the formate or of the acetate, in combination with monomer units from the
10 group consisting of ethylenically unsaturated carboxylic acids.

Individual amphoteric surfactants or a combination of different amphoteric surfactants may be used.

15 For the purposes of the present invention, it is also possible to use surfactants of different classes, for example anionic surfactants with cationic surfactants, amphoteric surfactants with nonionic surfactants, etc., in the composition according to the invention. Surfactants from one, two, three or four different surfactant classes (nonionic, anionic, cationic and amphoteric) may be used.

20 The electrolytic treatment according to the invention can furthermore be carried out in the presence of assistants known per se to the person skilled in the art. For example, the extract of the *Quillaja saponaria* tree may be mentioned in this context. This extract comprises the triterpenoid saponin. The concentration of the extract in the electrolysis
25 is chosen so that the concentration of the triterpenoid saponin in the electrolyte solution is from 0.3 to 10 ppm.

A further subject of the invention is the use of nonionic surfactants in electrolytic treatments of metal-containing solutions, the surfactant reducing the surface tension of
30 the electrolyte solution at a surfactant concentration of 0.2% by weight and a temperature of 24°C in an aqueous solution comprising 190 g/l of sulfuric acid and 157 g/l of copper sulfate, which is diluted with water in a ratio of 1:10. The nonionic surfactants furthermore preferably have a foam volume of at least 10 ml, particularly preferably at least 25 ml, especially preferably at least 40 ml, in a solution comprising
35 50 g of an aqueous solution with 190 g/l of sulfuric acid and 157 g/l of copper sulfate with 0.5% by weight of the surfactant, based on the solution, after shaking twenty times for 5 seconds in each case.

40 In a preferred embodiment, the nonionic surfactant is selected from the group consisting of alkoxyated C_4 - to C_{22} -alcohols, alkylpolyglucosides, N-alkylpolyglucosides, N-alkylglucamides, fatty acid alkoxyates, fatty acid polyglycol

esters, fatty acid amine alkoxylates, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, N-alkoxypolyhydroxy-fatty acid amides, N-aryloxypolyhydroxy-fatty acid amides, polyisobutene alkoxylates, polyisobutene/maleic anhydride derivatives, fatty acid glycerides, sorbitan esters, polyhydroxy-fatty acid derivatives, polyalkoxy-fatty acid derivatives and bisglycerides.

Further details relating to the nonionic surfactants can be found in the above statements regarding the process according to the invention.

The present invention furthermore relates to a process for the electrolytic treatment of metal-containing solutions, at least one nonionic surfactant being used in the electrolyte solution, the surfactant being selected from the group consisting of alkoxylated C₄- to C₂₂-alcohols, alkylpolyglucosides, N-alkylpolyglucosides, N-alkylglucamides, fatty acid alkoxylates, fatty acid polyglycol esters, fatty acid amine alkoxylates, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, N-alkoxypolyhydroxy-fatty acid amides, N-aryloxypolyhydroxy-fatty acid amides, polyisobutene alkoxylates, polyisobutene/maleic anhydride derivatives, fatty acid glycerides, sorbitan esters, polyhydroxy-fatty acid derivatives, polyalkoxy-fatty acid derivatives and bisglycerides.

In addition to the abovementioned nonionic surfactants, surfactants selected from the group consisting of

- block copolymers of ethylene oxide and propylene oxide,
- block copolymers of ethylene oxide, propylene oxide and butylene oxide,
- block copolymers blocked at one or both ends and comprising ethylene oxide and propylene oxide or ethylene oxide, propylene oxide and butylene oxide,
- natural extracts from the *Quillaja saponaria* tree, and the compounds which are referred to as saponin and are commercially available under the name Mistop[®] can also be used.

Regarding the individual surfactant classes and the specific information relating thereto, reference is made to the above statements.

In a first preferred embodiment, the nonionic surfactant comprises alkylpolyglucosides having 6 to 22 carbon atoms in the alkyl chain and 1 to 20 glucose units.

In a second preferred embodiment, the nonionic surfactant comprises C₁₂₋₁₈-fatty alcohol ethoxylates which have been reacted with from 2 to 80 ethylene oxide units.

The invention is further illustrated by the following examples:

Examples

5

Determination of the surface tension

To determine the surface tension a tensiometer K 100 (ring method) of the company Krüss, Hamburg was employed. Measurements were carried out at 24°C and a surfactant concentration of 0.2 % by weight in the aqueous base formulation. The base
10 formulation consisted of an aqueous solution of 190 g/l sulfuric acid (calculated 100 %) and 157 g/l copper sulfate, which is diluted with water in a ratio 1:10. The surface tension of the base formulation is 72 mN/m, this value was taken as 100 % value. The reduction of the surface tension by employing the surfactant system in % is summarized in Table 1, column 1.

15

Determination of the foam volume

The foam volume of 50 g of a 0.5 % by weight aqueous solution of 190 g/l sulfuric acid and 157 g/l copper sulfate was determined after shaking 20 times at room temperature during 5 seconds. The results are summarized in Table 1, column 2. In each case the
20 total volume was determined and reduced by the volume of the initial solution (about 50 ml).

Effect on the formation of acidic mist

To determine the acidic mist during Cu electrolysis the gas phase over the electrolytical
25 cell was hermetically shut. A stream of nitrogen was introduced through an opening in a height of about 30 cm over the cell, which could escape, together with the gases and mist formed during electrolysis, through a second opening opposite to the first opening through two absorption bottles connected in series and filled with 2 molar NaOH.

30 After an operational period of 36 h the remaining NaOH content and the volume of the washing liquid was determined. From this the amount of the emitted sulfuric acid could be determined. The percentual decrease of the amount as opposed to the amount determined without addition of surfactants, demonstrates the advantage of the process according to the invention and is shown in Table 1, column 3.

Table 1

Surfactant System	Reduction of surface tension [%]	Foam in [ml] after shaking 20 times	Reduction of H ₂ SO ₄ content in the mist [%]
No addition	0	<5	0
Alkylpolyglucoside (Lutensol GD 70)	60	55	30
Lutensol GD 70/C ₁₂ C ₁₄ fatty alcohol +25 EO 1/1	56	50	52
Castor oil ethoxylate (Emulan EL)/Lutensol GD 70 1/1	55	45	45
C ₁₂ C ₁₄ fatty alcohol + EO	40	40	25
Lutensol GD 70/C ₁₃ Oxoalcohol + 6 EO + 3PO 1/1	50	28	32
fatty alcohol ethoxylate (Emulan P)	60	20	55
Nonylphenol + 7 EO	45	30	28
C ₁₃ Oxoalcohol + 8 EO	53	30	18
Hexanol +6 EO	20	20	15
Pluronic PE 9200	47	35	17
C ₁₃ C ₁₅ end groups capped with methyl	56	15	27
C ₁₃ Oxoalcohol + 6,2 EO + 2,8	60	10	32

- 5 The employed brands Lutensol, Emulan and Pluronic are commercial products of BASF Aktiengesellschaft, Ludwigshafen.

The abbreviations +EO, +PO, and +BuO mean alkoxylation products with ethylene oxide, propylene oxide and butylene oxide as block copolymers.

- 10 The geometry of the employed cell and the parameters of electrolysis are shown in Table 2:

- 28 -

Table 2

	cathode surface / cell volume	ca. 15 m ⁻¹
	concentration of the surfactant system	50 ppm
	Cu-concentration	45 g/l
5	H ⁺ ion concentration in the electrolyte	180 g/l
	temperature	ca. 50°C
	current density	300 A/m ² (± 10 %)

10 The visual inspection of the cathodes did not show any negative impact of the use of the surfactants on the quality of the electrodes or the deposited copper.

CLAIMS:

1. A process for the electrolytic treatment of metal-containing solutions, wherein at least one nonionic surfactant is used in the electrolyte solution, the surfactant reducing the surface tension of the electrolyte solution at a surfactant concentration of 0.2% by weight and a temperature of 24°C in an aqueous solution with 190 g/l of sulfuric acid and 157 g/l of copper sulfate, which is diluted with water in a ratio of 1:10, by from 20 to 60%, wherein the nonionic surfactant is selected from the group consisting of alkylpolyglucosides and optionally further comprising alkoxylated C₄- to C₂₂-alcohols, N-alkylpolyglucosides, N-alkylglucamides, fatty acid alkoxylates, fatty acid polyglycol esters, fatty acid amine alkoxylates, optionally endcapped fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, N-alkoxypolyhydroxy-fatty acid amides, N-aryloxypolyhydroxy-fatty acid amides, polyisobutene/maleic anhydride derivatives, fatty acid glycerides, sorbitan esters, polyhydroxy-fatty acid derivatives, polyalkoxy fatty acid derivatives and/or bisglycerides and the electrolytic treatment serves for separating substances, working up ores and/or purifying metals.
2. The process according to claim 1, wherein the surfactant has a foam volume of at least 10 ml in a solution comprising 50 g of an aqueous solution with 190 g/l of sulfuric acid and 157 g/l of copper sulfate with 0.5% by weight of the surfactant, based on the solution, after shaking twenty times in the course of 5 seconds.
3. The process according to claim 1 or 2, wherein the electrolytic working-up is effected starting from an acidic aqueous solution of the metal as the electrolyte solution.

- 30 -

4. The process according to claim 3, wherein the acidic aqueous solution of the metal is obtained by the following process steps:

(a) leaching of the metal from a metal-containing starting material by a treatment thereof with acids or alkalis, a metal-containing mother liquor being obtained;

(b) treatment of the metal-containing mother liquor with an organic phase which comprises an extracting agent (complexing agent) suitable for the metal to be extracted, the metal being transferred to the organic phase;

(c) treatment of the organic phase with an acidic aqueous solution, the metal being transferred to the acidic aqueous solution.

5. The process according to claim 3 or 4, wherein the acidic aqueous solutions of the metal are chromium- or copper-containing solutions comprising sulfuric acid.

6. The process according to any one of claims 1 to 5, wherein the nonionic surfactant is an alkylpolyglucoside having 6 to 22 carbon atoms in the alkyl chain and 1 to 20 glucose units.

7. The process according to any one of claims 1 to 5, wherein the additional nonionic surfactant is a C₁₂₋₁₈-fatty alcohol ethoxylate which has been reacted with from 2 to 80 ethylene oxide units.

8. The process according to any one of claims 1 to 7, wherein the concentration of the nonionic surfactant in the electrolyte solution is from 0.001 to 0.5% by weight, based on the solution.

- 31 -

9. The process according to any one of claims 1 to 8, wherein a nonionic surfactant selected from the group consisting of block copolymers of ethylene oxide and propylene oxide, block copolymers of ethylene oxide, propylene oxide and butylene oxide, block copolymers blocked at one or both ends and comprising ethylene oxide and propylene oxide or ethylene oxide, propylene oxide and butylene oxide, and saponins, is additionally used.

10. The use of nonionic surfactants in electrolytic treatments of metal-containing solutions, wherein the surfactant reduces the surface tension of the electrolyte solution at a surfactant concentration of 0.2% by weight and a temperature of 24°C in an aqueous solution with 190 g/l of sulfuric acid and 157 g/l of copper sulfate, which is diluted with water in a ratio of 1:10, by a value of from 20 to 60%, wherein the nonionic surfactant is selected from the group consisting of alkylpolyglucosides and optionally further comprising alkoxylated C₄- to C₂₂-alcohols, N-alkylpolyglucosides, N-alkylglucamides, fatty acid alkoxylates, fatty acid polyglycol esters, fatty acid amine alkoxylates, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, N-alkoxypolyhydroxy-fatty acid amides, N-aryloxypolyhydroxy-fatty acid amides, polyisobutene alkoxylates, polyisobutene/maleic anhydride derivatives, fatty acid glycerides, sorbitan esters, polyhydroxy-fatty acid derivatives, polyalkoxy-fatty acid derivatives and/or bisglycerides and the electrolytic treatment serves for separating substances, for working up ores and/or for purifying metals.

11. The use according to claim 10, wherein the surfactant has a foam volume of at least 10 ml in a solution comprising 50 g of an aqueous solution with 190 g/l of sulfuric acid and 157 g/l of copper sulfate with 0.5% by weight of the surfactant, based on the solution, after shaking twenty times for 5 seconds in each case.

- 32 -

12. The use according to claim 10, wherein a nonionic surfactant selected from the group consisting of block copolymers of ethylene oxide and propylene oxide, block copolymers of ethylene oxide, propylene oxide and butylene oxide, block copolymers blocked at one or both ends and comprising ethylene oxide and propylene oxide or ethylene oxide, propylene oxide and butylene oxide, and saponins, is additionally used.

13. A process for the electrolytic treatment of metal-containing solutions, wherein at least one nonionic surfactant is used in the electrolyte solution, the surfactant being selected from the group consisting of alkylpolyglucosides and optionally further comprising alkoxylated C₄- to C₂₂-alcohols, N-alkylpolyglucosides, N-alkylglucamides, fatty acid alkoxylates, fatty acid polyglycol esters, fatty acid amine alkoxylates, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, N-alkoxypolyhydroxy-fatty acid amides, N-aryloxypolyhydroxy-fatty acid amides, polyisobutene alkoxylates, polyisobutene/maleic acid anhydride derivatives, fatty acid glycerides, sorbitan esters, polyhydroxy-fatty acid derivatives, polyalkoxy-fatty acid derivatives and/or bisglycerides and the electrolytic treatment serves for separating substances, working up ores and/or purifying metals.

14. The process according to claim 13, wherein the nonionic surfactant is an alkylpolyglucoside having 6 to 22 carbon atoms in the alkyl chain and 1 to 20 glucose units.

15. The process according to claim 13, wherein the additional nonionic surfactant is a C₁₂₋₁₈-fatty alcohol ethoxylate which has been reacted with from 2 to 80 ethylene oxide units.

- 33 -

16. The process according to any one of claims 13 to 15, wherein a nonionic surfactant selected from the group consisting of block copolymers of ethylene oxide and propylene oxide, block copolymers of ethylene oxide, propylene oxide and butylene oxide, block copolymers blocked at one or both ends and comprising ethylene oxide and propylene oxide or ethylene oxide, propylene oxide and butylene oxide, and saponins, is additionally used.

17. The use of nonionic surfactants in electrolytic treatments of metal-containing solutions, wherein the nonionic surfactant is selected from the group consisting of alkylpolyglucosides and optionally further comprising alkoxylated C₄- to C₂₂-alcohols, N-alkylpolyglucosides, N-alkylglucamides, fatty acid alkoxylates, fatty acid polyglycol esters, fatty acid amine alkoxylates, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, N-alkoxypolyhydroxy-fatty acid amides, N-aryloxypolyhydroxy-fatty acid amides, polyisobutene alkoxylates, polyisobutene/maleic anhydride derivatives, fatty acid glycerides, sorbitan esters, polyhydroxy-fatty acid derivatives, polyalkoxy-fatty acid derivatives and/or bisglycerides.

18. The use according to claim 17, wherein the nonionic surfactant is an alkylpolyglucoside having 6 to 22 carbon atoms in the alkyl chain and 1 to 20 glucose units.

19. The use according to claim 17, wherein the additional nonionic surfactant comprises C₁₂₋₁₈-fatty alcohol ethoxylates which have been reacted with from 2 to 80 ethylene oxide units.

20. The use according to any one of claims 17 to 19, wherein a nonionic surfactant selected from the group consisting of block copolymers of ethylene oxide and propylene oxide, block copolymers of ethylene oxide, propylene oxide

- 34 -

and butylene oxide, block copolymers blocked at one or both ends and comprising ethylene oxide and propylene oxide or ethylene oxide, propylene oxide and butylene oxide, and saponins, is additionally used.

21. Process according to any one of claims 1 to 9, wherein the surfactant reduces the surface tension by from 25 to 55%.