ADDITIVE FOR CHROMIUM ELECTROLYTES

Inventors: Lorenz Laser, Langenfeld (DE); Matthias Weiss, Altfussheim (DE); Frank Honselmann, Weingarten (DE)

Correspondence Address:
FOLEY AND LARDNER LLP
SUITE 500
3000 K STREET NW
WASHINGTON, DC 20007

Assignee: GOLDSCHMIDT TIB GMBH

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ABSTRACT
The fluorine surfactant-free, long-term-stable and biodegradable additive for chromium electrolytes lowers the surface tension and hence improves the chromium deposition process, especially in the application for the electrolytical chromium-plating. Preferred additives are CH$_n$(CH$_2$)$_n$SO$_3$H and the salts thereof with n from 10 to 18. These additives are also useful as component in polymer mordants as pretreatments for polymer metallizations.
The present invention relates to the field of additives for chromium electrolytes, especially to the field of the additive surfactants for chromium electrolytes, and to the field of the additives for chrome acid solutions applied for polymer metallizations.

For electrochemical chromium-plating, which typically takes place in chromium electrolytes at high concentration of aggressive chrome acid, a wide variety of different additives are proposed in order to prevent the formation of aggressive spray mists being caused by the formation of hydrogen under the electrolysing conditions. However, it has been found to be difficult in practice to find compounds (additives) which, on the one hand, have the intended favourable properties but, on the other hand, survive the aggressive conditions in the chromium-plating unchanged or at least over a longer time period.

Particularly suitable for the reduction of spray mist are foam-forming wetting agents (surfactants) which, by lowering the surface tension, not only reduce the spray losses but also greatly reduce the entrainment of the chromium electrolyte. For this purpose, for example perfluoroalkylsulfonic acids (PFOSAs) have been proposed. These products are also stable to the highly oxidative properties of chrome acid. However, their use is especially in view of the environment—problematic and already banned in many applications. These fluorine surfactants are not biodegradable, since they do not undergo any photolytic, hydrolytic, oxidative or reductive transformation whatsoever. They are biodegraded neither aerobically nor anaerobically. Owing to their physicochemical properties, perfluoroalkylsulfonic acids remain as end metabolites and are not degraded any further.

DE-B 1 034 945 has proposed already up to 10 g/l alkylmethylsulphonates (i.e. salts of bis or monooalkylmethan sulfonic acid) as additives, which are said to have the properties of a surfactant and simultaneously bring about process-improving influences with regard to the smoothing of the chromium layer. However, these additives are unsuitable in practice, since they decompose in the course of chromium-plating within a very short time.

From DE-C 37 23 198 up to 10 g/l of perfluoralkyl groups containing esters of phosphoric acid are known as additives, which are additionally added to a chromium electrolyte, having already a content of 125 mg/l tetracylammonium perfluoroethyl sulfonate besides 250 g/l CrO and 2.5 g/l sulphate ions. It is said that no spray mist is present under a surface tension below 30 mN/m and a temperature of 55°C.

DE-C 39 33 896 describes the addition of saturated aliphatic sulfonic acids or their salts or their halogen derivatives having maximum 2 C atoms and maximum 6 sulfonic acid groups during the electrolysing chromium-plating. The addition of fluoro compounds are also mentioned. The working current density ranges from 10 to 1200 A/dm². In specific examples 10 mg/l ammonium fluoroocetate is applied as wetting agent based on 300 g/l CrO and 1.3% (related to CrO) HSO₄, the current density is 50 A/dm² and the temperature is 55°C; the additive is a saturated aliphatic sulfonic acid having 1 C and 1 sulfonic acid group (3.2 g/l).

The galvanic chromium electrolytes of DE-A 43 05 732 contains 0.4 to 10 g 1,3-propanedisulfonic acid-2-sulfonic acid and/or 1,2,3-propentrisulfonic acid or the salts thereof besides 150 to 400 g/l CrO and 1 to 4% by weight (related to CrO) HSO₄. In a specific example 3 to 5 g additive are applied at 55°C and a current density of 50 A/dm².

The galvanic chromium electrolyte of DE-C 44 30 923 contains 2 to 10 g/l methanesulfonic acid and 2 to 20 g/l MgSO₄ as additive to CrO. In a specific example there are also 0.1 ml/l tetracylammonium perfluoroethyl sulfonate and 1 g/l sugar present. The chromium deposition is conducted at 40°C and a current density of 1.82 A/dm² and during 1 h.

From DE-C 198 28 545 a chromium electrolyte is known containing besides 100 to 600 g/l CrO and sulphate ions in a relation of Cr⁺⁺⁺SO₄⁻⁻ from 90 to 120 to 1 additionally 0.01 to 3.0 g/l Na₂-hydroxyethan sulfonate or its free acid. At a current density of 30 to 90 A/dm² the chromium deposition is conducted in 3 steps from 44 to 57°C during more than 1 h.

The chromium layers of DE-A 102 55 853 are produced in an electrolyte containing 50 to 600 g/l CrO, 0.5 to 10 g/l H₂SO₄, 1 to 20 g/l of an aliphatic sulfonic acid having 1 to 6 C atoms and 10 to 200 g/l of a molybdate, vanadate or zirconate. In the examples the electrolyte contains 250 g/l CrO, 2.5 g/l H₂SO₄, 4 g/l methan sulfonic acid and 100 g/l (NH₄)₆Mo₇O₂₄·4H₂O; the electrolyse is conducted at 55°C and at a current density of 40 A/dm² during 30 min. or at 50 A/dm during 120 min.

The electrolyte of DE-B 10 004 019 370 does not contain—compared with the beforementioned solution—molybdates, vanadates or zirconates. In the examples methan sulfonic acid (as a solution of 70%) in an amount of 9 ml/l at 60 to 70°C during 30 min. at 30 to 80 A/dm² is applied. The current efficiency is at ±12% (as in the beforementioned solution).

The chromium electrolytes known from the prior art are either only suitable for very specific applications, or show the disadvantages—already discussed before—caused by a fluoro part in the additive molecule.

It is therefore an object of the present invention to find an additive for chromium electrolytes as well as for chrome acid solutions applied for polymer metallizations which reduces the disadvantages detailed above.

This object is achieved by an additive for aqueous chrome acid solutions, being free of fluorine surfactants and being biodegradable and having in a chrome acid solution which contains the said additive a surface tension of ±35 mN/m, and having in the application in the electrolytical chromium-plating, determined at 45°C and 6000 Ah of charge passage, in the chrome acid solution which contains the said additive a stability of ±4 h.

It should be noted that the term “additive” within the present invention can relate either to an individual substance or to a substance mixture; for reasons of readability and clarity, however, “additive” is only referred to in the singular within the present invention. If the additive used is a substance mixture, what is meant in general is that the substance mixture has the properties described, but the individual components of the mixture may also only have the properties described.

In the context of the present invention, “stability” means especially the lasting efficacy of the additive with regard to the surface tension under the chemically demanding conditions of a chromium electrolyte in the application in the electrolytical chromium-plating. In particular, in the context
of the present invention, “stability” over a certain period means that the surface tension increases by not more than 5 mN/m over this time.

[0017] In particular, in the context of the present invention, “chromium electrolyte(s)” and/or “chromic acid solution(s)” are understood to mean chromium electrolytes or chromic acid solutions which—besides chromic acid and water—comprises catalysts and/or further acids among other components.

[0018] The content of chromic acid in the solution and the electrolyte, respectively, related to CrO₃—is normally between 120 and 450 g/l.

[0019] It has been found that, when such an additive according to the present invention is added to chromic acid solutions in most applications, but especially in chromium-plating operations, at least one, usually more than one, of the following advantages can be achieved:

[0020] The use of the inventive additive improves the operation of the chromium electrolytes in a lasting manner.

[0021] The use of the additive leads to the formation of significantly smaller gas bubbles, which is associated with a drastic reduction in the emission a nuisance.

[0022] It is likewise possible to considerably reduce entrainment losses.

[0023] Depending on the process, when the additive is used, the dispersibility of the electrolytes in many applications is improved.

[0024] The additive does not adversely affect the properties of the chromium layer, not even with regard to layer properties such as hardness, crack network or structure.

[0025] A chromic acid solution, which contains e.g. 0.1 g/l of additive and 250 g/l of chromic acid, preferably has a surface tension of ≤28 mN/m, even more preferably ≤25 mN.

[0026] A chromic acid solution, which contains e.g. 0.1 g/l of additive and 400 g/l of chromic acid, preferably has a surface tension of ≤35 mN/m, even more preferably ≤30 mN/m.

[0027] An additive according to the present invention has at 45°C, in a chromium electrolyte which contains 0.1 g/l and 270 g/l of chromic acid preferably has a stability of ≥8 h, even more preferably of ≥12 h.

[0028] The additive is free of fluorine surfactants. This is understood to mean especially that the additive does not contain any organofluorine compound, or that the proportion of organofluorine compounds in the additive is below the detection limit. Furthermore, the additive is biodegradable. This is understood to mean especially that, according to OECD criteria, ≥99.5%, preferably ≥99.8%, of the additive has degraded in the screening test after 8 days. In many applications, such an additive contributes to minimizing expenditure with regard to preventing the contamination of the environment, or even to making it entirely superfluous.

[0029] A chromium electrolyte, which contains e.g. 0.1 g/l of additive and 250 g/l of chromic acid, preferably has a current density of 30 A/dm² to 60 A/dm², even more preferably 40 A/dm² to 50 A/dm².

[0030] A chromium electrolyte, which contains e.g. 0.2 g/l of additive and 350 to 400 g/l of chromic acid, preferably has a current density of 5 A/dm² to 25 A/dm², even more preferably 8 A/dm² to 20 A/dm².

[0031] In a preferred embodiment of the present invention, the additive comprises at least a surfactant selected from the group consisting of long-chain alkylmonosulphonic acids, long-chain alkylhydroxysulphonic acids, long-chain alkylpolyaminosulphonic acids, salts of the long-chain alkylmonosulphonic acids, salts of the long-chain alkylhydroxysulphonic acids and salts of the long-chain alkylpolyaminosulphonic acids.

[0032] In this context, “long-chain” is understood to mean at least 4 C atoms. The long-chain alkyl radicals are preferably unbranched, but it is also possible to use branched alkyl-Imono-, di- and poly-sulphonic acids and salts thereof. The salts used are alkali metal salts, alkaline earth metal salts, NH₄⁺ salts, NR⁺ salts (where R=C₁ to C₄ alkyl). Polysulphonic acids have 3 to 6 sulfonic acid group per molecule.

[0033] In a preferred embodiment of the present invention, the additive comprises, as surfactant at least one compound CH₁(CH₂)nSO₃H or salts thereof, where n is 10 to 18. In practice, these compounds often have a particularly elevated stability and are preferred in this respect. More preferably, the additive comprises such surfactants, where n is 12 to 17; even more preferably n is 14 to 16.

[0034] The present invention also relates to use of the inventive additive as a smoothing agent in chromium electrolytes. Usually the concentration of additive is between 0.05 g/l and 20 g/l, preferably from 0.1 g/l to 10 g/l, and more preferably from 1 g/l to 3 g/l.

[0035] The present invention also relates to use of the inventive additive as an additive in polymer mordants. It has been found that, surprisingly, the inventive additive can be used not only in chromium electrolytes but also in this pre-treatment of polymer metatizations. In these mordants, the additive has a wetting effect and lowers the surface tension of the chromic acid-containing mordants. The positive influence on chromic acid mist formation and entrainment is comparable to the effects described above for chromium electrolytes. The amounts of surfactant in a chromic acid-containing mordant are basically identical with its amounts in chromium electrolytes.

[0036] The aforementioned components to be used in accordance with the invention, and those described in the working examples, are not subject to any particular exceptional conditions in their size, three-dimensional configuration, material selection and technical design, such that the selection criteria known in the field of use can be used without restriction.

[0037] Further details, features and advantages of the subject-matter of the invention are evident from the description of an inventive example.

EXAMPLE

[0038] In a bath containing 400 g/l of chromic acid, 5 g/l of phosphoric acid, 3 g/l of potassium nitrate, 3 g/l of rare earth fluorides (e.g. cerium, lanthanum) and, as the inventive additive, 2 g/l of sodium pentadecanesulphonate (i.e. in the general formula is n=14), at a temperature of 20 to 25°C, and a current density of 20 A/dm², a black chromium coating was performed.

[0039] It was possible to lower the surface tension to a value of 29.8 mN/m by the addition of the inventive additive. The chromic acid solution continued to be stable after an application time of 4 h during the electrolytical chromium-plating, i.e. the surface tension is only increased by much less than 5 mN/m.
In the subsequent studies, it was found that the chromium layer deposited had a very uniform appearance. In particular, the dispersibility of the electrolyte was improved. The testing of several sheets gave a dispersion of the chromium layer which was improved by an average of 1.0 to 1.5 cm according to corresponding tests in a Hull cell.

Materials and Testing Methods

The surface tension was measured with a K8 tensiometer from Krüss GmbH in Hamburg. The unit works by the Du Noüy ring method. The force of a liquid lamella drawn up by the ring is measured. The liquid is raised until there is contact of the ring with the surface. With the aid of a torsion balance, the force required to raise the platinum ring is measured. The further the ring is pulled out of the liquid, the greater this is. At the point of the highest force applied, when the liquid lamella breaks off, there is a force equilibrium from which the surface tension of the liquid can be calculated. The ring geometry is taken into account by means of an instrument-specific calibration by the manufacturer.

The current density is determined by means of a measurement of the currents with an ampereter and reference to the known surface geometry of the components to be chromium-plated.

The dispersibility of an electrolyte is determined by the evaluation of sheets after tests with the electrolyte in a Hull cell. The dispersion of the chromium layer is determined by measuring the expansion of the coated surface on the sheet after it has passed through the test run. The measurement is effected with a ruler. In general, several sheets are coated and measured under the same conditions in order to obtain reliable averages.

Additive for chromic acid solutions, being free of fluorine surfactants and biodegradable and having in a chromic acid solution which contains the said additive a surface tension of \( \geq 30 \) mN/m, and having in the application in the electrolysise chromium-plating, determined at 45° C. and 6000 Ah of charge passage, in the chromic acid solution which contains the said additive a stability of \( \geq 4 \) h.

Additive according to claim 1, comprised in a chromic acid solution and used in the electrolysise chromium-plating, this chromic acid solution has a current density of \( 35 \) A/dm\(^2\) to \( 60 \) A/dm\(^2\).

Additive according to claim 1, comprising at least one surfactant from the group consisting of long-chain alkylmonosulphonic acids, long-chain alkylsulphonic acids, long-chain alkylpolysulphonic acids, salts of the long-chain alkylmonosulphonic acids, salts of the long-chain alkylsulphonic acids and salts of the long-chain alkylpolysulphonic acids.

Additive according to claim 1, comprising at least one surfactant being \( \text{CH}_n(\text{CH}_2)_{\text{n}+1}\text{SO}_3\text{H} \) or salts thereof, where \( n \) is 10 to 18.

Method of use of an additive according to claim 1 as a smoothing agent in chromium electrolytes.

Method of use according to claim 5, wherein the concentration of the additive is between 0.05 g/l and 20 g/l.

Method of use of an additive according to claim 1 as an additive in polymer binders as pretreatments for polymer metallizations.

Method of use of an additive according to claim 3 as a smoothing agent in chromium electrolytes.

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