A NOVEL ADDITIVE FOR CHROMIUM ELECTROLYTES

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 polymer metallizations.

For electrochemical chromium-plating, which typically takes place in chromium electrolytes at high concentration of aggressive chromic acid, a wide variety of different additives are proposed in order to prevent the formation of aggressive spray mists. However, it has been found to be difficult in practice to find compounds which, on the one hand, have favourable properties but, on the other hand, survive the aggressive conditions in the chromium-plating.

Particularly suitable for the reduction of spray mist are foam-forming wetting agents 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, a wide variety of different products have been proposed, for example perfluoroalkylsulphonic acids (PFOAs). These products are also stable to the highly oxidative properties of chromic acid. However, their use is 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, perfluoro alkylsulphonic acids remain as end metabolites and are not degraded any further.

DE 1034945 has proposed alkylmethylsulphonates 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.

It is therefore an object of the present invention to find an additive for chromium electrolytes which reduces the disadvantages detailed above.

This object is achieved by an additive according to Claim 1. Accordingly, an additive, especially a smoothing additive for chromium electrolytes, is provided, characterized in that a chromic acid solution which contains 0.1 g/l of additive and 250 g/l of chromic acid has a surface tension of ≤ 30 mN/m, and 0.1 g/l of additive,

at 45°C and 6000 Ah of charge passage, in a chromic acid solution which contains 270 g/l of chromic acid, has 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 each case is that the substance mixture has the properties described, but the individual components of the mixture may also 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 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.

In particular, in the context of the present invention, "chromium electrolytes" and/or "chromic acid solution operations" are understood to mean chromium electrolytes or chromic acid solutions which comprises catalysts and/or further acids.

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

- The use of the inventive additive improves the operation of the chromium electrolytes in a lasting manner.
- The use of the additive leads to the formation of significantly smaller gas bubbles, which is associated with a drastic reduction in the emission nuisance.
- It is likewise possible to considerably reduce entrainment losses.
- Depending on the process, when the additive is used, the dispersibility of the electrolytes in many applications is improved.

- The additive does not adversely affect the properties of the layer, not even with regard to layer properties such as hardness, crack network, structure, etc.

A chromic acid solution which contains 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.

A chromic acid solution which contains 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.

0.1 g/l of additive at 45°C in a chromium electrolyte which contains 270 g/l of chromic acid preferably has a stability of ≥ 8 h, even more preferably of ≥ 12 h.

In a preferred embodiment of the present invention, 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.

In a preferred embodiment of the present invention, the additive is biodegradable. This is understood to mean especially that, according to OECD criteria, $\geq 99.5\%$, preferably $\geq 99.8\%$, 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.

A chromium electrolyte which contains 0.1 g/l of additive and 250 g/l of chromic acid preferably has a current density of ≥ 30 A/dm^2 to ≤ 60 A/dm^2, even more preferably ≥ 40 A/dm^2 to ≤ 50 A/dm^2.

A chromium electrolyte which contains 0.2 g/l of additive and 350 to 400 g/l of chromic acid preferably has a current density of ≥ 5 A/dm^2 to ≤ 25 A/dm^2, even more preferably ≥ 8 A/dm^2 to ≤ 20 A/dm^2.

In a preferred embodiment of the present invention, the additive comprises a material selected from the group of long-chain alkylmonosulphonic acids, long-chain alkyldisulphonic acids, long-chain alkylpolysulphonic acids, salts of the

long-chain alkylmonosulphonic acids, salts of the long-chain alkyldisulphonic acids, salts of the long-chain alkylpolysulphonic acids and mixtures thereof.

In this context, "long-chain" is understood to mean C_4 and greater. The long-chain alkyl radicals are preferably unbranched, but it is also possible to use branched alkylmono-, -di- and -polysulphonic acids and salts thereof.

The salts used in a preferred embodiment of the present invention are alkali metal salts, alkaline earth metal salts, NH_4^+ salts, NR_4^+ salts (where R = alkyl) and mixtures thereof.

In a preferred embodiment of the present invention, the additive comprises, as at least one component, the compound $CH_3(CH_2)_nSO_3H$ or salts thereof, where $n \geq 10$ and $n \leq 18$. In practice, these compounds often have a particularly elevated stability and are preferred in this respect.

More preferably, the additive comprises, as at least one component, the compound $CH_3(CH_2)_nSO_3H$ or salts thereof, where $n \geq 12$ and $n \leq 17$; even more preferably, the additive comprises, as at least one component, the compound $CH_3(CH_2)_nSO_3H$ or salts thereof, where $n \geq 14$ and $n \leq 16$.

The present invention also relates to use of the inventive additive as a smoothing agent in chromium electrolytes. In a preferred embodiment of the present invention, the concentration of additive is between ≥ 0.05 g/l and ≤ 20 g/l, more preferably ≥ 0.1 g/l and ≤ 10 g/l, and most preferably ≥ 1 g/l and ≤ 3 g/l.

The present invention also relates to use of the inventive additive as an additive in polymer mordants. The inventors have found that, surprisingly, the inventive additive can be used not only in chromium electrolytes but also in the pretreatment of polymer metallizations. 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 present invention also relates to use of an additive which comprises, as at least one component, the compound $CH_3(CH_2)_nSO_3H$ or salts thereof, where $n \geq 10$ and $n \leq 18$, more preferably $n \geq 12$ and $n \leq 17$, even more preferably $n \geq 14$ and $n \leq 16$, or mixtures thereof, as an additive in polymer mordants.

The aforementioned components to be used in accordance with the invention, and those claimed and 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.

Further details, features and advantages of the subject-matter of the invention are evident from the subclaims and from the description of an inventive example which follows, in which - in a purely illustrative and non-restrictive manner - one use of an inventive additive is detailed.

Example I:

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, at a temperature of 20-25°C and a current density of 20 A/dm^2, a black chromium coating was performed.

It was possible to lower the surface tension to a value of 29.8 mN/m by the addition of the inventive additive.

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 1.0-1.5 cm according to corresponding tests in a Hull cell.

MATERIALS AND METHODS

The surface tension was measured with a K8 tensiometer from Krüss 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 amperemeter 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.

CLAIMS:

1. Additive for aqueous chromic acid solutions, being free of fluorine surfactants and biodegradable, being $CH_3(CH_2)_nSO_3H$ or salt thereof, where n is 12 to 17, wherein said surfactant is the sole surfactant, and having in a chromic 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 chromic acid solution which contains the said additive a stability of ≥ 4 h.

2. Additive according to Claim 1, where n is 14 to 16.

3. Additive according to Claim 1 or 2, wherein a chromic acid solution comprising said additive and used in the electrolytical chromium-plating, this chromic acid solution has a current density of 35 A/dm^2 to 60 A/dm^2.

4. Use of an additive according to one of Claims 1 to 3 as a smoothing agent in chromium electrolytes.

5. The use according to Claim 4, wherein the concentration of the additive is between 0.05 g/l and 20 g/l.

6. Use of an additive according to one of Claims 1 to 3 as an additive in polymer mordants as pretreatments for polymer metallizations.