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ELECTRODEPOSITING BATH AND PROCESS

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This invention relates to novel electrochemical baths and processes employing same. More particularly it relates to electroplating baths wherein the principal or substantially the sole anion employed for the transport of electrical current is derived from an alkane sulfonic acid.

One object of my invention is to provide novel and improved electrochemical baths. Another object is to provide a novel anion for the transport of electrical current in electroplating baths. A further object is to provide electrolytic baths wherein the principal or substantially the sole anion employed for the transport of electrical current is derived from an alkanesulfonic acid. Still another object of my invention is to provide electrolytic baths wherein the principal or sole anion is an alkanesulfonate ion wherein the alkyl group contains between 1 and 5 carbon atoms.

An additional object is to provide electrolytic baths containing as the principal anion an alkanesulfonate ion containing between 1 and 5 carbon atoms in the alkyl group and a minor proportion of an alkanesulfonate containing between about 10 and about 30 carbon atoms in the alkyl group. Still another object of my invention is to provide electrolytic baths adapted to electrodeposit metals upon an aluminum cathode without the necessity of operations adapted to remove the alumina film which is usually present on aluminum. A further object is to provide electrolytic baths especially suitable for electroplating nickel and lead. Other objects will become apparent from the ensuing description of my invention.

I have discovered that alkanesulfonic acids having between about 1 and about 5 carbon atoms in the alkyl group form water-soluble salts of various metals and that these salts are excellent electrolytes in electroplating baths. Electrochemical operations such as electrodeposition of metals proceeds smoothly and with high efficiency when alkanesulfonate anions containing between 1 and 5 carbon atoms in the alkyl group are employed as the principal or sole anionic constituent of the bath.

I have further found that alkanesulfonates having between 1 and 5 carbon atoms in the alkyl group are stable in alkaline, acid or neutral solutions, both hot and cold, and that such solutions undergo no appreciable hydrolysis under ordinary conditions. Where the alkyl group in the alkanesulfonic acid contains more than 5 carbon atoms, metal salts thereof are generally

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"soapy," relative viscous and too low in water solubility to be attractive for plating.

Alkanesulfonic acids suitable for employment for the purposes of my invention may be prepared by a variety of methods. Especially suitable methods comprise the catalytic oxidation of mercaptans or aliphatic sulfides having the formula $R_1S_nR_2$ wherein R_1 or R_2 are alkyl groups and "n" is a positive integer between 1 and 6. Air or oxygen may be used as the oxidizing agent and various nitrogen oxides the employed as catalysts, the oxidation being effected at temperatures below about 300° F. These catalytic oxidation processes are described and claimed in United States Letters Patent 2,433,395 issued to W. A. Proell and B. H. Shoemaker on December 30, 1947, and 2,433,396 issued to W. A. Proell on December 30, 1947. The present application is a continuation in part of S. N. 590,841, now U. S. Patent 2,433,396.

The electrochemical baths are best prepared by dissolving in water an alkanesulfonate salt of the metal which it is desired to treat. Another method of preparing the bath, which method is ordinarily not as desirable, is to prepare a solution of the sulfonate of the metal to be treated by a double decomposition reaction, i. e., by reacting an aqueous solution of a sulfonate of a different metal with a non-sulfonate salt of the metal to be treated. The proportion of sulfonate to be used in the bath can be varied over a wide range, depending upon the particular metal which is to be electrochemically treated, the solubility of the specific sulfonate, the bath temperature and other bath variables such as the voltage and current density, the type of process in contemplation, etc. Generally the sulfonate content of the electrolytic baths of this invention may vary from about 10% by weight up to the saturation value.

Baths containing alkanesulfonate ions containing between 1 and 5 carbon atoms in the alkyl group may be employed for metal plating and related processes such as electrodeposition, electrorefining, electrolytic pickling, electroanalysis, electroforming, electropolishing of metals and of alloys, e. g., stainless steels, electrocleaning and electro-etching, electrotype preparation and similar operations characterized by more or less metal transfer from the electrolyzing solution. The metallic ion of the electrochemical bath may be lead, nickel, chromium, copper, zinc, iron, cobalt, cadmium, and silver, among others. A wide variety of materials may be coated when used as cathodes in the electrochemical baths of this invention.

The electrolytic baths of this invention are particularly suitable for electroplating lead and nickel. It is known in the art that both lead and nickel can be satisfactorily plated from solution. However, in the case of lead, only a few suitable salts are known since the common salts, e. g., sulfate and chloride are insoluble, or unsuitable for other reasons. Thus lead plating solutions are preferably acidic and lead is usually electroplated from such media as lead fluoborate or lead fluosilicate solutions. Such solutions are expensive and quite toxic due to volatile acid (HF). It has been proposed to use lead sulfamate; indeed electrolysis of sulfamate solutions gives a bright, dense coat. But sulfamate solutions hydrolyze rapidly at 50-80° C. and deposit lead sulfate sludge. I have found that the lead alkanesulfonates containing between 1 and 5 carbon atoms in the alkyl group are water soluble and contain ionic lead. Thus lead n-buthanesulfonate will dissolve to the extent of 39.6 grams per 100 grams water at 25° C. and is more soluble in warm water. This lead salt is readily purified and can be heated for 24 hours at 100° C. in aqueous solution without hydrolysis. The solubility of lead ethanesulfonate in water is 67.3 grams per 100 grams of solution at 25° C. For these reasons, alkanesulfonic acids containing between 1 and 5 carbon atoms in the alkyl group make excellent media for the electrodeposition of lead.

It is also known in the art that nickel is difficult to plate because it tends to become passivated in conventional sulfate baths and refuses to give anode attack. I have found that even in the absence of an electrical current, nickel alloys, such as monel metal (except 18-8 stainless steel), are rapidly attacked by hot concentrated alkanesulfonic acids containing between 1 and 5 carbon atoms in the alkyl group. This evident lack of passivity under very favorable conditions for passivity suggests that the use of the lower molecular weight alkanesulfonic acids in nickel baths would expedite plating and improve efficiency. This expectation has been realized experimentally, as set forth in the examples which follow.

Further, I have found that in certain instances, electrochemical baths containing alkanesulfonate ions having between 1 and 5 carbon atoms in the alkyl group can be improved by incorporating a small proportion, usually between about 0.01 and about 5% by weight based on said alkanesulfonate, of an alkanesulfonate having between about 10 and about 30 carbon atoms in the alkyl group. I prefer to employ alkanesulfonates containing between about 15 and about 22 carbon atoms in the alkyl group as an adjunct to the alkanesulfonates containing between 1 and 5 carbon atoms in the alkyl group. Thus, the employment of mixed high and low molecular weight sulfonate ions has been found to yield improved results in lead plating baths as will be described more fully in one of the examples set forth hereinafter.

I have successfully plated brass, copper, iron and aluminum with nickel to obtain adherent bright coatings free of cracks. The electrolyte in these plating operations was a 10% aqueous solution of nickel ethanesulfonate having a pH of about 6 to 6.5. This electrolyte was found to have high throwing power. Electroplating was effected at about 25-27° C., employing a voltage of about 3 volts. In all cases, thick, bright nickel deposits free of cracking were obtained with current densities as high as 7 to 14 amperes per

square foot. Current densities as high as 20 to 25 amperes per square foot were satisfactory to prepare thin coats of nickel.

Nickel alkanesulfonate baths produced in accordance with this invention appear to be self-stabilizing. Maximum anode and cathode efficiencies, of the order of 100%, are obtained at pH values of about 5 or 6. In more alkaline media, anode efficiency drops rapidly, while in more acidic media, cathode efficiency drops rapidly. Regardless of the initial pH of the electrolytic bath, either anode or cathode efficiency will be high, which will cause a change in pH until that pH is reached at which anode and cathode efficiencies are about equal, after which the pH of the electrolyte remains constant.

An automobile key was thinly plated with nickel employing the technique described supra. Upon employing this key in normal service, it was found that the plate wore very well, no flaking occurring after many months. Nickel deposits on iron and aluminum were distinctly matte when prepared from a nickel ammonium sulfate bath, as contrasted with the bright coatings which I have obtained from nickel ethanesulfonate baths.

Lead was plated on copper, employing as the electrolyte a 30% aqueous solution of mixed lead alkanesulfonates wherein the alkyl group contained between 1 and 4 carbon atoms. The mixture of alkanesulfonic acids used in preparing the lead salts employed as the electrolyte was prepared by catalytically oxidizing a mixture of disulfides having between 1 and 4 carbon atoms in the alkyl group, obtained by extracting a mercaptan-containing petroleum naphtha with a caustic solution containing a solutizer followed by oxidation of the mercaptans extracted by the caustic. Both the solutizer process for obtaining the mixed disulfides and their oxidation with air and a nitrogen oxide catalyst are described in United States Letters Patent 2,433,395 and 2,433,396. The pH of the electrolyte was between 5 and 4. Adherent lead coatings were obtained on copper and on aluminum cathodes at room temperature (about 27° C.) employing a voltage of about 0.52 and current density of about 6 amperes per square foot. The coatings obtained with the lead salts of the crude mixed sulfonic acids, as described above, were unexpectedly better than those obtained under otherwise identical conditions, but employing a lead salt of a pure, individual alkanesulfonic acid, e. g., methanesulfonic acid. The mixed acids showed unusual fine grain and fine throwing power. With nickel, the reverse is true, i. e., more satisfactory deposits are obtained from pure, individual nickel sulfonates such as nickel ethanesulfonate.

I have found that brighter and more strongly adherent lead deposits may be obtained by the inclusion in the electrolytic bath of small proportions of alkanesulfonic acids or salts having at least 10 carbon atoms in the alkyl group. For example, I have electrolyzed a bath containing 30% of lead methanesulfonate and about 1% of sodium alkanesulfonates prepared by sulfonating propylene polymers and containing a number of molecular species ranging in carbon content from 17 to 22 carbon atoms in the molecule. Electrodeposition of lead on a copper cathode was effected at 27° C. for 5 minutes with 0.5 volt and a current density of 6 amperes per square foot. The lead deposit was a beautiful gray-white, almost polished in its lustre. A light rub with cloth gave the lead deposit a fine polish. The lead deposit was extremely adherent and

showed no trace of sponginess on edges or at any other location. The same electrolysis without the C₁₇-C₂₂ alkanesulfonate gave a sponge of lead which fell off the cathode.

Similar desirable lead plating results can be obtained by employing lead alkanesulfonates of sulfonic acids derived from oxidation of mixed disulfides containing between 1 and 5 carbon atoms in the alkyl group and a small proportion of an alkyl mercaptan or disulfide containing at least ten carbon atoms in the alkyl group. Good results were obtained with this type of mixed lead sulfonates at 27° C., 0.50 volt and current density of 25 amperes per square foot in about 30% solution. It was found that the cathode efficiency was about 100% and the anode efficiency was above 100%. The anode was etched in a very peculiar fashion, individual lead crystals being dissolved. This latter effect suggests that electrorefining with this solution should yield a very pure lead.

I have observed some indications that a small proportion of glue, which is a conventional addition agent in lead plating baths, reduces the adherency of the lead deposit from the lead alkanesulfonate bath.

Electroplating tests with a silver ethanesulfonate bath indicated that satisfactory silver plating should be obtained.

I have prepared mixed neutral cadmium alkanesulfonates containing between 1 and 4 carbon atoms in the alkyl group. The mixture of alkanesulfonic acids used in preparing the cadmium salts was prepared by catalytically oxidizing a mixture of alkyl disulfides, substantially as described for the preparation of mixed lead alkanesulfonates. A 25% solution of the mixed cadmium alkanesulfonates was electrolyzed, employing a cadmium anode. At two volts and a current density of 6 amperes per square foot, a fine gray adherent deposit of cadmium was obtained on the brass cathode; varying the current density from 1 to 6 amperes per square foot caused little change. Acidification of the electrolytic bath to a pH of about 5 with mixed alkanesulfonic acids containing between one and four carbon atoms in the alkyl group resulted in appreciable brightening of the cadmium deposit. Desirable operating conditions are a pH of about 6 and current density of about 6 amperes per square foot. The throwing power of the cadmium sulfonate solutions under these conditions is good. Under these conditions a very fine grained, adherent cadmium deposit is obtained which upon light rubbing with fine abrasive powder yields a lustrous surface.

While the above examples have set forth specific embodiments of my invention, it is to be understood that my invention is not to be limited thereto. It should further be understood that various addition agents which are known in the art may be added to the electrolytic baths of this invention on occasion.

Numerous modifications and adaptations of my invention will no doubt suggest themselves to one skilled in the art and these are within the scope and spirit of this invention. Also, my novel baths may be employed for the electrolytic oxidation of organic compounds and anodic oxidation of metals. They may also be applicable in the electrolytic white lead manufacturing process. Aqueous solutions of alkanesulfonic acids containing between 1 and 5 carbon atoms in the alkyl group may be employed for leaching lead, silver, zinc,

copper and other ores, followed by electrolysis of the leaching liquor to recover metals.

I claim:

1. An electroplating bath for the electrodeposition of a metal ion comprising essentially an aqueous solution containing said metal ion capable of being deposited by electrolysis to yield a normally solid electrodeposit, an alkanesulfonate ion having between 1 and 5 carbon atoms in the alkyl group as the principal anion, the concentration of the metal alkanesulfonate in said solution being at least about 10 percent by weight and not greater than the saturation concentration of said alkanesulfonate in said solution, and between about 0.01 and 5% based on said alkanesulfonate of an alkanesulfonate ion having between about 10 and about 30 carbon atoms in the alkyl group.

2. The electroplating bath of claim 1 wherein the aqueous solution comprises essentially lead ions.

3. The electroplating bath of claim 1 wherein the aqueous solution comprises essentially nickel ions.

4. The electroplating bath of claim 1 wherein the aqueous solution comprises essentially cadmium ions.

5. The electroplating bath of claim 1 wherein the aqueous solution comprises essentially silver ions.

6. The electroplating bath of claim 1 wherein the aqueous solution comprises essentially zinc ions.

7. The process of electrodepositing a metal which comprises electrolyzing an aqueous solution comprising essentially ions of a metal capable of being deposited by electrolysis to yield a normally solid electrodeposit, alkanesulfonate ions containing between 1 and 5 carbon atoms in the alkyl group as the principal anions, the concentration of the metal alkanesulfonate in said solution being at least about 10 percent by weight and not greater than the saturation concentration of said alkanesulfonate in said solution, and between about 0.01 and about 5 per cent based on said alkanesulfonates of an alkanesulfonate having between about 10 and about 30 carbon atoms in the alkyl group.

8. The process of claim 7 wherein the aqueous solution comprises essentially lead ions.

9. The process of claim 7 wherein the aqueous solution comprises essentially nickel ions.

10. The process of claim 7 wherein the aqueous solution comprises essentially cadmium ions.

11. The process of claim 7 wherein the aqueous solution comprises essentially silver ions.

12. The process of claim 7 wherein the aqueous solution comprises essentially zinc ions.

13. An electroplating bath comprising essentially an aqueous solution of a nickel salt of an alkanesulfonic acid having 1 to 5 carbon atoms in the alkyl group in a concentration between about 10 weight percent and saturation concentration and an alkanesulfonic acid having 1 to 5 carbon atoms in the alkyl group in quantity sufficient to produce a pH of about 5 in said solution.

14. The process of electrodepositing nickel which comprises electrolyzing a medium comprising essentially an aqueous solution of a nickel alkanesulfonate, said alkanesulfonate having 1 to 5 carbon atoms in the alkyl group and being present in said solution in a concentration between about 10 weight percent and saturation concentration of said alkanesulfonate in said

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solution, said solution containing also an alkane-sulfonic acid having 1 to 5 carbon atoms in the alkyl group in quantity sufficient to produce a pH of about 5 in said solution.

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