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3,677,907

CODEPOSITION OF A METAL AND FLUOROCARBON RESIN PARTICLES

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18 Claims

ABSTRACT OF THE DISCLOSURE

Fine particles of fluorocarbon resins such as Teflon particles can be readily codeposited with metals when they are dispersed in aqueous plating baths, when there is also present in the baths a fluorocarbon surfactant such as perfluoro n-octanoic acid, perfluoro n-octyl sulfonic acid, perfluoro p-ethyl cyclohexyl sulfonic acid, or their salts. Such 2-phase composite plates have good anti-seizing and anti-friction properties.

This invention relates to the cathodic codeposition of multitudinous fine particles of fluorocarbon or modified fluorocarbon resins dispersed as fine powders in aqueous electroplating baths containing dissolved therein fluorocarbon surface-active agents. It relates especially to the codeposition of these fluorocarbon resin powders with nickel, cobalt, iron and their binary and ternary alloys, and with copper, silver, gold brass, lead, and lead-tin and lead-tin-copper alloys from the respective metal plating baths containing dissolved therein a fluorocarbon surfactant.

We have found that fine powders of fluorocarbon resins when dispersed for example in a Watts nickel bath will not appreciably codeposit on vertical surfaces unless a fluorocarbon surface-active agent is also present in the bath. It is necessary to have a fluorocarbon surface-active agent dissolved in the aqueous electroplating bath before it is possible to densely codeposit the fine particles of the fluorocarbon resins on vertical surfaces.

Fluorocarbon solid surfaces have the lowest coefficient of friction of any solid. This is due to their extremely low surface energies or surface tensions. Therefore the incorporation of multitudinous particles of fluorocarbon resins in the electrodeposited surfaces of nickel, cobalt, iron, copper, lead, lead-tin, brass, silver, bronze, etc. leads to surfaces which have excellent anti-seizing properties and good lubricity even when dry. Teflon particles (polytetrafluoroethylene), modified Teflon such as Vydax (which is a fluorocarbon telomer), Kel-F powder (polytrifluorochloroethylene) are examples of fluorocarbon or modified fluorocarbon powders which can be obtained in a finely divided state. The important factor for obtaining the maximum in dry lubrication and anti-seizing properties is a high volume percent of the codeposited particles. Also, it is important that these fluorocarbon resin powders contain a preponderance (over 50%) of fluoro groups attached to the carbon atoms of the polymeric resins. Thus, chloro groups, or oxygen or oxygen containing groups or hydrogen or nitrogen containing groups can be present, but as relatively minor constituents.

The particle sizes of the powders that codeposit from the nickel, nickel alloy, copper, lead, lead-tin, etc. aqueous electroplating baths range from about 2 to 3 mils down to submicroscopic particles. Often there are coarser resin particles present in the dispersed powders in the plating baths, but these do not readily codeposit on vertical surfaces. It was also found that in general, it was advantageous to wash the fluorocarbon resin powders with isopropyl alcohol before mixing them into the plat-

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ing baths containing the dissolved fluorochemical surface-active agents. This step aided the rapid wetting of the fluorocarbon resin powders by the fluorocarbon surfactants.

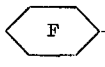
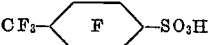
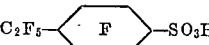
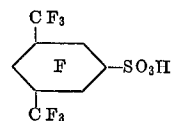
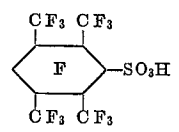
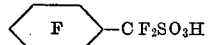
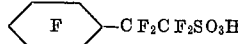
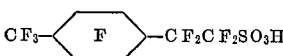
These fluorocarbon resin powders codeposit on vertical surfaces as well as on shelf areas with the most uniform codeposition occurring with the finest powders even with very thin plate of 0.05 to 0.1 mil thicknesses. However to plate out a maximum of the particles of 0.1 mil to 2 mils (2.5 to 50 microns) sizes, thicknesses of plate of 0.1 mil to about 0.5 or even to 1 mil thicknesses should be used. The formation of a densely populated metal surface with codeposited resin particles persists with continued plating past 2 mils thicknesses with consistent codeposition.

The plating solutions of the present invention are metal plating baths in which the fluorocarbon resin particles are dispersed and which also contain, in addition to the metal ions to be plated, at least one fluorocarbon surfactant. These solutions may be electroplating baths for plating nickel, cobalt, iron, the binary and ternary alloys of these, copper, silver, gold, brass, lead, lead-tin or lead-tin-copper alloys, and the like. Such plating baths are conventional and well known to those in the art.

It is desirable that such baths contain the fluorocarbon resin particles in an amount of at least about 1 gram/liter, and preferably in an amount of about 2 to 150 grams/liter. The fluorocarbon surfactant is desirably present in the bath in an amount of at least about 0.01 grams/liter and preferably in an amount within the range of about 0.01 to 5 grams/liter. Various fluorocarbon surfactants may be used so long as they are soluble in the plating baths and are not detrimental to the plating of the fluorocarbon resin particles and/or the metal. Examples of some of the fluorocarbon surfactants which may be used to obtain a dense codeposition of the resin particles with the metal are given in Table I.

TABLE I

Fluorocarbon Surface-Active Agents

- 1)  perfluorocyclohexyl sulfonic acid (Na, +K, + etc., salt)
- 2) 
- 3) 
- 4) 
- 5) 
- 6) 
- 7) 
- 8) 

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- 9) $\text{CF}_3(\text{CF}_2)_n-\text{CF}_2\text{SO}_3\text{H}$, where $n=2-8$
 10) $\text{ClCF}_2(\text{CF}_2)_n-\text{CF}_2\text{SO}_3\text{H}$
 11) $\text{CF}_3(\text{CF}_2)_n-\text{CF}_2\text{COOH}$
 12) $\text{ClCF}_2(\text{CF}_2)_n-\text{CF}_2\text{COOH}$
 13) $\text{Cl}(\text{CF}_2\text{CFCl})_n-\text{CF}_2\text{COOH}$
 14) $\text{HCF}_2(\text{CF}_2)_n-\text{CF}_2\text{COOH}$
 15) $\text{HCF}_2(\text{CF}_2)_n-\text{CF}_2\text{PO}(\text{OH})_2$
 16) $\text{HCF}_2(\text{CF}_2)_n-\text{CH}_2\text{OSO}_3\text{H}$
 17)
$$\text{CF}_3(\text{CF}_2)_n-\text{CF}_2-\overset{\text{O}}{\parallel}\text{C}-\overset{\text{H}}{\text{N}}-\text{C}_6\text{H}_4-\text{N} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \end{array}$$

 18) $\text{CF}_3(\text{CF}_2)_n-\text{CH}_2\text{OC}_2\text{H}_4(\text{OC}_2\text{H}_4)_{n_1}\text{OH}$
 19) $\text{CF}_3(\text{CF}_2)_n-\text{CH}_2\text{NH}_2\text{HCl}$
 20)
$$\text{CF}_3(\text{CF}_2)_n-\text{CH}_2-\overset{\text{O}}{\parallel}\text{N}-\text{C}(\text{CH}_3)_2\text{SO}_3\text{Na}$$

 where $n=2-8$, $X=1-4$, $n_1=1-50$

In some cases it is desirable to use the normal hydrocarbon surfactants together with the fluorocarbon surfactants. For example, in the acidic type of nickel baths, like the Watts bath or the high chloride nickel bath, the fluorocarbon surfactants, even though they lower the surface tension more than the best type of hydrocarbon surfactants for nickel and nickel alloy baths, they do not prevent hydrogen gas pitting. That is, the fluorocarbon surface-active agents do not have detergent properties for the usual types of organic contamination (dust, traces of organic materials from vat linings, etc.) that may cause hydrogen gas bubbles to stick to the cathode, thus causing pitting in the cathode. The usual hydrocarbon surfactants for nickel plating such as sodium 2-ethyl hexyl sulfate, and sodium n-octyl sulfate to sodium lauryl sulfate, solubilize in their micelles the ordinary hydrocarbon type impurities, unlike the micelles of the fluorocarbon surfactants. However, the fluorocarbon surfactants are unique in their ability to wet the fluorocarbon resin particles, and make possible the extensive codeposition of the dispersed fluorocarbon powders.

In some cases it is also desirable to codeposit inorganic bath-insoluble fine particles such as barium sulfate or strontium sulfate or mica along with the fluorocarbon resin particles, in order to add strength to the composite plate, without decreasing the high lubricity and anti-seizing properties of the plate. In fact, just the dense codeposition of particles such as barium or strontium sulfate provides very important lubricity and anti-stick properties, because of the slip qualities of these particular powders. However, if over about 50 g./l. of barium sulfate is used in the baths containing about 50 g./l. of the fluorocarbon dispersed particles, then the codeposition of the barium sulfate particles will predominate over fluorocarbon particles.

When air agitation is used to keep the particles dispersed in the bath, the shorter chain surfactants in general are preferred to avoid over-foaming. With mechanical agitation, the longer chain surfactants can be used as well as the shorter chain types. The use of anti-foaming agents is generally not desirable, but certain ones, like octyl alcohol cause no troubles.

In the case of acid copper plating baths it is also necessary to have present in the bath besides a fluorocarbon surfactant, a "promoter" addition agent to cause the extensive codeposition of the fluorocarbon resins on vertical surfaces. The promoter addition agents for the acid copper plating baths are salts of monovalent cations such as those of thallium, cesium, rubidium, sodium, potassium, ammonium, lithium, amines, especially aliphatic polyamines or imines, such as tetraethylene pentamine, or amino acids such as alanine, or EDTA. Actually the use of amino acids and especially chelating agents of the type

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of EDTA help in the codeposition of the fluorocarbon particles not only in acid copper plating baths where they are the most helpful, but also in zinc sulfate baths, nickel plating baths, alkaline cyanide silver and copper plating baths, in brass plating baths, and in pyrophosphate copper plating baths.

Below are listed some examples of electroplating baths for codepositing fluorocarbon resin particles with metals.

EXAMPLE I

	Concentration in grams per liter
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	200-300.
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	40.
15 Teflon particles (1 micron to about 50 microns particle size) -----	30-100.
Perfluoro p-ethyl cyclohexyl sulfonic acid -----	0.1-2.
p-Toluene sulfonamide -----	0-2.
20 Benzene sulfonamide -----	0-2.
o-Benzoyl sulfimide -----	0-2.
8-Methoxy coumarin -----	0-0.5.
Temperature—100 to 160° F. -----	pH 2.5-5.2.
Cathode current density -----	20-60 amps/sq. ft.
25 Air agitation.	

EXAMPLE II

	Concentration in grams per liter
30 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ -----	100-250.
H_2SO_4 -----	5-100.
Teflon particles (1 micron to about 50 microns particle size) -----	2-150.
Perfluoro n-octyl sulfonic acid -----	0-0.01.
35 Perfluoro p-ethyl cyclohexyl sulfonic acid -----	0.1-2.
EDTA -----	5-20.
Temperature—60 to 130° F. -----	Agitation—air or mechanical.
40 Cathode current density -----	10-100 amps/sq. ft.

EXAMPLE III

High cathode efficiency brass bath (90%+)

	Concentration in grams per liter
45 CuCN -----	90.
Zn(CN) ₂ -----	7.5.
NaCN -----	105.
50 NaOH or KOH -----	60.
EDTA -----	10-20.
Teflon particles (1 micron to about 50 microns particle size) -----	3-100.
Perfluoro ammonium n-octanoate or Perfluoro potassium p-ethyl cyclohexyl sulfonate -----	0.5-2.
Temperature—170 to 175° F. -----	
Cathode current density -----	10-40 amps/sq. ft.
60 Mild air agitation or gentle mechanical agitation.	

The above brass bath yields about an 80-20 copper-zinc brass alloy plate with the codeposited Teflon particles present. By using different ratios of copper to zinc, it is possible to deposit higher zinc alloy brasses such as 70-30 and 60-40 copper-zinc brasses. Also by adding small concentrations of lead carbonate or lead acetate to the baths, it is possible to incorporate a small percentage of lead into the brass deposits which also helps in anti-friction applications.

70 The electroplating baths for the codeposition of the fluorochemical resin particles should have relatively high cathode efficiencies, cathode efficiencies of at least about 90% being preferred. Additionally, however, electrodeless (electrodeless) copper or nickel or cobalt (or the alloys of the iron group) plating baths, which also incorporate flu-

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orocarbon resin particles and the fluorocarbon surfactants, such as perfluoro p-ethyl cyclohexyl sulfonic acid or its salts, may also be used.

EXAMPLE IV

By way of example of the use of such electroless baths, a bath is formulated containing the following components in the amount indicated:

	Concentration in grams/liter	
Basic nickel carbonate	10.	10
Hydrofluoric acid	6 ml./liter.	
Citric acid	5.5.	
NH ₄ HF ₂	10.	
Sodium hydrophosphite	20.	15
Ammonium hydroxide	30 ml./liter.	

To this bath was added the Teflon particles and fluorocarbon surfactant as in Example I and the bath was operated at a temperature of from 170–180° F. to obtain a co-deposit of Teflon particles and electroless nickel plate on a steel surface immersed therein.

EXAMPLE V

The following baths were formulated with the components and in the amounts indicated:

(A)

	Grams/liter	
Potassium aurocyanide	4–12	30
Potassium cyanide	30	
Potassium carbonate	30	
Potassium arbasic phosphate	30	

(B)

	Grams/liter	
Stannous Tin	6.0	35
Lead	88.0	
Free fluoroboric acid	100.0	
Free boric acid	25.0	40
Peptone	0.5	

(C)

Silver cyanide	4.8 oz./gal.	
Potassium cyanide	8.0 oz./gal.	
Potassium carbonate	2.0 oz./gal.	45
Metallic silver	3.5 tray oz./gal.	
Free cyanide	5.5 oz./gal.	

To each of these baths was added the Teflon particles and fluorocarbon surfactant as in Example I. The baths were then operated under the following conditions of codeposit the respective metals and Teflon particles, as in Example I:

(A)

Temperature	120–150° F.	55
Current density	up to 5 amp/sq. ft.	
Gold or steel anodes.		

Acid gold baths operated at pH values from 3–6 may also be used instead of alkaline ones, for example:

Gold	4–12 g./l.	
Citrates	90 g./l.	
pH	3–6.	
Cathode current density	1–10 amps/sq. ft.	65
Anodes	carbon or platinum.	

(B)

Temperature	60–100° F.	
Cathode current density	30 amps/sq. ft.	70
Lead-tin alloy anodes.		

(C)

Temperature	70–80° F.	
Current density	5–15 amps/sq. ft.	75
Silver anode.		

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What is claimed is:

1. A method of electroplating which comprises codepositing dispersed fine fluorocarbon resin particles with a metal from an aqueous metal plating bath having cathode efficiencies higher than about 90% and having dissolved in said plating bath a fluorocarbon surfactant in a concentration of at least about 0.01 gram/liter, and having at least 1 gram/liter of the fluorocarbon resin particles dispersed in the metal plating bath.

2. A method in accordance with claim 1 wherein said fluorocarbon resin particles are essentially polytetrafluoroethylene of particle size less than about 50 microns.

3. A method in accordance with claim 1 wherein said fluorocarbon surfactant is essentially perfluoro n-octyl sulfonic acid in a concentration of 0.01 to 1 gram/liter.

4. A method in accordance with claim 1 wherein said fluorocarbon surfactant is perfluoro p-ethyl cyclohexyl sulfonic acid in a concentration of 0.05 to 2 grams/liter.

5. A method in accordance with claim 1 wherein said metal plating bath is essentially an acidic nickel electroplating bath.

6. A method in accordance with claim 1 wherein said metal plating bath is an alkaline silver electroplating bath.

7. A method in accordance with claim 1 wherein said metal plating bath is essentially an electroless nickel plating bath.

8. A method in accordance with claim 1 wherein said metal plating bath is essentially a gold electroplating bath.

9. A method in accordance with claim 1 wherein said metal plating bath is essentially a lead-tin alloy electroplating bath.

10. An aqueous metal plating bath comprising a plating bath of cathode efficiency greater than about 90% and containing dispersed therein at least 1 gram/liter of fine fluorocarbon resin particles and having dissolved in said plating baths a fluorocarbon surfactant in a concentration of at least about 0.01 gram/liter.

11. A bath in accordance with claim 10 wherein said fluorocarbon resin particles are essentially polytetrafluoroethylene of particle size less than about 50 microns.

12. A bath in accordance with claim 10 wherein said fluorocarbon surfactant is essentially perfluoro n-octyl sulfonic acid in a concentration of 0.01 to 1 gram/liter.

13. A bath in accordance with claim 10 wherein said fluorocarbon surfactant is perfluoro p-ethyl cyclohexyl sulfonic acid in a concentration of 0.15 to 2 grams/liter.

14. A bath in accordance with claim 10 wherein said metal plating bath is essentially an acidic nickel electroplating bath.

15. A bath in accordance with claim 10 wherein said metal plating bath is an alkaline silver electroplating bath.

16. A bath in accordance with claim 10 wherein said metal plating bath is essentially an electroless nickel plating bath.

17. A bath in accordance with claim 10 wherein said metal plating bath is essentially a gold electroplating bath.

18. A bath in accordance with claim 10 wherein said metal plating bath is essentially a lead-tin alloy electroplating bath.

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