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ELECTROPLATING

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This invention relates to electroplating and more particularly to a method for preventing foaming of "anti-pitting" agents of the surface tension lowering type in plating operations wherein the article being plated is agitated, or the solution is agitated by the frequent removal of the articles being plated.

Heretofore, it has been found in electroplating articles in plating solutions with metals such as cobalt, copper, nickel, lead, iron, zinc, etc., that a great improvement in the metal plating can be produced by adding "anti-pitting" agents of the surface tension lowering type to the plating baths.

When employed in non-agitated plating solutions this type of "anti-pitting" agent, among the best of which are higher sulphonated alcohols, perform very satisfactorily. However, when such higher sulphonated alcohols are employed in plating solutions in which the article being plated (the cathode) is removed frequently, or rotated partly immersed, trouble is experienced with foaming of the solution which frequently overflows the plating bath and seriously interferes with the plating operation.

An object of the invention is therefore a process by which higher sulphonated alcohol "anti-pitting" agents may be employed in electroplating solutions without excessive foaming.

Another object of the invention is a non-foaming plating solution containing "anti-pitting" agents or other addition agents which have a tendency to foam excessively particularly when agitated.

In accordance with the invention these and other objects are attained by adding to a suitable electroplating solution containing non-pitting agents such as sulphonated alcohols, or other surface tension lowering substances, a small percent of insoluble higher aliphatic alcohols.

I have found that the aliphatic alcohols and their isomers from $C_5H_{11}OH$ to $C_{10}H_{21}OH$ inclusive are particularly valuable as foam preventing agents for use in electroplating baths containing non-pitting agents such as higher sulphonated alcohols. Of these octyl alcohol, $C_8H_{17}OH$, is especially useful. These materials do not interfere with the plating operation as do oils and are therefore particularly adaptable for use in electroplating solutions where it is necessary that the cathode be frequently removed or rotated partly immersed.

Suitable higher sulphonated alcohols and other sulphonated substances suitable for use as anti-pitting agents which without the addition of ali-

phatic alcohols will cause excessive foaming when used in agitated plating solutions are: alkyl sulphononic acids such as lauryl sulphononic acid, and salts of alkyl sulphononic acids such as sodium lauryl sulphonate and sodium palmatyl sulphonate; aromatic sulphononic acids such as benzene sulphononic acid and aryl sulphononic acid salts such as benzene sodium sulphonate, and naphthalenic sulphononic acids and salts thereof such as sodium naphthyl sulphonate.

I have also found that the anti-pitting agent available on the market under the trade name "Harshaw Non-Pitting Agent" and also the non-pitting or wetting agents known as "Du Ponal", "Igepon T" and "Daconal", (all of which I believe to be higher sulphonated alcohols or mixtures containing sulphonated alcohols) will foam excessively when employed in acid plating solutions when the solution is agitated as heretofore described, and that the addition of a small amount of insoluble aliphatic alcohols and their isomers within the group comprising $C_5H_{11}OH$ to $C_{10}H_{21}OH$ inclusive to the plating solution will prevent excessive foaming of such anti-pitting agents without perceptibly changing the plating characteristics of the plating solution and, in fact, improving the action of the anti-pitting agents.

The following are examples of non-foaming electrolytic baths suitable for plating nickel on an article which is rotated at comparatively high speeds while partially immersed in the solution:

Example 1

$NiSO_4 \cdot 7H_2O$	140 g/l	
$NiCl_2 \cdot 6H_2O$	40 g/l	
H_3BO_3	40 g/l	35
Sulphonated higher alcohol (C_nH_{2n-1SH})	3 g/l	
Octyl alcohol ($C_8H_{17}OH$)	4 g/l	

Example 2

$NiSO_4 \cdot 7H_2O$	140 g/l	40
$NiCl_2 \cdot 6H_2O$	40 g/l	
H_3BO_3	40 g/l	
"Harshaw" non-pitting agent	25 cc/l	
Octyl alcohol ($C_8H_{17}OH$)	4 g/l	45

Example 3

$NiSO_4 \cdot 7H_2O$	140 g/l	
$NiCl_2 \cdot 6H_2O$	40 g/l	
H_3BO_3	40 g/l	
"Du Ponal"	3 g/l	50
Octyl alcohol ($C_8H_{17}OH$)	4 g/l	

While the preferred amounts of the contents of the electroplating bath are given in the above examples, the content of $NiSO_4$ may be within the range of 100-300 grams per liter, the $NiCl_2$ be-

tween 20-100 grams per liter, the H_3BO_3 between 15-40 grams per liter, the sulphonated higher alcohols or "Du Ponal" between 1-20 grams per liter, the octyl alcohol between 2-10 grams per liter, and the "Harshaw non-pitting" agent in Example 2 between 10-40 cc. per liter, and a good plating without foaming may be obtained.

The following are examples of non-foaming electrolytic baths suitable for plating copper on an article which is rotated at comparatively high speeds while partially immersed in the solution:

Example 4

$CuSO_4 \cdot 5H_2O$	200 g/l
H_2SO_4	70 g/l
Sulphonated higher alcohol ($C_nH_{2n-1}SH$)	3 g/l
Octyl alcohol ($C_8H_{17}OH$)	4 g/l

Example 5

$CuSO_4 \cdot 5H_2O$	200 g/l
H_2SO_4	70 g/l
"Harshaw" non-pitting agent	25 cc/l
Octyl alcohol ($C_8H_{17}OH$)	

Example 6

$CuSO_4 \cdot 5H_2O$	200 g/l
H_2SO_4	70 g/l
"Duponal"	3 g/l
Octyl alcohol ($C_8H_{17}OH$)	4 g/l

In addition to the specific amounts employed in the above examples of copper plating solutions, satisfactory plating without foaming may be obtained when the bath contains $CuSO_4$ in the range of 100-300 grams per liter, H_2SO_4 from 3 to 75 grams per liter sulphonated higher alcohol "Duponal" 1-20 grams per liter, octyl alcohol 2-10 grams per liter and in the case of Example 5, "Harshaw" non-pitting agent 10-40 cc. per liter.

The above examples are given for purposes of illustration and are not limitations of the invention. I have found that the addition of one or more of the aliphatic alcohols and their isomers from $C_5H_{11}OH$ to $C_{10}H_{21}OH$ in amount within the range of from 0.2% to 10% and preferably within a range of 0.2% to 1% based on the amount of foam producing addition agent such as sulphonated higher alcohols, etc. in either an acid or basic plating solution will form a low surface tension film on the surface of the bath and will effectively prevent the foam forming materials from interfering with the plating operation.

This invention is not limited only to nickel or copper plating but is also applicable to any acid plating solution such as cobalt, copper, nickel, lead, iron, zinc, etc. Chromium plating solutions, however, are an exception because their powerful oxidizing action destroys the organic alcohols.

Mildly alkaline plating solutions such as used for cadmium, copper, brass, silver, zinc, etc., may also be made non-foaming by adding a small percentage of the above described insoluble aliphatic alcohols to the solution containing non-pitting agents such as higher sulphonated alcohols and the like.

The following are examples of non-foaming alkaline electrolytic plating baths in accordance with the invention.

Example 7

$CuCN$	22.5 g/l
$NaCN$	34 g/l
Na_2CO_3	15 g/l
"Igepon T"	3 g/l
Octyl alcohol	4 g/l

Suitable ranges for the contents of this bath are $CuCN$ 15-60 grams per liter, $NaCN$ 15-90 grams per liter, Na_2CO_3 10-100 grams per liter,

"Igepon T" 1-20 grams per liter, octyl alcohol 2-10 grams per liter.

Example 8

$AgCN$	35 g/l
KCN	37 g/l
K_2CO_3	38 g/l
"Igepon T"	3 g/l
Octyl alcohol	4 g/l

Suitable ranges for the contents of this bath are $AgCN$ 15-45 grams per liter, KCN 17-20 grams per liter, K_2CO_3 15-70 grams per liter, "Igepon T" 1-20 grams per liter, octyl alcohol 2-10 grams per liter.

It will be understood that in place of employing a single aliphatic alcohol in the above examples to prevent foaming of the electroplating bath, it is within the inventive concept to employ more than one of these alcohols in the same bath. However, in such event the total aliphatic alcohol content should be within the preferred range of approximately 0.2% to 10%.

By employing my invention I have been able to greatly facilitate and improve electroplating of articles in baths containing non-pitting or bright plating addition agents particularly when the article is rotated or removed frequently in the course of the plating operation.

What is claimed is:

1. The method of preventing foaming of electroplating baths containing addition agents which tend to produce foaming, which comprises adding to the bath a small amount of a saturated monohydric aliphatic alcohol having 5 to 10 carbon atoms said alcohol being insoluble in said plating bath.

2. The method of preventing foaming of electroplating baths containing addition agents which tend to produce foaming, which comprises adding to the bath a small amount of octyl alcohol, said alcohol being insoluble in said plating bath.

3. The method of preventing foaming of electroplating baths containing addition agents which when agitated during the plating operation tend to produce foaming, which comprises adding to the bath a small amount of a saturated monohydric aliphatic alcohol having a 5 to 10 carbon atom alkyl radicle, said alcohol being insoluble in said plating bath.

4. The method of preventing foaming of electroplating baths containing addition agents which when agitated during the plating operation tend to produce foaming, which comprises adding to the bath a small amount of octyl alcohol, said alcohol being insoluble in said plating bath.

5. The method of preventing foaming of electroplating baths containing higher sulphonated alcohol addition agents which comprises adding to the bath a small amount of a saturated monohydric aliphatic alcohol having 5 to 9 carbon atoms, said alcohol being insoluble in said plating bath.

6. The method of preventing foaming of electroplating baths containing higher sulphonated alcohol addition agents which comprises adding to the bath a small amount of octyl alcohol, said alcohol being insoluble in said plating bath.

7. The method of preventing foaming of electroplating baths containing higher sulphonated alcohol addition agents which comprises adding to the bath a small amount of a saturated monohydric aliphatic alcohol having 6 to 8 carbon atoms, said alcohol being insoluble in said plating bath.