The present invention is directed to bright nickel plating baths and more particularly to the use of an improved agent in a normal type of nickel bath to improve the brightness of platings made therefrom.

In the past it has been customary to electroplate bright nickel coatings and a considerable variety of addition agents to the usual nickel bath have been proposed. While such substances had some effectiveness, they either were incapable of providing a completely bright deposit or if the deposits were bright, they were brittle in form, particularly when the coating was of substantial thickness. Some of the brightening agents used, such as chlorine or bromine substituted aldehydes, reduced the throwing power of the nickel bath, tended to give deposits which were passive and difficult to cover well with chromium and they also tended to be brittle where the deposits were relatively heavy. Also under conditions which made it necessary to replace the nickel, or to plate nickel over nickel, the deposits obtained from a bath containing the aldehyde type of addition agents, which are used in relatively high concentrations, the nickel plate tended to become passive, making an activating treatment necessary.

There was also suggested the use of alkyl polyamines, which were asserted to be effective in obtaining a high degree of brightness required by the trade. Such compounds were reacted with various substances such as acrylonitrile, epichlorhydrin, in order to increase their molecular weights. It has been found that such high molecular weight compounds have an adverse effect on the ductility of the deposit and in addition do not give full brilliance to the deposits. Although alkyl polyamines such as triethylene tetramine and tetraethylene pentamine give deposits of excellent ductility, such deposits do not have maximum brightness but tend to be hazy. When used in higher concentrations, brightness of the deposit is increased, but darkening of the coating results particularly in the low current density areas accompanied by a decrease in the ductility of the deposit.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in prior compositions of the type described, it being among the objects of the present invention to provide a composition of a nickel bath containing certain substances whereby the coatings obtained therefrom are smoother than the basis metal.

It is also among the objects of the present invention to provide a composition of the type described which results in coatings of extreme brightness together with a high degree of ductility.

It is further among the objects of the present invention to provide a composition which is highly effective and provides an improved bright deposit even in low current density areas.

The basis of the present invention is the use of certain unsaturated acetylenic compounds added to the usual nickel bath in relatively small amounts. Such acetylenic compounds, which are reacted with alkyl polyamines, are added to the bath in conjunction with certain compounds.

The sulphonic acid compounds are those of benzoic, toluene and naphthalene containing from 1 to 3 sulphonic groups, the latter having the following general formula: \(-SO_2R\). In such compounds \(R\) represents OH, NH, NH2 and alkali metal. Compounds of this type are known in the prior art and they include sulphonates, sulphonamides and sulphonimides, such as are described in Schlotter Patent No. 1,972,693, Brown No. 2,191,813 and Lind 2,238,861.

There may also be added to the bath polyalkylene amines and condensation products of said polyalkylene amines with aldehydes, the polyalkylene amines having 2 to 12 amino groups and containing alkylene groups having from 1 to 6 carbon atoms, and there being present in the amines from 2 to 10 such alkylene groups.

In particular the use of a mixture of the sulphur-containing compounds described above with the polyamine reaction products of acetylenic compounds overcomes the undesirability of the darkening previously encountered at low current densities of the prior compositions. At the same time, the present composition results in the highly desirable characteristic of ductility of the deposit. They have the further advantage of making the bath more tolerant to high concentrations of the addition agent without any adverse effects on the ductility of the deposit, and they do not increase the passivity of the nickel plate over that obtained from the Watts type bath without addition agents.

The preparation of the acetylenic compounds is known and such preparation is described by Victor Wolfe in Annalen, vol. 576, 1952, pages 35 to 45.

The compounds according to the present invention probably have the following general formula:

\[
\text{XH} \quad \text{(CH2)2} \quad \text{NH} \quad \text{C} \quad \text{(CH2)n} \quad \text{NH} \quad \text{X}
\]

wherein \(X\) is a radical taken from the class consisting of \(\text{R} - \text{C} = \text{C} - \text{X}\) and \(\text{R} - \text{C} = \text{O} - \text{CH} = \text{CH} - \text{CH} = \text{O} - \text{R}\).

In which \(R\) represents H and \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H}n\), \(n\) is a numeral from 0 to 10 and \(X\) is X or hydrogen. Thus it can be seen that the total number of carbon atoms making up the group heretofore referred to as \(X\) varies from 2 to 15.

The following substances are typical of the unsaturated or acetylenic compounds which are reacted with polyamines:

- Propargyl chloride
- Propargyl bromide
- 3-Cl-3-methyl-1-butyne
- 5-Br-3-methyl-4-pentene-3-ol

Various polyamines having relatively low and even relatively high molecular weights may be reacted with the acetylenic compounds and the following illustrates the general character of the amines which may be used.

- Ethylenediamine
- Diethylenetriamine
- Triethylenetetramine
- Tetraethylenepentamine
- Pentapropylenehexamine
- Polyethylenamine 1200
- Polyethyleneamine 1800
The following are examples which illustrate the manufacture of the reaction products used in the present invention.

**Example 1**

4 mols. of propargyl bromide are introduced drop by drop into 1 mol. of triethylenetetramine, the reaction mass being cooled in order to avoid undue rise of temperature. As a result of the reaction, fumes of hydrobromic acid are evolved. After such evolution ceases, the reaction mass is heated to about 60° C. to complete the reaction. The reaction product is N,N,N',N'-propargyl triethylenetetramine.

**Example 2**

5 mols. of 3-chloro-3-methyl-1-butyne are introduced into 1 mol. of tetraethylenepentamine. The mixture is gradually heated, preferably on a water bath, to about 90° C. in order to cause the reaction to proceed. Fumes of hydrochloric acid are evolved and the reaction proceeds without any further addition of heat since the reaction is exothermic. The product is most likely

3N,3N,3N'-3-methyl-1-butyne : tetraethylenepentamine

**Example 3**

2 mols. of 5-bromo-3-methyl-4-pentyne-3-01 are incorporated into 1 mol. of diethylenetriamine and the mixture is heated to 80° C. upon the reaction starts and proceeds to completion. Fumes of hydrobromic acid are evolved and the reaction is completed when such evolution ceases. The product may be designated as

5N,5N,5N'-3-methyl-4-pentyne-3-01 diethylenetriamine

In the course of the reaction, the acetylenic compound is attached to amino nitrogen, usually to one of the terminal nitrogen groups and one or more of the internal nitrogen groups. It is also possible that acetylenic radicals attach themselves to both of the terminal nitrogen groups.

It has been found that the best plating results are obtained when the molar ratio of the acetylenic halide used is equivalent to the total number of amino groups in the polyamine. For example, the reaction product of 1 mol. of ethylenediamine and 2 mols. of the acetylenic halide gives the optimum results and the reaction product of 1 mol. of triethylenetetramine with 4 mols. of the acetylenic halide also gives the best results. While better results are obtained when all or most of the NH₂ groups are reacted with the acetylenic compounds, improved operation is obtained even when some of the NH₂ groups remain unreacted.

It is also possible to start with an acetylenic dihalide such as 3,5-dibromo-4-pentyne-3-01. In this case only ½ mol. of the acetylenic dihalide is necessary for each amino group. The product resulting from this reaction is most likely the following general formula:

\[
\text{H₂C₃CH₂[N₃C₆H₆N]₅CH₃}
\]

It is to be understood that the acetylenic addition agents which are used in accordance with the present invention are incorporated in the bath in conjunction with the sulfonium compounds set forth above, in accordance with the prior art, such compounds including sulphonates, sulphonamids and sulphonimides. The use of such acetylenic compounds in the compositions described, not only improved the leveling characteristics of the plating bath but also do not adversely affect the covering power of the bath or the ductility of the deposit even when the ammonia therewith is present in amounts as much as six times the optimum concentration used in the prior art. In fact, there is a considerable improvement in the current density characteristics of the plating bath when reaction products of polyamines and acetylenic compounds are used.

The standard bath in which the compounds of the present invention are introduced is illustrated by the following formula:

\[
\text{NiSO₄·6H₂O} \quad \text{Na₃C₅O₄} \quad \text{K₂HPO₄}
\]

The amounts stated are in grams per liter. The wetting agents are the usual ones common in the art and include such compounds as sodium lauryl sulphate, sodium tetradecyl sulphate, sodium ethyl hexysulphate and sodium octysulphate. The following are examples of compositions which are added to the above described standard bath to obtain the beneficial results of the present invention.

**Example 4**

Na naphthalene trisulphonate : 30 N,N,N',N', propargyl-triethylenetetramine : 02

**Example 5**

Ni naphthalene disulphonate : 15

**Example 6**

1.6 Na naphthalene trisulphonate : 12

5N,5N,5N',3-methyl-4-pentyne-3-01 triethylenetetramine : 0.007

**Example 7**

p-Toluene sulphonamide : 0.5 N,N,N', propargyl diethylenetriamine : 02

The conditions of the baths will vary within certain limits which are recognized as being suitable for the purpose. The pH of the various solutions varies from approximately 3.0 to 4.2 and the temperatures of the baths vary from about 130° F. to 170° F. Excellent platings which are highly ductile and of extreme brightness are obtained thereby. The nickel salts used in the bath may be replaced in whole or in part by other soluble salts thereof, such as sulphamate, fluoborate, and the like. The polyamines may have molecular weights of say, 1200 to 1800 with good results.

We claim:

1. In a nickel plating bath comprising an aqueous solution of a compound taken from the class consisting of nickel sulfate and nickel chloride, the improvement which comprises the addition of the reaction product of a soluble acetylenic compound having from 2 to 15 carbon atoms and taken from the class consisting of acetylenic halides and acetylenic alcohol halides, with an alkylen polyamine having 2 to 12 amino groups, the alkylene groups having 2 to 3 carbon atoms, said soluble acetylenic compound being present in an amount of from .001 g./l. to 1.0 g./l., said product containing at least one carbon-to-carbon triple bond and being an acetylenic polyamine.

2. A nickel plating bath according to claim 1 wherein there is added to said bath an aromatic sulfo compound in which the aromatic group is taken from the class consisting of benzene, toluene and naphthalene, said sulfo compound containing from 1 to 3 sulfonylic groups, said sulfonylic groups having the general formula SO₃R where R is taken from the class consisting of OH, NH, NH₂, and alkali metal.

3. A bath in accordance with claim 1 in which the number of acetylenic groups is from 1 to the number of amino groups present.

4. A bath in accordance with claim 3 in which the polyamine is diethylenetriamine.
5. A bath in accordance with claim 3 in which the polyamine is ethylenediamine.

6. A bath in accordance with claim 3 in which the polyamine is triethylenetetramine.

7. A bath in accordance with claim 3 in which the polyamine is tetraethylenepentamine.

8. A bath in accordance with claim 3 in which the polyamine is pentaethylenhexamine.

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