

[54] GALVANIC NICKEL BATH FOR  
DEPOSITING SILK-DULL NICKEL COATS

[75] Inventors: Waldemar Immel, Solingen;  
Wennemar Strauss,  
Erkrath-Unterbach, both of  
Germany

[73] Assignee: Dr. W. Kampschulte & Cie,  
Solingen, Germany

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Primary Examiner—G. L. Kaplan  
Attorney, Agent, or Firm—Walter Becker

[57] ABSTRACT

A galvanic nickel bath for precipitating silk-dull nickel coats, which includes anion active primary and/or secondary phosphoric acid esters of polyalkylene oxide adducts adapted to be produced from ethylene oxide and/or propylene oxide and/or butylene oxide, or of the salts of such propylene oxide adducts.

3 Claims, No Drawings

## GALVANIC NICKEL BATH FOR DEPOSITING SILK-DULL NICKEL COATS

The present invention relates to a galvanic nickel bath for precipitating dull, glare or dazzle free nickel coats with a certain content of basic luster substances. The production of articles the surface of which is made glare-free by the galvanic precipitation of silk-dull nickel coats is to an ever increasing extent requested by consumers in a wide range of technical fields. A silk-dull nickel coat is characterized by a velvet-like luster and by a reduced reflection as compared to nickel coats having a high luster and strong reflection.

It is known to produce such silk-dull coats by mechanical treatment of the surface of the respective article either prior to or following the deposit of a lustrous strongly reflecting coat by dulling. The various heretofore known drawbacks of this method have been overcome by the manufacture of galvanic nickel baths which make it possible to obtain the precipitation of silk-dull coats directly out of the bath. In this connection there are to be distinguished such nickel baths to which insoluble pulverous particles are added which will be enclosed in the otherwise smooth nickel coat thereby producing a rough velvet like surface, from nickel baths which contain organic additions which result in a dull shiny deposit of nickel with reduced reflecting ability.

With the last mentioned galvanic nickel baths it is known to add non-ionogenic alkylene oxide adducts to galvanic nickel baths of customary composition having a content of basic luster substances. In this connection the bath contains such substituted or non-substituted ethylene oxide or propylene oxide or ethylene oxide-propylene oxide adducts in a concentration of from 5 - 100 mg/l which at a temperature of from 40° - 75°C form a finely dispersed emulsion in the bath electrolyte. These addition compounds include, for instance, the high molecular polyethylene oxides, polypropylene oxides, mixing adducts of ethylene oxide and propylene oxide, addition compounds of ethylene oxide and propylene oxide or ethylene oxide and propylene oxide in any desired sequence on one or multi-valent saturated and unsaturated straight chained and branch chained aliphatic, cycloaliphatic, aromatic and heterocyclic alcohols, ethyl hydrosulfides (mercaptanes), aldehydes, ketones, acetals, amines, carbonic acids, carbonic acid amides and phenols.

Furthermore the composition of the customary nickel baths is known which consists of nickel salts, such as nickel chloride, nickel sulfate, nickel fluoroborate or nickel sulfamate and customarily contains a buffer, such as boric acid. A frequently employed bath is the so-called Watt-bath with nickel chloride, nickel sulfate and boric acid.

With these known galvanic nickel baths for a direct precipitation of silk-dull coats of the type described above, the drawback has been encountered that on the one hand there exists the danger that the satin former, when operating with air, will float and that in addition thereto with profiled and greatly curved workpieces in certain current density ranges no uniform deposit can be obtained. Inasmuch as the articles which are to be provided with a nickel coat are in most instances profiled, so that for this reason extremely low current densities occur during the galvanizing process, the resulting lack of uniformity of the coat represents a rather important drawback. Above all, at low current den-

sities, with the heretofore known baths involved, dark and up to black deposits are obtained which sometimes appear only as dots but sometimes also cover extensive areas. This is true in particular for the current density range below 1 Amp/dm<sup>2</sup>.

It is, therefore an object of the present invention to provide a galvanic nickel bath for depositing silk-dull nickel coats which, even at low current densities, will assure the production of a proper uniform coat while the precipitation of dark deposits onto the articles to be galvanized will be avoided.

These objects have been realized according to the present invention by the fact that the galvanic nickel bath contains anionactive primary and/or secondary phosphoric acid esters of polyalkylene oxide adducts adapted to be produced from ethylene oxide and/or propylene oxide and/or butylene oxide, or by the fact that the galvanic nickel bath contains the salts of such polyalkylene oxide adducts.

The present invention concerns the teaching that anionactive primary and secondary phosphoric acid esters of polyalkylene oxide adducts prepared by the known reaction of polyalkylene adducts and P<sub>2</sub>O<sub>5</sub>, when added to nickel baths containing basic luster substances, especially nickel baths of the Watt-type, during the galvanizing process will yield silk-dull nickel deposits. By polyalkylene oxide adducts intended for reaction with P<sub>2</sub>O<sub>5</sub>, there are meant addition compounds of ethylene oxide, propylene oxide, butylene oxide or mixtures of these alkylene oxides in any desired sequence with low molecular organic compounds, such as ethyleneglycol, propyleneglycol, ethyleneglycol, etc., which with reference to active hydrogen represent bi- or polyfunctional low molecular organic compounds.

Preferably, the galvanic nickel bath according to the invention contains the phosphoric acid esters in a concentration of from 20 - 80 mg/l. The galvanic nickel bath according to the present invention makes possible the generation of a silky luster on articles in the form of a uniform coat even when low and very low current densities are involved. Black deposits do not occur so that above all with highly profiled and curved workpieces to be coated considerable advantages are realized by the present invention over the state of the art as it existed prior to the invention.

From the numerous phosphoric acid esters which may be used in connection with the generation of a silky luster in a nickel bath, there may be mentioned the following

### EXAMPLE

To a nickel bath of the Watt-type which as basic luster substance contains 1 g/l of saccharin, there are added 40 mg/l of a mixture of primary and secondary phosphoric acid esters which mixture was obtained by reaction of the adduct of 30 mol propylene oxide and 30 mol ethylene oxide on propyleneglycol with P<sub>2</sub>O<sub>5</sub> in a molar ratio (mean with regard to P<sub>2</sub>O<sub>5</sub>) of 2.5 : 1 as high viscous, higher molecular liquid. When galvanizing in the range of from 0.5 - 5 Amp/dm<sup>2</sup>, at a temperature of 60°C bath temperature, silk-dull nickel deposits of maximum uniformity were obtained on polished brass. With a layer or coat thickness of 10 um, the peak-to-valley height of the nickel amounted to 0.25 um.

It is, of course, to be understood that the present invention is, by no means, limited to the particular example set forth above but also comprises any modifications within the scope of the appended claims.

It is also to be noted that the bath according to the present invention may be employed for depositing silk-dull nickel coats on various other basic materials.

What we claim is:

1. A galvanic aqueous, acidic bath for precipitating silk-dull nickel coats, containing active phosphoric esters in concentration of 20-80 mg/l, which are pre-

pared by reacting the adduct of 30 mol propylene oxide and 30 mol ethylene oxide on propylene glycol with  $P_2O_5$  at a mol ration of 2.5:1.

2. A galvanic nickel bath according to claim 1, which contains 1 g/l of saccharin.

3. A galvanic nickel bath according to claim 1, in which the bath contains nickel salts selected from the group consisting of nickel chloride, nickel sulfate, nickel fluorborate and nickel sulfamate.

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