

PROTECTIVE AND DECORATIVE COPPER AND NICKEL COATINGS "VELOUR", "VELVET", "SATEEN"

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Abstract

Low reflective decorative mat "velour" and "velvet" coatings provide a qualitatively new exterior of metal articles as a result of deposition from solutions containing the stabilized emulsion. The compositions "SATEEN" and "VELOUR" contain organic agents purposely designed for deposition of coatings with a different degree of a roughness (10-100 μm). The additional finishing of such coatings enhances decorative properties of the velvet surface. After the stage of electrochemical coloring coatings imitate the most attractive view, such as "gold" or «old bronze».

Introduction

Recently more and more rigid requirements are placed upon to the protective and protective-decorative coatings, as well as good mechanical characteristics, corrosion resistance and aesthetic queries are to be present in the modern depositions. This provokes the challenge in new approaches in electroplating.

In modern practice the copper deposit self-maintainedly is not applied almost neither as a protection, nor as a decorative deposit. It is explained to that the copper easily oxidates on air, and especially at heating up. The surface of copper is coated with green scurf of the basic and chloride salts under an operation of carbonic acid and chlorides were in an atmosphere or in liquid environments. The copper is coated with grey or dark brown scurf CuS by the effect of sulphurous compounds [1].

However copper deposits widely apply as an underlayer in multilayer coatings on products, manufactured from steel, zinc and aluminium alloys before nickel, chromic or silver electrodeposition and ensure the best ganging of a substrate with a coating. It allows to reduce width of a topcoat (for example, of nickel) and enables to gain the best decorative effect [2]. In galvanoplastics the copper deposits have received wide application for manufacture of metal duplicates from metal and non-metallic artworks of art products.

Besides, the copper deposits are apply to a furnish of different devices and products with consequent oxidation or other aspects of handling. As such aspects of handling can be used: chemical or electrochemical colouring, patination, and also preliminary mechanical surface treatment (decorative grinding, polishing and scratch-

brushing). Thus the obtained coatings can be of different colours depending on their width, composition and used conditions.

Chemical and electrochemical colouring is one of methods of a decorative finishing of products in copper or copper deposits. This method consists in electrochemical cathode handling of a products in special alkaline electrolytes containing complex ions of divalent copper. Film of copper oxide which width is proportionate to lengths of waves monochromatic making of white light is formed and slowly grows on copper at cathodic current density which is not exceeding $0,01A/dm^2$. In accordance with propagation the film sequentially is dyed in different spectral colours, each of which is easy for fixing during an electrolysis [3].

Colour and appearance of a products surface are the basic decorative performances, which are determined by an expedient of their deriving and are one of resorts of art expressiveness in industrial design [3]. It is possible to select three basic performances of expressiveness of a surface of products - lustre, roughness degree and figure, which can be obtained by a mechanical or chemical expedient [4].

The methods of deriving of mat, microrough and textured surfaces by electroplating of special deposits explicate in several directions. One of them - deriving of deposits such as "sateen" [5-6], which are a variety of composite plates. The size of particles which are in suspension in an electrolyte, can oscillate in limits $0,02 - 0,4 \mu m$. The stability of composition of similar deposits depends on stability of a disperse phase.

Other direction - deriving of decorative mat deposits such as "velour" and "«velvet" with application solutions containing not a solid heterogeneous phase but a stabilized emulsion. Thus formation of microdimples on the deposit give a mut surface by dispersion of a luminous flux [4-7].

The surface roughness magnitude can vary not only from a nature of a disperse phase, but also from its concentration. For maintenance of emulsions in a stable state in an electrolyte add an emulsifier - substance capable to reduce sharp transferring from one not immixing fluid to another.

The features of plating mat and semibright copper deposits such as "sateen", "velour" and "velvet", variants of their consequent furnish and decorative effects, obtained at it surveyed are discussed in this article.

Experimental

We used a standard electrolyte of acidic copper plating ($CuSO_4 \cdot 5H_2O - 180-250$ gpl, $H_2SO_4 - 50-70$ gpl) at a relation $S_a: S_k = 1:1$. The current efficiency makes 98-100 %. As an anode material will be used phosphorous-containing copper. The anodes put in covers from acidproof fabric.

High-molecular compounds and polyols are used as the components formed finely dispersible emulsions and allowing to electroplate "velvet" copper deposits. As a result of application of similar substances the deposit becomes mat or semibright with enough high roughness.

We design compositions "SATEEN" and "VELOUR" on the basis of organic compounds for precipitation of "sateen" and "velour" deposits with a different degree of a roughness (from $1-100 \mu m$). The introduction $1-20$ ml /l of these components in a standard acidic electrolyte of copper plating allows to gain a deposition with a required roughness, which varies depending on a condition of an electrolysis. The inconvertible electrodeposition of "copper-

"velour" is ensured with maintenance of temperature 55 ± 3 at continuous agitating and at current density of $1-6 \text{ A/dm}^2$. Deposit "sateen" is shaped in the same range of i_k at temperature $42 \pm 3 \text{ }^\circ\text{C}$ and at agitating.

The presence of two Tafel's slopes on the polarization curves allows to assume an opportunity of staging process of copper reduction at the slowest stage of disproportionation. Besides it is necessary to take into account adsorption of the additive on a sample surface. The unexpected increase of an overpotential testifies to essential influence of an adsorption in all range of polarization at agitating. The precipitation of a deposit "velour" is accompanied by nonmonotone change of magnitude of an overpotential of copper restoring at a variation of density of the component both at low (fig. 1), and at high i_k (fig. 2).

At a room temperature the deposit "velour" is formed only at very major ($> 50 \text{ g/l}$) concentration of the velourforming component. The increasing of temperature naturally reduces the magnitude of an overpotential [8]. Besides the increasing of temperature can cause chemical conversions of the components and transformation of velourforming polymolecular associates and, as a consequence, to lowering an overpotential.

One more aspect of decorative copper deposit obtained from a standard electrolyte of an acidic copper plating, containing the stabilized emulsion, are deposits with developed surface morphology reminding fractal structures [9]. Brilliance, degree of a roughness and explicitly marked surface of deposits substantially depend on concentration of the newly designed component R-1, condition of an electrolysis and also of agitating. For example, the change of fluid rate and streamline at agitating an electrolyte during an electrolysis considerably influences the degree of an obtained deposit roughness and figure. The general conditions of deposits precipitation: agitating of an electrolyte, temperature $35-40 \text{ }^\circ\text{C}$, current density (i_k) = $4 - 6 \text{ A/dm}^2$.

The finishing of designed deposits not only does not hide but also strengthens decorative effect of a velvety surface.

For example, as a supplementary finishing of velvet copper deposits we used bright nickel electroplating from a suitable electrolyte ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O} - 300 \text{ g/l}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} - 40 \text{ g/l}$, $\text{H}_3\text{BO}_3 - 20 \text{ g/l}$, brightener). The thin layer of nickel underlines the roughness of a velour copper underlayer, creating the illusion of a silver-mat velvety product surface. The roughness of a nickel deposit varies according to the type of a copper substrate ("sateen", "velour", "velvet"). Both the electrodeposition of laminas ($1-3 \text{ }\mu\text{m}$) of chrome and vacuum arc deposition of titanium oxide or nitride by PVD method atop of deposits such as "velvet", "sateen" and "velour" also intensifies decorative effect and essentially (by 15-70%) raises corrosion resistance of articles [10].

The decorative finishing of articles with copper deposits such as "velvet", "sateen" and "velour" by electrochemical colouring was carried out by us in a suitable solution ($\text{CuSO}_4 - 50-60 \text{ g/l}$, sugar - $80-90 \text{ g/l}$, $\text{NaOH} - 40-50 \text{ g/l}$), at $t=35-45 \text{ }^\circ\text{C}$, $i = 0,01-0,02 \text{ A/dm}^2$. The article with a copper deposit is sequentially dyed in a time interval from 2 to 25 minutes in brown, violet, dark blue, blue, light green, yellow, orange, red - lilac, greenish-dark blue, green, pinkish-red colour. Articles with a velvety surface after colouring them for imitation "gold" and "old bronze" looked most effectively.

Conclusions

The carried out examinations have shown that is possible to precipitate microrough deposits from emulsion electrolytes. The degree of a surface roughness varies according to a condition of an electrolysis (current density and temperature). The designed compositions allow to form decorative deposits with given morphology of a surface: from velvet up to fractal-shaped.

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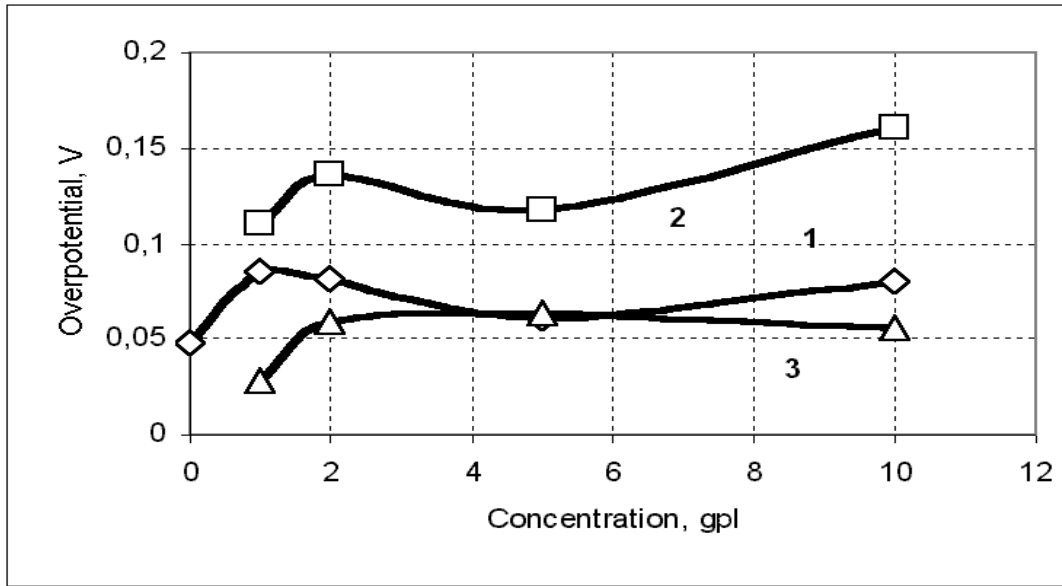


Fig. 1. The influence of additive concentration on the overpotential of copper reduction (1,2 – 25 °C; 3 – 50 °C; 1 – without agitation; 2,3 – with agitation)

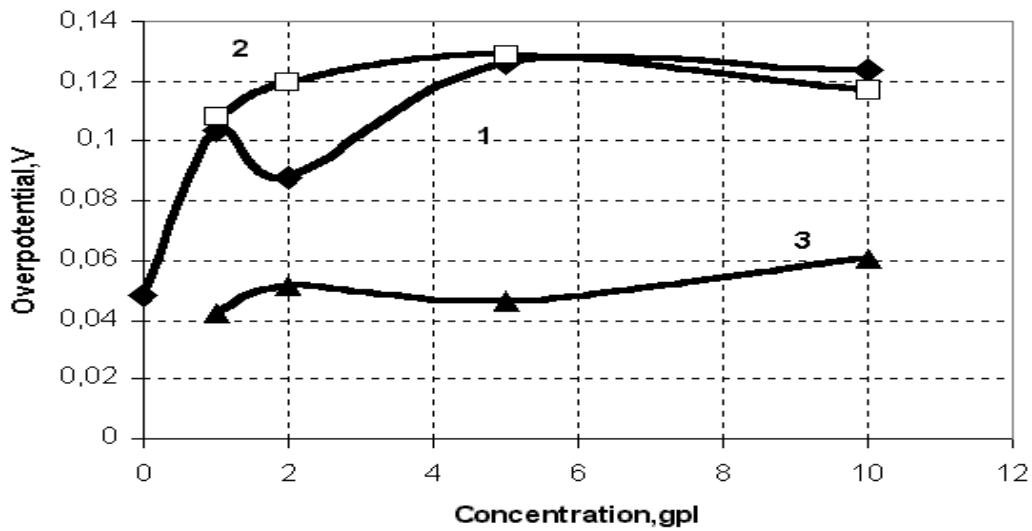


Fig. 2. The influence of additive concentration on the overpotential of copper reduction (1,2 – 25 °C; 3 – 50 °C; 1 – without agitation; 2,3 – with agitation)