New nickel- and hexavalent chromium free matte coating for decorative applications

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Introduction

Satin matte chromium plated parts look more beautiful and valuable. And they are well accepted in the market. Today the matte effect is produced by a special matte nickel layer coated with chromium for interior parts. Multi nickel layer systems are used for outdoor exposition(semibright, matte and microporous nickel followed by chromium).

In the state of art, matte nickel plating exhibits great economic significance used in decorative plating due to its attractive appearance and the relatively low cost. However, the nickel metal price limits its application and discounts its worth. Therefore, the development of an alternative satin matte plating process without nickel is very important for decorative applications.

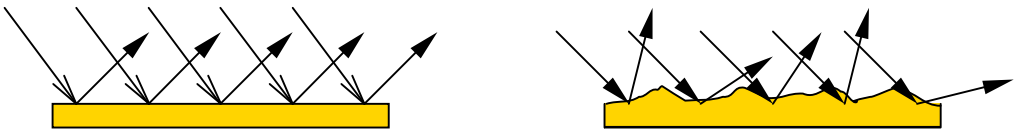
We frequently get more and more requests from the household industry to develop such attractive surfaces without the use of nickel. This is to address nickel leaching from such parts during household use.

Some companies like to advertise that they offer “green” products like nickel-free and hexchrome-free processes. There is no need to have the products nickel-free because the leaching in water or artificial sweat is quite low.

To understand how matte nickel plating works we will discuss the principles first. The term pearl brite is used to characterize a coating surface that appears smooth uniform and satin matte with an aesthetic lustre and appearance. The process to produce this attractive satin matte metal coating, is an advanced alternatively to the traditional bright metal plating. In state of art, research and development of the matte plating are mainly focus on nickel plating, which combined with semi-bright nickel and chromium layer has been widely applicated on jewelry, medical equipment, furniture, and automotive industry.

General idea of satin matte coatings

The most attractive characteristic of satin matte coatings is the glare-free effect. This means that a coating surface that provides more or less a satin brightness, i.e. a relatively bright finish but does not produce a dazzling effect.



(a) flat surface reflection (b) rough surface nonpoint reflection

Figure 1: Illustration of the reflection on different surface

From an optical point of view light is transmitted parallel to the surface of all articles. If the surface is very flat, the light will be reflected parallel to the eyes of the observer and this article appears is than sparkling. As the intensity of the light source is too strong, the intensity of the reflected beam increases and the observer will feel dazzled. However, when the surface is not very flat but with much small waviness, nonpoint reflection occurs instead of parallel reflection. The reflex transmits in all random directions and the intensity of the reflex will be reduced strongly, which brings harmony/lambency to the eye of the observer. Figure 1 illustrates this effect.

The satin matte coatings are particularly suitable for office and buildry like door furniture and light fittings, where its unobtrusive appearance blends in with the surroundings. High fidelity equipment, cameras, mobile phones, automobile or other quality domestic goods also use satin matte coating widely.

Figure 2: Satin matte plated articles

Mechanism of the matte satin-finish plating

Satin-finish metal coatings have been produced using several different methods. In one method, the surface of a metal substrate is mechanically blasted with an abrasive medium such as aluminium oxide to provide a textured surface, which is then electroplated with bright nickel or chromium. Another method involves the deposition of satin matte nickel finishing directly from the nickel bath without mechanical treatment. The nickel bath used is a typical nickel plating bath with the addition of a large amount of insoluble inorganic powdery material with a particle size of about 0.1 to 3 μm, such as kaolin, talcum, barium sulfate, etc. These particles will diffuse to the cathode surface and adsorb there, and then incorporate into the metal deposition and result in a satin matte deposited structure. These two methods are generally not preferred because of their relatively higher price, lower efficiency or unsatisfactory appearance [1].

A desired process for uniform satin matte finish has been developed in nickel plating with a much lower price than the old processes [1]...[5]. Surfactant is added into the electroplating bath to form a finely divided dispersion in the electrolyte at operative temperature. This dispersion can be formed in two ways depending on the properties of the added surfactant. Ionic surfactants react with the anions in the electrolyte and form small insoluble solid particles dispersed in the electrolyte as suspension. Nonionic surfactants that show a low solubility in the electrolyte will disperse as agglomerated micelles or as an emulsion. The dispersed particles or droplets will adsorb on the cathode surface due to diffusion, convection or electrical attractions. They will influence the physical properties of the cathode surface such as surface tension and charge distribution or directly incorporate into the metal deposition and result in a satin matte deposited structure. Generally speaking, the nonionic surfactants are more preferable than the ionic surfactants because of its electrically neutral structure, which makes them significantly less sensitive to the presence of the electrolytes in the system and to the solution pH. Nonionic surfactants are always synthetic flexibility of being able to design the required degree of the solubility into the molecule by the careful control of the size of the hydrophilic group. In addition, the adsorption of them on the cathode surface shows less destroys in the cathode surface property and the metal deposition than that of the ionic surfactant.

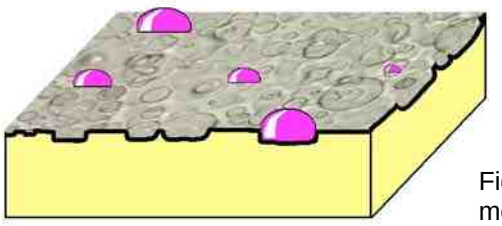


Figure 3: Satin matte plating mechanism

The dispersed droplets or micelles can have a size in the range from a few nanometers to hundreds or thousands of nanometers. In order to achieve an acceptable roughness and homogeneity for the

deposited coating, it is important that the surfactant is dispersed throughout the electrolyte homogeneously with a desired size. As a rule, a freshly prepared electrolyte will typically exhibit the desired finely divided dispersion surfactant. However, after a period of time, the finely divided droplets or micelles will coalesce or agglomerate into larger micelles and the roughness of the matte coating will increase consequently. If nothing further is to counter the growth of the micelles, the roughness depth will increase to an unacceptable level with an unacceptable appearance. What is worse, serious agglomerate defects will appear at the coating due to large agglomerates sticking to the cathode surface and destroy the normal deposition mechanism. When the sticking happens at the beginning of the deposition, the deposit will be compromised. Therefore, the control of the stability of the electrolyte is of great significance.
To improve the appearance of the satin matte coating and ensure the process, a suitable carrier, such as saccharin, is necessary to be added individual or in combination with the additives into the bath [3]. And to obtain a brightening effect in conjunction with the antiglare effect of the deposits, the electrolyte additionally could also contain some brighteners.

Bronze, Sn/Co and other tin alloys are the most popular alternatives to nickel in decorative plating nowadays [6, 7 and 8]. Considering the technical possibility and costs of the process, research has been done to develop a process to create an attractive matte coating structure in acid copper plating. Because of the limitation of bad tarnish and corrosion resistance of bare, unprotected copper coatings, other metal coatings, such as white bronze, chromium, palladium, silver or gold can be used to improve the life span and attraction of the matte copper coatings. The combination of these coatings forms a nickel-free satin matte coating system. The main purpose of this thesis is focus on developing a plating process to produce nice Satin matte copper coatings with acceptable time stability of the plating bath.

Satin matte copper

We found two ways to produce such satin matte surfaces. The first option is to use a matte copper from the PWB plating field and plate a white or yellow bronze on top. For some applications the color and corrosion resistance is accepted by the designers. Those who require more corrosion resistance and a bright or blackish color can plate the right trivalent chromium on top. The matte effect of the PWB copper is a little different in high and low current density areas. Therefore parts with a complex shape are not easy to plate with uniform coating.

The second version and we believe the best is a new developed matte copper which has the same appearance like the well known satin matte nickel products in the market. The satine matte effect is made by special additives. The pearl brite copper was born. These parts are looking really nice. and designers in different household article producing companies are inspired about the appearance. The corrosion resistance of the layer system matte copper, white bronze (cyanide version: BRONZEX WJ® or acid: BRONZEX WMR® and trivalent chromium as final layer is not as high as necessary for exterior applications, but meet the specifications for interior parts.

The make-up and maintenance is quite similar that of matte nickel. After about 8 hours the additives start to agglomerate to bigger particles and the coating looks rougher. That is the point where the additives are filtered out like a normal satin matte nickel system. Concentration of additives and temperature are able to control the roughness. The controlled feed and filter out in a by-pass type system is possible as demonstrated in production with continuous satin matte nickel.

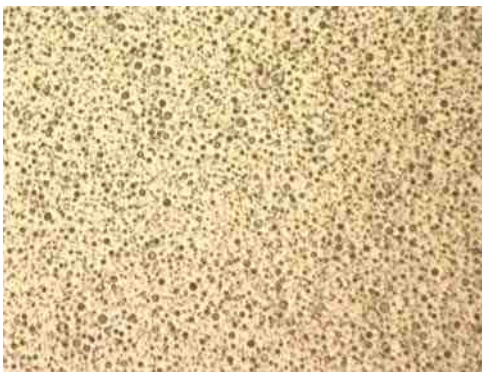


Figure 4: Satin matte copper

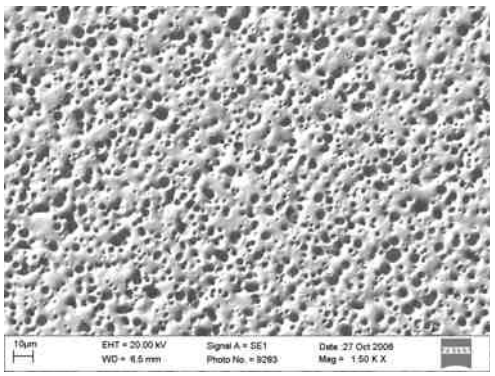


Figure 5: Satin matte copper and Bronzex WMR®

Figure 6: Satin matte parts plated with matte copper, bronze, and trivalent chromium in comparison with a bright part.

Conclusions

The new satin matte copper plated with a white bronze and on demand with trivalent chromium enables us to produce a nickel-free, hexchrome-free satin matte coating.
In the same way the plating process with bright copper or any other suitable bright layer followed by a bronze layer and trivalent chromium results in a bright nickel-free systems made in a hexchrome-free process.

All versions to produce such a nickel-free surface are patent pending.

Literature

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