

AN ARTICLE HAVING A COATING WHICH GIVES

THE ARTICLE A BLACK SILVER APPEARANCE

5 This invention relates to an article having a coating which gives the article a black silver appearance.

Articles having a coating which gives the article a black silver appearance are known. One known method
10 for producing such articles comprises immersing a material previously coated with a metal such for example as zinc, aluminium or nickel, or immersing a metal itself, for example zinc, aluminium or nickel, in a solution mainly composed of sodium chromate or sodium
15 bichromate, thereby forming a chromium oxide coating. Another known method comprises immersing material previously coated with metal such for example as zinc, aluminium or nickel, or immersing a metal itself, for example zinc, aluminium or nickel, in a nickel chloride
20 solution passed with hydrogen sulphide, thereby forming a nickel sulphide coating. These known methods of chemical treatment are disadvantageous in that the starting materials are restricted in that the thickness of the coating layer formed thereby is extremely thin,
25 being at most about 0.1 micron, and in that the coating

layer lacks a dense texture. Accordingly, the produced articles have suffered problems such as those of corrosion resistance and abrasion resistance.

5 It is an aim of the present invention to provide an article in which the above mentioned problems are obviated or reduced.

10 According to the present invention there is provided an article having a coating which gives the article a black silver appearance, the coating being a cermet coating of chromium and alumina or of nickel/chrome alloy and alumina.

15 Preferably, the coating comprises 5 to 50% by weight of alumina.

20 The coating may be formed by vapour deposition, sputtering or ion plating.

25 Apart from the coating, the article may be made of a synthetic resin, a metal or a ceramic material. The synthetic resin, the metal or the ceramic material may be provided with a primer coating. The primer coating may be a nickel or chromium primer coating. Other primer coating materials may be used. The primer coating may be formed by plating or coating.

30 The article of the present invention may be any desired and suitable article such for example as spectacle frames, stationery items, personal ornaments

and various kinds of accessories and exterior items.

The coating may give the article a metallic gloss which is highly decorative in appearance, and which has excellent corrosion resistance, abrasion resistance and close bondability. Furthermore, the article may be such that it can consistently be reproduced with the required quality, and at reduced costs compared to known methods.

The highly decorative nature of the metallic gloss provides a gracious and high quality feeling. The cermet coating may have a high density and, as mentioned above, it is excellent in corrosion resistance, abrasion resistance and close bondability. The above mentioned consistent reproducibility is achieved, at least in part, because the coating can be provided in a uniform manner. Moreover, a large range of starting materials can be employed and the coating is easily formed.

In order to facilitate a full and complete understanding of the invention, reference will now be made to the following Examples.

EXAMPLE I

This Example gives details of a study of various composite cermets of metal-oxide.

When using a composite cermet of metal-oxide ceramic as a coating material, it is desirable that the

composition, given the metal as X and the oxide ceramic as $Y_{x_2}O_{y_2}$, can satisfy the following relationship in view of the formation of free energy:

$$|X_{x_1}O_{y_1}| < |Y_{x_2}O_{y_2}| \quad (I)$$

This means that the metal of the cermet should not reduce the oxide ceramic on sputtering. If a reduction proceeds during sputtering, conversion of cermet into ceramic occurs and, as a result, the optical transparency of the material for the coating is increased, causing interference of light in the coating and thus making it difficult to obtain a uniform tone for the coating as well as making it difficult to reproduce a substantially identical tone in subsequently produced coated articles.

By considering not only the decorative properties of the produced coated articles, but also their required corrosion resistance and abrasion resistance, chromium Cr and nickel/chrome alloy (NICHROME - Trade Mark) were selected as the metal to be used. With regard to the selection of an oxide ceramic capable of satisfying the relationship defined by equation (I) with respect to chromium or nickel/chrome alloy, the following compounds were considered: zirconium oxide, vanadium oxide,

alumina, niobium oxide and tantalum oxide. With such compounds the formation of free energy has the following relationship:

$$| \text{ZrO}_2 | < | \text{V}_2\text{O}_5 | < | \text{Al}_2\text{O}_3 | < | \text{Nb}_2\text{O}_5 | < | \text{Ta}_2\text{O}_5 | \quad (\text{II})$$

In this case, while equation (I) can be satisfied for ZrO_2 and V_2O_5 , a reaction occurs during sputtering and this tends to cause a small loss in the uniformity of the tone. Further, for Nb_2O_5 and Ta_2O_5 , the reaction does not occur substantially in the sputtering and the coating has less difference in tone as compared with a coating of chromium or nickel/chrome alloy alone, and it gives no special effect as a decorative coating.

Thus, as a result of the above, chromium and nickel/chrome alloy were selected as suitable metals and alumina Al_2O_3 was selected as the oxide ceramic.

EXAMPLE II

A decorative casing made of ABS resin was placed in a high frequency magnetron sputtering device and a composite target comprising 70% of chromium and 30% by weight of alumina was used. After reducing the pressure in the magnetron sputtering device to a vacuum of about $(1.0 - 2.0) \times 10^{-3}$ Pa, argon gas was applied to increase the pressure to $(6.0 - 7.0) \times 10^{-1}$ Pa. Then sputtering

was applied at a high frequency output of 8 Watt/cm².
The film forming rate was 0.78 micron/hour and the
thickness of the coating thus formed was 0.2 micron.

5 The temperature of the material heated during film
formation remained from room temperature up to 50°C, the
material caused no thermal deformation and showed good
close bondability. A highly decorative black silver
10 coating having a metal gloss was formed.

EXAMPLE III

Chromium metal and alumina were disposed
separately as targets. Shutters were attached to both
15 of the targets and sputtering was applied whilst
controlling the alumina ingredient ratio to 30% by
weight by the degree of opening for both of the
shutters. Other conditions were the same as those in
20 Example II and the coating thus formed was also as
described above in Example II.

EXAMPLE IV

25 Sputtering was applied using a composite target
comprising 70% by weight of nickel/chrome alloy and 30%
by weight of alumina, and under the same conditions as
in Example II. The thus formed coating was a highly
30 decorative black silver layer, with good close
bondability.

In Example IV, the composition for nickel/chrome

alloy was set to 80% nickel and 20% chromium. It is to be appreciated that other weight percentages may be employed for the nickel/chrome alloy. Also, when placing nickel/chrome alloy and alumina in separate targets and applying sputtering in the same manner as in Example III, a satisfactory coating layer similar to that mentioned above in Example III was obtained.

In all of Examples II to IV, the coating had an intense metallic nature and was excellent in its close bondability.

EXAMPLE V

Examples II to IV were repeated using vacuum deposition and ion plating as two alternatives to the sputtering employed in Examples II to IV. When using an electron beam for the evaporation source, both in the vacuum deposition and in the ion plating, two electron guns and crucibles were disposed respectively in one device and ion plating was applied for chromium (or nickel/chrome alloy) and alumina independently under appropriate conditions for the evaporation rate to form a layer. One of these conditions for the evaporation rate was that the alumina ingredient ratio in the layer was from 5 to 50% by weight. When using one electron gun and crucible, a target previously set to a proper ingredient ratio may be placed and evaporated

simultaneously.

The material of the article to which the coating is applied can be, for example, a synthetic resin, a metal or a ceramic material. There is no particular restriction on the type of material that can be employed. The material may be plated, for example, nickel plated or chromium plated, prior to applying the cermet coating. Alternatively, if desired, the material may be coated with a metal such, for example, as chromium, nickel/chrome alloy or nickel by sputtering, vacuum deposition or ion plating prior to applying the cermet coating. Generally, the material may be treated in the above and other ways with the aim of improving the close bondability of the subsequently applied coating. Where the material is a metal of poor corrosion resistance, a primer coating of a metal or a ceramic layer may be disposed between the material and the cermet coating with the aim of improving the corrosion resistance of the finally produced article.

The amount of alumina used in the coating may determine the optical transparency of the formed coating and therefore the decorative nature and the colour tone

of the finally produced article. As indicated above,
the alumina is preferably employed in the range of 5 to
50% by weight but greater or lesser amounts of alumina
may be employed if desired.

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CLAIMS

1. An article having a coating which gives the
5 article a black silver appearance the coating being a
cermet coating of chromium and alumina or of
nickel/chrome alloy and alumina.

10 2. An article according to claim 1 in which the
coating comprises 5 to 50% by weight of alumina.

3. An article according to claim 1 or claim 2 in
which the coating is formed by vapour deposition,
15 sputtering or ion plating.

15 4. An article according to any one of the preceding
claims in which apart from the coating, the article is
made of a synthetic resin, a metal or a ceramic
material.

20 5. An article according to claim 4 in which the
synthetic resin, the metal or the ceramic material is
provided with a primer coating.

25 6. An article according to claim 5 in which the
primer coating is a nickel or chromium primer coating.

7. An article according to claim 5 or claim 6 in
which the primer coating is formed by plating or
30 coating.

8. An article as claimed in claim 1 and having a
coating which gives the article a black silver
appearance substantially as herein described.
