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PROCESS FOR BLACK FINISHING METALS

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The present invention relates to metal finishes and, particularly, to black finishes used for ornamentation purposes and, in certain applications, as a protective coating to reduce the effects of abrasion, corrosion, oxidation and the like.

It frequently is desirable to provide a black finishing coating on a metallic surface either for purposes of ornamentation or to protect the surface, or for both ornamentation and protection. A so-called "black-nickel" finish has heretofore been used for this purpose. This finish is prepared by immersing the surface to be finished in a nickel-salt solution and making it the cathode in an electrolytic process. Numerous difficulties are encountered in providing a satisfactory black-nickel finish since the inexact nature of the resulting deposit is such that it is difficult to predict the final color, which may run from a dark brown to a satisfactory black color. The reasons for this are that the deposit is extremely critical as to the value of the current used in the process, as to the concentration of several constituents of the solution, and as to the technique employed in carrying out the process. Additionally, a black-nickel finish has the disadvantage that it can only be considered a decorative finish and has practically no value as a protective finish, thus requiring the use of an additional protective coating of lacquer, baked enamel, or the like.

It is an object of the present invention to provide a new and improved black finish and finishing process for metals.

It is an additional object of the invention to provide a new and improved finish and finishing process for metals and one in which the finish is easily and quickly applied and possesses a high degree of resistance to abrasion and chipping.

It is a further object of the invention to provide a new and improved finish and finishing process for metals and one in which the finish exhibits highly tenacious properties and offers substantial protection to the surface of the metal.

It is an additional object of the invention to provide a new and improved finish and finishing process for metals wherein the finish is unusually durable and pleasing in appearance.

It is a further object of the invention to provide a new and improved finish and finishing process for metals which does not require an electric current in the process by which the finish is formed.

In accordance with the invention, a process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium comprises electrochemically depositing on the sur-

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face from a solution of a copper salt and a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, and treating the deposit in a hydrogen-peroxide solution.

For a better understanding of the present invention, together with other and further objects thereof, reference is had to the following description, and its scope will be pointed out in the appended claims.

The present invention contemplates the provision, on a metallic surface of zinc or cadmium or a combination of these metals, of a black decorative and protective finish comprising primarily a tenacious fine-grained coating of a copper oxide. This coating is quite durable and possesses a high degree of resistance to abrasion. It is not subject to chipping, and experience has shown that its protective properties reside not alone in the presence of the coating on the metallic surface but in imparting to the surface a resistance to oxidation and corrosion not previously possessed by the surface. The color of the coating may be controlled within limits from a deep jet black to a soft black.

The finishing coating of the present invention requires the use of two baths, and preferably the use of three baths, in which the surface to be finished is immersed. The three baths are referred to hereinafter in the specification and claims as Baths A, B and C, of which Baths A and C are essential and the additional use of Bath B is preferred. The composition of these baths will now be described.

Bath A

This bath comprises a $\frac{1}{2}$ per cent. to 1 per cent. by weight water-soluble copper salt and a $1\frac{1}{2}$ per cent. to $2\frac{1}{2}$ per cent. by weight water soluble alkali-metal or alkaline-earth-metal chlorate.

In regard the first ingredient, a cupric salt and particularly copper sulphate is preferred. The concentration above noted for the copper salt is that which furnishes the best black finish with reasonable length of life of the solution. Larger concentrations of copper salt produce increasingly browner tones in the finish due to the larger granular structure of the deposit. Concentrations of the copper salt less than 1 per cent. produce the blackest obtainable finish, but are quickly exhausted due to the low concentration of copper in the solution.

In regard the second ingredient, namely the

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alkali-metal or alkaline-earth-metal chlorate, potassium chlorate is preferred. However, a relatively large class of chlorates is useful. Of the alkali-metal chlorate type, chlorates of potassium, sodium, lithium, caesium, rubidium, are useful. Alkaline-earth-metal chlorates are represented by magnesium, calcium, barium, strontium. The concentration of this ingredient cannot be too high. Concentrations of less than 1 per cent. tend to produce a brownish tinge in the finished deposit.

Bath B

This bath comprises a water-soluble alkali-metal or alkaline-earth-metal permanganate of which permanganates of the aforementioned alkali-metals and alkaline-earth-metals are typical. Potassium permanganate is preferred. A satisfactory concentration is 1 per cent. to 2 per cent. by weight, although stronger concentrations have longer life and any greater concentration may be used up to a saturated solution at 25 per cent.

Bath C

This bath comprises a hydrogen peroxide solution. A thirty per cent. by weight aqueous solution is preferred.

The procedure to be followed in finishing a metallic surface by deposition thereon of a coating in accordance with the present invention will now be considered.

Where the metal surface to be finished is not one of cadmium or zinc, the first step in the coating process is to coat the surface with cadmium or zinc, or a combination of these metals, in a manner well understood in the art. Cadmium is preferred due to the ease with which it may be applied and to the fact that an electrolytic process is used in its application. The cadmium or zinc surface is now immersed in Bath A for approximately 15 seconds, the bath being maintained at a temperature approximately within the range of 60 degrees to 70 degrees centigrade. Immersion for too short a time does not provide a sufficiently heavy coating; too long immersion provides a coating tending to have reduced adhesive properties.

The surface to be finished is then immersed in Bath B for approximately 10 seconds, this being about the minimum time for satisfactory results. The article can be immersed in this bath substantially longer without harm to the process. This bath is used at normal room temperature, 20 or 21 degrees centigrade.

The article is then drained for approximately 10 seconds and immersed in Bath C for approximately 10 seconds, this being about the minimum time for satisfactory results. It is to be noted that the article should not be immersed in this bath appreciably beyond the length of time specified since prolonged immersion tends unduly to corrode the base metal. The temperature of this bath should not exceed approximately 28 degrees centigrade.

The article is then successively and repeatedly immersed in Baths A, B and C, as above described, until the desired intensity of black is produced. Ten cycles of such immersion has in practice been found generally satisfactory. Continued cycles do not substantially increase the depth of the coating since it appears to be impervious to liquid after about ten such cycles.

The article is next rinsed in clear water and dried in air, oven drying being not necessary al-

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though not harmful to the finish. While the finish is wet it presents a smooth black surface. When dry, however, a loose greenish-brown powder appears over the surface. This excess deposit is removed preferably by the use of a buffing cloth and a fine black rouge.

An additional organic black coating, such as a black lacquer or black synthetic baking enamel, may be sprayed over the finish, if desired, as additional protection to the finish itself.

The manner in which the deposit is formed on a zinc or cadmium metallic surface is not clearly understood but is believed to occur as follows. Since zinc and cadmium are both higher in the electromotive series than copper, metallic copper in Bath A is deposited out of solution and onto the zinc or cadmium surface by an electrochemical action. The alkali-metal or alkaline-earth-metal chlorate, which is a constituent of this bath, is an oxidizing agent and oxidizes the metallic copper immediately after it has been deposited out of solution, thus to form a microscopic layer of copper oxide. This electrochemical deposition is terminated before the layer of copper oxide thus formed becomes too thick.

The immersion of the article in Bath B produces a reaction the exact nature of which is unknown. It is probable that some manganese dioxide is deposited out onto the layer of copper oxide. Observation indicates that this bath performs the function of increasing the adhesion of the deposit. The use of this bath is not essential in the process described, and may be omitted, but has been found greatly to increase the adherence of the deposit in certain cases as, for example, where the finishing coating is provided on cadmium or zinc which has been electroplated onto a poor quality of steel.

The function of Bath C is to destroy any existing potassium permanganate which is carried over from Bath B, and which would give the deposit a purplish tinge, and additionally to increase both the blackness and adherence of the deposit. The exact nature of the reaction which occurs, particularly in regard to the property of this bath to increase the blackness and adherence of the deposit, is not known. It would seem that the bath at least reduces any permanganate carried over from Bath B to manganous chloride and manganous sulphate or either, both of which are almost colorless, and reduces the chlorates carried over from bath A to potassium chloride, which is colorless.

A finish provided in accordance with the invention possesses not only a pleasing appearance, but additionally is characterized by unusual durability, tenacity, and a high degree of resistance to abrasion and chipping, thus to provide substantial protection to abrasion, corrosion and oxidation of the coated metal surface. Additionally, the finish of the invention has the advantage that it may be formed on a cadmium or zinc surface without the need of an electric current in the process employed.

While there has been described what is at present considered to be the preferred embodiment of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is, therefore, aimed in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. A process for coating a metallic surface

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formed of a metal from the group consisting of zinc and cadmium which comprises electrochemically depositing on said surface from a solution of a copper salt and a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, and treating said deposit in a hydrogen-peroxide solution.

2. A process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium which comprises electrochemically depositing on said surface from a solution having a temperature within the approximate range 60 degrees to 70 degrees centigrade and comprising a copper salt and a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, and treating said deposit in a hydrogen-peroxide solution.

3. A process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium which comprises electrochemically depositing on said surface from a solution of copper sulphate and a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, and treating said deposit in a hydrogen-peroxide solution.

4. A process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium which comprises electrochemically depositing on said surface from a $\frac{1}{2}\%$ to $1\frac{1}{2}\%$ copper salt solution with a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates added thereto a coating primarily of a copper compound, and treating said deposit in a hydrogen-peroxide solution.

5. A process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium which comprises electrochemically depositing on said surface from a solution of copper sulphate and potassium chlorate a coating primarily of a copper compound, and treating said deposit in a hydrogen-peroxide solution.

6. A process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium which comprises electrochemically depositing on said surface from a solution of a copper salt and a $1\frac{1}{2}\%$ to $2\frac{1}{2}\%$ by weight chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, and treating said deposit in a hydrogen-peroxide solution.

7. A process for coating a metallic surface

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formed of a metal from the group consisting of zinc and cadmium which comprises electrochemically depositing on said surface from a solution of a copper salt and a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, and treating said deposit in a 30% solution of hydrogen peroxide.

8. A process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium which comprises, electrochemically depositing on said surface from a solution of a copper salt and a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, treating said deposit in a solution comprising a permanganate from the group consisting of alkali-metal and alkaline-earth-metal permanganates, and then treating said deposit in a solution of hydrogen peroxide.

9. A process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium which comprises, electrochemically depositing on said surface from a solution of a copper salt and a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, treating said deposit in a solution of potassium permanganate, and then treating said deposit in a solution of hydrogen peroxide.

10. A process for coating a metallic surface formed of a metal from the group consisting of zinc and cadmium which comprises, electrochemically depositing on said surface from a solution of a copper salt and a chlorate from the group consisting of alkali-metal chlorates and alkaline-earth-metal chlorates a coating primarily of a copper compound, treating said deposit in a 1% to 2% solution comprising a permanganate from the group consisting of alkali-metal and alkaline-earth-metal permanganates, and then treating said deposit in a solution of hydrogen peroxide.

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REFERENCES CITED

The following references are of record in the file of this patent:

FOREIGN PATENTS

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