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SURFACE TREATMENT OF ZINC AND CADMIUM

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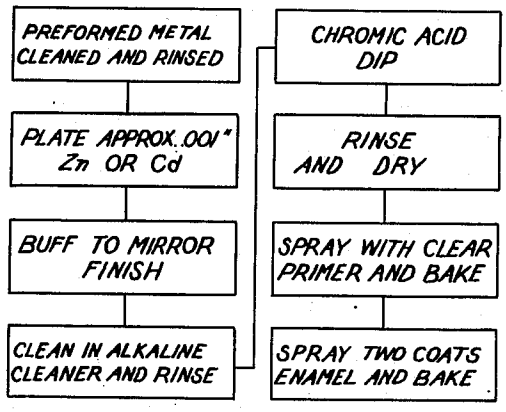


FIG. 1

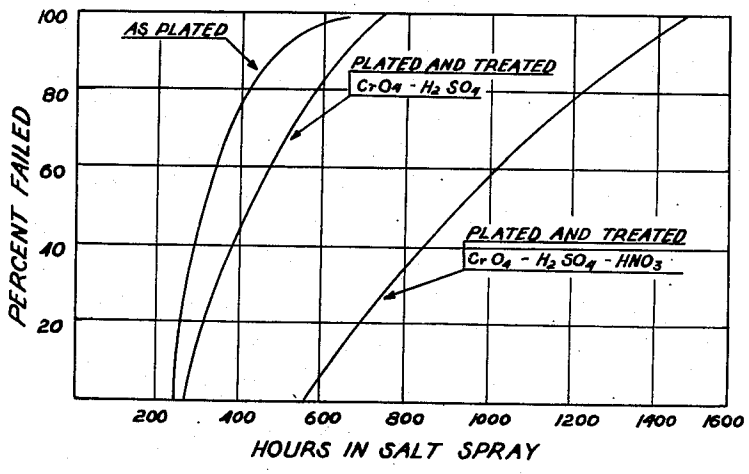


FIG. 2

R. H. McCarroll
L. L. McCloud
H. C. L. Hanson
INVENTORS

BY Edwin C McRae and Robert F. Harris.
ATTORNEYS.

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SURFACE TREATMENT OF ZINC AND CADMIUM

Russell H. McCarroll and John L. McCloud, Dearborn, and Harry E. J. Hanson, Detroit, Mich., assignors to Ford Motor Company, Dearborn, Mich., a corporation of Delaware

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5 Claims. (Cl. 148—6)

This invention relates to a method of applying protective and decorative metal coatings to base metals and is more particularly related to treatment of metallic automobile body parts known as brightwork. It also contemplates the further surface treatment of these bright parts to increase their durability, finish, and brightness.

An object of this invention is to use on the base metal an electrically-deposited, protective metal coating which may be treated to produce highly lustrous as well as stable and corrosion-resistant finishes. A further object of this invention is to use as the plating metals those chosen from the class of zinc, cadmium, and the like. Yet another object of the invention is to obtain a zinc or cadmium coating which is comparable in brightness, reflectivity and color to those heretofore obtained in using chromium or nickel. Another object is to obtain similar bright finishes on die castings.

Experiments have long been under way to find suitable substitutes for the common, and costly, copper, nickel, chromium plating heretofore used.

The stress of the present national emergency has given additional impetus to the search since chromium, nickel, and copper have been among the first material restricted to military uses. With the elimination of the three metals named from the available field, every source and type of brightwork commonly used from the beginning of the automotive industry has been cut off.

Under such circumstances, there are two alternatives. One is to avoid entirely the use of brightwork and obtain decorative contrast by means of different color combinations. But no matter how well this is carried out, the effect achieved leaves something to be desired in the absence of the accent which properly placed brightwork alone can give. The other alternative is to seek among the commoner and more available metals those which could take the place of chromium, nickel, or copper and which would give platings that are comparable in effect and luster durability to those formerly used.

Following the second course, metals in the class of zinc, cadmium, and the like were first considered because they had been used in rough plating where luster, durability, and high polish were not important, as in machine parts. Despite this use, these metals have not been successfully applied to obtain polished and highly lustrous stable plating.

In former practice, the zinc or cadmium plating was electrodeposited from basic or acidic solutions and was further treated or brightened by other agents in a plating bath or applied in an after-plating dip. The first class of agents includes organic compounds which whiten the plated structure and cause an over-all uniform appearance. Other agents were based on the chromic acid dip which is essentially a brightener but which does not work well on buffed surfaces. In both cases, the treated surfaces are deficient in brilliance and luster.

Broadly considered, this invention constitutes two steps: the formation of a bright, lustrous, durable metal surface which will take a protective coating; and the application of a transparent coating which will adhere to the polished surface and maintain its integrity under conditions of shock and temperature incident to ordinary use. However, the requisite qualities, heretofore, have been antagonistic. Thus, brightening a zinc surface weakened its durability. Polishing the surface made it almost impossible to get a satisfactory "tooth" for paint. The protective coating itself—if durable enough for wear—required either too high a baking temperature to be supported by zinc or would peel or become disassociated from the base. Each of these conflicting factors must be reconciled and subordinated to the end desired. The method of this invention shows the way to the attainment of a bright and durable coating of the metals named. Moreover, it is equally applicable to die-cast bases, which normally contain large percentages of zinc, and to plated coatings of zinc, cadmium or other similar metals; and, while zinc is referred to specifically in the following description, it is to be understood that the other metals noted are included in this invention.

With these and other objects in view, the invention consists of the combination of the various steps of the method and the composition of the various agents used therein, as described in this specification, claimed in the claims, and illustrated in the accompanying drawing, in which:

Figure 1 is a flow sheet for producing zinc-plated, bright trim.

Figure 2 is a comparative graph showing the corrosive resistance of plated metals given various dips and treatments.

Attention is now directed to Figure 1 in which the steps are shown to obtain a piece of automotive brightwork, such as a molding strip, using a zinc plate. The preformed metal base is cleaned and rinsed, and is then zinc-plated in any of the usual baths, either acidic or alkaline,

as for instance a cyanide plating bath of approximately the following composition:

	Ounces per gallon
Zinc cyanide	8
Sodium cyanide	4
Caustic soda	7

In conjunction with the plating bath, perfectly satisfactory zinc anodes may be formed by remelting the scrap die castings, which will include zinc, tin, aluminum, lead, copper, and other metals. Although the amount of sludge is increased, the resultant coating appears to be harder and more impervious than obtained from pure zinc anodes. Other results are also comparable as it has been noted that die castings themselves can be given the same treatment as plated materials.

The depth of the deposited coating is approximately .001'' before buffing, which reduces it to about .005''. The buffing step is very important in that it determines the polish of the finished article and hence is largely responsible for its final appearance. The buffed article is cleaned in a mild alkaline bath and rinsed.

The following step is particularly important because of its influence on the three prime factors involved: the durability, the brightness, and the "tooth" of the finished surface. In essence, this step includes the dipping of the article in a chromic-acid bath which is distinguished by the fact that it also contains a combination of other acidic radicals. Certain chromic-acid baths are widely used to brighten dull plating and are well-known under several trade names but none, to our knowledge, is effective on buffed work to enhance the surface and increase its "tooth." For example, in Figure 2 the several curves show the durability of test plates with different dips under the standard salt-spray test.

For the first curve, the plated article was exposed to the spray without further treatment. For the second, the plated article was treated by a subsequent dip in chromic acid and sulphuric acid in proportion according to one of the most common commercial dips. In the third curve, the plated article was dipped in the composition of this invention. The gain in durability in the last instance is clearly shown.

This bath is essentially an aqueous solution of chromic acid or a similar acid which is relatively inactive with zinc, and two very reactive acids—such as sulphuric and nitric—the combined amount of the latter two present being preferably about 1 per cent by weight of the chromic content, a preferred composition being:

Chromic acid—16 oz. per gal.—120 gr. per liter
Sulphuric acid—½–1 cc. per gal.—0.25–0.50 gr. per liter
Nitric acid—2–3 cc. per gal.—0.8–1.2 gr. per liter
Time of dip—15–20 seconds

Brightening, of course, would seem to be a function of the solubility of the plate, in the chromic acid dip, for while the chromic acid does not attack the plate, the other radicals are very reactive with it and in their presence—whether as catalysts or otherwise, the solubility is markedly increased and the brightening effect follows. But brightening postulated on solution of the coating alone results, first, in a diminution of the protective value by reduction in thickness of the coating remaining, and second, by deterioration on the surface appearance. In ordinary brightening of rough work, as practiced heretofore, the second point was obviously not of great importance, but when the surface is buffed and polished, it is paramount. We have found that an active acid radical concentration, in excess of 0.2% by weight in the dip, adversely affects the surface as does a chromic radical concentration in excess of about 15%.

The "tooth" of the surface has been referred to above as designating the ability of the plated or die-cast surface to take and hold a paint or enamel coating. It is not to be understood that "tooth" necessarily means a roughened or broken surface for even the rougher zinc surfaces are notoriously lacking in paintability and it has been customary to treat them further before applying the coating. Here, no treatment can be used which would destroy the polished surface. In short, a surface must be deveoped which is both polished in appearance and yet affords a good base for enamel. Finally, there is evidence of interaction between the plate and the coating which, in time, destroys the bond between the plate and what initially appeared to be a satisfactory coating. Therefore, the plate surface must have the requisite "tooth" while remaining polished, and it must be passive to the coating throughout the life of the part.

We are not in a position to state with definiteness the exact action of the dip disclosed in meeting each of the factors. It will be noted that the chromic acid content and the chromic active and radical ratio are both well below those commonly used. The combination of active acid radicals rather than the use of but one radical appears to make the interaction more intense. It would seem that the combined active acids attack the plate more quickly and vigorously, thereby brightening it without greatly diminishing the plate thickness, the solubility of which is decreased because of the low chromic-acid content. That is, the active acid attack is finely dispersed. This would account, to some extent, for the increased durability (which is shown by Figure 2), for the increased "tooth" and for the maintenance of the polished surface. Thus, if the individual areas of acid attack are very small, the surface—although microscopically roughened for "tooth"—still retains a polished appearance to all intents; and as brightness is obtained with a minimum of plate solution at any point the durability is enhanced.

This does not, however, account for the increased durability of treated plate over untreated plate, nor for the chemical passivity of the plate with respect to the subsequently applied coating. It is probable that a very fine deposit of a metallic chromate is formed on the plate by interaction with the acids. The chromate, in the form in which it is deposited, would necessarily be much thinner and more adherent than oxide coatings ordinarily formed. Thus, the brightness would not be adversely affected. There may even be an apparent increase in brightness due to the lightening of the color. Too, an adherent coating of a nonreactive chromate would explain the passivity toward the enamel coating and the increased "tooth" as well.

On the other hand, there may be a pronounced oxidation of the surface and the pure zinc so exposed is responsible for the brightness; in the oxidized state, it is actually less reactive, hence it is passive with respect to the surface coating and otherwise stabilized. Similarly, the want of "tooth" in usual zinc plate may be a characteristic of the coated oxide, the oxidized zinc itself

presenting no difficulties. These theories, it is true, are apparently mutually inconsistent but surface phenomena of the type involved are not resolved by any simple experiment. It is probable that an exact determination will be arrived at only through protracted investigation using the medium of the electron-diffraction camera or similar apparatus. Suffice to say that the treatment gives the results set forth, that parts so treated are in use, and that circumstances now demand production and not academic discussion of whys or wherefores.

To continue, the dipped article is rinsed and dried and is ready for the application of the protective coating. Again, transparent lacquers or enamels have been used in the metal arts; but, and again we point the distinction, not to our knowledge has there been a transparent enamel coating which, when applied to a polished zinc plate, would adhere thereto and stand up under the conditions imposed on automobile brightwork. Part of this durability is due to the preparation of the surface which has been described. The remainder is found in the composition of the transparent enamel used. This has a base of glycerol phthalate or other alkyd resin with an addition of about 30% of a melamine resin in a solvent such as a high solvency petroleum naphtha to give desired viscosity. This enamel has requisite clarity and durability without brittleness. No less important is that the compounded enamel will bake in about an hour at temperatures not exceeding 250° F. It has been discovered that plated or die-cast articles of the metals under consideration tend to be porous and will blister under higher temperatures, destroying both the surface polish and the protective coating bond. A part of the melamine may be replaced by urea resin to obtain a somewhat harder finish while retaining the other advantages. The admixture of the melamine resin up to substantially half the resin content is particularly desirable. As a variation, gold tinted enamel may be substituted with pleasing results.

By following the steps outlined and utilizing the treating compositions described, it is now possible to obtain bright, lustrous, and durable trim either directly from die castings or with plated surfaces employing only the relatively non-strategic metals named.

We claim as our invention:

1. A bath for the surface treatment of metals selected from a group consisting of cadmium and zinc which comprises an aqueous solution containing as essential elements approximately 120 grams per liter of chromic acid, from .25 to .50 gram per liter of sulphuric acid and from .80 to 1.20 grams per liter of nitric acid.

2. A method for the surface treatment of metals selected from the group consisting of zinc and cadmium to produce a high lustre durability and a surface capable of being painted, comprising, the step of immersing the metal in an aqueous bath containing as essential elements about 120 gr. chromic acid per liter, about 0.25 to 0.50 gr. sulphuric acid per liter and about 0.8 to 1.2 gr. nitric acid per liter, the ratio of said chromic acid to the combined amount of the sulphuric and nitric acids being approximately 100 to 1.

3. A method for the surface treatment of metals selected from the group consisting of zinc and cadmium to produce a high lustre durability and a surface capable of being painted, comprising, the step of immersing the metal in an aqueous bath containing as essential elements about 120 gr. chromic acid per liter, about 0.25 to 0.50 gr. sulphuric acid per liter and about 0.8 to 1.2 gr. nitric acid per liter, the ratio of said chromic acid to the combined amount of the sulphuric and nitric acids being approximately 100 to 1, the nitric acid being present in amount in excess of the sulphuric acid.

4. A method for the surface treatment of metals selected from the group consisting of zinc and cadmium to produce a high lustre durability and a surface capable of being painted, comprising, the steps of immersing the metal in an aqueous bath containing as essential elements about 120 gr. chromic acid per liter, about 0.25 to 0.50 gr. sulphuric acid per liter and about 0.8 to 1.2 gr. nitric acid per liter, the ratio of said chromic acid to the combined amount of the sulphuric and nitric acids being approximately 100 to 1; and maintaining said metal in said bath for a period not to exceed 60 seconds.

5. A method for the surface treatment of metals selected from the group consisting of zinc and cadmium to produce a high lustre durability and a surface capable of being painted, comprising, the steps of immersing the metal in an aqueous bath containing as essential elements about 120 gr. chromic acid per liter, about 0.25 to 0.50 gr. sulphuric acid per liter and about 0.8 to 1.2 gr. nitric acid per liter, the ratio of said chromic acid to the combined amount of the sulphuric and nitric acids being approximately 100 to 1, said combined content of sulphuric and nitric acid being substantially less than 0.2 of 1% of said aqueous solution, the nitric acid being present in excess of the sulphuric acid; and maintaining said metal in said bath for a period not to exceed 60 seconds.

RUSSELL H. McCARROLL.
JOHN L. McCLOUD.
HARRY E. J. HANSON.