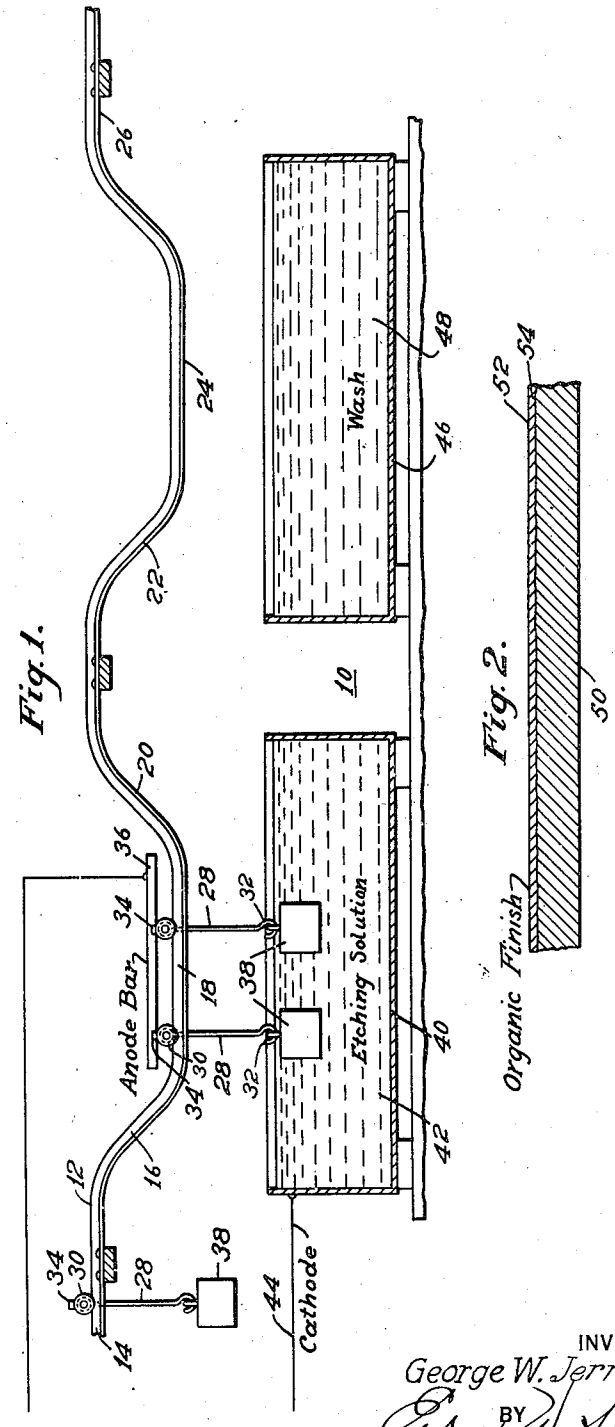
Feb. 22, 1949. G. W. JERNSTEDT 2,462,197

ETCHING METHOD

Filed Sept. 27, 1944 2 Sheets-Sheet 1



WITNESSES:

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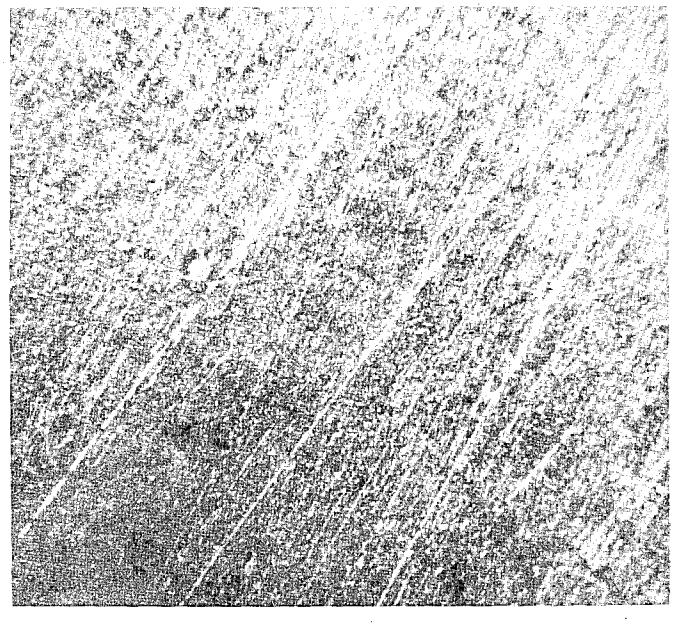
ETCHING METHOD

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Fig. 3.



Fig. 4.



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2,462,197

ETCHING METHOD

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4 Claims. (Cl. 204—141)

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This invention relates to a treatment for metal surfaces particularly an electrolytic treatment to provide for predetermined etching of the surface.

This application is a continuation in part of my copending patent application, Serial No. 398,035, filed June 14, 1941 (now abandoned).

In the application of organic finishes to metal surfaces, particularly upon copper and copper base metals, the adherence of the organic finish is ordinarily not entirely satisfactory. Brightly finished brass sheet, for example, when coated with enamels or lacquers and subjected to bending or further working loses the adhesion of the enamel or lacquer to the brass surface with consequent flaking of the organic finish. Even in cases where the organic finish does not flake off the brass on bending, the bond becomes so weakened that a slight rubbing or scratching will cause the organic finish to flake off readily.

The object of this invention is to provide for treating metal surfaces to produce a surface structure for better adhesion of organic finishes.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

For a fuller understanding of the nature and objects of the invention, reference may be had to the following detailed description, taken in conjunction with the accompanying drawing, in which:

Figure 1 is a schematic elevational view of an apparatus for carrying out the invention;

Fig. 2 is a fragmentary sectional view showing a metal sheet provided with an organic finish;

Fig. 3 is a photomicrograph of the surface of a sheet of brass treated according to the invention; and

Fig. 4 is a photomicrograph of the surface of a sheet of untreated cold rolled brass.

In the production of smooth finished copper alloy sheets, such as brass sheets for example, the sheet metal is frequently subjected to cold rolling and other surface treatment which results in a smooth surface but which has insufficient "tooth" or roughness for the best adhesion of subsequent organic finish coatings. It is desirable, on the other hand, in fabricating members from such copper base alloys, to apply to the member some decorative finish. Ordinary sprayed or brushed paint and lacquer coatings when applied to highly finished copper base alloy sheets do not adhere to the metal with sufficient tenacity to insure an adequate life for the finish. Where the member is subjected to slight bending or tensile stresses, the finish will either crack and flake off or else lose its adhesion

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to the copper base sheet and upon being subjected to slight mechanical abrasion will easily be removed. The failure of the organic finish is undesirable. Accordingly the manufacturer is frequently forced to substitute metals which are more expensive than copper base alloys in order to avoid this objectionable feature.

According to this invention copper base alloys in the form of sheets, machined parts, forgings and other smooth surfaced shapes are subjected to an electrolytic treatment whereby the surface of the metal is given a "tooth" or microscopic roughening sufficient for a greatly enhanced adherence of organic finishes. When provided with such a surface, the metal may be bent and subjected to other stresses without premature failure of the coating of organic finish by flaking and the like. Furthermore, the organic finish on electrolytically treated surfaces will withstand considerably more abrasion before loss of the organic finish than on untreated surfaces.

In some cases shot or sand blasting of copper alloy sheets has been resorted to in order to prepare a better surface for subsequent coatings of organic finish. Shot blasting will distort thin sheet metal and damage delicate members whereas electroetching can be safely applied to the thinnest sheets and most fragile parts. Further the shot or sand blasting is not always uniform. In many cases the treatment of copper alloy electrolytically is less expensive.

Briefly the electrolytic treatment comprises the anodic etching of copper base alloy members in an aqueous solution of phosphoric acid and nitric acid. This treatment will produce a sufficient microscopic alteration of the metal to roughen and pit the surface to provide a greatly improved adherence of organic finishes to the surface.

In carrying out the process, reference should be had to Fig. 1 showing a suggested mode of treating copper base metals. Other possible modes and forms of apparatus will be obvious to those skilled in the art. The apparatus 10 for carrying out the etching operation includes an endless conveyor track 12 whereby copper base members to be electrolytically etched are carried through the entire process of operations. At portion 14 of the conveyor 12 is located a loading station for loading articles 38 upon conveyors 28 for subsequent processing. The members 38 are suspended upon hooks 32 of the conveyor 28 provided with wheels 30 for travel along track 12. When the wheeled conveyors 28 travel from loading station 14 of track 12, they ap-

proach a descending portion 16 to permit the lowering of the articles 38 into an etching solution tank 40. The members 38 are suspended in the etching solution for the horizontal length 18 of the track 12. During travel along length 18, an insulated contact 34 on the conveyors 28 makes contact with an anode bar 36 whereby electrical current flows from the bar 36 to contact 34 through conveyor 28 to the hook 32 and thence to the member 38 to be etched. After each conveyor 28 has remained a predetermined length of time upon portion 18 of the track 12, the conveyors are caused to move upwardly along rise 20 of the track.

Passing further the conveyors 28 descend on portion 22 of the track to a lower horizontal portion 24 whereby the members 38 are dipped into a water wash solution 48 contained within tank 46. The wash solution 48 removes the etching acids. The members 38 are then brought up out of the wash solution to the unloading portion 26 of the track 12. After drying in an oven or by other suitable means, the members are in condition for further processing.

The etching solution tank 40 is made the cathode by connecting thereto a direct current cathode conductor 44 to a portion of the tank 40. The tank 40 is made of some conducting metal which will be resistant to the etching solution. A lead liner, for example, is satisfactory for the purpose, but steel cathode liners are preferred.

The etching solution 42 is an equeous electrolyte containing from 20% to 85% phosphoric acid (H_3PO_4) by weight from 0.1% to 25% nitric acid by weight. The solutions with higher concentrations of phosphoric acid are employed for copper base metals which contain the higher percentages of copper.

The main function of the nitric acid in the electrolytic solution appears to be to remove a surface layer of soft non-adherent copper particles which form during the electrolytic treatment.

The electrolyte of phosphoric acid and nitric acid operates satisfactorily when applied to copper base alloys having substantially no impurities, particularly metallic impurities such as lead, arsenic, and iron. If these metallic impurities are present in the copper base alloy, a surface smut may be left on the electro-etched copper alloy. It has been found that the addition of oxidizing compounds of chromium and oxygen, such for example, as chromic acid, sodium chromate and potassium dichromate, to the electrolyte will prevent formation of the smut. The amount of the chromium and oxygen compound may be as much as 5% of the weight of the bath.

In operating the etching bath it has been discovered that best results are obtained when the amperage per square foot of surface being treated varies between 20 and 100 amperes. With current of this strength, a good etch for the subsequent application of organic finishes is obtained in from 2 to 10 minutes. Four minutes of treatment has been found in many cases to produce highly effective results.

In treating a relatively pure brass composed of 67½% copper, the balance being substantially all zinc, the electrolyte solution was prepared from 1450 milliliters of 85% H_3PO_4 and 150 milliliters of 70% HNO_3 diluted with water to a volume of one gallon. The solution contained roughly 45% by weight phosphoric acid and 3% by weight nitric acid.

In the treatment of a relatively impure 40–60 brass, for example, a solution having 50% phosphoric acid, 1% nitric acid and ½% potassium dichromate by weight gave a highly effective etch in four minutes at a current density of 40 amperes per square foot.

The proportions of the electrolyte composition obviously may be modified for different amounts and kinds of impurities and the copper base alloys being subjected to the treatment.

After the copper base alloy metal has been electrolytically etched, washed and dried, an examination of the surface will reveal a marked dulling of the original bright finish due mainly to the fact that the surface has been preferentially etched to produce a roughening which is substantially microscopic in character. The etched surface produced by the treatment is in much better condition for the reception of organic finishes than the original highly finished surface. In the preparation of dials for instruments and recorders and similar apparatus, for example, the etched surface will hold a white enamel background finish and black enamel indicia much better than the untreated copper alloy. The finish will adhere as well to the electrolytically etched copper base metal as it will to more expensive alloys heretofore deemed necessary for the purpose.

Referring to Figure 2 of the drawing, there is shown an enlarged sectional view of a plate 50, of brass or the like, with an electrolytically etched surface 54. An organic finish 52 is keyed to the plate 50 by the microscopic roughened surface 54. The coated unit of Figure 2 constitutes a desirable improvement in the art.

Referring to Figures 3 and 4, there is shown photomicrographs at a magnification of about 300× of the surfaces of an alloy of 67½% copper, the balance being substantially zinc, after having being electro-etched according to the present invention and the original cold rolled surface respectively. Examination of the photomicrograph of Figure 3 shows that the surface has many fine pits distributed uniformly over the entire surface. The pits are disposed without regard to crystals of the brass, high spots or other gross features. It is these fine pits that provide for good paint adhesion without any roughness apparent in the paint coating. In Figure 4 the rolled surface exhibits a relatively smooth structure that does not provide a coating of paint means to effect a good bond thereto. The difference in flatness between the surfaces is imperceptible except under a microscope. Visually the electro-etched surface of Figure 3 has a dull appearance as compared to that of Figure 4. It is believed that no treatment known to the art heretofore etched to roughen the metal surface without regard to crystal structure by etching pits over the entire surface as uniformly as shown in the photomicrograph of Figure 3.

The following is illustrative of the improvement in adhesion secured by the invention. A sheet of brass $\frac{1}{32}$ inch thick had half of its surface etched while the other half remained unaltered. The entire member was then coated with a standard white lacquer and the coated metal baked to harden the organic lacquer. The opposite edges of the coated sheet were then bent substantially back upon themselves with the organic finish being upon the external side of the bend. In the case where the etching has been employed, the organic finish did not flake off or indicate any other evidence of failure at the bend. On the other hand where the organic finish had been applied

to the unetched surface the organic finish was cracked and small flakes had become disrupted. Lightly rubbing the organic finish at the bend with the fingernail failed to remove any of the lacquer from the etched metal portion while on the unetched metal the lacquer came off easily and freely. A great improvement in the adhesion of the organic finish for the metal has thus been secured by electrolytically etching the surface.

Since certain changes may be made in the above invention and different embodiments of the invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or taken in connection with the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. The method of electroetching the surface of a copper base alloy member containing at least 60% copper comprising making the member the anode in an electrical circuit, applying to the surface of the member an aqueous electrolyte having as its essential ingredients from 20% to 85% by weight of phosphoric acid, from 25% to 0.1% by weight of nitric acid and the balance water, and passing an electrical current through the circuit including the member and the aqueous electrolyte to etch the surface of the member to produce a substantially uniform microscopic roughening and pitting of the surface to enable organic finishes to adhere more tenaciously.

2. The method of electroetching the surface of a copper base alloy member containing at least 60% copper comprising making the member the anode in an electrical circuit, applying to the surface of the member an aqueous electrolyte having as its essential ingredients from 20% to 85% by weight of phosphoric acid, from 25% to 0.1% by weight of nitric acid and the balance water, and passing an electrical current of from 20 to 100 amperes per square foot of surface of the member through the circuit including the member and the aqueous electrolyte to etch the surface of the member to produce a substantially uniform microscopic roughening and pitting of the surface to enable organic finishes to adhere more tenaciously.

3. The method of electroetching the surface of a copper base alloy member containing at least 60% copper, the alloy having impurities therein tending to form a surface smut on etching, comprising making the member the anode in an electrical circuit, applying to the surface of a member an aqueous electrolyte having as its essential ingredients from 20% to 85% by weight of phosphoric acid, from 25% to 0.1% nitric acid, from effective amounts up to 5% by weight of a

water soluble oxidizing compounds of chromium and oxygen selected from the group consisting of chromates, dichromates and chromic acid to oxidize the impurities that would otherwise form a smut and the balance water, and passing an electrical current through the circuit including the member and the aqueous electrolyte to etch the surface of the member to produce a substantially uniform microscopic roughening and pitting of the surface to enable organic finishes to adhere more tenaciously.

4. The method of electroetching the surface of a copper base alloy member containing at least 60% copper, the alloy having impurities therein tending to form a surface smut on etching, comprising making the member the anode in an electrical circuit, applying to the surface of the member an aqueous electrolyte having as its essential ingredients from 20% to 85% by weight of phosphoric acid, from 25% to 0.1% nitric acid, from effective amounts up to 5% by weight of a water soluble oxidizing compound of chromium and oxygen selected from the group consisting of chromates, dichromates and chromic acid to oxidize the impurities that would otherwise form a smut and the balance water, and passing an electrical current of from 20 to 100 amperes per square foot of surface of the member through the circuit including the member and the aqueous electrolyte to etch the surface of the member to produce a substantially uniform microscopic roughening and pitting of the surface to enable organic finishes to adhere more tenaciously.

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