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METHOD OF ETCHING ALUMINUM

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This invention is primarily directed to problems arising in the manufacture of those aluminum or aluminum alloy products, such as printing plates, where a selected design or pattern is formed on an aluminum surface by methods comprising blocking off a portion of the surface with a resistant coating and thereafter submitting the exposed portions of the surface to the action of an etching medium. The planned result of such methods is to produce a clearly and sharply defined design or pattern on the aluminum surface. The problems and difficulties usually encountered center around control of the action of the etching medium. In commercial operations of this character the etching medium tends to attack the resistant coating, or resist, particularly at the edges of that coating. This results in loosening of the coating and consequent etching, or, as it is sometimes called, undercutting, of metal which is supposed to be protected by the resist. Under such conditions the boundaries between the etched and unetched portion are not clean-cut and the etched design or pattern is not clearly defined. The resistant coating, or resists, referred to are those commonly used in the trade, such as enamels, shellacs, asphalts and the like.

The present invention consists in an improvement on such methods. The improvement consists in the use of an aqueous solution of a hydroxide selected from the group consisting of barium and strontium hydroxides. The advantages obtained by the use of these improved methods may be generally indicated as uniform etching action, reduced attack on the commercially used resists and the commercial production of etched designs or patterns on aluminum surfaces which are, generally, more sharply and clearly defined and delineated than those produced by commercial methods previously used. The aqueous solutions which form the etching medium should contain at least 0.5 per cent. by weight of the indicated hydroxides, or either of them, and may contain amounts ranging therefrom up to the limit of solubility of such hydroxides in the solution. Preferably, however, solutions containing 1 to 5 per cent. by weight of hydroxide are used in commercial operations because higher concentrations are harder to control because of their stronger etching action. For the same reason operating temperatures of less than 170° F. are preferred, but a warm solution gives better results than a cold one, and operating temperatures of about 90° to 130° F. have given the best results. The advantages above indicated are obtained on aluminum surfaces and on those consisting predominantly

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of that metal, i. e., containing about 80 per cent. or more by weight of aluminum. However, as in the case of heretofore known processes of this general character, results will vary somewhat with the composition of the alloy.

The etching action may take place chemically, but electrochemical etching is preferred. In the former case the surface is simply immersed or otherwise covered with the etching medium until the desired attack has taken place. In the latter case the surface to be etched is made anode in an electrolytic cell in which the electrolyte is the etching medium and electrical energy is impressed on the cell, a voltage range of 5 to 30 being usually satisfactory, although an operating range of 10 to 20 volts is preferred.

Agitation of the etching medium during the processing and the presentation of a grease and dirt free aluminum surface to the etching medium are desirable, as is usual in aluminum etching processes. Any smudge, sludge or deposit remaining on the surface after the etching is complete can usually be removed by the use of a stream of water or by a gentle abrading action. These and similar details are common to many etching processes and are not critical to the practice of the present invention, the advantages of which principally flow from the use of the etching medium above defined.

In some cases it is useful and desirable to add to the aqueous solution of barium or strontium hydroxide about 1 to 10 per cent. by weight of glycerines and glycols, sugars, ammonium hydroxide, or a compound containing an amine radical selected from the class consisting of urea, triethanolamine and morpholine. Such substances appear to produce a smoother etching action by the hydroxide and to sometimes insure a sharper definition of the boundaries of the etched portions of the aluminum surfaces under treatment when the etching action is produced by chemical action alone. When, as is preferred, the etching action is electrochemical, sometimes called anodic, these substances perform the additional function of producing favorable current-voltage conditions during the etching action. For instance, in the preferred operating range of 10 to 20 volts the current may vary as much as an ampere per square inch when the hydroxide solution does not contain the substances above named. However, when such substances are present, the current characteristics improve. For instance, the addition to a 5 per cent. by weight solution of barium hydroxide of 1 per cent. by weight of triethanolamine maintains the current at a sub-

stantially constant level through a range of 10 to 20 volts. While the advantages obtained by the use of these added substances are substantial, the hydroxide solution has, without such addition, the attributes and advantages hereinabove indicated.

Above are set forth the general aspects of the invention. In its more specific, and much preferred, operation barium hydroxide serves as the etching medium and the etching is done electrochemically instead of chemically. Particularly good results are obtained by this specific procedure where the portion of the aluminum surface which is not to be etched is covered by a light-sensitive resist, for instance by chromated albumen or shellac, such as is used in the photoengraving art in the preparation of half-tone printing plates. While such resists are particularly susceptible to the etching operation, they are not substantially affected by the barium hydroxide solution. In another preferred aspect of the invention the surface to be etched is first treated chemically or electrochemically to form thereon an oxide coating. The resist is applied to the proper portion of the oxide coated surface, and the whole is then subjected to electrochemical etching in a barium hydroxide solution. However, previous to imposing electrical energy on the cell in which this electrochemical etching is to take place, the surface to be treated is allowed to remain in contact with the barium hydroxide solution until the oxide coating on the surfaces which have not been coated with resist has been dissolved. Thereafter electrical energy is imposed on the cell and the etching is completed. This procedure may also be used where the surface is not oxide coated, to remove dirt, grease or other foreign substances from the surface prior to the beginning of the electrochemical reaction.

The term "oxide coating" as used herein and in the appended claims is a well known designation in the art which describes a layer of aluminum oxide artificially produced on the aluminum or aluminum alloy surface by treatment of the surface with acids, such as sulphuric, chromic, etc., or alkalis, such as sodium carbonate or the alkali sulphates and acid sulphates, etc., all with or without the addition of other substances and some with and some without the use of externally applied electrical energy. But the term "oxide coating" does not include the very thin film of aluminum oxide which is naturally formed upon that metal or its alloys by reason of contact with the air.

These oxide coatings as well as electro-plated films of metal, such as nickel or chromium, may likewise be used to protect printing surfaces prepared in accordance with this invention.

I claim:

1. The method of etching aluminum surfaces, which includes making the surface an anode in an electrolytic cell, the electrolyte of which is an aqueous solution having as the essential etching component at least 0.5 per cent by weight of a compound selected from the group consisting of barium hydroxide and strontium hydroxide.

2. The method of etching aluminum surfaces, which comprises making the surface an anode in an electrolytic cell the electrolyte of which is an aqueous solution having as the essential etching component a compound selected from the group consisting of barium hydroxide and strontium hydroxide, said compound being present in said solution in amounts of at least 0.5 per cent by

weight and said solution also containing from about 1 to about 10 per cent by weight of glyc-
erine.

3. The method of etching aluminum surfaces, which comprises making the surface an anode in an electrolytic cell the electrolyte of which is an aqueous solution having as the essential etching component a compound selected from the group consisting of barium hydroxide and strontium hydroxide, said compound being present in said solution in amounts of at least 0.5 per cent by weight and said solution also containing from about 1 to about 10 per cent by weight of sugar.

4. The method of etching aluminum surfaces, which comprises making the surface an anode in an electrolytic cell the electrolyte of which is an aqueous solution having as the essential etching component a compound selected from the group consisting of barium hydroxide and strontium hydroxide, said compound being present in said solution in amounts of at least 0.5 per cent by weight and said solution also containing from about 1 to about 10 per cent by weight of a compound selected from the class consisting of urea, triethanolamine and morpholine.

5. The method of preparing a printing plate having an aluminum surface, which comprises coating a portion of said aluminum surface with an etch resisting material, and subjecting the uncoated portion of said surface to the action of an etching medium, consisting of an aqueous solution having as the essential etching component at least 0.5 per cent by weight of a hydroxide selected from the group consisting of barium hydroxide and strontium hydroxide.

6. The method of claim 5 characterized by the fact that the etch resisting material is light-sensitive.

7. The method of claim 5 characterized by the fact that the etch resisting material contains a chromate.

8. The method of preparing an aluminum surface for printing, including the steps of providing said surface with an artificially produced oxide coating, partially coating the oxide coated surface with an etch resisting material and thereafter making the partially coated surface an anode in an electrolytic cell, the electrolyte of which is an aqueous solution having as the essential etching component a hydroxide selected from the group consisting of barium hydroxide and strontium hydroxide, said hydroxide being present in said solution in amounts of at least 0.5 per cent by weight, and contacting said partially coated surface with said electrolyte in said cell prior to the imposition of electrical energy on said cell until the artificial oxide coating has been dissolved from the uncoated portions of said surface, and thereafter imposing electrical energy on said cell.

9. The method of etching aluminum surfaces which includes making the surface an anode in an electrolytic cell the electrolyte of which is an aqueous solution having as the essential etching component at least 0.5 per cent by weight of barium hydroxide.

10. The method of preparing a printing plate having an aluminum surface which comprises partially coating said aluminum surface with an etch resisting material and making the uncoated portion of the surface an anode in an electrolytic cell, the electrolyte of which is an aqueous solution having as the essential etching component at least 0.5 per cent by weight of a hydroxide se-

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lected from the group consisting of barium hydroxide and strontium hydroxide.

11. The method of preparing an article having an aluminum surface, such as a surface for printing, which comprises partially coating said aluminum surface with an etch resisting material, immersing said article in the electrolyte of an electrolytic cell consisting of an aqueous solution having as the essential etching component at least 0.5 per cent by weight of a hydroxide selected from the group consisting of barium hydroxide and strontium hydroxide, and thereafter passing an electric current through said article as the anode.

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