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METHOD OF WRITING ON UNSEALED ANODIZED ALUMINUM

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It is often desirable to produce a permanent light-fast marking on a permanent metal base for identification badges or the like.

One known procedure for treating aluminum surfaces to produce a more or less permanent image thereon involves the preparation of a porous oxidized surface on the aluminum, treatment of the resulting surface to incorporate a light sensitive medium therein and exposure of the resulting article in a manner resembling conventional photographic practice. This procedure, taught in United States Patents 2,115,339, 2,126,017 and 2,766,119 represents a complex process in which particular care must be taken to avoid exposure of sensitive chemicals to light and which therefore entails the use of a darkroom or its equivalent.

Other methods are known for imparting permanent markings to aluminum, e.g. by mechanical means or by chemical etching, but the resulting images are not as readily legible as those in the above-mentioned photographic processes and in addition they require specialized apparatus which adds to the ultimate cost of the product.

This invention relates to permanent marking by writing or printing or both on the porous surface of an unsealed anodized layer of aluminum, by a simple procedure requiring neither the expensive chemicals nor the expensive apparatus of the foregoing prior art approaches and to the permanently marked aluminum articles so produced.

Briefly the invention comprises the impregnation of such a porous surface with a dilute solution of a strong reducing agent and then writing or printing on the impregnated surface with a salt of an easily reducible metal, whereby an image prints out almost immediately. The procedure may be reversed, if desired by using a solution of the salt as the impregnant and writing or printing with the reducing agent. Because of the relative instability of the easily reducible metal salts suitable for the present process, it is preferred that they comprise the writing fluid.

Substrates which have been found to be amenable to this invention include aluminum and alloys in which the major component is aluminum, such as those described in Tables III and IV on page 793 of the 1948 Handbook published by the American Society of Metals. It will therefore be understood that the term "aluminum" as hereinafter employed, is intended to cover not only the metal but also any alloys in which it is the predominant constituent.

The formation of an absorbent oxide or hydrated oxide film on such materials is old and well known and may be accomplished by any of several techniques known to those skilled in the art. For example, the oxide or hydrated oxide coating may be produced by treating the surface chemically, e.g. by contacting the surface with a solution of an alkali carbonate and a soluble dichromate, as described in Tosterud Patent 1,946,150. Alternatively, as described in the same patent, the oxide or hydrated oxide may be produced by anodic oxidation of the surface in oxalic acid or sulfuric acid, or other appropriate liquid medium. Whether chemical or electrochemical means are chosen to produce the absorbent film is immaterial, provided that a sufficiently thick absorbent film is formed. Depending on the process, the porous layer may vary

from 0.1 to 1.0 mil in thickness. Within this range, the thickness is less important than the absorbency of the porous layer. The thin aluminum oxide which forms naturally when the metal is exposed to air is not of sufficient thickness to satisfactorily retain the image forming materials in the amounts found necessary to obtain the benefits of the present invention.

Regardless of the anodizing process employed, the freshly formed anodized surface need merely be rinsed with water in order to qualify as the porous surface desired for the impregnation which follows. Preferably the rinsed surface is permitted to air dry before use.

In a preferred process the dry porous surface comprised of an anodized layer about 0.5 mil thick is immersed in a dilute solution of a strong reducing agent. Excess liquid is removed from the surface by passage through rollers or by other suitable means and the surface is allowed to air dry. Such a pre-sensitized plate may be stored for long periods if desired without deterioration.

Inorganic and organic reducing agents have been found to be satisfactory as impregnants for the porous surface. By way of example, the following reducing agents have all been found suitable when used in conjunction with the proper reducible salt:

Organic—
- Hydroquinone
- Phenyl hydrazine
- p-Phenylenediamine
- Hydrazine

Inorganic—
- Sodium sulfite
- Sodium bisulfite
- Potassium meta bisulfite
- Trivalent Ti compounds
- Trivalent V compounds
- Divalent V compounds

The solution of reducing agent may be in either an aqueous or nonaqueous solvent. Water, or a lower alcohol such as methanol or ethanol, are preferred solvents, but any known solvent for the selected reducing agent may be used without any apparent detrimental effect on the process. Reducing agent-concentrations of between 1% and 5% by weight, in such solvents have been satisfactorily employed.

The relative oxidation and reduction potentials of the reducing agent determines to some extent the reducible compound selected. In general organic and inorganic salts of silver, mercury, copper, the platinum metals, gold, zinc, cadmium, tin, lead bismuth and antimony have been used with reducing agents of the proper reducing potency. Concentrations of metal salts in the range of 3% to 25% by weight, in water or in alcohol or similar vehicles have been found to provide satisfactory writing fluids.

While most soluble salts may be used, the nitrates, acetates, citrates and tartrates are preferred. Chlorides tend to initiate an undesirable corrosion of the film and are not preferred for this reason.

The permanent marking is effected by writing with a wooden stylus or steel nib dipped in the writing fluid or by transferring the desired image onto the impregnated surface by means of stencils, dies or other printing techniques.

The image appears almost immediately (i.e. less than 1 second) and is made permanent by the usual methods of sealing, e.g. by holding the image bearing surface for about 20 to 30 minutes in boiling water. No bleeding or bleaching takes place.

In the table below specific examples have been given of reducible salts used with specific reducing agents. The examples are to be construed as illustrative and not as limitative.

Table I

Example	Column 1 Reducing Agent and Concentration	Column 2 Metal Salt and Concentration	Column 3 Other (Thickener, Wetting Agent, etc.)
1	Hydroquinone, 1% in CH_3OH.	$AgNO_3$, 10% in water.	Glycerol, 2%; Methyl cellulose, 1.0%.
2	Hydroquinone, 2% in CH_3OH.	Mercuric Acetate, 15% in water.	Polyvinyl alcohol, 1.0%; Ethylene Glycol, 3.0%; Aerosol OT, 0.3%.
3	Na_2SO_3, 3% in water.	Copper Acetate, 5%; Silver Nitrate, 5% in water.	Methyl cellulose, 1.0%; Glycerol, 2.0%.
4	Phenyl hydrazine, 2% in alcohol.	Lead Acetate, 10% in water.	Methyl cellulose, 1.0%; Glycerol 2.0%.

To either of the formulations exemplified in Columns 1 and 2 above, there may be added various optional ingredients to improve the process. For example between 1 and 10% of a humectant may be added to the solution of reducing agent or metal salt to retard the rate of drying, glycerol and other glycols being selected for availability and economy.

Similarly, in some instances, ease of writing is improved by the presence of a thickener in the writing fluid. Such materials as polyvinyl alcohol, methyl cellulose, modified polyvinyl acetate, gum tragacanth, gum arabic or other water- or alcohol-soluble gums and similar materials have been found to produce an improved result when present in the writing fluid in amounts of from 0.5% to 5.0% by weight.

Furthermore, it has also been found desirable to include between 0.1% and 1.0% by weight of a wetting agent in the writing fluid although this too is not essential. When a humectant, wetting agent or thickener is used, it is preferably incorporated in the solution used to mark the impregnated surface. Thus it may be incorporated in the metal salt solution when the surface has been presensitized by impregnation with a dilute solution of a strong reducing agent, or it may be incorporated in the solution of the reducing agent when the surface is processed by first impregnating with the reducible metal salt.

In a co-pending application, Serial No. 816,664, filed of even date herewith, now Patent No. 3,017,285, there is described a related invention wherein the permanent writing and printing are accomplished on sealed anodized aluminum surfaces. The process described in that application differs from that disclosed in the present application principally due to the necessity for unsealing the pores in the anodized layer in order to provide an absorbent surface for treatment.

I claim:

1. In a method of marking an aluminum surface which includes producing on said surface an adherent and adsorbent porous oxide coating by anodizing said surface and then treating the pores of said surface coating successively with a solution of a reducible metal salt and a solution of a reducing agent for said reducible salt, wherein the first of said solutions to be applied is applied to uniformly impregnate the entire porous oxide-coated surface and impregnates the same and the second of said solutions to be applied produces an immediately visible marking on said impregnated surface directly as a result of contacting the impregnated surface with the second of said solutions to be applied; the improvements which comprise: including in the second of said solutions to be applied, between 0.5% and 5% by weight of a thickener compatible with said solution, and applying said thickener-containing solution to only those portions of the impregnated oxide surface which are to be marked, whereby the marking resulting from the application of the second solution applied to said surface is confined to those portions of the impregnated porous oxide surface to which the thickener-containing solution is applied.

2. The method of claim 1 in which the metal salt is a reducible salt selected from the group consisting of the nitrates, acetates, citrates and tartrates of a metal selected from the group consisting of silver, mercury, copper, the platinum metals, gold, zinc, cadmium, tin, lead, bismuth and antimony.

3. The method of claim 2 in which the metal salt is in solution in a solvent selected from the group consisting of water and a lower alcohol.

4. The method of claim 1 in which the reducing agent is a dilute solution of hydroquinone in methanol and the reducible salt is a 10% solution of silver nitrate in water.

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