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3,017,285

METHOD OF WRITING ON ANODIZED ALUMINUM

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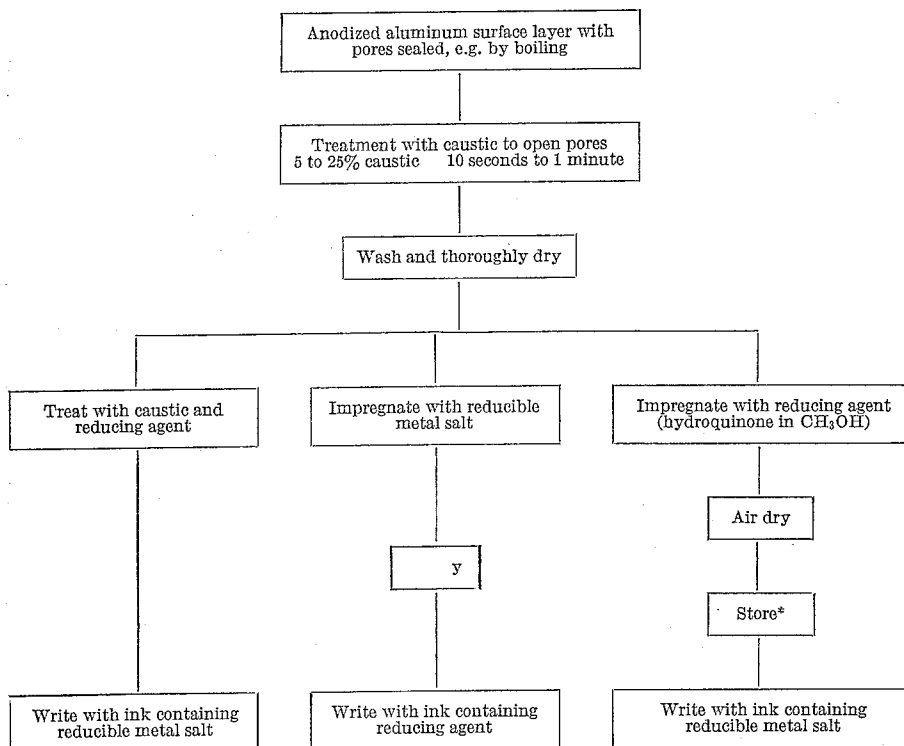
It is often desirable to produce a permanent light-fast marking on a permanent metal base for identification badges or the like.

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 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 marked aluminum articles, so produced.

A schematic simplified flow diagram of the process is as follows:



*Storage is optional.

Briefly the invention comprises the impregnation of a suitable porous surface of an anodized layer of aluminum

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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 material 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 relatively thick film (about 0.5 mil) is formed. 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.

In a co-pending application, Serial No. 816,701, filed of

even date herewith, there is disclosed a process of permanent writing and printing on unsealed anodized aluminum

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surfaces, i.e. surfaces prepared as above described, and merely rinsed with water prior to processing.

One conventional finishing treatment applied to anodized aluminum surfaces is "sealing" wherein the pores are sealed for example by prolonged exposure to steam or boiling water.

In order to practice the present invention it is necessary that the pores be reopened and this is most readily accomplished by etching the sealed surface with a water or alcohol solution of a strong alkali such as NaOH, KOH or phenyl trimethylammonium hydroxide in which the concentration of alkali hydroxide is in the range of 5-25% for between 10 seconds and 1 minute. Thereafter the surface is washed in running water for a few minutes and then thoroughly dried, preferably at an elevated temperature. The porous surface is then impregnated with a dilute solution of a strong reducing agent. Both 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, and generally concentrations of the order of 1 to 5% in water or organic solvents are found to be suitable.

Organic:	Inorganic:
Hydroquinone	Sodium sulfite
Phenyl hydrazine	Sodium bisulfite
p-Phenylenediamine	Potassium meta bisulfite
Hydrazine	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 lower alcohol, e.g. methanol and ethanol are preferred solvents, but any known solvent for the selected reducing agent may be used without any apparent detrimental effect on the process. One preferred reducing agent is a 1% to 2% solution of hydroquinone in methyl alcohol. After impregnation the resulting article is air dried and may be stored without decomposition, almost indefinitely. Printing or writing is thereafter accomplished by impressing the desired image on the treated surface with an ink containing a suitable reducible salt.

The relative oxidation and reduction potentials of the reducing agent determine 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.

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 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.

Instead of etching and impregnating in the manner described above, the sealed anodized surface may be treated with a fluid composed of the following (all percentages being by weight):

	Percent
Thickener	0.5-5
Humectant	1-10
Wetting agent	0.1-1.0
Strong alkali and vehicle	Balance

The only essential constituent of the composition is the alkali which may advantageously be a water- or alcohol-solution of a NaOH, KOH or phenyl trimethylam-

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monium hydroxide in which the concentration of alkali hydroxide is in the range of 5% to 25%.

The thickener, humectant and wetting agent are optional, albeit preferred constituents.

Thus the wetting agent, if present, should be one which is compatible with alkali. Drying of the fluid is retarded by incorporation of suitable humectants such as glycerol and the glycols in the proportions stated above. Further, to improve ease of writing a thickener such as polyvinyl alcohol, methyl cellulose, modified polyvinyl acetate, gum tragacanth, gum arabic or other water- or alcohol-soluble gums, or the like may be used.

The following specific formulations are illustrative of suitable formulations. (All parts and percentages are by weight.)

- (1) 10% solution NaOH containing 0.5% Aerosol OT.
- (2) 10 parts NaOH, 3 parts ethylene glycol, 1 part polyvinyl alcohol, 0.5 part Aerosol OT, and 100 parts water.
- (3) 10 parts NaOH, 3 parts ethylene glycol, 1 part polyvinyl alcohol, 0.5 part Aerosol OT, and 100 parts methyl alcohol.

The caustic ink was applied to the surface with a steel pin when the writing was carried out by hand. A pen with a wooden nib may also be utilized. If printing or hand stamping is involved, compositions containing humectants are used because of the thinness of layer of transfer. In each case, the ink or printing fluid was applied to the sealed surface and allowed to remain in contact for a period of 30 seconds to one minute, after which the caustic was washed or wiped off with a cloth. After air drying for one or two minutes, preferably under an infrared lamp, a 10% solution of silver nitrate was applied either by dipping or wiping. If dipping was utilized, an immersion time of five to twenty seconds is sufficient. The black color was then developed by dipping in a 1% solution of hydroquinone in methyl alcohol or by wiping with a cloth dampened with the same solution. As soon as the black color develops fully, the surface of the place was then wiped with a damp cloth.

The technique may be modified by incorporating the reducing agent such as hydroquinone in the caustic writing fluid initially so that a concentration between 1 and 2% of hydroquinone is available. This may be added to the caustic solution in an alcohol medium. In this case, the black color is then developed by dipping or wiping with a 10% solution of silver nitrate or other reducible salt.

One chemical feature of the process should be especially noted. In etching the surface with a strong caustic solution, there is a good possibility that even with vigorous washing, some caustic may still remain in the pores especially when the writing is done almost immediately after the caustic etching. By using a metal salt which on decomposition to the metal produces some acid, as for example nitric acid, this caustic is neutralized and stability and permanency of the surface is thereby improved.

I claim:

1. A method of marking an aluminum substrate having a porous anodized surface layer wherein the pores in said surface layer have been sealed, which comprises: opening the pores in said surface by contact with a solution of a strong alkali selected from the group consisting of alkali metal hydroxides and organic ammonium hydroxides; impregnating the opened pores of said surface with a dilute solution of a strong reducing agent and thereafter contacting portions of the impregnated surface with an ink composition consisting essentially of a salt of an easily reducible metal in a liquid vehicle.

2. An aluminum plate marked by the process of claim 1.

3. An alkaline composition useful in preparing an aluminum article having a porous oxide surface for subsequent impregnation thereof in a marking process and

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which comprises: a solution of a hydroxide from the group consisting of alkali metal hydroxides and organic ammonium hydroxides, in which the concentration of said hydroxide is between 5% and 25% by weight, and at least one of the following additional constituents: a thickener, selected from the group consisting of polyvinyl compounds, methyl cellulose and soluble gums; a humectant, selected from the group consisting of glycols and glycerol; and an alkali-compatible wetting agent.

4. A method of marking an anodized aluminum-base material having a porous anodized surface layer, the pores of which are sealed, which comprises: applying a caustic solution of an alkali selected from the group consisting of alkali metal hydroxides and organic ammonium hydroxides to selected portions of said surface for between about 10 seconds and 60 seconds; washing the so treated surface with water; drying the washed surface; applying a solution of an easily reducible salt to the surface; and thereafter developing a visible mark on said surface by application of a reducing agent thereto.

5. The process of claim 4 wherein the reducible salt is silver nitrate and the reducing agent is a dilute solution of hydroquinone in methyl alcohol.

6. The process of claim 4 wherein the reducing agent is included in the caustic solution used in the initial treatment of the surface.

7. A composition of matter comprising: between about 1% and 10% by weight of ethylene glycol; between about 0.5% and 5% by weight of polyvinyl alcohol; between 0.1% and 1% by weight of an alkali-compatible wetting agent; and the balance consisting essentially of a strong alkali, selected from the group consisting of

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alkali metal hydroxides and organic ammonium hydroxides, dissolved in a liquid vehicle the concentration of alkali in said composition being between 5% and 25% by weight.

8. The composition of claim 7 wherein the vehicle is water.

9. The composition of claim 7 wherein the vehicle is a lower alcohol.

10. The composition of claim 7 wherein the alkali is NaOH.

11. A process of preparing an article having a porous anodized aluminum surface layer, the pores of which are sealed, for subsequent marking which comprises: etching the surface with a strong alkali, selected from the group consisting of alkali metal hydroxides and organic ammonium hydroxides, for between 10 seconds and 1 minute; washing the etched surface in running water; drying the washed surface; impregnating the pores in said dried surface with a reducing agent; air drying the resulting impregnated article and storing the so formed article.

12. The process of claim 11 which comprises in addition impressing on the air-dried resulting impregnated article the desired image by means of an ink consisting essentially of between 3% and 25% by weight of an easily reducible metal salt in a suitable liquid vehicle.

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