United States Patent Office 2,995,443
Patented Aug. 8, 1961

2,995,443

ALUMINUM PLATE WITH PLURAL IMAGES AND METHOD OF MAKING SAME

Robert A. Kempe, Chagrin Falls, Ohio, assignor to Metalphoto Corporation, Cleveland, Ohio, a corporation of New Jersey

No Drawing. Filed Aug. 8, 1957, Ser. No. 676,925
2 Claims. (Cl. 96—43)

This invention relates to an article of manufacture and to the method of producing it. More specifically it relates to an aluminum member which is provided with ornamental and useful indicia in addition to the image or information formerly imparted to the surface of the aluminum member. One use of objects produced with this combination of markings is as a means of rendering tamper-proof such articles as identification badges, reproductions of passports and other documents, and other uses will become apparent from the following description.

The production of aluminum photographic plates is known and is described in expired United States Patents 2,115,339 and 2,126,017 and more recently in United States Patent 2,766,119. In general, these prior art processes include the initial formation of an aluminum oxide layer on the surface of the aluminum or aluminum-base alloy photographic plate; the subsequent impregnation of the oxide layer with photosensitive material; exposure and development of the sensitized plate and finally the sealing of the developed image in the plate, to form a permanent image. It will be apparent that it is relatively easy to duplicate, imitate, or counterfeit objects produced by these direct prior art processes.

I have now discovered a procedure in which a plurality of images are produced in a specific sequence of operations, the net effect of which is to produce an object which cannot be readily duplicated and which cannot be altered without leaving a distinct record of any efforts to change the information recorded on the aluminum surface.

Briefly, my invention comprises a preliminary treatment in which one type of information is imparted to the aluminum substrate in a form which is rendered virtually nonerasable by superimposing a second type of information on the first information. The second information may be placed on the plate bearing the first indicia by any of the processes of the above mentioned patents, or by other techniques commonly known and practiced in the present. Since the second image exists in an otherwise transparent layer, the resulting object is one in which both the first and second images are plainly visible and hence any evidence of tampering or attempts to alter the finished object will be apparent when the finished object is scrutinized.

A schematic representation of the invention comprises the following tabulation of the steps in the process

(1) Clean aluminum sheet and free from soil.
↓
(2) Mark surface of clean sheet with first image (mechanically, chemically or electrically).
↓
(3) Clean to remove any residue from marking step.
↓
(4) Anodize (steps 4 et seq. per U.S. 2,766,119).
↓
(5) Photosensitize.
↓
(6) Expose.
↓
(7) Develop to form image in pores of anodized layer.
↓
(8) Fix image.

The first image may be placed on the aluminum or alumium-base alloy substrate by any of several suitable techniques. It may consist of markings imparted mechanically, electrically or chemically or by a combination of two or more of these. The image may consist of an infinitely repeated grid or pattern and may be either a fanciful design or combinations of one or more letters, words or numbers, or it may consist of the use of both a repeated pattern and letter or number arrangement.

Regardless of the markings chosen, it is important that the metal plate presented for marking be clean and free from soil. Usually rinsing the plate material in a degreasing bath followed by a water rinse suffices as preparation prior to marking.

Suitable marking by mechanical means includes mechanical scratching, scribing, engraving, abrading, or rolling the metal blank between rollers impressing a pattern on the metal. As examples of chemical marking, photo-resist etching followed by removal of the resin surface and chemical etching have been found suitable.

The method for producing the first image preferred by me involves electrochemical etching. In this method a mark is made on the cleaned unanodized surface of aluminum by the use of a marking fixture, applied to the surface. The plate to be marked and the marking fixture are immersed in a suitable electrolyte (e.g. a 5% solution of NaCl in water). The marking fixture bears the image which it is desired to impart to the aluminum surface, and usually consists of a stencil which may be glued to the base metal. When an electric current is passed through the stencil or marking fixture and the plate to be marked, the desired image appears. With a direct current, a permanent frosted white pattern corresponding to the pattern on the marking fixture appears. With a voltage of about 5 volts and a current density of about 1 ampere per square decimeter of stencil, only 2 or 3 seconds are required to produce the desired marking. With an alternating current a darkened pattern is obtained. The amount of marking which is produced is readily controlled by a suitable choice of electrolyte, voltage and current density. The stencils may be prepared by die impression or by photoresist technique. It is also possible to use stencils which are not glued directly to the surface which are maintained in contact by pressure of a marking stylus. In this particular case, the point of the marking stylus consists of a porous resin sponge such as nylon or cellophane. The current is passed as before and gentle rubbing of the sponge over the stencil provides the necessary image.

Once the blank has been provided with the desired first image, it is cleaned to remove any residue from the marking operation and to prepare it for the anodizing operation which constitutes the next step in the process. When a mechanical method of marking is employed, cleaning with a soft cloth to remove any loose particles of metal should precede the wet cleaning. One wet cleaning procedure which has been found suitable includes dipping the marked aluminum plate in an acid chromate solution, rinsing in water, and then dipping it in a mild alkali and then in a strongly acid solution, prior to a final rinse in water, to complete the preparation for anodizing.

There are a large number of known anodizing processes described in the technical literature and in many patents. Although it is possible to form an oxide coating on an aluminum blank by purely chemical treatment, I prefer to anodize the aluminum by electrolytic means. Three electrolytic processes which have been found suitable use electrolytes based on sulfuric acid, chromic acid and oxalic acid, respectively.

With sulfuric acid a 7% solution of H_2SO_4 maintained at about 20° C. is satisfactory. The cleaned aluminum

plates bearing the previously imparted markings are immersed in the electrolyte and made the anode for one hour at a current density of approximately two amperes per square decimeter. After anodization, the plate is thoroughly washed in running water and then in a dilute aqueous solution of sodium hydroxide (about 1% NaOH), and after a final rinse under running water it is dried at 60° C. or below.

With chromic acid anodizing, a 3% solution of chromic acid in water serves as the electrolytic bath and is operated at a controlled temperature of 40° C. The bath is voltage controlled being gradually raised through the one hour anodizing period from about 5 volts at initiation up to about 50 volts at the close. After anodization is complete, the plate is removed from the electrolytic bath, washed thoroughly in running water, followed by dipping in a 1% solution of sodium hydroxide and then washed in running water and dried as before. The chromic acid process suffers from the disadvantage that although transparent and durable, oxide coatings are produced on the aluminum, the color of the coating tends to be somewhat gray thereby reducing contrast in subsequent photographic operations.

Of the various anodizing techniques, the preferred procedure is that employing complexed oxalic acid baths. The complexed oxalic acid base anodizing bath may contain either potassium oxalate or sodium oxalate in proper concentration regulated to a suitable pH by the addition of oxalic acid. One preferred procedure is as follows: A solution of 3,000 grams of potassium oxalate in 100 liters of water is prepared. Oxalic acid is then dissolved therein until a pH of 2.8 is reached. The solution is heated to 55° C. and the aluminum sheet anodized with vigorous stirring at a current density of two amperes per square decimeter, at a voltage of 40 volts. A suitable thickness of clear oxide layer is obtained by treatment as indicated above for a period of 30 minutes. After removal from the anodizing solution, the plates are washed in running water for 5 minutes and then allowed to air dry.

After the aluminum plates bearing the first identifying markings are provided with a transparent durable porous film of aluminum oxide have been washed and dried, they are ready for the photosensitization whereby a second image is placed on the plates.

A plate of aluminum anodized as above was immersed for 10 seconds in a 5% solution of chromic acid maintained at 60° C. After it was removed from the chromic acid, the plate was washed and dried. Thereafter, all of the operations about to be described were carried out in a darkroom. A solution was prepared containing 30 grams of silver nitrate, 0.5 gram of photographic grade gelatin, and 0.02 gram of potassium dichromate per 100 cubic centimeters of distilled water by mixing the ingredients and stirring until the solution was complete. In the darkroom, the dry anodized plate was soaked in this solution for 10 minutes and allowed to drain and the excess solution removed from the surface by passage through tight rubber rollers. The plate was then air dried and soaked for one minute in a solution consisting of 5 grams of potassium bromide, 5 grams of potassium dichromate, and 100 cubic centimeters of water. Any surface coating of silver bromide which might have formed in this treatment was wiped away while the plate was immersed in running water. The thoroughly washed plate was then oven dried at 50° C. and stored in the dark until use. In a modification of the foregoing, a plate treated with the chromic acid solutions and the silver nitrate-gelatin-dichromate mixture, as described above, was soaked for 10 seconds in a saturated solution of sodium chloride containing 5% potassium dichromate. After thorough washing, this plate was placed in a bath containing 12½ grams of potassium bromide and 2 grams of sodium dichromate, all dissolved in a liter of distilled water. It was retained in this bath for one minute. After rinsing in running water, the wet plate was immersed in a 1% solution of potassium bromide for one minute. It was then washed thoroughly, dried, and stored in the dark until use.

For plates which are to be exposed and developed almost immediately after preparation, the anodized plate containing the previously inscribed image has been processed in a slightly modified manner. It was first immersed in a 5% solution of chromic acid at 60° C. for 10 seconds and after washing and drying, all subsequent operations with the plate were carried out in the darkroom. In the darkroom, a solution consisting of 30 grams of silver nitrate and 0.5 gram of photographic grade gelatin dissolved in 100 cubic centimeters of water was prepared. The dry anodized plate was soaked in this solution, allowed to drain, and the excess solution wiped from the surface by passing through rubber rollers. The plate was again air dried and soaked for one minute in a solution consisting of 10 grams of potassium bromide dissolved in 100 cubic centimeters of water. Any surface coating of silver bromide which might come from this treatment was wiped away while the plate is immersed in running water. The thoroughly washed plate is passed through rubber rolls and then oven dried at 50° C. Such a plate should be exposed and developed within 100 hours after its preparation.

Instead of the specific photosensitizations described above, any of the procedures described in the three United States patents may be used, or any other equivalent procedure for photosensitizing the plates may be employed.

To complete the badge or other article of manufacture, a photographic negative containing the second portion of the information to be placed on the badge is placed in contact with the sensitized aluminum plate already bearing the first portion of the desired information.

The film negative or stencil is prepared by conventional techniques and may contain a photograph of the individual or specific information as numbers or letters or combinations of the two, or it may consist of symbols or any combination of numbers, letters or symbols.

Exposure and development of the second image on the aluminum plate is accomplished by a conventional contact printer, in which the light is caused to illuminate the aluminum plate to the extent permitted by the stencil or film negative. An exposure of 15 seconds from a 40 watt tungsten filament lamp about 8 inches from the metal plate suffices.

After exposure the photographic image is developed, fixed and sealed within the anodized layer. One typical procedure, given by way of illustration, was as follows:

(*a*) A standard metol-hydroquinone developer was used. A time of 5 minutes at 72° F. was necessary for achieving full density.

(*b*) The plate was rinsed in running water for 1 minute.

(*c*) The plate was then fixed for 2 minutes in a hypo bath containing an acid hardener, and the plate was again rinsed in running water.

(*d*) The plate was then immersed in a gold chloride thiocyanate toner consisting of 50 grams of 1% gold chloride solution and 100 grams of ammonium thiocyanate per liter of solution. The plate was retained in the toner solution until the color of the image became black, usually about two minutes and the plate was then rinsed in running water.

(*e*) The plate is then completed by immersing the plate in boiling water for 30 minutes, which seals the image and concludes the process.

Optionally, the background of the plate may be colored by immersing the plate in a solution of a dye after the image has been fixed. Any of the dyes normally used for coloring anodized aluminum may be used. After it has been dyed, the plate is rinsed in running water and then sealed. Obviously, the choice of dyed, toned, or

natural aluminum color background constitutes merely one of several alternative modes of practicing my invention.

While I have disclosed, by way of illustration, the use of a silver salt photosensitive system, diazo systems may be substituted in the preparation and development of a photographic image without departing from the scope of my invention.

Having now described my invention in accordance with the patent statutes, I claim:

1. A method of manufacturing an aluminum photographic plate which comprises: cleaning the surface of an aluminum sheet material to provide an unblemished base, free from soil; forming a relief image on said aluminum surface by removal of a portion of said surface; anodizing the resulting article to provide the image bearing surface with a thin, transparent, porous oxide coating and impregnating the pores of said coating with a photosensitive material.

2. The method of claim 1 in which the relief image is formed on the surface by etching, the photosensitive material is a silver salt containing a minor amount of gelatine and a second image is formed by exposure and development of the photosensitive material.

References Cited in the file of this patent

UNITED STATES PATENTS

2,766,119	Freedman et al.	Oct. 9, 1956
2,854,336	Gutknecht	Sept. 20, 1958

OTHER REFERENCES

Wallbank: "British Jour. of Photography," vol. 90, June 18, 1943, page 226.

Hartsuch: "Chemistry of Lithography," Lithographic Technical Foundation, N.Y., 1952, pp. 98 and 114.

Tory: "Photolithography," Graphic Arts Monthly, Chicago, Ill., 1953, pp. 149 and 177.