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METHOD OF MANUFACTURING METALLIC IMAGES ON ALUMINUM AND ALUMINUM ALLOYS

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ABSTRACT OF THE DISCLOSURE

An aluminum sheet is oxidized to form a porous aluminum oxide layer. This layer is then treated with a light sensitive material capable of forming a light reaction product which in the presence of water converts mercurous ions to mercury. The thus sensitized layer is exposed to light and then treated with an aqueous solution of a mercurous compound forming a latent mercury image at the exposed portions. The latent mercury image is then physically developed by treatment with a solution of a metal salt such as a silver salt and a reducing agent. This abstract is not intended to be a description of the invention defined by the claims.

This invention relates to a method of producing internal and external metallic images by photographic means on aluminum and aluminum alloy carriers.

It is known to produce photographic images on carriers which are at least superficially hydrophilic by sensitizing these carriers with photosensitive compounds which produces light-reaction products capable of depositing mercury metal from mercurous ions in the presence of moisture to form a latent mercury image and then physically developing this latent image in a developer containing a noble metal salt dissolved in water and a reducing agent for this salt. See for example, U.S. Patents 2,067,690, 2,764,484, 2,838,398, 2,868,643 and 2,923,626.

This method is referred to as the "nuclear-introduction method." The solution containing mercurous-ions with which the carrier is brought into contact after exposure is referred to as the "nuclear-introduction bath." An improvement in the photographic sensitivity is possible by adding also silver ions to the nuclear-introduction bath. In this case the treatment with the nuclear-introduction bath may give rise to the formation of a latent silver amalgam nuclear image.

In the physical development it is also possible to form in situ a dye-image together with the metallic image, the latter being removable after development is completed. See U.S. Patent 2,750,292.

The photosensitive compounds which, after exposure, can liberate metallic mercury in the form of a physically-developable nuclear image from mercurous compounds by means of disproportionating according to the equation

$$Hg_2^{++} \rightleftarrows Hg^{++} + Hg$$

include the aromatic diazosulphonates, which are preferably used in combination with a so-called "anti-regression agent," that is a compound which, when added to the layer, prevents the reformation of diazosulphonate from its light-reaction product by binding either the sulphite, or the diazonium-radical, or both of them so that it remains possible for the sulphite to react with the mercurous compound while forming mercury nuclei.

Other usable photosensitive compounds which satisfy the above-mentioned conditions are, for example, o-hydroxybenzene-diazonium compounds, o-hydroxynaphthalene diazonium compounds, aromatic diazocyanides, o- and p-nitro-mandelic acid nitrile, the bisulphite compounds of o- and p-nitrobenzaldehyde and a series of inorganic complex compounds from which one or more of the following ions or molecules are liberated by exposure: CN^-, CNS^-, NO_2^-, $SO_3^=$, $S_2O_3^=$, NH_3, pyridine and its derivatives and thiourea and its derivatives, which ions and molecules are bonded to at least one central metal ion.

It is known to use aluminum superficially converted into aluminum oxide by anodic oxidation as a carrier material for silver halide photographic systems. It is also possible to use aluminum alloys for this purpose.

The impregnation with silver halide is effected by submerging the hydrophilic oxide-layer successively into a solution of a halide and into a solution of silver nitrate whereby the silver halide deposits in the layer. After drying and exposure, use is preferably made of acid physical developers to prevent the layer from being attacked by alkalinic chemical developers. After fixing, silver images of a brown color are obtained which gradually become black by treatment with a dilute solution of gold chloride. However, due to the precipitation reaction occurring in the pores, it is difficult to provide a sufficient amount of photosensitive material in the layer. Thus it was found that only one third of the volume of the pores was filled with AgBr after a layer has undergone 39 times the cycle of the treatment with a 10% solution of KBr and a 10% solution of silver nitrate. In addition, upon chemical development of layers thus obtained fog formation is liable to occur the prevention of which requires KBr concentration in the developer higher than is usual. Further, it is difficult to obtain images having a uniform optical density by chemical as well as physical development.

Thus the use of silver halide systems in anodically-oxidized aluminum suffers from several severe drawbacks.

Nevertheless anodized aluminum has a number of properties which render its use as a photographic carrier material extremely attractive. It is a dimensionally stable material which, if correctly after-treated, is also resistent to the action of acids and salt solutions. Also it can resist comparatively high temperatures and endures a temperature up to 600° C. without objection. In addition, it has reasonable resistivity against scratches and shocks because of the hard oxide layer.

It is also known that aluminum is heavily attacked by mercury compounds. Aluminum metal is protected from atmospheric attack and thus passivated by a natural coherent oxide film. The protective film is deteriorated and if there is no possibility for this film to be restored, a heavy chemical attack will take place. This is the case for example if the aluminum is brought into contact with solutions of mercurous salts. This contact results in aluminum amalgam being formed which activates the contact area and causes the aluminum metal to be converted within a short time into alumina of low coherence even in dry air. (Riesenfeld, Lehrbuch der Anorganischen Chemie, Zurich 1946, page 463.) This aluminum amalgam is also known to be a strong reducing agent which is capable of depositing metallic mercury and/or silver from solutions containing soluble mercury and/or silver compounds, such as nuclear introduction baths and physical developers. Thus in literature the use of mercurous

compounds in photographic baths intended to be used in the photography in anodically-oxidized aluminum is therefore expressly excluded.

So although it initially looked as if aluminum is decidedly unsuitable as a carrier material in the nuclear-introduction method wherein the use of baths containing a mercurous compound is indispensable, applicants have surprisingly found that it was still possible with the use of this method, if concentration of the mercurous salt in the nuclear-introduction bath was about 0.1 mol/litre, to obtain photographic images in and/or on aluminum of greater or smaller porosity obtained at the surface of aluminum or an aluminum alloy by anodic oxidation thereof. A repeated impregnation was then not required and even without the use of a gold-chloride bath, fog-free beautiful black images were obtained without the layer noticeably being attacked by the mercurous salt, if the treatment with the nuclear-introduction bath was completed in from 1 to 5 seconds. Since insoluble compounds of silver halide are not used in the nuclear-introduction method, it was also possible to omit the usual process of fixing the developed layer. Any silver ions present in the layer after the development could be removed by rinsing in distilled water.

However, it has been found that it is usually not possible without further expedients to obtain these images without an accompanying heavy fog.

A principal object of the invention is furthermore to provide a solution of this fog problem and thus render possible the use of the nuclear-introduction method in a general sense with the use of a carrier of aluminum or an aluminum alloy made superficially hydrophilic by the provision of a porous layer of aluminum. This and other objects of our invention will be apparent from the description that follows.

According to our invention we have found that aluminum or aluminum alloy may be chosen for the carrier if the surface is oxidized so that an outer porous oxide is formed which is separated from the metal by an intermediate non-porous layer and by preventing or suppressing the adsorption of mercury ions by the aluminum metal carrier.

This mercuric adsorption effect may be prevented by carrying out one or more of the following steps: adjusting the concentration of the mercuric ions in the nuclear introduction bath being adjusted to be at least about 10^{-4} molar, treating the outer porous oxide layer before sensitization with the solution of a mercuric compound and treating the latent image prior to development with a solution of an organic hydroxy acid which acid does not form a permanent precipitate with mercury and silver ions.

During the investigation preceding the establishment of the invention, it has become clear that the fog which usually occurs may have at least two causes:

(1) The absence of a sufficient separation between the porous oxide layer and the underlying metal, so that mercury and/or silver ions from the treatment baths may come into contact with the aluminum and, due to reaction therewith, give rise to the formation of fog nuclei.

Thus, in order to carry out the method of the invention it is essential for the porous oxide layer to be separate from the metal by an intermediate layer which is substantially not porous. If the porous oxide layer is provided chemically, for example by treatment in a hot solution of soda in chromate, the separation from the basic metal is insufficient and a non-porous intermediate layer must be provided in a separate treatment by anodically after-oxidizing the carrier with its oxide layer in a suitable electrolyte. The use of a borax-boric acid electrolyte is extremely suitable for providing or strengthening a substantially non-porous intermediate layer.

(2) The mercuric-adsorption effect. This is to be understood to mean the effect that, due to preferential adsorption of mercuric-ions from the nuclear-introduction batch, on the aluminum-oxide adsorbents, fog nuclei may be formed in the vicinity thereof by disproportioning.

From literature it is known that mercuric-ions are preferently adsorbed on aluminum oxide. It is also known that at equilibrium a solution of a mercurous salt in water contains mercuric-ions in addition to mercurous-ions in a ratio of about 1:100. If mercuric-ions are preferently adsorbed on the aluminum-oxide adsorbents then in the vicinity thereof the following reaction will take place in the solution:

$$Hg_2^{++} \rightarrow Hg^{++} + Hg$$

so that the solution locally becomes oversaturated with mercury.

The range of concentrations of the mercurous compound in the nuclear-introduction bath in which the method according to the invention is applicable extends from about 5×10^{-4} molar to about 2×10^{-1} molar. However, for reasons of homogeneity in density and photographic sensitivity, the range of concentration from about 5×10^{-3} molar to about 5×10^{-2} molar is preferred. With several layers which are otherwise separate from the carrier metal by means of a non-porous intermediate layer of sufficient thickness, the mercuric-adsorption effect does not give rise to fog formation when using mercurous concentrations located at the upper limit of, or just above, the aforementioned preferred range of concentrations. In these cases the over-saturation occurring as a result of the effect is evidently too small to give rise to the formation of nuclei within the short time in which the nuclear introduction is established. However, since within the preferred range the photographic sensitivity passes through a maximum and the concentrations near the lower limit of this range are very useful in view of the formation of external nuclear images, and since with all these concentrations the mercuric-adsorption effect gives rise to fog formation, it is always necessary to take one or more of the following steps for preventing and/or neutralizing the effect.

The mercuric-adsorption effect will be prevented if, before or during the nuclear introduction, the oxide layer is able to become saturated sufficiently with mercuric-ions without resulting in a decrease of the concentration of mercuric-ions on the nuclear introduction bath below the equilibrium value. This may be achieved by adding the mercuric-ions to be adsorbed in addition to those present in the equilibrium to the nuclear-introduction bath, or by subjecting the oxide layer, prior to sensitization, to a short separate treatment in a dilute solution of a mercuric salt, followed by carefully rinsing in distilled water. As a rule, the adjustment of the concentration of mercuric-ions in the nuclear-introduction bath to a value of at least about 10^{-4} molar is preferred. The adsorptive properties of the relevant oxide layer are determinative of how far the adjustment of the concentration of mercuric-ions must exceed the said limit. One will preferably not exceed that concentration which is precisely capable of completely suppressing the fog, since a further increase results in a rapid decline in photographic sensitivity for reasons readily understood. The maximum mercuri-concentration to be used is, for example, 2×10^{-3} molar when using an oxide layer obtained with the aid of an oxalic-acid electrolyte. The foregoing is, of course, also dependent upon the thickness of the relevant oxide layer. It is a wise policy, if necessary, to determine beforehand the optimum concentration of the mercuric-ions in the nuclear-introduction bath by means of a series of test baths containing increasing mercuric-concentrations which keeping an eye on the effect that is produced on the fog and the sensitivity.

For the treatment of the oxide layer preceding the sensitization thereof the concentration of the mercuric-

ions in the treatment bath is usually chosen not higher than 5×10^{-4} molar and the duration of the treatment not longer than 5 seconds. In certain cases, however, it is necessary to use still lower concentrations in view of the photographic sensitivity. As previously mentioned, it is important that the mercuric treatment is followed by carefully rinsing in distilled water to remove the excess of mercuric-ions in the layer which is fatal for the sensitivity of the layer.

The mercuric-adsorption effect may also be prevented or neutralized by adding an organic hydroxy-acid to the nuclear-introduction bath, or by treating the latent nuclear image before its intensification into an image having the desired optical density or the desired amount of image metal with a solution of such an acid. Examples of such acids which may be used are citric acid, glycolic acid, tartaric acid, glyceric acid and malic acid. Especially when added to the nuclear introduction bath, these acids should be employed in a concentration such as to prevent a permanent deposit in the bath. Thus, preferably a concentration of the mercurous compound of 5×10^{-4} molar to 5×10^{-3} molar and for the acid preferably a concentration of 10^{-1} molar to 3×10^{-1} molar is used in the bath. Citric acid and glycolic acid are the preferred acids to be employed in these baths as they result in images which are completely free from fog. The use of these baths is also favorable for the formation of an external nuclear image.

The fog formation may also be prevented by the treatment of a latent nuclear image with a solution of the last-mentioned acids, especially in the case of oxide layers manufactured with the use of sulphuric acid electrolyte. The concentration of the acids in the after-treating bath is preferably about 0.3 mols/litre. The duration of the treatment may then be about 1 minute. Although it is assumed that the activity of said acids is connected inter alia with influencing of the activity of the active ions the accurate mechanism of the action is not known.

The aluminum and the aluminum alloys suitable for the method according to the invention are unalloyed aluminum having a purity preferably higher than 99.5% of Al, Al-Si-Mg alloys, Al-Mn-Mg alloys or Al-Mg alloys containing at the most 5% of Mg.

Before carrying out the superficial oxidizing process, the aluminum may have to be subjected to one or more pretreatments, according to the quality of the initial product of the desired structure of the oxide layer. A large number of such pretreatments are described in the handbooks.

The aluminum surface must be carefully degreased and, if necessary, etched in order to remove the natural oxide film. Irregularities in the surface such as occur, for example, due to drawing, rolling or pressing and which also become visible in the oxide layer must be removed, for example by chemical or electrolytic polishing. The chemical process may be carried out, for example, by submerging in hot concentrated phosphoric acid with additions of nitric acid, sulphuric acid and salts of heavy metals. A thin irridescent film is thus formed which can be removed by treatment in cold chromic acid or by treatment with nitric acid.

A matted surface is obtained, for example, by treatment with a hot concentrated solution of phosphoric acid and hydrofluoric acid or fluorides.

Several methods are available for the oxidation of the surface. The resulting oxide layer must have a certain porosity and be separated from the metal by an intermediate layer which is not porous since otherwise it is not sufficiently protected from the action of the treatment baths. Oxide layers which are best usable may be obtained by anodic oxidation with electrolytes such as oxalic acid, sulphuric acid, chromic acid, phosphoric acid and mixtures of sulphuric acid and oxalic acid or chromic acid.

The treatment in oxalic-acid electrolyte is carried out best at a temperature from about 20° to 40° C., and a current density of 1 to 2 amp./cm.^{2} in a 5 to 8% solution of oxalic acid. The voltage of the bath adjusts itself to about 40 volts. The oxide layers obtained therewith have a very light yellowish color. These layers yield a sensitive photographic material on which deep black images may be obtained.

A colorless oxide-layer is obtained by the use of sulphuric acid as the electrolyte. Preferably about 18% by weight of sulphuric acid are used, a current density of about 1 amp./cm.^{2}, a voltage of 15 volts and a temperature of 18° C. for the bath. The sensitivity of the photographic material which can be manufactured with the aid of such oxide layers is, however, lower than that of the material previously mentioned and the images have a warmer color. The sensitivity considerably increases, however, and the color of the images becomes deeper if a comparatively short after-anodization is carried out in oxalic-acid electrolyte.

Usable porous oxide layers may also be obtained by chemical oxidation, for example by treatment in a hot solution of soda and chromate. However, as previously mentioned, these layers have to be anodically after-anodized, though for a comparatively short period, in order to provide a non-porous intermediate layer.

The photographic images in the oxide layer once having been obtained, the oxide layer may be "sealed" in known manner in order to make the image resistant to atmospheric attack and prevent the formation of spots due to dust or fat. To this end, the material is treated with boiling distilled water or with hot solutions of electrolyte. A very suitable sealing bath contains cobalt acetate, nickel acetate and boric acid.

The nuclear image obtained in and/or on the oxide layer by the method according to the invention can be intensified into an image having the desired optical density or the desired amount of image metal by means of a purely-physical development. For this purpose use is preferably made of an acid physical development. It is also possible, however, to use a coloring physical development and thus manufacture color images which create new possibilities in the decorative domain. It is then necessary, however, to use silver developers since the layer is not resistant to the action of alkaline mercury developers. Besides, the pH value of the coloring physical developer is preferably chosen not higher than 10. Examples of such color-physical developers are described in U.S. Patent 2,750,292. A treatment of the latent nuclear image prior to the development with a solution of citric acid or glycolic acid is in this case also always necessary to prevent color fog.

The nuclear-introduction bath containing citric acid or glycolic acid may be combined with the developer by adding one or more silver salts, a photographic reducing agent and, if necessary, a development stabilizer. This results in the simplification of the method. The total concentration of the silver salts in such a developer is preferably about 10 times as high as that of the mercurous salts.

According to a further elaboration of the method according to the invention, the mercury or silver-amalgam nuclear image may also be intensified, after activation, by means of chemical reduction of a copper, nickel and/or cobalt salt with the aid of a reducing agent for this salt, into an image consisting of copper, nickel, cobalt or an alloy of nickel and cobalt. The activation preferably consists in a short treatment with a physical silver developer if it is desired to prepare copper images by chemical reduction. If nickel or cobalt images or images consisting of an alloy of nickel and cobalt have to be manufactured the activation may take place by means of a short physical development with, or an electro-chemical exchange for, gold or one of the platinum metals, but

preferably for this purpose also use is made of a short physical development with silver, followed by catalyzing the silver surface in a known manner, for example by means of a solution of a salt of one of the platinum metals or, if an external image is concerned, by means of contact with a catalytic metal such as iron or aluminum.

In the case of further intensifications with copper, nickel and/or cobalt of a nuclear image which has already been pre-intensified with silver into an external image, it is preferable to seal the oxide layer prior to catalyzation or, if this is not necessary, before bringing the layer into contact with the metalizing bath. It is thus completely possible to overcome fog difficulties which may result from the adsorption of silver ions and/or noble-metal ions on the aluminum oxide.

In view o fthe alkalinity of the usual chemical copper-plating baths it is necessary to choose a bath having a rate of deposition such that the time of contact can be limited to at the most about 10 minutes (see Example 14).

If aluminum sheet material, after the anodic oxidation is cut into smaller pieces which are to be employed in the method of the invention the portions of the material which are not protected by a natural or a synthetic oxide film are found to be chemically attacked even within the short period in which the material is in contact with the more concentrated nuclear-introduction baths. In order to protect these pieces, after the anodic oxidation, the unprotected portions thereof are chemically oxidized or covered in another way with a material resistant to mercurous salts, such as a lacquer. The chemical oxidizing process may take place, for example, in a hot solution of chromic acid. This is especially necessary if a disproportionating developer is used and hence the carrier is in contact with mercurous compounds for a comparatively long period.

Excellent protection may be obtained if the carrier is anodically oxidized in an electrolyte or borax-boric acid bath.

Either internal or external electrically-conductive images may be obtained, as is also known from the use of the nuclear-introduction method with the use of other hydrophilic carriers or carriers which are at least superficially hydrophilic, see U.S. Pat. 2,764,484, French Pat. 1,262,878, and French Pat. 1,269,393 by means of the method according to the invention and hence with the use of a carrier consisting of aluminum or an aluminum alloy the surface of which has been oxidized so that a porous oxide-layer exists which is separate from the metal by an intermediate layer which is substantially not porous.

For manufacturing an internal image such as is desirable for normal photographic uses, start is made from a predominantly internal nuclear image which is intensified by means of a stabilized purely-physical development into an image having the desired optical density. Factors enhancing the formation of an internal image are for example: the use of a hydrophilic layer having a concentration of the photo-sensitive substance such that light absorption also takes place in portions of the layer situated at a greater depth, the avoidance of over-exposure, the use of nuclear-introduction baths containing silver-ions and having a comparatively high concentration of mercurous-ions, and the avoidance of over-development.

If the exposures are made a little longer or intenser and if the development is continued for a longer time it is possible to make an internal nuclear image grow out of the carrier into an external, electrically-conductive image.

On the other hand, an external, electrically-conductive image may be manufacture by starting from a predominantly external nuclear image or from a nuclear image situated predominantly closely beneath the surface of the carrier. In the first case, only a non-stabilized purely-physical developer can be used for the intensification, in the second case the nuclear image beneath the surface can be caused to grow rapidly out of the carrier also by the use of a stabilized developer. Factors enhancing the formation of an external nuclear image or one situated beneath the surface are for example: the use of hydrophilic layer having a comparatively high concentration of the photo-sensitive material, carrying out the exposure with the use of radiation which is absorbed very well by the photo sensitive compound with the exclusion of radiation penetrating the layer to a great depth, and the use of nuclear-introduction baths having a comparatively low concentration of mercurous-ions or of nuclear-introduction baths to which citric acid or glycolic acid has been added.

A special feaure of the method according to the invention is that it permits the manufacture of external, electrically-conductive images which are short-circuited to the aluminum carrier as well as those which are not short-circuited.

When starting from internal nuclear images, if the stabilized development is continued for a sufficiently long time external electrically-conductive images short-circuited to the aluminum substratum are usually obtained which images can be further intensified by electroplating without trouble even when built up of isolated parts. On the other hand, when starting from external or sub-superficial nuclear images, especially if comparatively thin oxide-layers are used, it is possible to obtain external, electrically-conductive images isolated from the substratum which images are thus characterized in that they are separated from the basic metal by means of a dielectric.

External, electrically-conductive images excellently isolated from the aluminum substratum may be obtained by the procedure of first causing anodic oxidation in an electrolyte known for obtaining porous oxide-layers such as for example, an electrolyte of oxalic acid or sulphuric acid and the strengthening of the non-porous intermediate layer by anodization in an electrolyte as usually employed for providing a non-porous oxide layer, such as the known electrolyte of borax-boric acid.

By starting from external nuclear images and with the use of non-stabilized physical development it is also possible to obtain external images which can be loosened from the substratum and, if desired, transferred to another substratum, which is important, for example, for the manufacture of printed circuits.

The method of the invention is thus extremely versatile and flexible. It can be used not only for electrotechnical and electrical purposes but also, for example, for the manufacture of name plates, text plates and advertising plates, scale divisions for measuring instruments and wireless apparatus, etc. When using a photographic negative it is possible more particularly to make a small series in a cheap manner. In combination with known coloring methods, the method may also be useful for the manufacture of objects of decorative art. At last, it allows the manufacture of beautiful images with transition densities or so-called half-tones. Objects and images thus manufactured are durable even when exposed to atmospheric influence and moisture.

Our invention will now be described in greater detail with reference to the following examples:

EXAMPLE 1

An aluminum plate consisting of an alloy of aluminum containing 2% to 3% of Mg, in which the content of impurities of Si, Fe, Mn and Zn were each at the most 0.01%, Cu at the most 0.02% and the total of the impurities at the most 0.06% by weight was mechanically polished and treated in sulphuric acid (180 to 200 gs. per litre) at 85° C. for 0.5 to 0.75 minute. Next the plate was submerged in nitric acid (1:1), rinsed in distilled water and held submerged for 1 to 2 minutes in a polishing bath heated to 100° C., which was the following composition:

816 ml. of concentrated phosphoric acid (d=1.73)
126 g. of sodium nitrate
86 g. of potassium sulphate and
14 g. of cadmium acetate

Then the plate was submerged in nitric acid (1:1) at room temperature for 1 minute and thoroughly rinsed in distilled water. Finally, the plate was immerged in a solution of 0.5 g. of CrO_3 per litre of water, again rinsed in distilled water and dried.

After these pre-treatments, the plate was anodically oxidized at 20° C., in a solution of 5% of oxalic acid in water at a DC-voltage of 40 to 45 volts and a current density of 1 amp./cm.^{2} for 60 minutes, rinsed in distilled water for 2 minutes, in 5% chromic acid of 60° C. for 1 minute, again rinsed in distilled water and dried.

The plate thus treated was sensitized by impregnating for 2 minutes in a solution of the following composition:

0.15 molar o-methoxybenzenediazosulphonic acid sodium
0.1 molar of cadmium lactate and
0.004% by weight of "Lissapol N"
streaked off between rubber strips and dried.

The plate thus sensitized was exposed behind a line-negative to a 125 watt high-pressure mercury-vapor lamp placed at a distance of 30 cms. for 10 seconds, then submerged for 2 seconds in a nuclear-introduction bath consisting of a solution of 0.05 molar mercurous-nitrate and 0.03 molar silver nitrate and 0.1 molar nitric acid in distilled water and then rinsed in distilled water for 5 seconds. Next the plate was developed for 3 minutes in a solution of the following composition.

0.2 molar ferrous-ammonium sulphate
0.1 molar ferric-nitrate
0.05 molar citric acid
0.1 molar silver nitrate
0.04% by weight of "Lissapol N" and
0.02% by weight of "Armac 12D"

and rinsed in distilled water for about 10 minutes. At last, the plate was sealed for about 40 minutes at a temperature of 98% for 100° C. in a bath containing per litre of water:

5.5 gs. of nickel acetate
1.0 g. of cobalt acetate
8.5 gs. of boric acid and
10 gs. of 1% "Ultravon W" solution

and the pH value of which was adjusted to 5 to 6, rinsed and dried ("Ultravon W" is a moistening agent containing sodium neptadecylbenzimideazolemonosulphate as an active component). A black fog-free image on a glossy blank surface was obtained.

EXAMPLE 2

An aluminum plate containing from 0.5% to 2% of Mg was anodically oxidized for 30 minutes in a solution of the following composition:

40 g. of titanium potassium oxalate
8 g. of boric acid
1 g. of citric acid
1.2 g. of oxalic acid in 1 litre of water

The pH value of this bath was adjusted from 1.8 to 2.0 and the temperature from 55° to 60° C. The anodization was carried out at an initial voltage of 80 to 90 volts, which was progressively raised to 120 volts. The current density was initially 3 amps./dm.^{2} and progressively decreased to a value of 1 to 1.5 amps./dm.^{2}. The plate was sensitized in the manner described in the previous example, streaked off, dried and exposed to a 125-watt high-pressure mercury-vapor lamp placed at a distance of 30 cms. for 2 seconds, treated with the nuclear-introduction bath mentioned in the previous example, rinsed, physically developed for 2 minutes in an aqueous solution consisting of 0.2 molar ferrous-ammonium sulphate, 0.08 molar ferric-nitrate, 0.05 molar silver nitrate, 0.05 molar citric acid, 0.04% of "Lissapol N" and 0.02% of "Armac 12D," rinsed, sealed in boiling distilled water for 60 minutes and dried. A black fog-free image on an opal-white background was obtained.

EXAMPLE 3

A cylinder manufactured of an aluminum alloy containing 0.5% to 2% of Mg, 0.5% to 1.5% of Si and 0.2% to 1.5% of Mn and in which the impurities of Fe and Cu were less than 0.4% and 0.05% respectively and the total of the other impurities was less than 0.1%, was submerged in dilute sulphuric acid (180 to 200 g./litre) of 85° to 90° C. for 1 minute and then in nitric acid (1:1) of room temperature. Next it was rinsed in distilled water for 3 minutes and etched in a solution of ammonium bifluoride 100 gs./litre) of about 20° C. for 5 minutes. After rinsing thoroughly, the cylinder was treated at 100° C. in the polishing bath from Example 1 for 10 seconds, submerged in nitric acid (1:1) of room temperature for 1 minute, rinsed in distilled water for 5 minutes, and treated with a solution of 0.6 gs. of CrO_3 per litre at room temperature for 15 to 30 seconds.

After rinsing and drying, the cylinder was anodically oxidized in a bath containing 30 gs. of oxalic acid and 20 g. of potassium oxalate per litre for 45 minutes. The voltage of the bath was 30 to 45 volts, the current density 1.5 amps./dm.^{2} and the temperature of the bath was 50° C. After anodization, the cylinder was rinsed in distilled water, submerged in a 5% by weight solution of chromic acid at 60° C. for 1 minute, again rinsed with distilled water and dried.

A dull oxide-layer was formed on the aluminum by this treatment.

Next, the cylinder was impregnated for 2 minutes in a solution of the composition:

0.15 molar o-methoxybenzenediazosulphonic-acid sodium
0.1 molar cadmium lactate and
2% by weight of "Lissapol N"

The excess of the solution was removed by dripping off. After drying, the cylinder was exposed to a high-pressure mercury-vapor lamp. The negative comprised a guilt copper sleeve which exactly fitted around the cylinder and in which a scale division was cut out. After exposure, the cylinder was submerged in the nuclear-introduction bath from Example 1 for 3 seconds, rinsed in water and physically developed at 20° C. for 8 minutes in the solution of the following composition:

0.01 molar p-methylaminophenol sulphate
0.01 molar silver nitrate
0.08 molar citric acid
0.02% by weight of "Armac 12D" and
0.02% by weight of "Lissapol N"

Then it was rinsed and dried. A dull, blank aluminum cylinder having a black scale division was obtained.

EXAMPLE 4

An aluminum plate having a purity of at least 99.7% in which the impurity of Si+Fe together with at the most 0.3% and that of Cu+Zn together at the most 0.08%, was degreased with carbon tetrachloride, immerged successively in ethanol and in concentrated nitric acid, rinsed with water and treated at 100° C. for 5 minutes in a bath of the following composition:

45 g. of anhydrous sodium carbonate
15 g. of sodium chromate and
1.5 g. of Na_2HPO_4, 12 aq. per mls, of water

Then the plate was submerged in 32.5% nitric acid until it required a purely white color, well rinsed in distilled water, treated in a 5% solution of chromic acid at 60° C. for a few seconds, again rinsed in distilled water and dried.

The plate was anodically oxidized further for 30 minutes in the electrolyte bath used in Example 3. The voltage

of the bath was from 30 to 38 volts, the current density 1.5 amps./dm.^{2} and the temperature 50° C. After anodization, there was rinsed in water, in 2% NaOH for a few seconds, again in water, then in 5% chromic acid at 60° C. for a few seconds, again in water and dried.

The plate was sensitized in the manner described in Example 1 and exposed behind a negative to a 125-watt high pressure mercury-vapor lamp at a distance of 30 cms. for 20 seconds.

The exposed plate was submerged in the nuclear-introduction bath from Example 1 and then developed for 4 minutes by means of a physical developer of the following composition:

0.05 molar p-methylaminophenol sulphate
0.1 molar citric acid
0.05 molar silver nitrate
0.025% of "Armac 12D" and
0.01% of "Lissapol N"

Then the plate was sealed in the same manner as in Example 1, rinsed and dried. An image is now obtained having a somewhat different structure from that in the case where the aluminum plate is anodically oxidized only. The background is blank.

EXAMPLE 5

An aluminum plate anodized as in Example 1, after drying, was submerged in a bath containing 5×10^{-4} molar mercuric nitrate and 10^{-3} molar nitric acid for 5 seconds, rinsed in distilled water for 3 minutes and dried.

The plate was sensitized in the same manner as in Example 1 and then exposed behind a sensitometer wedge to a 125-watt high-pressure mercury vapor lamp at a distance of 30 cms. for 10 seconds, then submerged for 3 seconds in an aqueous solution containing:

0.005 molar mercurous nitrate
0.003 molar silver nitrate
0.01 molar nitric acid

and then rinsed in distilled water for 5 seconds. The plate was subsequently physically developed for 3 minutes and treated further as described in Example 1.

A fog-free print of the wedge was obtained which varied from black to blank. If the pre-treatment with mercuric-ions was omitted, a copy with a heavy fog resulted.

EXAMPLE 6

An aluminum plate pre-treated, anodized and sensitized as described in Example 1 was exposed behind a sensitometer wedge to a high-pressure mercury-vapor lamp placed at a distance of 60 cms. for 15 seconds and then treated for 3 seconds in a nuclear-introduction bath consisting of an aqueous solution of:

0.005 molar mercurous nitrate
0.003 molar silver nitrate
0.01 molar of nitric acid and
7.5×10^{-4} molar mercuric nitrate

rinsed in distilled water for 10 seconds and, at last, developed and treated further in the manner described in Example 1. A fog-free print of the wedge was obtained. If no salt was added to the nuclear-introduction bath a heavy fog occurred.

EXAMPLE 7

An aluminum plate pre-treated, anodized and sensitized in the manner described in Example 1 was exposed behind a sensitometer wedge to a high-pressure mercury-vapor lamp placed at a distance of 60 cms. for 10 seconds and then treated for 3 seconds in a nuclear-introduction bath of the composition:

0.0005 molar mercurous nitrate
0.003 molar silver nitrate
0.001 molar nitric acid and
0.01 molar citric acid

rinsed in distilled water for 10 seconds and then physically developed and treated further as described in Example 1. A fog-free print of the wedge was again obtained, which was not the case if the citric acid was omitted from the nuclear-introduction bath.

EXAMPLE 8

An aluminum plate pre-treated in the manner described in Example 1 was anodized at 20° C. in a 18% by weight solution of sulphuric acid at a voltage of 14 to 15 volts and a current density of 1 amp./dm.^{2} for 60 minutes. Next this plate was rinsed in distilled water for 2 minutes, treated in a 5% solution of chromic acid at 60° C. for 1 minute, again rinsed in distilled water and dried. The plate was sensitized in the manner of Example 1, streaked off between rubber strips, dried, exposed to a high-pressure mercury-vapor lamp at a distance of 60 cms. for 1 minute and treated in the nuclear-introduction bath from Example 5. After rinsing in distilled water for 10 seconds, the plate was held submerged in an aqueous solution of 0.3 molar glycolic acid for 1 minute, again rinsed and physically developed for 5 minutes in a developer of the composition:

0.2 molar ferrous-ammonium sulphate
0.1 molar ferric nitrate
0.05 molar silver nitrate
0.05 molar citric acid
0.04% by weight of "Lissapol N" and
0.02% by weight of "Armac 12D"

rinsed in distilled water for 3 minutes and dried. A fog-free image was obtained; if after the nuclear introduction the treatment with glycolic acid did not take place, a heavy fog occurred.

EXAMPLE 9

An aluminum plate pre-treated, anodized and sensitized in the manner described in Example 1 was exposed behind a sensitometer wedge to a high-pressure mercury-vapor lamp placed at a distance of 30 cms. for 5 minutes, submerged for 3 seconds in the following nuclear introduction bath:

0.005 molar mercurous nitrate
0.01 molar silver nitrate
0.01 molar nitric acid
0.001 molar mercuric nitrate

rinsed in distilled water, submerged in an aqueous solution of 0.3 molar citric acid for 1 minute, again rinsed, physically developed for 5 minutes in the developer from Example 8, rinsed in distilled water for 3 minutes and dried.

A fog-free print of the wedge was obtained. If no additional mercuric salt was added to the nuclear introduction bath and if the treatment with citric acid after the nuclear introduction was omitted, a heavy fog occurred.

EXAMPLE 10

An aluminum plate pre-treated as in Example 1 was anodized in sulphuric acid as described in Example 8, rinsed and further anodized in a bath of oxalic acid for 5 minutes as described in Example 1 and after-treated and sensitized in the manner described in the same example. The plate was exposed behind a sensitometer wedge to a 125-watt high-pressure mercury-vapor lamp at a distance of 30 cms. for 1 minute, submerged in the nuclear-introduction bath from Example 5 for 2 seconds, rinsed in a solution of 0.3 molar citric acid for 1 minute, in distilled water for 10 seconds, developed for 3 minutes in the developer from Example 1, rinsed in distilled water and eventually dried.

A print of the wedge was obtained which varied from black to blank with considerably deeper blackenings than in the case where after-anodization in oxalic acid did not take place. Besides, the photographic sensitivity had increased due to this after-anodization.

EXAMPLE 11

In an aluminum plate polished by anodization in the manner of Example 1, after sensitization, exposure behind a line-negative (radio scale) to a 125-watt high-pressure mercury-vapor lamp at a distance of 30 cms. for 1 minute, and treatment in the nuclear introduction bath from Example 1, photographic color images were obtained in the following manner. The plate provided with the latent nuclear image was rinsed in a freshly prepared solution of 0.3 molar citric acid for 1 minute, rinsed with distilled water for 10 seconds, and developed in an ammoniacal, stabilized, coloring physical developer at 20° C. for 6 minutes. To remove the metallic image produced in situ together with the dye-image, an aqueous 10% by weight solution of potassium ferric cyanide was used. The dye-image was fixed with the aid of an aqueous solution containing 20% by weight of sodium thiosulphate and 0.8% by weight of potassium metabisulphite.

At last, the plate was rinsed in tap water for 20 minutes and treated with the cobalt-nickel sealing bath from Example 1 for 40 minutes.

The ammoniacal, stabilized coloring physical developer was of the following composition:

Solution A

1% by weight of sodium thiosulphate
0.45 molar ammonia and
0.8% by weight of silver nitrate.

In preparing this solution, first the silver nitrate must be dissolved, then the ammonia added to it and only thereafter the thiosulphate. The dissolving process being completed, the solution is supplemented to the desired volume with distilled water.

Solution B.—Color-component solution

B_1: magenta color component—2% by weight of 1-phenyl-3-methyl-5-pyrazolon in ethanol.

B_2: blue color component—1% by weight of 2.4-dichloro-1-naphthol in ethanol.

B_3: yellow color component—0.8% by weight of 2.5-dichloroacetoacetanilide in ethanol.

Solution C.—5% by weight solution of "Genochrom" in water

25 mls. of solution A were mixed with 20 mls. of a 1% by weight solution of "Lissapol N," 2 mls. of a 1% by weight solution of "Armac 12D," 0.2 mls. of solution C and to this mixture the following amounts of one or more of the solutions B were added:

(1) For a yellow image 1 ml. of yellow color component, the metallic image being removed afterwards. Time of development 10 minutes.

(2) For a blue dye-image 1 ml. of blue color component; time of development 10 minutes; metallic image removed.

(3) For a magenta dye-image 1 ml. of magenta color component; time of development 10 minutes; metallic image removed.

(4) For a green dye-image 1 ml. of yellow color component +1 ml. of blue color component; time of development 10 minutes; metallic image removed.

(5) For a violet dye-image 1 ml. of magenta +0.5 ml. of blue color component; time of development 10 minutes; metallic image removed.

(6) 1 ml. of magenta component +1 ml. of blue component yielded, after removal of the metallic image, a dark blue dye-image; time of development 6 minutes.

(7) 1 ml. of yellow component +0.5 ml. of blue component yielded, after removal of the metallic image, a yellow-green dye image; time of development 6 minutes.

(8) 1 ml. of magenta component +0.5 mls. of yellow component yielded, after removal of the metallic image, a yellow-orange dye-image; time of development 6 minutes.

(9) 1 ml. of magenta component+0.5 mls. of blue component+0.5 mls. of yellow component produced a dark brown image. After removal of the metallic image, a silver-grey dye-image was obtained; time of development 6 minutes.

(10) 1 ml. of yellow component+1 ml. of blue component+0.5 mls. of magenta component yielded, after removal of the metallic image, a grass-green dye-image; time of development 6 minutes.

In all these cases fog-free color images on a glossy blank underground were obtained.

Special effects could be obtained by not removing the metallic images. Color images may also be manufactured on an aluminum plate matted by etching and subsequently anodized.

It is also possible to make prints of negatives having half-tones; in this case the metallic image is preferably not removed, resulting in images which are more beautiful and richer in contrast.

EXAMPLE 12

An aluminum plate polished by anodization in the manner as in Example 1 was sensitized by impregnating in a 0.3 molar solution of o-methoxybenzenediazosulphonic-acid sodium in methylglycol for 2 minutes, then streaking off and drying. The plate was subsequently exposed behind a negative of a printed circuit to a 125-watt high-pressure mercury-vapor lamp placed at a distance of 30 cms. for 90 seconds, submerged for 2 seconds in a nuclear-introduction bath containing

5×10^{-4} molar mercurous nitrate
0.01 molar silver nitrate
0.001 molar nitric acid
0.1 molar citric acid

and rinsed in distilled water for 5 seconds. Subsequently the plate was developed at 20° C. in the physical developer from Example 3 until an external, electrically-conductive silver image was obtained the resistance of which was less than 1 ohm per square. During this process the developer was refreshed several times. After rinsing, drying and sealing in the manner described in Example 1, an acrylonitrile-butadiene copolymer glue on the basis of acrylonitrilbutadienes was smeared on the image side of the plate, followed by drying of the plate in an oven at 160° for 10 minutes. Then the silver image was transferred to hard paper by pressing the aluminum plate into the paper at 160° C. at a pressure of 60 kgs./cm.^{2} for 20 minutes. After cooling, the aluminum plate and the hard paper were separated. The external silver image was thus passed into the hard paper.

EXAMPLE 13

An aluminum plate anodized in the manner of Example 8, after rinsing, was anodized further in a bath containing 10 g. of borax and 40 g. of boric acid per litre at 20° C., for 1 hour. The voltage of the bath in the first minute was slowly raised from 0 to 100 volts and then maintained at 100 volts. The current density was carefully maintained below 0.2 amp./dm.^{2}. After rinsing in distilled water for 5 minutes and drying, the plate was sensitized in the manner of Example 1, exposed behind a negative to a high-pressure mercury-vapor lamp at a distance of 30 cms. for 60 seconds and then developed at 20° C. for 10 minutes in a disproportionating developer consisting of:

0.015 molar p-methylaminophenolsulphate (0.5% by by weight)
0.1 molar citric acid
0.01 molar silver nitrate (0.2% by weight)
0.0005 molar mercurous nitrate
0.001 molar nitric acid

rinsed in distilled water for 10 minutes, sealed and dried.

An external silver image was obtained having a resistance less than 30 ohms per square, which image was electrically isolated from the aluminum plate.

EXAMPLE 14

An aluminum plate anodized and sensitized in the manner described in Example 1 was exposed behind a grid, used as a negative, to a 125-watt high-pressure mercury-vapor lamp placed at a distance of 30 cms. for 10 seconds, treated in a nuclear-introduction bath of the composition:

0.005 molar mercurous nitrate
0.003 molar silver nitrate
0.01 molar nitric acid
0.25 molar citric acid

After rinsing in distilled water the plate was developed in the physical developer from Example 1 at 20° C. for 10 seconds.

After rinsing, the resulting light brown "slightly developed" latent nuclear image was intensified for 6 minutes in an electroless copper-plating bath of the following composition:

0.14 molar copper sulphate
0.2 molar triethanol amine
0.65 molar NaOH and
2 molar formaline

Next the plate was thoroughly rinsed in distilled water and dried. An external, electrically-conductive copper image having a resistance of 3 ohms per square was obtained in the abovementioned manner on a glossy underground.

If the "slightly developed" nuclear image was intensified in the copper plating bath for 2 minutes only, a fog-free, internal deep black copper image was obtained.

EXAMPLE 15

An aluminum plate was anodized and after-treated in the manner described in Example 1, then sensitized by impregnating for 2 minutes in a 0.3 molar solution of o-methoxybenzene-diasosulphonic acid sodium in methylglycol, streaking off and drying, then exposed behind a grid negative to a 125-watt high-pressure mercury-vapor lamp placed at a distance of 30 cms. for 30 minutes and treated with the nuclear-introduction bath from Example 14. After rinsing in distilled water for 10 minutes, the nuclear image was developed at 20° C. with a developer of the composition:

0.01 molar p-methylaminophenol sulphate
0.08 molar citric acid and
0.05 molar silver nitrate

until a visible, external silver image was produced, rinsed in distilled water and sealed in the manner described in Example 1 .

After rinsing, there was submerged for 1 minute in an aqueous solution of

0.01 molar palladium chloride,
0.01 molar hydrochloric acid and
1 molar potassium chloride

rinsed in distilled water, submerged in a 1 molar solution of potassium chloride for 10 minutes, again rinsed in distilled water and, at last, treated for 6 minutes in a solution heated to 95° to 99° C., which contained per litre:

30 g. of nickel chloride
10.5 g. of citric acid
10 g. of sodium hypophosphite (1 aq.).

The pH value of said bath was adjusted from 4.5 to 5 with the aid of NaOH. The deposition of nickel took place selectively.

EXAMPLE 16

A black silver image obtained on an aluminum plate anodized in the manner of Example 2 was provided with a gold colored background in the following manner:

After the development of the silver image, the aluminum plate was held submerged in an aqueous solution of ferric-ammonium oxalate (2 gs. per litre) at 65° C. for 20 minutes. The pH value of said bath was adjusted from 5.5 to 6.3. The color could be intensified by subsequently submerging the plate in a 0.1% by weight aqueous solution of gallic acid for 1 minute. This color is light-resistant; after this treatment the material was treated further in the manner described in Example 1.

While we have described our invention in connection with specific embodiments and applications, other modifications thereof will be readily apparent to those skilled in this art without departing from the spirit and scope of the invention as defined in the appended claims.

What we claim is:

1. A method of producing a photographic contrast on a base consisting essentially of aluminum comprising the steps, oxidizing the surface of a base consisting essentially of aluminum in a manner so as to provide a porous aluminum oxide outer layer separated from the metal by a substantially non-porous intermediate layer, sensitizing said porous outer layer with an organic material the light decomposition product of which reacts with mercurous ions in the presence of water to form a latent mercury image, exposing desired portions of said sensitized layer to light of desired intensity, treating said exposed layer with an aqueous solution containing mercurous ions in a concentration of at least about 10^{-4} molar to form a mercury latent image and then physically developing said mercury image by applying to said layer an aqueous solution of a salt of a metal selected from the group consisting of mercury, siliver, gold, platinum and palladium and a water soluble organic reducing compound for said salt said reducing compound capable of reducing said salt to metal on said latent mercury image.

2. The method of claim 1 wherein an organic hydroxy acid is incorporated into the latent mercury image prior to physical development.

3. The method of claim 3 wherein the organic hydroxy acid is selected from the group consisting of citric acid and glycolic acid.

4. A method of producing a photographic contrast on a base consisting essentially of aluminum comprising the steps oxidizing the surface of a base consisting essentially of aluminum in a manner so as to provide a porous aluminum oxide outer layer separated from the metal by a substantially non-porous intermediate layer, treating said aluminum oxide outer layer with an aqueous solution containing mercuric ions, sensitizing said porous outer layer with an organic material the light decomposition product of which reacts with mercurous ions in the presence of water to form a latent mercury image, exposing desired portions of said sensitized layer to light of desired intensity, treating said exposed layer with an aqueous solution containing mercurous ions in a concentration of at least about 10^{-4} molar to form a mercurous latent image and then physically developing said mercurous image by applying to said layer an aqueous solution of a salt of a metal selected from the group consisting of mercury, silver, gold, platinum and palladium and a water soluble organic reducing compound for said salt said reducing compound capable of reducing said salt to metal on said latent mercury image.

5. The method of claim 4 wherein the concentration of mercuric ions is less than 5×10^{-4} molar.

6. The method of claim 1 wherein the solution containing mercurous ions in addition contains silver ions and a silver-amalgam latent image is formed.

7. The method of claim 4 wherein an organic hydroxy acid is incorporated into the latent mercury image prior to the physical developing.

8. The method of claim 7 wherein the physical developer contains in addition a color coupler.
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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,390,988 July 2, 1968

Cornelis Johannes Dippel et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 12, "cm^2" should read -- dm^2 --. Column 9, line 4, "0.5 g." should read -- 0.6 g. --. Column 11, line 75, "0.01" should read -- 0.1 --.

Signed and sealed this 13th day of January 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents