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3,424,580

PHOTOGRAPHIC PROCESS FOR THE DIRECT PRODUCTION OF POSITIVE IMAGES ON METAL

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ABSTRACT OF THE DISCLOSURE

A photographic process for the direct production of nonerasable positive images on metal, particularly aluminum, the surface of which has been anodized, including modification of known anodizing processes to eliminate sulfate ions, or the use of novel anodizing processes, and including the use of novel aluminum alloys.

This invention relates to a photographic process for the direct production of nonerasable positive images on metal and to special treatments of such metal surfaces so as to render the images nonerasable.

It is the primary object of this invention to provide a photographic process for the direct production of positive images on a metal surface, primarily aluminum, where the image thus produced can be retained in fully developed density without the defect of being removable by vigorous rubbing with a dry or wet cloth and which further is capable of being sealed in or on the surface of such metal so as to yield a permanency of image reproduction comparable to the permanency of the metal itself.

It is a further object of this invention to provide a means of producing a direct positive image of permanent nature on metal in which the image may be applied either through a negative or by reflexographic techniques.

It is a further object of this invention to provide a photographic process for the direct production of positive colored images.

Further objects of the invention will be apparent from the following description.

The basic process by which I apply an image to a metal surface, irrespective of the mode of treatment of that metal surface, is commonly designated as "diffusion transfer" and has been amply described in the patent literature as indicated partially in Table 1 following.

TABLE 1

Inventor:	United States Patent No.
Rott	2,352,014
Rott	2,665,986
Meeussen et al.	2,673,800
Weyde	2,699,393
Weyde	2,709,135
Weyde	2,712,995
Weyde	2,875,052
Weyde	2,937,945
Roth	3,042,514
Weyde	3,043,691
Rogers et al.	3,077,400
Haydn et al.	3,080,230
Weyerts et al.	3,146,102
Weyde	3,149,970

In general, the diffusion transfer process involves a photographic process for the direct production of positive images, according to which a light sensitive silver halide emulsion layer, after being exposed imagewise to an object, is developed in the presence of a silver halide solvent, said silver halide emulsion layer being in close contact during said developing process with a light insensitive re-

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ception layer containing nuclei for development. During this process the exposed part of the silver halide emulsion layer is developed to a negative image of the object to which it has been exposed, while at the same time part of the unexposed silver halide is dissolved by the silver halide solvent. This dissolved silver halide diffuses to the reception layer, where it is reduced to a positive image by the developer under the catalytic influence of nuclei for development, deliberately added to said reception layer. As nuclei for development there may be used, for instance, colloidal silver, colloidal gold, colloidal silver sulfide or other known substances which either are nuclei for development by themselves or which produce such nuclei for development during the developing process. These nuclei for development are sometimes called "fogging agents" which are known to be substances capable of promoting the reduction of silver halides without requiring the action of light. Other fogging agents than those previously listed include sulfites, hydrophosphites, stannous chloride and a variety of organic sulphur compounds such as thiosinamine, phenylmercaptotetrazole, and mercaptobenzothiazole.

The usual developer and transfer agent now commonly utilized for the diffusion transfer process is generally designated as "a monobath." Such a monobath contains the usual latent silver image developers such as alkaline hydroquinone and Metol mixtures with or without the addition of potassium bromide and also contains silver halide solvents such as sodium sulfite or sodium thiosulfate or combinations of the two. In addition, the developer may also contain accelerators of development which cause a previously exposed silver halide emulsion to blacken much more rapidly than usual such as minor quantities of 2-phenyl-3-pyrazolidone or phenylmercaptotetrazole or combinations of the two. Auxiliary agents for acceleration of the development process such as aminophenols and substituted hydroquinones may also be utilized alone or along with the organic compounds mentioned. Such complex developers for high speed development are described in U.S. Patents 3,188,209, 3,077,400 and 3,146,102.

The words "negative" and "positive" as used in the above description are intended to mean that if the emulsion layer is exposed to a negative object, there will be produced a direct negative in the reception layer, whereas if the emulsion layer is exposed to a positive object, a direct positive will be obtained. In other words, the diffusion transfer process is such that the image seen on the photographic receiving layer after the process is completed is reasonably identical with the image seen by the human eye. In the normal operation of the diffusion transfer process, in order to render the positive image freely visible, the silver halide emulsion layer will normally be removed from the reception layer after development by peeling.

The silver halide emulsions used for the production of the light sensitive layer may be silver chloride emulsions, silver chloride bromide emulsions or silver bromide emulsions containing silver iodide, with or without visible light dye sensitizers.

The diffusion transfer process is particularly useful for the production of positive images on both sides of a sheet-like support and for reflexographic type of copying. Further, as defined in the patents listed above the diffusion transfer process is also suitable for the production of colored images either in monochrome by reducing the metallic silver in the reception material with Farmer's reducer and redeveloping in the presence of a color coupler, or by utilizing multilayer techniques for the production of full color pictures as defined in U.S. Patents 3,077,400, 3,146,102 and 3,188,209. Various disclosures in the prior art, as for example, U.S. Patent 2,352,014, state that substantially any type of surface in-

cluding metal may be utilized as a reception material and this statement is repeated many times in the descriptive portions of the patents referred to. However, U.S. Patent 3,079,858 (last line of column 3 and first line of column 4) recognizes the fact that in order to obtain an image on a metal surface a binding agent such as gelatin must be present on such surface.

I have found that when the diffusion transfer process utilizes a metal as a receptor even though the metal may contain in its chemical makeup significant percentages of silver or gold, the image transfers to the metal surface as would be expected and as described in the prior art. But on drying, such image is easily removed by mild rubbing with a cloth or with a cotton swab and particularly easily if the surface is wet. I have further found that the reason for the temporary binding of the transferred silver image to the metal surface is due to the simultaneous transfer of gelatin which acts as a binder for such silver image and the transfer of such gelatin along with the silver salts is well recognized and described in U.S. Patent 3,079,858. Of course, by applying a lacquer over the surface of such temporarily bound silver image it is possible to retain the silver image on the surface of the metal but again this image is susceptible to destruction by abrasion and by the ordinary aspects of weathering. I have further found that if a porous metal surface is used such as aluminum anodized in sulphuric acid, the common commercial anodizing process utilized, the same disadvantage of an image reposing on the surface is obtained, the majority of which can be easily wiped off after it is dried. A very faint, barely visible pale yellow-brown image remains after such wiping process and this faint yellow-brown image cannot be intensified by the usual intensification processes involving gold salts known to those skilled in the art. This same inability for penetration of the pores of the anodized aluminum surface is found to be exhibited no matter what the anodizing process if even traces of sulfate ion are present in the liquids used for anodizing purposes. Since the most common commercial process for anodizing aluminum is the sulphuric acid process and since sulfates are common impurities in industrial waters, the inability of the usual anodized aluminum to yield the desired permanent transfer of the nonexposed silver halide complex is substantially universal.

I have found, and this is the primary object of this invention, that if sulfate radical is eliminated either in the anodizing process itself or by a special treatment of the anodized surface even though initially anodized in sulphuric acid that the defects referred to in the previous paragraphs can be eliminated. Transfer takes place with astonishing readiness and a deep lustrous black image capable of being intensified with gold or platinum salts in a manner known to those skilled in the art is obtained. The image cannot be rubbed off and the plate containing such image is capable of being sealed so as to protect the image from weathering and other abrasion effects and forces, for indefinite periods.

I have found that aluminum foils anodized with a sulphuric acid electrolyte in a manner known to those skilled in the art to produce a specially absorptive surface for a dye take-up is not capable of absorbing the silver salts into the pores to produce a black image by the standard diffusion transfer process, possibly for reasons given in the foregoing sections. I have further found that if this nontakeup type of anodized aluminum foil is treated in a dilute oxalic acid solution (particularly if such dilute oxalic acid solution contains a minor percentage of sodium or potassium oxalate) at an elevated temperature of the order of 50° C. for a period of 5 to 10 minutes some improvement in the ability of the receptor foil to take up the diffusion transfer image is developed but not to the extent that might be considered commercially acceptable. However, it is significant to note that the amount which is taken up is not only sealed into the pores but can be

toned to a light brown-black with the use of gold or platinum salts.

I have found that other techniques of anodizing, some of them novel in nature, radically improve the capability of anodized aluminum to act as a receptor in a diffusion transfer process. By specific modification of either the aluminum itself through the medium of alloying, and/or through the medium of modifying the anodizing process, I can produce a receptive plate which will take up the silver to its maximum extent, can be toned completely and sealed so as to produce a permanent image. By anodizing specific alloys of aluminum, I can produce nuclei for development of the silver halide-sodium thiosulfate complex commonly available from the diffusion transfer process without any special surface treatment of the metal plate itself. I can also utilize a complex aluminum alloy which not only produces the desired nuclei for development of the silver halide-sodium thiosulfate complex commonly available from the diffusion transfer process without any special surface treatment of the metal plate itself. I can also utilize a complex aluminum alloy which not only produces the desired nuclei for development of the silver halide-sodium thiosulfate complex but also yields an almost white porcelain finish after sealing; which is particularly attractive from a photographic standpoint. I can produce this porcelain-like, almost white finish by use of techniques known to those skilled in the art through the medium of the Ematal process and novel modifications thereof. In those cases where the aluminum alloy has not been specially treated so that the desired nucleating agents are not available directly as a consequence of anodizing, I can nucleate a properly prepared anodized layer with such materials as colloidal silver, colloidal gold, colloidal palladium, colloidal platinum, silver sulfide and similar nucleating agents which have been defined in the prior art though in a manner somewhat different from that established in the prior art.

I have found a significant modification of the Ematal process yields an improved result. This involves the use of niobium or tantalum hydrogen oxalate as an additive to an oxalic acid bath with or without the addition of an alkali metal oxalate. Anodizing conditions are the same as those described for the Ematal process but a particularly pleasing shiny, porcelain-like finish is obtained as the end result of the process in the presence of these salts. Combinations of titanium and niobium or zirconium and tantalum oxalates in an oxalic acid bath appear to yield a somewhat synergistic effect in that the development of the desired anodized layer can be produced in roughly half the time normally required.

Anodizing procedures

I will first define the various anodizing processes which are suitable for the practice of my invention.

The anodizing processes in most common use for decorative and protective applications are summarized on pages 216 and 217 of the book entitled "Finishing of Aluminum," by S. Wernick and R. Pinner, published in 1959 by Robert Draper Ltd. of Teddington, England. There are five major processes listed in this summary. The first involves a chromic acid electrolyte in which the concentration of CrO_3 may be varied from 2.5 up to 10 percent. The second is the sulfuric acid process in which sulfuric acid contents from 5 to 20 percent are utilized. The third is the oxalic acid process which may or may not contain alkali metal oxalates in which the oxalic concentration may be varied between 3 and 10 percent. The fourth is the Ematal process which involves a 3 to 5 percent concentration of oxalic acid combined with a 3 to 5 percent concentration of the oxalates of titanium, zirconium or thallium and the fifth is the boric oxide process used for the manufacture of condensers. Of these processes those deliberately designed for the production of porous surfaces for the takeup of dyes, for example, are the sulfuric acid, the oxalic acid and to a very limited extent the Ematal process.

A standard sulfuric acid process for maximum dye absorption, for example, utilizes an electrolyte comprising 10 percent sulfuric acid, a current density of the order of 20 amperes per square foot, a voltage of the order of 10 to 20 volts, a temperature in the range of 20 to 30° C. for a period of 10 to 30 minutes in which case a film thickness in the range of 0.2 to 1.2 mils is obtained. An ideal thickness for imparting silver images to a receptor sheet is about 0.4 mil obtained after 20 minutes of anodizing. It has been indicated previously that such a sheet has been found to be a poor receptor for the diffusion transfer process but is somewhat improved but not to the desired extent by soaking in hot oxalic acid.

My first novel process for producing a fully acceptable receptor sheet for the silver halide diffusion transfer process involves the following conditions: a 1 percent sulfuric acid electrolyte (prepared by adding 1 gram of 98 percent sulfuric acid to 99 cc.'s of water) is utilized at a temperature of 50° C., a voltage in the range of 20 to 25 volts, a current density in the range of 16 to 18 amperes per square foot, for a time period of 25 minutes. Vigorous air agitation is used throughout the anodizing procedure. The plate is removed from the hot anodizing bath, rinsed once in deionized water maintained at 50° C., and then immersed in a 3 percent solution of oxalic acid in deionized water for a period of 10 minutes at 50° C. using air agitation during such immersion. Mechanical agitation is also effective. After washing it in hot water and allowing it to dry, the aluminum foil so anodized is found to be an excellent receptor for the diffusion transfer process.

A second anodizing process, not novel in itself, has also been found to produce a surface which is entirely satisfactory as a receptor surface. This involves anodizing the aluminum foil in an oxalic acid solution containing 3 to 5 percent oxalic acid by weight in deionized water in which said oxalic acid may or may not contain 1 to 3 percent of the oxalates of sodium or potassium. With such a bath the current density normally used is generally of the order of 10 to 15 amperes per square foot at a voltage in the range of 40 to 50 volts, at a temperature of 50 to 55° C. for a period of about 30 minutes. After washing and drying, such a surface is an excellent receptor for permanent nature for the silver halide complex of the diffusion transfer process.

This oxalic acid process may be modified to produce a porcelain-like finish by use of the Ematal process. This involves the use of an oxalic acid solution which contains the alkali metal double oxalates of titanium, zirconium or thallium. The bath is operated at 20 to 30 amperes per square foot, 120 volts, a temperature of 50° C., for an operating time of 20 to 40 minutes. The pH in the solution is critical and must be kept between 1.6 and 3.0. Again, such a surface is an excellent permanent receptor for the diffusion, transfer process.

Nucleation aluminum alloys

I have found that if a straight oxalic acid bath in the concentration of 3 to 5 percent is utilized at 50° C. and if the aluminum being anodized contains fractions of a percent of metals such as silver, gold, palladium, or platinum, such alloys yield a satisfactory anodizing surface and are self-nucleating without any further treatment providing that, after drying at the end of the anodizing operation, the plate is then maintained at approximately 100° C. for about 10 minutes. The amount of precious metal alloying need not exceed 0.1 percent and a significant degree of nucleation is achieved with a concentration of the order of 0.01 percent by weight.

I have further found that if the aluminum contains in the range of 1 to 4 weight percent of the elements titanium, zirconium, niobium, tantalum, or thorium, oxalic acid anodizing in accordance with standard practice but in the absence of alkali oxalates yields a porcelain-like finish after hot water sealing and after washing and

prior to sealing such a surface represents a good receptor for the diffusion transfer process.

Finally, I have found that if this group of alloys containing self opaquing agents, as it were, are in turn alloyed with the minor percentages of the noble metals mentioned previously that not only is an opaque finish achieved on the finished product but at the same time the sheet is self-nucleating and does not require special treatments as will be defined in later portions of this description. The amount of opacity developed in the anodized layer increases as the amount of thorium, titanium, zirconium, niobium, and tantalum is increased but if these alloying agents added to aluminum are increased much above 5 percent the alloy is too brittle to roll easily into foil form, then in order to achieve the desired porcelain enamel type of finish, one must resort to either pure 2S aluminum base, anodized in accordance with the Ematal process, followed by special treatments to develop nucleation or to use an aluminum alloy containing a trace of a precious metal anodized by the Ematal process.

The manner in which the anodized aluminum surface is self-nucleated through modifications of the compositions of the aluminum alloy has been defined previously. In those instances where chemically pure aluminum is the base for the anodizing process, such an aluminum foil having been anodized by the preferred processes previously described, the anodized layer then requires special treatment in order that it may act properly as a nucleating surface for the diffusion transfer process. Salts of the noble metals such as silver, gold, palladium, and platinum have been found to be most effective for the purpose and stable water soluble salts are the most useful. In the case of silver the preferred salt is silver nitrate; in the case of gold, platinum and palladium these are the water soluble halides of these metals complexed with ammonium thiocyanate. The suitable range of concentration in deionized water for the salts are, in the case of silver, a weight percentage of 0.1 to 1.0; and in the case of gold, platinum and palladium, weight percentages of the halide salts themselves are found to be effective at concentrations as low as 0.01 percent and may extend up to about 1.0 percent. The ammonium thiocyanate complex is generally prepared by adding 1 to 2 moles of ammonium thiocyanate per mole of the halide compound and such solutions are stable in deionized water. To achieve the best results the dry plate after anodizing by one of the preferred processes described previously is immersed in the solution of the precious metal just indicated for a period of 20 to 120 seconds. Excess solution is then wiped off with a squeegee or a rubber roller after which the plate is immersed in a bath containing a strong reducing agent, such as hydrazine, formaldehyde, hydroquinone, stannous chloride or the like. Suitable concentrations of these baths for reduction purposes are as follows: 0.1 percent in the case of hydroquinone; 5 percent in the case of formaldehyde; 5 percent in the case of stannous chloride. Immersion in such reducing baths is continued at room temperature for 1 to 2 minutes after which the plate is thoroughly washed in running water and allowed to dry thoroughly.

With silver nitrate and to a lesser extent with the ammonium thiocyanate complexes of the noble metals, an improved effect is obtained without the use of the reducing agent. In this case, after the treatment with the silver, gold, palladium or platinum salt and removing excess salt by squeegeeing or rubber rolling, the plate is allowed to dry thoroughly at room temperature, after which it is heated at 100° C. for a period of 10 minutes, and a smooth, uniform pale yellow-brown color is obtained. The plate is then cooled to room temperature, washed in running water and again allowed to dry and it is found that excellent nucleating surface is achieved by this technique. In each case, the purpose of the treatment is to impart a small but significant percentage of a colloidal metallic nucleating agent.

All the receptor surfaces described in the prior art of

a workable nature such as paper or even metal require the use of a hydrocolloid such as gelatin, polyvinyl alcohol, or similar materials in order to make the diffusion transfer process work. It should be noted that no such hydrocolloid is required for adequate transfer or complete nucleation in the case of the present description. Minor amounts of hydrocolloid such as gelatin, polyvinyl alcohol, hydroxyethylcellulose, methylcellulose, carboxylated polymethylenes, and the like, can be used in my process, not necessarily for improvement of transfer but to improve binding of the image in the pores during the various subsequent processing that might be desired such as gold toning or color development. When such hydrocolloid is used it must be used in very small quantities to be effective and concentrations not exceeding 0.2 percent as a water solution of such hydrocolloid in which the porous anodized layer is dipped represent the maximum amount which can be utilized and concentrations in the range of 0.05 percent to 0.1 percent are preferred.

Diffusion transfer process according to the present invention

In the generalized practice of my invention, a light-sensitive paper is provided coated on one side with a silver halide emulsion in gelatin in the usual manner. Depending on the manner in which it is desired to use such an emulsion the silver halide may be the chloride, the bromide, the bromiodide, or any one of these and particularly bromiodide, sensitized to the visible with the usual type of sensitizing dyes such as the cyanines. The dry anodized aluminum plate, anodized and nucleated in the preferred manner which have been defined in previous paragraphs and the light sensitive silver halide sheet are assembled together with a plastic hinge. This plastic hinge is simply a piece of pressure sensitive tape in which the adhesive comprising the pressure sensitive surface is unaffected by water at room temperature. The tape may be cellophane, vinyl or Mylar base and Mylar is preferred because of its strength. In assembly, and in the darkroom the "negative" paper with the silver halide gelatin emulsion coated on one side is laid face down on a clean, smooth surface. The anodized surface which has been prepared to act as the receptor surface and with the proper nucleating agents already incorporated is also laid face down on the same surface so that the edges of the two sheets butt against each other. The hinge is prepared by taping the top edge (away from the photosensitive side) of the "negative" sheet to the top edge of the aluminum foil and again the side away from the anodized surface. Thus, when the hinge is completed and the package closed by bending the hinge in the direction towards the pressure sensitive surface, the light sensitive side of the "negative" and picture-taking material is then in contact with the nucleated anodized side of the foil. In order to carry out the processing the assembly is opened up which permits the "negative" light sensitive surface to be exposed as desired, either in a camera, to a negative or reflexographically. The exposure and conditions of exposure will depend on the nature of the silver halide emulsion which is applied. After exposure has been completed, the anodized aluminum (not the light sensitive paper transfer sheet) is then immersed in a monobath type of developer. Several such formulae are known and the following may be considered typical: 1000 cc.'s of water, 15 grams of hydroquinone, 1 gram of 2-phenyl-3-pyrazolidone, 10 grams of caustic soda, 40 grams of anhydrous sodium sulphite, 1 gram of potassium bromide, 15 grams of sodium thiosulfate, 0.01 gram of 1-phenyl-5-mercaptotetrazole (sometimes called 5-phenylmercaptotetrazole). The anodized aluminum foil is immersed in this bath at room temperature for 30 seconds taking care not to wet the "negative" still light sensitive (though containing a latent image) sheet with this monobath developer solution. After the 30 second immersion the aluminum foil is removed from the solution just

described and allowed to drain completely. Thereafter, the light sensitive and exposed sheet is brought into contact with the monobath wet anodized layer and this contact is accomplished by closing the hinge only partially and the contact is completed by running the assembly through a set of rubber rollers which applies very light pressure very uniformly all over the surface. By holding the sandwich open as the material is being fed into the rollers all air bubbles which might be caught in the surface are swept out. After passing through the roller equipment the assembly is allowed to stand for 10 seconds, after which the combination is placed in cold running water for 30 seconds and the "negative" paper removed. The plate is then washed in running water and any traces of paper or gelatin left from the transfer operation removed with a wet cotton swab. A brown-black "positive" image is now available in the pores of the anodized aluminum. This image may be toned with gold salts or transformed to a colored image through bleaching and color development by techniques well known in the art.

The pressure sensitive tape hinge and sandwich construction described in the foregoing is an important portion of my invention. The aluminum surface, even though it is an anodized layer, is very smooth and slippery and in bringing the anodized layer into contact with the latent image layer to accomplish the total transfer of the image with the somewhat caustic developer, the paper tends to slide, reducing resolution and in some cases blurring the image. By use of the sandwich technique described above, sliding and blurring of the image is prevented.

As a final stage of the operation the washed anodized aluminum sheet, now containing the desired image, is sealed—that is the image is sealed into the anodized layer by immersing the plate in boiling water containing ½ percent of nickel acetate, ½ percent of cobalt acetate and 2 percent of boric acid. The sealing is complete in about 5 minutes. The plate may also be sealed in hot water after a 15 minute immersion therein.

EXAMPLES

Having described my invention the following examples are indicative of preferred practice.

Example 1

A sheet of 2S aluminum is anodized at 50° C. in the 1 percent sulphuric acid bath described previously, then washed for a period of 10 minutes in 3 percent oxalic acid, again at 50° C., and then washed and dried. Thereafter, the sheet is dipped in a 0.5 percent water solution of silver nitrate, retained in the silver nitrate bath for 30 seconds, the plate removed from the bath, the excess solution wiped off and the plate then placed in a 0.1 percent solution of hydroquinone for 20 seconds after which the plate is allowed to drain and dry. A hinged set of plates is then prepared comprising the thus treated anodized plate and a sheet of paper treated on one side with a silver emulsion which has been sensitized to visible light with a carbocyanine dye in which the emulsion is a silver bromiodide halide principally. The hinged set is prepared in the darkroom with the emulsion side and the anodized surface of the plate lying end to end and face down against a smooth clean, flat surface. The hinge is prepared by pasting a strip of pressure sensitive 3 mil Mylar joining the two abutting edges.

The set is then opened so that only the photographic paper is available in the exposing device with the gelatin photosensitive side exposed to light beam. Exposures are made through a negative with the tungsten illumination for a period of 2 seconds using a 500 watt No. 2 photoflood. The specific silver halide paper utilized for the purposes designated in the trade as Apeco No. 1, as manufactured by The American Photocopy Company of Chicago, Ill. This paper is also called "negative" paper No. 1 Auto-stat and similar papers are produced by a variety of manu-

facturers as a negative portion of a usual diffusion transfer set. After exposure the sheet is removed from the exposure device and the anodized aluminum *alone* is dipped in a monobath-developer-fixer as previously described and retained in such solution at room temperature for 12 seconds. The plate is allowed to drain and the set is now manipulated so that the top hinged edge of the light sensitive but now exposed paper comes in contact with the monobath treated anodized layer of the aluminum plate. The hinged edge is inserted into a set of rubber rollers and the sheets are kept apart up to the moment of contact at the rubber rollers so as to sweep out any air between them. After removal from the rubber roller set, the combination is allowed to stand for 15 seconds after which it is placed in cold running water for 30 seconds and the negative paper peeled off. A deep brown-black positive image (duplicating the relative light and dark areas of the original) is now visible on the aluminum sheet. The negative paper is removed from the hinged set and discarded by peeling it from the surface of the anodized aluminum and the surface of the anodized aluminum is cleaned by gentle swabbing with a piece of wet cotton and then dipped immediately into a 1 percent solution of the complex of gold chloride and ammonium thiocyanate at a pH of approximately 8 wherein it is retained for 1 minute. This yields a deep blue-black image through the toning and intensification process available from the gold salt as commonly practiced in photographic arts. After toning, the plate is washed for about 30 seconds in running water and then is placed in a boiling solution of water containing 0.5 percent of nickel acetate, 0.5 percent of cobalt acetate and 1 percent of boric acid, wherein the plate is retained for 5 minutes and then removed and allowed to dry. A black photographic image is now available sealed into the pores of an anodized aluminum sheet.

Example 2

Same as in Example 1 except that the hydroquinone reduction step is omitted. After treatment with 0.5 percent solution of silver nitrate as described in Example 1, the plate is allowed to drain and then is dried at room temperature after which it is heated at 100° C. in a dry atmosphere for 10 minutes. After cooling, the photographic processing as defined in Example 1 is repeated and again an excellent transfer is obtained as before with the exception that the transfer before toning yields an image with a somewhat deeper hue than in the case where the silver nitrate has been reduced to colloidal silver by hydroquinone as defined in Example 1.

Example 3

A sheet of 2S aluminum is anodized at 55° C. in an electrolyte comprising 5 percent oxalic acid and 3 percent potassium acid oxalate for a period of 30 minutes, washed in running water and allowed to cool and dry, thereafter the sheet is dipped in a solution containing 0.1 percent of the 1 to 1 molecular complex of palladium chloride and ammonium thiocyanate and retained in such solution for 30 seconds, after which the plate is removed from the solution and allowed to dry. Thereafter, the sheet is placed in a 3 percent solution of stannous chloride containing 2 percent hydrochloric acid and held in such solution for 15 seconds, after which the plate is washed in running water for 30 seconds at room temperature and allowed to dry. The hinged set with the Apeco photosensitive paper No. 1 is prepared and processed photographically as before, except in this case the exposure is made by reflexographic techniques in which case the photosensitive paper is placed emulsion side up on top of the sheet to be copied and a blanket exposure of the entire photosensitive surface with a photo flood at a distance of 18" is carried out for a time of 6 seconds. Thereafter, the photographic processing and developing is carried out as in Example 1 and an image is obtained directly from the transfer process which is blue-black in color and does not require gold toning to achieve

its full intensity. Sealing renders the image permanent and abrasion resistant.

Example 4

A sheet of 2S aluminum is anodized by the Ematal process in which the electrolyte comprises 3 percent oxalic acid and 2 percent potassium titanium oxalate in deionized water and anodizing is carried out at 55° C. for 30 minutes. Nucleation of this plate carried out with a 0.2 percent solution of the 1/1 molecular complex between platinum chloride and ammonium thiocyanate at a pH of 8, which after draining is reduced with a 2 percent solution of hydrazine hydrochloride to deposit colloidal platinum in the pores of the anodized layer. The plate is washed and dried and photographically processed as in Example 1 by exposure to a negative. A blue-black image is obtained directly on transfer which is then sealed.

After sealing, an exceptionally bold blue-black image is available on a faintly blue-white porcelain-like background yielding the impression of a relief image.

Example 5

A sheet of 2S aluminum is anodized as described in Example 1 and after washing and drying, the anodized sheet is treated with a 0.2 percent solution of the 1/1 molecular complex between gold chloride and ammonium thiocyanate at a pH of 8 for 30 seconds. After draining, the sheet is then placed in a 5 percent formaldehyde solution in water for 15 seconds, after which the sheet is washed in running water and permitted to dry. Photographic processing from exposure, through monobath development and transfer is carried out as in Example 1. A lustrous blue-black image is obtained on a porcelain-like background which after sealing, again yields the impression of being in relief, even though the image is planographic.

Example 6

A sheet of an aluminum alloy comprising roughly 99.9 percent aluminum and 0.1 percent silver is anodized in the oxalic acid solution as defined in Example 3 and after anodizing is thoroughly washed and dried and then heated in dry air at 100° C. for 10 minutes and then cooled. Using the hinged pack as defined in Example 1 and proceeding through the photographic processing developing and transfer as therein defined, an excellent transfer is produced which can be gold toned to a lustrous black image and sealed permanently in the anodized layer by hot water sealing. It is noted that in this case there is no need for special treatment with noble metal salts for nucleation purposes.

Examples 7, 8 and 9

Example 7 utilizes a 0.1 percent gold alloy of aluminum; Example 8 a 0.1 percent platinum alloy of aluminum and Example 9 a 0.1 percent palladium alloy of aluminum. Each are anodized with the oxalic acid bath described in Example 3, heated for 10 minutes at 100° C. and after cooling photographically processed for diffusion transfer purposes without added nucleation devices as pointed out in Example 6. In each case, excellent transfer is obtained and the image is a deep black without the need for gold salt intensification after transfer. On sealing a lustrous black image of permanent character is obtained.

Examples 10, 11, 12, 13 and 14

Alloys of aluminum in sheet form are utilized comprising 97.9 percent of aluminum, 2.0 percent of one of the metals taken from the group zirconium, titanium, thorium, niobium, and tantalum; and 0.1 percent silver. These are anodized in the oxalic bath described in Example 3 and heat treated under the conditions therein detailed. After anodizing, washing and drying the photographic processing, hinging and diffusion transfer described in Example 1 is repeated. The image transfers in an excellent manner without the need for chemical nu-

cleation of the plate and after toning with the gold chloride ammonium thiocyanate complex achieves a blue-black color, which after sealing is available against a porcelain type background which gives the impression of the image being in relief. The surfaces obtained by this technique are comparable to those achieved by use of the Ematal process based on the anodizing of pure aluminum as described in Example 4.

Example 15

An aluminum alloy comprising approximately 97.9 percent aluminum, 1.0 percent tantalum, 1.0 percent zirconium, and 0.1 percent gold was anodized in accordance with the practice taught in Example 3. Again, the nucleation step through the use of chemical treatments was omitted and after photographic processing and diffusion transfer as described in Example 1, a blue-black image was obtained directly on transfer which was sealed with hot water sealing without further toning, yielding a lustrous blue-black image on a pleasant appearing whitish background where the image, though planographic, gives the impression of being in relief.

Example 16

A 2S aluminum foil was anodized in a 4 percent oxalic acid, 2 percent potassium oxalate, and 2 percent niobium hydrogen oxalate solution, in deionized water at 55° C. at 50 volts and 15 amperes per square foot for 30 minutes.

Example 17

Same as Example 16 except tantalum hydrogen oxalate was used in place of the niobium compound.

Examples 18 and 19

Foils anodized as in Examples 16 and 17 respectively are nucleated, hinged and processed photographically as in Example 1. After sealing, a blue-black image is obtained on a porcelain appearing background yielding the impression of a relief image.

Example 20

A 2S aluminum foil was anodized at 50° C. in a 4 percent solution of axalic acid containing 4 percent sodium titanium oxalate and either tantalum or niobium hydrogen oxalate at 25 amperes per square foot for 30 minutes at a pH of 2.5. A much whiter finish was obtained than the bluish-white characteristic of the Ematal product.

The novel anodizing procedures and the novel alloys disclosed herein are described and claimed in patent applications filed concurrently herewith.

I claim:

1. In a diffusion transfer process for the direct production of positive images on metal surfaces which includes:

- (1) preparing a light sensitive silver halide emulsion layer;
- (2) exposing the same imagewise to a subject the image of which is to be produced;
- (3) developing the resulting latent image in the presence of a silver halide solvent; wherein said silver halide emulsion layer is in close physical contact with a light insensitive reception layer during said developing process, the improvement which comprises: providing as the light insensitive reception layer an anodized aluminum surface free from any traces of sulfate.

2. The process of claim 1 wherein the light insensitive reception layer of anodized aluminum is rendered free of sulfate by anodizing said aluminum surface in a dilute solution of sulfuric acid and thereafter treating the resulting anodized layer with a solution containing oxalic acid.

3. The process of claim 1 wherein the light insensitive layer is anodized in a solution of oxalic acid which contains up to 3 percent of at least one alkali metal oxalate.

4. The process of claim 1 wherein the light insensitive reception layer is anodized in a 3 to 5 percent solution of

oxalic acid in deionized water at a current density of 10 to 15 amperes per square foot and at a temperature of between 50 and 55° C. for a period of about 30 minutes.

5. The process of claim 1 wherein the light insensitive reception layer is produced by anodizing an aluminum sheet or foil in a 1 percent sulfuric acid electrolyte at about 50° C., at a voltage of 20 to 25 volts and a current density of 16 to 18 amperes per square foot for about 25 minutes and the anodized surface is then soaked in a heated oxalic acid solution.

6. The process of claim 1 wherein the light insensitive reception layer is anodized in a solution of oxalic acid which solution contains at least one alkali metal double oxalate selected from the group consisting of alkali metal oxalates of titanium, zirconium and thallium.

7. The process of claim 1 wherein the light insensitive reception layer is anodized in an oxalic acid solution which includes at least one oxalate selected from the group consisting of titanium and zirconium oxalates and at least one oxalate selected from the group consisting of niobium hydrogen oxalate and tantalum hydrogen oxalate.

8. The process of claim 1 wherein the light insensitive reception layer is an anodized surface of an aluminum base alloy containing a small amount of at least one alloying element selected from the group consisting of silver, gold, palladium, platinum, titanium, zirconium, niobium, tantalum and thorium.

9. The process of claim 1 wherein the metal is an aluminum alloy containing between 0.01 percent and 0.1 percent by weight of a metal which acts as a nucleating agent and selected from the group consisting of gold, silver, platinum and palladium.

10. The process of claim 1 wherein the metal is an aluminum alloy containing between 1 percent and 4 percent by weight of an opaquing metal selected from the group consisting of Ti, Zr, Nb, Ta, and Th.

11. The process of claim 1 wherein the light insensitive reception surface is provided with a nucleating metal by immersion in a water solution of a water soluble salt of a nucleating metal selected from the group consisting of Ag, Au, Pd, and Pt for between 20 and 120 seconds, after which the anodized surface is immersed in a strong reducing agent.

12. The process of claim 9 wherein after drying at the end of the anodizing operation the surface is maintained at approximately 100° C. for about 10 minutes.

13. The process of claim 1 wherein the diffusion transfer from said silver halide emulsion sheet to said anodized surface is effected by assembling said sheet to said surface with a plastic hinge by placing said sheet and said surface on a flat support side by side one another with the sensitive surfaces face down, and taping the top edges of the two together so that when lifted from the support, the sensitive side of the silver halide emulsion sheet and the anodized image reception surface may be placed in face to face contact with the hinge holding one side of the two together for transfer of said image into the pores of said anodized surface.

14. The process of claim 13 wherein the silver halide emulsion layer is exposed to a subject; then the anodized surface is immersed in a monobath type of developer; then the emulsion layer and the anodized layer are brought together by closing the plastic hinge partially and then applying pressure to the assembled members from the hinged side to the opposite side; and after a suitable time sufficient to permit the resulting silver image to be taken into the pores of the anodized surface, removing the silver halide emulsion sheet from the assembled combination; and then washing and sealing the surface of the anodized plate.

15. The process of claim 14 wherein the plate is toned before sealing.

16. An anodized surface containing in its pores a silver halide sodium thiosulfate water soluble complex.

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17. An anodized surface containing a non-erasable image in the pores of said surface.

18. An aluminum article comprising an aluminum alloy containing a small amount of at least one metal selected from the group consisting of opaquing metals and nucleating metals and having a porous anodized surface containing a non-erasable image therein.

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