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Complete Specification entitled (54) METHOD OF REPRODUCING IMAGES USING FISSION FRAGMENTS AND/OR ALPHA RAY ETCH TRACKS FROM TONED PHOTOGRAPHS

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The following statement is a full description of this invention, including the best method of performing it known to us :

1746/75-L

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X800-85-ND-25 P.C.

This invention relates to the reproduction of photographic images. There is a very great and continuing need to transfer photographic images to surfaces which are not normall photoreceptive.

This need is illustrated by the multiple reproduction of photographs in newspapers, magazines and books, by the transfer of decorative pictures or patterns to packaging materials, glassware, pottery, ceramic tiles, etc., by the reproduction of durable measuring scales on scientific instruments, and by the use of photographic techniques in the fabrication of electrically conducting and semiconducting circuits for electronic equipment.

Faithful reproduction of photographic images on such surfaces presents no serious problems when the photograph consists of portions which are either completely opaque or completely transparent. The method generally employed is to coat the material which is to receive the image with a thin layer of a substance which can be made insoluble (usually by polymerization) when exposed to light. Such materials are generally referred to as photopolymerizable etch-resists. When such a thin layer is exposed beneath a two tone (black and white) photograph, parts of the layer which are exposed to light become insoluble and adhere strongly to the underlying surface and parts which are screened by the black parts of the photograph are unchanged and can be washed away later to leave the corresponding areas of metal surface unprotected. These unprotected areas can then be marked by suitable inks or chemical etchants so as to reproduce the original photograph.

When the photograph consists not of two tones (black an white) but of many shades of grey as is normally the case,

this process cannot be applied in a direct manner since the etch-resist is either present on the surface or it is absent. It cannot be partially present to partially protect the surface against subsequent chemical attack.

To overcome this problem, a gridded screen is normally used to break up the light passing through the negative into a large number of small black and white areas. This causes the etch=resist to remain soluble in places and be later washed away as a large number of small pits. The surface density of such pits is roughly proportional to the density of the part of the photograph which overlayed them but there is no direct positional relationship between the original silver grains on the original photograph and the etch-pits which later form in the corresponding area of the matrix. Normally screens having about 150 lines per inch are employed in the conventional process and 200 lines per inch is about the maximum which can be employed by a skilled engraver. This limits the resolution of fine detail in the transferred picture.

In the application of the present invention, a photograph is toned with a chemical substance which reacts with the silver grains. After toning, the silver grains spontaneously emit or indirectly by being irradiated are made to emit densely ionising radition such as fission fragments or alpha particles. This densely ionising radiation can produce a 'radiation damage image' in any surface with which the photograph is placed in close contact. In many such surfaces this 'radiation damage image' will have electrical, magnetic and chemical properties which are different from areas of the surface which have remained unaffected by radiation. These different properties of the 'radiation damage image' have many applications in the use-

ful arts. Thus the different electrical and magnetic properti of the image can be applied directly in the fabrication of electrical circuits. The charged chemical properties of the image can be made manifest by the increased speed with which the areas damaged by radiation react with chemical reagents in liquid or gaseous form. One very useful manifestation of the increased reactivity of the 'radiation damage image' is in the application of etchants to produce an intaglio image in many types of surface against which the toned photograph has been pressed.

Thus the invention provides a method of precision doping or precision etching in highly localized areas of a surface to be employed in the useful arts.

The main benefits resulting from the invention are that no diffusing screens are necessary to cause loss of fine details and the etch-pits or doped areas of the transferred image have a direct positional relationship to silver grains on the original photograph thereby permitting a much more faithful reproduction to be achieved. To the best of our knowledge, no other method of reproducing intaglio images which has ever been devised permits such a direct positional relationship between the element of the transferred picture and the silver grains of the original photograph.

When an etch resist covers a metal plate or cylinder and parts of it have been washed away to produce a series of small holes by the conventional process described above or by the process of the present invention, the metal itself can be etched through these holes to produce a series of pits which can be used to transfer ink to an absorbent surface such as paper. This is the most frequently used method of preparing an

intaglio type plate or cylinder for the rapid multiple reproduction of photographic images as in rotagravure printing. The method of the present invention is a method whereby the ink spots transferred to the paper bear a direct positional relationship with the silver grains in the original photograph.

In lithographic printing, the ink transfer relies on the fact that certain areas of the plate are preferentially wetted by the ink and ink transfer is not controlled by the depth of etchpits. The new process can be applied equally well to lithographic printing since the changed chemical properties of the 'radiation damage image' can manifest themselves in the form of increased receptivity to printing ink (this phenomenon is related to the well-known process whereby plastic sheets used for wrappings etc, can be made more receptive to printing ink by bombarding the surface with electrons).

Alternatively, as when using metallic surfaces for lithographic printing, an etch-resist may be used which has been penetrated by etch-track holes produced by a toned photograph. A chemical reagent is then allowed to operate through the etch-track holes to make the underlying plate ink-wettable in localized areas in a manner similar to that currently employed in the existing art. (See Example 3).

The invention depends on three main principles. These are:-

1. Photographs can be toned with other substances in such a manner that the silver grains of the photograph combine with or are displaced by some other material.

2. The material used to tone the photograph can be chosen from those isotopes which emit fission fragments or alpha particles by virtue of their radioactivity. The invention

also extends to certain elements which, although not emitting fission fragments nor alpha particles spontaneously, can be made to do so when bombarded with neutrons.

3. When densely ionizing radiation, such as fission fragments or alpha particles, strikes the surface of many types of solid, damage trails are produced which have different properties from the undamaged material. In many surfaces the damaged areas can be etched away to leave pits which are clearly visible under the microscope. Fission fragments have been observed to produce such effects in glass, mica, ceramics and many minerals and plastics. Alpha particles have been observed to produce this effect only in specially susceptible plastics such as nitrocellulose.

Fission fragments are emitted spontaneously by some radioisotopes e.g. californium-252 and many alpha active radionuclides are known e.g. polonium-210. Stronger fluxes of fission fragments can be obtained when fissile elements such as uranium-233, uranium-235 or plutonium-239 or Americium-242 are irradiated with neutrons. Stronger fluxes of alpha particles can also be obtained by irradiating the elements boron or lithium with neutrons.

In applying this invention, a photograph toned with one of these materials is pressed against the surface of a suitable solid. With the passage of time, (and sometimes but not always by means of neutron bombardment) the image becomes transferred to the surface in the form of damage trails caused by fission fragments or alpha particles. At this stage, the image is not visible even under the microscope and becomes visible only if developed by immersion in a suitable etching fluid. For some purposes, such as the transfer of decorative

images to mirrors or drinking glasses, no further treatment is required but in other cases the image can be made more visible or appealing by filling the etch-pits with a suitable ink of staining fluid. Using low viscosity inks and high pressure, images can be further transferred to absorbent surfaces such as paper to form the basis of a high fidelity printing process.

However, as prepared by these direct methods, the etch-pits are of very small dimensions (since they cannot exceed the penetration depth of the ionizing particle) and the process cannot be applied directly to metals (only non-conductors are capable of retaining damage trails which can subsequently be etched). This precludes the direct formation of intaglio metal printing plates. In addition the high pressure necesary to remove the ink from the very small pits coupled with the low mechanical strength of plates of plastic, glass, etc., can cause difficulties.

However, this difficulty has been overcome by the following method to prepare metal plates having deeper etch-pits. The method may also be applied to give deeper pits in non-metallic surfaces but metals are generally used for printing plates.

In this method, the material in which the damage trails are formed and etched is present in the form of a thin barrier layer on an underlying matrix. The barrier layer may be applied to the matrix as a solution which subsequently dries or polymerizes to give a protective coating. Alternatively, the barrier may be formed by chemical or electrochemical treatments as ex-

ampled by the formation of a protective oxide barrier layer on metals such as aluminium or titanium when they are anodised.

The barrier layer may be etched away at points where it has been traversed by alpha particles or fission fragments but it protects the underlying matrix in all other places. The etching fluid thus penetrates the barrier layer only at places where it has been traversed by an ionizing particle. This causes an etch pit to form in the underlying matrix within a few microns distance of a toned silver grain in the original photograph which overlaid it. In some cases, a different etching fluid may be used to attack the matrix after the first etch has produced holes in the barrier layer. Electro-etching techniques may also be used to attack either the barrier layer or the matrix or both of these. In all cases, whether one etchant or two are used and whether or not electro-etching is used, the depth of the etch-pits in the matrix can be varied as desired by varying the contact time with the etching fluid. A strong intaglio printing plate capable of rapid transfer of ink to paper without the use of excessive pressure can thus be prepared.

The method of this invention may be used to prepare relief images in which the image is raised above the surrounding surface instead of being sunk below it as in the intaglio case. Such relief images can also be used for printing. In addition, when such relief images are prepared using precious or non-corrodable metals very permanent and decorative photographs can be obtained which are of value in the manufacture of jewellery and the preservation of archival records.

One method of preparing such relief images is to prepare replicas of intaglio images prepared by the methods hereinbefore described. On such process for preparing decorative metal photographs, is to prepare an intaglio image on a glass plate by the methods previously disclosed and then to deposit silver

onto the intaglio image by one of the well known processes for preparing mirrors. Metals other than silver may also be used and the metal may be deposited by vacuum evaporation techniques or deposited from chemical solutions. The thin layer of metal on the glass plate is then increased in thickness by electroplating more of the same metal or some other metal upon it. When the metal is sufficiently thick to provide adequate strength, it is separated from the glass. Many such metal relief photographs can be prepared from the same etched glass plate.

Etchings in materials other than glass can also be used to provide the relief photograph. The relief photograph may also be prepared by means other than the silvering and electrodeposition process previously described. For example, preparation of a relief replica of the intaglio image by casting molten materials upon it or by casting with liquids which can be polymerized in situ to form solids is also possible.

A relief image may also be prepared by using a variation of the barrier layer technique which has previously been described.

In the manufacture of such a plate, holes are first etched through the barrier layer as in the manufacture of the intaglio plate but the second step, instead of etching the matrix through the holes, uses electrodeposition to build up the material of the matrix where the holes in the barrier layer permit this to occur. Off-set printing plates can be prepared in this manner. Lithographic printing plates can be prepared in a similar manner by electro-depositing a small amount of a hydrophobic metal such as copper on a surface of a hydrophillic

metal such as nickel (or vice versa).

As a variation of the method of involving the barrier layer a material can be used as a barrier which disintegrates on being heated, in those areas which have been irradiated. Etching of the underlying layer can then take place.

Particular applications of the method of this invention will now be described in the following examples.

EXAMPLE 1

Decorative Etching of Polycarbonate Plastic Sheet

A fine grain medium speed photographic negative is exposed and developed in the normal manner before being toned with the fissile isotope uranium-233 by the following procedure.

The toning solution is prepared from a 1% solution of potassium ferricyanide. To each 100 mls of this solution is added 10 mls of glacial acetic acid and 2.5 mls of a solution of uranyl nitrate containing 1 mg U^{233} per ml. Sufficient solution is prepared to cover the negative when coiled around the inner wall of a cylindrical container. The vessel is tightly stoppered and shaken with the negative for about two hours. The negative is then washed several times with demineralised water and then for one hour in running water. It is then washed for a few minutes in a 2% solution of ammonium thiocyanate until all trace of yellow colour has disappeared from clear regions of the gelatine. After a further 10 minutes wash in running water, the negative is dried.

It is then clamped with the emulsion in contact with a sheet of transparent polycarbonate plastic which is to be embossed. The negative is then irradiated with thermal neutrons at a flux of 5×10^{10} neutrons/(cm^2)/(sec) for 10 minutes so as to cause uranium atoms in the toned image to fission and bombard

the polycarbonate surface.

After removal from the neutron flux, the polycarbonate sheet is separated from the negative and etched for 15 minutes in a solution of 6.5 N sodium hydroxide at 50°C. This causes the original image to appear on the surface of the plastic. The image can be made more visible or more decorative by rubbing a suitable coloured ink into the etch-pits and removing the excess.

It should be noted that the irradiated negative can also be immersed in the etching solution and this will cause the emulsion containing the silver and uranium to dissolve away. If the base is constructed of material in which fission tracks can be etched, e.g. cellulose-based plastics an intaglio image identical with the one in the polycarbonate sheet will be formed and can be used for similar purposes.

In the case of glass based photographic plates, a sodium hydroxide solution will remove the emulsion from the glass but the glass plates must then be transferred to dilute hydrofluoric acid for etching.

EXAMPLE II

Preparation of a permanent relief photograph from noble metals

A fine grain medium speed photographic negative is exposed and developed in the normal before being toned with the spontaneously fissile isotope californium-252.

The negative is first hardened with formaldehyde and then shaken with a 5% solution of potassium ferricyanide to convert the image to silver ferrocyanide. The negative is thoroughly washed in running water and then allowed to stand

in a solution containing californium chloride for about 4 hours. The pH of the californium solution should be adjusted

to a value of 2.0 with nitric acid and it should contain about 1 microcurie of Cf-252 for each cm^2 of film which has to be treated. As californium deposits from solution, the photographic image slowly turns blue and this is a useful indication of the extent to which the reaction has occurred. The photograph is then rinsed with demineralised water and washed for about 30 minutes in running water. Negatives having high fog levels are much improved by a few minutes treatment in a 0.1% solution of thiourea adjusted to pH3 with oxalic acid before the final water wash. The photograph is then dried and pressed against a smooth glass surface in which fission fragments from the photograph can cause radiation damage. It is important that the glass surface should be free from scratches and it must on no account be cleaned with abrasive powders.

After an overnight exposure, the glass is separated from the photograph and etched in a dilute solution (5%) of hydrofluoric acid. The etching time varies somewhat with the type of glass and the length of the exposure but is generally about 30 minutes. When the intaglio image is clearly visible and shows good contrast, the plate is washed with demineralised water and dried.

The glass plate is then transferred to a vacuum enclosure and gold is deposited on the image by the well-known evaporative technique.

Only a very thin layer of gold can be deposited in this manner but, after the plate has been removed from the vacuum system, the gold thickness can be increased to any desired value by a standard electroplating procedure. When the gold has reached the desired thickness it can be separated from the glass and shows a raised relief image on its surface which is

permanently resistant against the effects of light and atmospheric contaminants.

The intaglio image in the glass can be used to prepare many such metal relief photographs and they can be made from noble metals other than gold if so desired.

EXAMPLE III

Preparation of a high fidelity lithographic printing plate.

A tri-metallic lithographic printing plate, of the type commonly employed in the trade and consisting of a thin layer of chromium plated on a thicker layer of copper and supported on a steel base plate, is coated with a thin layer of nitrocellulose approximately 4 microns in thickness. This can be accomplished by dipping the plate in a solution of nitrocellulose in a solvent such as ethyl acetate and then slowly withdrawing the plate and allowing the solvent to evaporate.

When the plate is completely dry, it is pressed against a photograph toned with californium-252 by the method described in the previous example. After a suitable exposure (which can be estimated by counting the alpha ray emission of the photograph with a suitable alpha ray counter) the nitrocellose barrier layer is etched with 5N sodium hydroxide solution at 30°C for about 60 minutes or until the picture can be seen on the plate. The plate is then thoroughly washed and then treated with one of the etching fluids used in the trade to dissolve chromium. Where this etchant penetrates the fission track holes, the chromium is removed and the picture becomes outlined in the underlying copper. When etching is complete the nitrocellulose etch resist is removed with a suitable solvent and the plate is treated with water and then with lithographic printing

ink. This ink adheres only to the picture outlined in very small areas of exposed copper metal and the ink can be transferred to paper in a standard printing press.

The foregoing examples are not intended as restrictions or limitations on the broad concept of this invention.

The amount of radiation damage is related to the inherent energy of the radiated particles. Generally speaking the closer the photograph to or the harder the photograph is pressed against the surface to be imaged the better the result. However an image can be obtained with a lesser degree of closeness. The word contiguous is used herein to define this situation.

The claims defining the invention are as follows:

1. The method of reproducing a photographic image on a normally non-photo-receptive surface comprising the steps of toning the photograph with substances which combine with or replace the silver grains so that the photograph emits either spontaneously or indirectly fission fragments or alpha particles in amounts related to the distribution of the silver grains in the photograph, placing the toned photograph contiguous with the surface on which the image is to be reproduced, for sufficient time for the emissions from the photograph to reproduce the image as a radiation-damage image on the surface, the damage areas having a close positional relationship to the silver grains in the original photograph, and utilising the changed properties of the radiation damage image to produce a visual reproduction of the photographic image.

2. The method according to claim 1 wherein the step of utilising the changed chemical properties of the radiation damage image comprises etching the radiation-damage image to form an intaglio image.

3. The method of reproducing a photographic image on mirrors, glassware, ornaments, jewellery, scientific instruments, electrical components or printing plates, which include the method claimed in claim 2.

4. The method according to claim 1 or 2 characterised by the use as toner material of the isotope californium-252 which produces spontaneous release of fission fragments.

5. The method according to claim 1 or 2 characterised by the use as toner material of the isotope uranium-233, uranium-235, plutonium-239 or americium-242 which emits fission

fragments when bombarded with neutrons.

6. The method according to claim 1 or 2 characterised by the use as toner material of the isotope polonium-210 which emits alpha particles spontaneously.

7. The method according to claim 1 or 2 characterized by the use as toner material of the isotopes of boron or lithium ~~such as boron-10~~ which emits alpha particles when bombarded with neutrons.

8. The method according to claim 2 wherein the surface to be treated is an ester of cellulose for use with alpha particles and mica, glass, ceramics, plastics and the like for use with fission fragments.

9. The method according to claim 2 or 8 wherein the intaglio images are coated with inks or stains.

10. The method according to claim 2 or 8 wherein the intaglio images have deposited thereon a reflective coating.

11. The method according to claim 2 or 8 wherein the intaglio images have deposited thereon an electrically conducting coating.

12. The method of reproducing a photographic image on a surface which is both not normally photo-receptive and not normally made etchable by radiated fission fragments or alpha particles, comprising the steps of toning the photograph with substances which combine with or replace the silver grains so that the photograph emits either spontaneously or indirectly fission fragments or alpha particles in amounts related to the distribution of the silver grains in the photograph, coating the surface to receive the image with a barrier layer of material which can be made etchable by radiated fission fragments or alpha particles, placing the toned photograph contiguous

with the barrier layer for sufficient time for the emissions from the photograph to reproduce the image by radiation-damage on the barrier layer, the damage areas having a close positional relationship to the silver grains in the original photograph, applying etching material which penetrates the image areas of the barrier layer to remove the imaged barrier layer and to etch an image on the underlying surface.

13. The method of reproducing a photographic image on a surface which is both not normally photo-receptive and not normally made etchable by radiated fission fragments or alpha particles, comprising the steps of toning the photograph with substances which combine with or replace the silver grains so that the photograph emits either spontaneously or indirectly fission fragments or alpha particles in amounts related to the distribution of the silver grains in the photograph, coating the surface to receive the image with a barrier layer of material which can be made etchable by radiated fission fragments or alpha particles, placing the toned photograph contiguous with the barrier layer for sufficient time for the emissions from the photograph to reproduce the image by radiation-damage on the barrier layer, the damage areas having a close positional relationship to the silver grains in the original photograph, applying etching material which penetrates the image areas of the barrier layer to remove the imaged barrier layer and applying a second etching material to etch an image on the underlying surface.

14. The method according tc claim 12 or 13 wherein the barrier layer is an oxide layer formed on a metal surface to be treated or is a layer of silica or titania ~~or the like~~ deposited by means of chemical reactions in a suitable liquid or vapour, or by vacuum deposition.

15. The method according to claim 12 or 13 wherein electro-etching is used to etch either or both the barrier layer or the underlying surface.

16. The method according to claim 12, 13 or 14 wherein the surface to receive the image is a printing plate which comprises a layer of hydrophobic material ~~such as copper~~ having a thin layer of hydrophillic material ~~such as chromium~~ adhered thereto ~~such as~~ by plating and the barrier layer is coated on the hydrophillic material, characterized in that the etch removes the hydrophillic material to expose the hydrophobic material in the form of the image.

17. The method according to claim 16 wherein the hydrophobic and hydrophillic layers are reversed.

18. The method according to claim 2 wherein the surface is not normally electroplatable characterized by the steps of depositing, ~~such as~~ by vacuum evaporation techniques or from chemical solutions or by casting a thin metal layer on the etched image area and electroplating on more metal to produce a raised relief image.

19. The method according to claim 2 wherein a raised relief image is prepared by casting a liquid material in contact with the intaglio image and allowing the material to solidify.

20. The method according to claim 13 or 14 wherein the surface is electroplatable characterized in that before the

barrier layer is finally removed the etched image area is electroplated to produce a relief image.

21. The method according to claim 18, 19 or 20 characterised by the further step of removing the relief image from the etched surface to obtain imaged replicas.

22. The method according to claim 20 or 21 wherein the replicas are printing plates, jewellery, ornaments, decorative fittings and the like.

23. The method according to claim 12 or 13 wherein the surface is a standard lithographic plate and the etching material makes the plate wettable by printing ink only.

24. The method according to claim 1 wherein the changed chemical properties of the radiation-damage image are utilised to produce a visual reproduction of the photographic image.

25. The method according to claim 1 wherein the changed electrical properties of the radiation-damage image are utilised to produce a visual reproduction of the photographic image.

26. The method of reproducing a photographic image on a surface which is both not normally photo-receptive and not normally made etchable by radiated fission fragments or alpha particles, comprising the steps of toning the photograph with substances which combine with or replace the silver grains so that the photograph emits either spontaneously or indirectly fission fragments or alpha particles in amounts related to the distribution of the silver grains in the photograph, coating the surface to receive the image with a barrier layer of material which can be made etchable by radiated fission fragments or alpha particles, placing the toned photograph contiguous with the barrier layer for sufficient time for the

emissions from the photograph to reproduce the image by

radiation-damage on the barrier layer, the damage areas having a close positional relationship to the silver grains in the original photograph, heating the barrier layer to evaporate the radiation-damage image area thereof and applying an etching material to etch the underlying surface.

27. Imaged surfaces and objects made by the method of claims 2, 9 to 13 or 21 or 26.

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