

July 2, 1963

R. W. BUETOW ETAL

3,096,197

MARKING METHOD

Filed Jan. 21, 1960

2 Sheets-Sheet 1

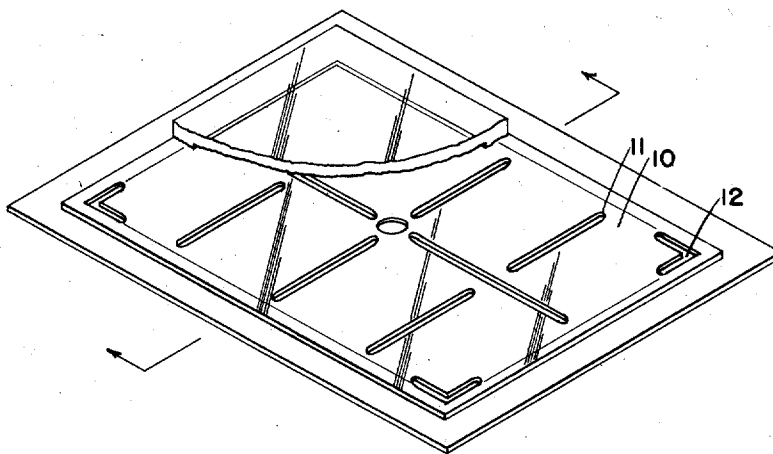


FIG. 1

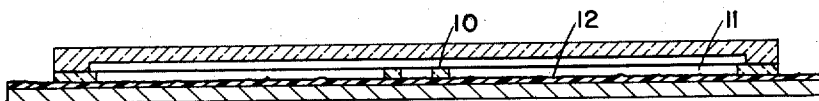


FIG. 2

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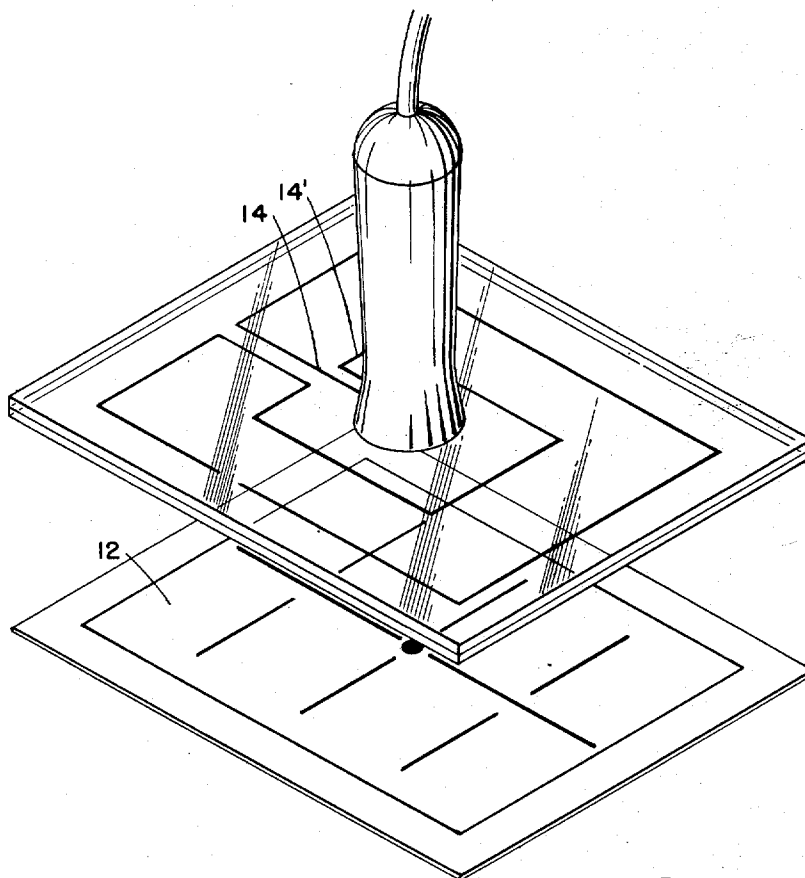


FIG. 3

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MARKING METHOD

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6 Claims. (Cl. 117—33.5)

This invention relates to methods for marking photographs, and more particularly relates to methods for accurately stenciling and imprinting reference marks, numerals or descriptive information on photographs, paintings or similar graphic articles without destruction of the surface of the article. Marking may be accomplished by applying a coating of reactive material on the article and producing a mark by reacting the coating with a suitable material.

When stenciling reference data on art work or photographs it is often desirable to obtain alignment of markings upon the work without first making facsimile copies to assure the proper alignment of the mark on the work. The application of this invention to the marking of mosaics of aerial photographs is of particular utility.

In accordance with the process of this invention, preliminary markings are made on photographs by coating the surface of a photograph with a transparent film of material and then producing a mark on the photograph by exposing the coating material through a stencil to a reactive vapor to produce markings which are visible in ultra violet light. After the markings are viewed in ultra violet light the stencil may be corrected when necessary before the photograph is permanently marked with a marking material which is normally visible. Permanent visible markings may be made by stenciling or printing the article with ink in conventional manner or by applying a fusible marking material to the article. Marking can also be accomplished by applying an additional coating to the photograph and forming an image by contacting the coating composition with certain metals or metal salt compositions.

It is an object of this invention to provide a method of marking articles with fluorescent marking materials.

It is another object of this invention to provide a method of permanently marking photographs without scratching the photographic emulsion.

It is another object of this invention to provide a means of marking photographs with the reaction product of a coating material and a metal or metal salt.

Other objects will become apparent from the drawings and from the following detailed description in which it is intended to illustrate the applicability of the invention without thereby limiting its scope to less than that of all equivalents which will be apparent to one skilled in the art. In the drawings like reference numerals refer to like parts and:

FIGURE 1 is a cutaway of a perspective view of a device for marking photographs;

FIGURE 2 is an elevation of the device of FIGURE 1;

FIGURE 3 is a perspective view of another embodiment of a device for marking photographs.

In FIGURES 1 and 2 stencil 10 is configured as an enclosure with perforations 11 therein and is preferably constructed of a transparent material such as glass, synthetic resin or cellulosic material, but may also be comprised of metal or other opaque material. Perforations

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11 are provided in stencil 10 to enable vapor to contact a reactive coating on photograph 12 to produce markings thereon. To insure that perforations 11 precisely correlate with points to be marked upon photograph 12 a marking may be made with a composition which is visible only in fluorescent light. Permanent visible markings may be subsequently imprinted on the photograph after alignment of the marks made with fluorescent material has been found to be satisfactory.

In FIGURE 3 is shown a wire printing device which may be heated by resistance to electric current flow there-through produced by connection to electric leads 14 and 14' and be contacted to a material coated on photograph 12.

In the preferred embodiment of this invention the surface of the photograph may be first coated with a film of reactive composition and a stencil be placed thereover before the photograph is exposed to a reactive vapor or liquid through the stencil. The product which is obtained from the reaction between the coating composition and the vapor fluoresces visible in ultra violet light, but is invisible in ordinary light. The photograph may then be stenciled with visible ink, or may be again coated and printed with a reaction product of the coating material.

Example I

An aerial photograph was prepared for marking by being dipped in a 2% solution of 2,4-dihydroxybenzaldehyde in water. The photograph was dried and a transparent stencil was laid on the face of the photograph and visual alignment of photograph and stencil was made. Exposure of the stencil to vapors of hydrazine and acetic acid produced markings of 5 mils $\pm$ 2 mils line width from a stencil perforation 3 mils in width. After exposure for one minute, the markings on the photograph fluoresced brilliant green when exposed to the rays of an ultra violet lamp, but were otherwise invisible.

Example II

An X-ray photograph was coated with a film of gelatin containing dissolved acidified salicyclic aldehyde. The coating was dried and a stencil was placed upon photograph before the assembly was exposed to hydrazine vapor. A reaction took place between the aldehyde and the hydrazine yielding an aldazine reaction product which fluoresced brilliant yellow during exposure to an ultra violet lamp.

Example III

A photograph coated with gelatin was exposed through a stencil to aldehyde vapors. The photographs were marked with faintly visible yellow and yellow orange fluorescent traces when viewed in ultraviolet light, but not in ordinary light. Operable materials included vapors of furfural, glutaraldehyde, and acetyl acetone. Other lower aldehydes were somewhat less suitable for imparting colored traces to the surfaces of printed matter and photographs when the articles were exposed to rich ultraviolet radiation in a background of subdued daylight.

Example IV

Markings visible in ordinary light were printed on photographs subsequent to marking by the method of Examples I-III by using complex ions formed by reaction of cobalt, chromium, nickel, iron, magnesium, aluminum or manganese with amine compounds or ammonia. A

photograph coated with a gelatin film was dipped into an aqueous solution of a salt, e.g. chloride, of one of the enumerated metals. Metal ions which diffused into the gelatin coating from the solution formed colored traces on the photograph after exposure of the photograph to vapors of either ammonia or amine compounds through a template masking the photograph.

Example V

Gelatin was admixed with sodium nitroprusside solution to provide a solution for visible marking of photographs. A photograph was dipped therein and dried. The photograph was exposed through a stencil to acetone vapors and a colored trace was formed. The marking was water sensitive and could be removed by washing.

Example VI

Acidic hematoxylin solution was coated on a photograph as in Example IV. A purple trace was developed upon exposing the coating to ammonia fumes through a stencil.

Example VII

A photograph was immersed in a solution of cupric sulfate and was dried. A stencil was laid on the photograph and the assembly was exposed to hydrogen chloride gas. Bleaching of the photographic silver occurred to yield visible light colored stenciled indicia.

Example VIII

The procedure of Example VII was repeated using solutions of Na_2CrO_4 and $\text{Cu}(\text{NO}_3)_2$ with amines of molecular weights of less than 100 as additives. Bleaching occurred as in Example VII.

Example IX

Two parts of CuSO_4 was dissolved in 4 parts of water and 1 part of ethylene glycol. Dimethyl formamide and tetra hydroxyethyl ethylene amine were added to insure that spontaneous bleaching would not occur. A wetting agent was added. Upon exposure to fumes of 10% hydrochloric acid bleaching took place.

Example X

Two parts of CuSO_4 , 10 parts water, 3 parts ethylene glycol, and 0.05 part of a wetting agent were mixed and several photographs were immersed in the mixture and dried. Immersion in the mixture for five minutes yielded a distinct trace with $\frac{1}{10}$ - $\frac{1}{4}$ second exposure times to hydrogen chloride. Fine lines were obtained with slits as narrow as 0.5 mil at shutter speeds of $\frac{1}{10}$ second.

Example XI

A solution of 1,5-diphenylcarbohydrazide and cellulose acetate was dissolved in nitroethane and deposited upon the face of an aerial photograph. The solvent was allowed to evaporate and the photograph was marked by bringing Nichrome cross hairs heated to between 300°-400° F. into contact with the coating. A purple trace image of the cross hairs appeared on the photograph. It is believed that ion transfer from the cross hairs to the coating occurred and imparted to the coating composition a characteristic color.

Example XII

1,4-dihydroxybenzaldehyde was dissolved in water in 1% concentration and a photograph was immersed in the solution and dried. An iron wire having a slight oxide coating was heated by electric current therein while the wire was pressed against the coated photograph. A brown colored image of the wire appeared on the photograph.

Example XIII

The procedure of Example I was repeated using a 1%

solution of gallic acid in place of dihydroxybenzaldehyde. A similar mark was obtained.

Example XIV

1% solutions of the following reagents in ethanol were deposited on photographs: rhodamine; 2-nitrosalicylic acid; dithioamide; 5-diphenylcarbazone; 6-mercaptobenzoic acid. Each of the photographs was contacted with a heated wire. Nichrome wire and iron wire which had not been freshly cleaned produced the most satisfactory marks. It was found that moist photographs could be marked more distinctly than thoroughly dried photographs with all wires. It is believed that all metals that will form a fine crystalline oxide can be used for operable marking.

Generally, compositions that can be used for marking photographs are those which are actinically insensitive and which can be chemically reacted to provide a durable, tack free adherent mark on the surface of a photograph.

While certain modifications and embodiments of the invention have been described, it is of course to be understood that there are a great number of variations which will suggest themselves to anyone familiar with the subject matter thereof and it is to be distinctly understood that this invention should not be limited except by such limitations as are clearly imposed in the appended claims.

We claim:

1. A process for marking an article of graphic art comprising

(a) a preliminary treatment for applying a fluorescent marking visible only in ultraviolet light to an article of graphic art, said preliminary treatment including

(1) coating said article of graphic art with a reactive first composition,

(2) applying a stencil to said article of graphic art,

(3) reacting the areas exposed by said stencil with a vaporous second composition, the reaction product of said first and second compositions being visible only in ultraviolet light;

(b) a secondary treatment for applying a permanent marking to said article of graphic art marked with said preliminary fluorescent marking including

(1) coating said article of graphic art with a third reactive composition,

(2) aligning said stencil to said fluorescent marking, and

(3) applying a fourth reactive substance in the exposed areas of said stencil, the reaction product of said third reactive composition and said fourth reactive substance giving a permanent marking visible in actinic light.

2. A process for marking an article of graphic art as claimed in claim 1 wherein said first reactive composition is a hydroxy aromatic derivative selected from the group consisting of salicylaldehyde, 2,4-dihydroxybenzaldehyde, and gallic acid; and said vaporous second composition is hydrazine.

3. A process for marking an article of the graphic art as claimed in claim 1 wherein said first reactive composition is gelatin and said second vaporous composition is selected from the group consisting of furfural, glutaraldehyde acetyl and acetone.

4. A process for marking an article of the graphic art as claimed in claim 1 said article of graphic art having a developed silver emulsion on one surface wherein said third reactive composition brought in contact with said emulsion is an inorganic salt selected from the group consisting of Na_2CrO_4 , $\text{Cu}(\text{NO}_3)_2$, Cu_4 , said third reactive composition containing an additive amine to retard spontaneous bleaching by said fourth reactive substance, and said fourth reactive substance being hydrogen chloride gas.

5. A process for marking an article of the graphic art as claimed in claim 1 wherein said first reactive com-

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position is gelatin and said third reactive substance is the chloride salt of a metal selected from the group consisting of cobalt, chromium, nickel, iron, magnesium and aluminum, and said fourth reactive substance is the vapor of a compound selected from the group consisting of ammonia and amine compounds. 5

6. A process for marking articles of the graphic art as claimed in claim 1 wherein said third reactive composition is 1,4-dihydroxybenzaldehyde dissolved in H₂O at a strength of 1% and said fourth reactive substance is a heated iron wire having an oxide coating. 10

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