May 29, 1956 T. A. SAULNIER, JR 2,748,288

ELECTRON PHOTOGRAPHY PLATE CONSTRUCTION

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Fig. 1.

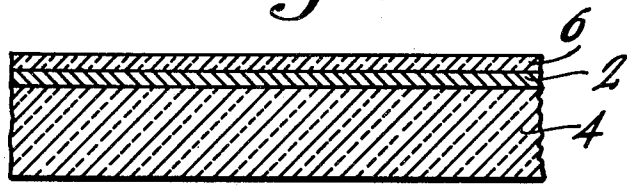


Fig. 2.

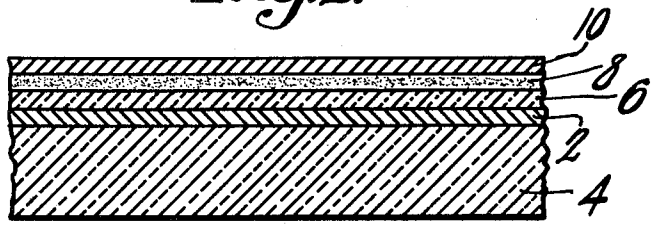
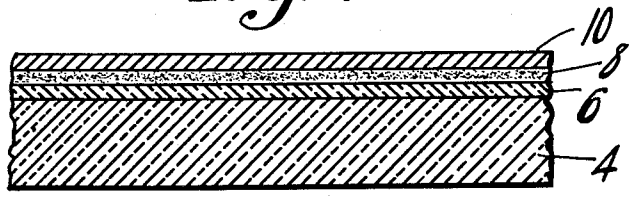


Fig. 3.



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ELECTRON PHOTOGRAPHY PLATE CONSTRUCTION

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16 Claims. (Cl. 250—65)

This invention relates in general to electron-sensitive photographic plates and more particularly to plates which are capable of recording electron images but which are relatively insensitive to ordinary light.

It has been found desirable to have some method of photographing images produced by electron optical systems where the electrons are generated by a thermionic emitter. This problem arises, for example, in plotting the positions at which phosphor dots are to be deposited on the viewing screen of one type of tricolor kinescope tube. One method utilized for plotting the positions of the dots is to expose a photographic plate through a predetermined grid of crossed wires to a thermionically generated beam of electrons scanned across the area of the plate. The apertures of the grid of wires permits passage of the electron beam at the points it is desired to place a phosphor dot on the completed screen. After the photographic plate has been properly exposed to the electron beam to form a multiplicity of latent dot images, the plate is developed and a print is then made on a medium, such as a silk screen, which is to be used for actual printing of the phosphor dots on a base member. This method of plotting is more fully described in a co-pending application of Harold B. Law, Serial No. 277,133, filed March 18, 1952 and assigned to the same assignee as the instant application.

In developing the foregoing process it was found that ordinary types of photographic plates are not suitable for at least two reasons. One reason is that a thermionic emitter generates visible light. An ordinary photographic plate is exposed immediately by the light and rendered useless to optically record electron images. Another reason is that an ordinary photographic plate is a good electrical insulator and when exposed to an electron beam accumulates an electrical charge which has an undesirable effect on the characteristics of the electron optical lens system used to plot the position of the phosphor dots. It was therefore found necessary to devise a photographic plate which is initially, at least, sensitive to record electron-optical images but relatively insensitive to visible light and is at the same time a fairly good electrical conductor.

One object of the present invention is to provide a photographic plate which is sensitive to electrons, electrically conductive, and relatively insensitive to ordinary visible light of predetermined wavelengths.

Another object is to provide an improved photographic plate which is sensitive to electron irradiation but relatively insensitive to the light generated by a thermionic emitter.

Another object is to provide an improved photographic plate for recording images formed by electron optical systems.

Still another object is to provide an improved electron-sensitive photographic plate which may be used in an electron optical system without producing undesirable effects on the lens characteristics of the system.

A still further object of the invention is to provide an improved electron-sensitive photographic plate capable of producing relatively high contrast images.

These and other objects may be accomplished by the practice of the present invention which comprises improved photographic plates and methods of making them. In a preferred embodiment of the invention, the plates comprise a base having a metal surface and a layer covering the metal surface of a material such as a synthetic resin or shellac which is insolubilized by electron bombardment. The synthetic resin or shellac may be electron-sensitized by any desired sensitizing agent such as potassium dichromate. The exposed surface of the material may also be advantageously provided with a relatively thin, semi-transparent film of a metal such as aluminum.

The invention will be described in greater detail with reference to the drawing of which:

Figures 1, 2 and 3 are schematic, cross-sectional, elevational views of respective embodiments of photographic plates constructed in accordance with the principles of the present invention.

Similar reference characters have been applied to similar elements throughout the drawing.

According to a first embodiment of the invention as illustrated in Figure 1, an improved type of electron-sensitive photographic plate may be made by first applying a coating 2 of silver upon the surface of a glass base 4. The coating of silver may be applied by any known technique such as evaporating by heating silver in vacuo, or by chemically depositing silver from an ammoniacal silver nitrate solution as commonly practiced in the manufacture of mirrors. The thickness of the silver layer is not critical but is preferably sufficient to render the layer opaque.

The silvered surface is rinsed and dried and coated with a relatively thin layer 6 of a material which is insolubilized by exposure to an electron beam. This may be a polymerizable resin such as shellac or photoengraver's cold-top enamel resist. The polymerizable material may be dissolved in a suitable solvent such as an alcohol or acetone to produce a solution having a viscosity such that when it is flowed over the silvered surface it will form a film of a desired thickness. It is preferred to make the film relatively thin so that it may be polymerized throughout its complete thickness by a relatively short exposure to an electron beam. Films a few microns thick are preferred although for applications where it is desired to provide relatively long electron exposures the films may be up to about 0.1 mm. thick.

It is also preferred to include a sensitizing agent such as potassium dichromate in the resin. The amount of such a sensitizing agent is not critical and may be withing the range generally useful in photoengraving. A suitable film material may be made according to the formula described in "Modern Photoengraving" by Flader and Mertle (1948) page 159. The material comprises dichromate-sensitized shellac in an alkaline water solution. The mixture is placed in a vessel having an aperture and is permitted to flow out through the aperture. The silvered glass plate is held at an angle of about 30° from the vertical with one edge closely adjacent the aperture so that the solution flows across the entire surface of the plate. The plate is passed once across the aperture and permitted to dry. Conventoinal spinning on of the coating may also be employed according to the practice in the photoengraving trade.

The plate thus produced is relatively insensitive to visible light except in the very short wavelength portion of the spectrum. It may be exposed without harm to relatively intense illumination by light of wavelengths longer than about 4500 Angstroms.

The photographic plate heretofore described may be utilized in a manner similar to the plates described and claimed in the previously mentioned co-pending application of H. B. Law. As explained in said co-pending application, the plate may be exposed to electron bombardment by an electron beam generated by a thermionic emitter such as a glowing wire filament. The plate itself is made anodic with respect to the filament. Exposures may be made over a relatively wide range of current densities, accelerating voltages and times. Generally an accelerating voltage of 10 to 20 kilovolts is satisfactory when utilizing effective current densities of 0.2 to 2.0 microamperes per square inch. The exposure time may vary from about 30 seconds to about 10 minutes depending on such factors as the thickness of the coatings on the plate, the sensitivity of the polymerizable material, the accelerating voltage and the effective current density.

The silver film provides a relatively high conductivity that minimizes the accumulation of electrons on the plate. An electrical contact may be made to the silver film by a point contact made by penetrating through the sensitive layer, or by scraping away a relatively small portion of the sensitive layer.

The filament gives off visible light within a broad range of wavelengths in the visible portion of the spectrum. Ordinary photographic emulsions are relatively sensitive to light within the broad range of the visible spectrum. In the present case, however, the sensitivity of the polymerizable material is restricted to a spectral range wherein the filament gives off relatively little light.

After exposure the plate is developed by washing in a solvent such as alcohol to dissolve unexposed portions of the resist material. A suitable developer is described on page 160 of "Modern Photoengraving." The developer removes the unexposed portions of the resist and does not dissolve the exposed portions that have been polymerized by the electron beam. The exposed portions may be further hardened by heating to about 70° C. or by drying by exposure to a desiccant. The portions of the silver film thus laid bare are removed by etching the surface in a silver etchant such as Farmer's solution. Any silver etchant may be used but it should be sufficiently mild so that it does not attack the polymerized resist material.

When substantially all the exposed portions of the silver film have been dissolved, the plate is rinsed and dried. It may be utilized as a negative to make a print on a transfer medium such as a silk screen or to produce a pattern directly upon a stencil material. The presence of the opaque silver film beneath the electon-sensitive material provides a relatively high degree of contrast between the exposed and the unexposed portions of the plate. The optical density of the polymerized electron-sensitive material is therefore not important in the practice of the invention according to this embodiment.

Photographic plates constructed according to the first embodiment of the instant invention are relatively easy to handle, relatively insensitive to visible light, and produce optical images of high contrast. They are subject, however, to a difficulty known as an ion spot. During exposure of the plate in an imperfectly evacuated or leaky vessel ions are often produced by the electron beam. Such ions may travel toward the plate and strike it in a concentrated group producing an exposed effect on a relatively small area of the plate.

A preferred embodiment of the invention, therefore, comprises an electron-sensitive photographic plate generally similar to the photographic plate heretofore described but including a thin semi-transparent metallic film disposed on the surface of the electron-sensitive material. A photographic plate constructed according to the preferred embodiment of the invention is illustrated in Figure 2 and may be constructed in a manner generally similar to the construction of the photographic plate heretofore described in connection with the first embodiment.

A glass base **4** is provided with a silver surface **2** and a coating **6** of an electron-sensitive material. On the surface of the electron-sensitive material there is flowed a relatively thin transparent coating **8** of a water-soluble sizing such as glue or starch. A film **10** of a metal such as aluminum is evaporated over the sizing. The metal film is preferably about 500–2000 Angstroms thick. The purpose of the metal film is primarily to prevent ions from striking the sensitive material during exposure. Its thickness is relatively critical. If the film is too thin, it will not act as an effective ion barrier. Electron exposures may be made through aluminum films up to at least 3600 Angstroms thick. However, films substantially thicker than about 2000 Angstroms are relatively impermeable to water and cannot be readily removed by dissolving the sizing.

A photographic plate produced according to the preferred embodiment may be exposed in an exactly similar manner as a plate produced according to the first embodiment. After exposure the plate is immersed in water. Water penetrates the porous aluminum film and dissolves the sizing. When the sizing is dissolved the aluminum film floats off the surface and is removed. The plate may then be developed in the same manner as the plate heretofore described in connection with the first embodiment.

In order not to disturb the sensitive coating when applying the sizing to it, it is desirable that the sizing be insoluble in the coating solvent and that the coating be insoluble in the sizing solvent. For example, if an alcohol-soluble resin such as shellac is utilized for the electron-sensitive layer, a water-soluble material such as glue or starch is satisfactory for the sizing layer. Conversely, if a water-soluble electron-sensitive material such as polyvinyl alcohol is used, the sizing may conveniently be a material such as notrocellulose that is insoluble in water but is soluble in an organic solvent such as amyl acetate. The use of a sizing having a different solution characteristic from the electron-sensitive material also facilitates the removal of the sizing and the metallic film from the exposed plate without damage to the electron-produced image.

A photographic plate according to a third embodiment of the invention is illustrated in Figure 3. This plate comprises an insulating base **4** bearing a coating **6** of a polymerizable material, but no conductive film between the base and the polymerizable material. A layer of a sizing covers the polymerizable material and separates it from an electron-transparent metal film **10**. The plate is generally similar to the plate according to the preferred embodiment but for the omission of the conductive layer **2** upon the base. In this plate the electron-permeable metal film acts as a conductive member and provides an electron discharge path to prevent the accumulation of an electrostatic charge on the insulating surface.

This plate may be exposed in an exactly similar manner as the plates heretofore described. Development is accomplished by removing the metal film by dissolving the sizing in a suitable solvent and dissolving the unexposed portions of the polymerizable material. The material is preferably dyed to increase the contrast of an image. The dye may be included in the material when it is first laid down on the base or during or after development as may be desired.

Many organic materials are polymerizable by electron energy. Materials such as natural and synthetic resins, collodion, gelatins, gum arabic and albuminous materials are especially sensitive to electron bombardment and are satisfactory for use in the practice of the instant invention.

The effects of electron bombardment on the molecular structures of these materials are not definitely known. The gross effect, however, is generally similar to the polymerization of resins by other means. Therefore the term polymerization is used in this application to mean any

molecular change induced in a material by electron bombardment that renders the material substantially insoluble in its normal solvents.

In the practice of the instant invention it is preferred to sensitize the polymerizable material with a sensitizing agent such as potassium dichromate. A sensitizing agent permits the forming of a latent image on the film by a relatively short exposure to the electron beam. Shortening of the exposure is desirable for the reasons given hereinafter and also to minimize the effect of the electron beam on the sizing. If the exposure is too long the electron beam may polymerize the sizing as well as the sensitive layer, thereby making it difficult to remove the protective metal film without damaging the sensitive layer.

In certain exposure processes such as that described by H. B. Law in his co-pending application heretofore mentioned, the electron exposure time is relatively short. For example, when exposing the photographic plate through a so-called shadow mask, a total scanning time of about thirty seconds to five minutes is utilized. The total scanning time is the time during which the electron beam is permitted to scan across the mask. In certain masks there may be as many as 300,000 spaced apertures, the apertures comprising about ⅓ or less of the total area of the mask. It may be seen, therefore, that if a total scanning time of thirty seconds is utilized the electron beam penetrates each hole for a time of only $\frac{1}{30,000}$ of a second. If the total scanning time is about five minutes, the exposure time per hole is about $\frac{1}{3,000}$ of a second. Photographic plates according to the instant invention that utilize unsensitized polymerizable materials generally require about four to eight minutes total scanning time in this process. Plates utilizing sensitized materials may be fully exposed by scanning for about thirty seconds. It is desirable to minimize the total scanning time in order to minimize the effect of variations in the electrical scanning circuits that occur over relatively short periods of time.

Generally, electron beams are generated and electron photographic exposures are made in relatively low pressure vacuums such as about .02μ to .04μ of mercury. It is, therefore, important that the materials used in the photographic plates according to the invention have relatively low vapor pressures. Materials having relatively high vapor pressures tend to vaporize in a vacuum, adversely affecting both the vacuum system and the photographic plate.

Although electron-sensitive photographic plates comprising glass bases have been described herein, photographic plates according to the invention may be constructed utilizing bases of other materials. For example, transparent materials such as Lucite or mica provide satisfactory bases.

An opaque base may be utilized if it is desired to leave the electron-formed image on the plate, or to transfer the image by means of reflected light. In this instance any of a large number of materials is satisfactory, and a metal may be advantageously utilized. When a plate according to the first-described embodiment of the invention is constructed on a metal base it is, of course, not necessary to provide a silver film, and the electron-sensitive material may be placed directly on the metal base. The surface of a metal base provides ample electrical conductivity for the purpose of electron exposure.

In respect of the first and the preferred embodiments of the invention a dye or other opacifying material may be added to the electron-sensitive material to produce a photographic plate having reudecd sensitivity to ordinary light. Inclusion of a dye may also be desirable to increase the contrast of the developed polymerized image when it is desired to make photographic prints by reflected light from the plate. However, the use of a dye is not an essential part of the instant invention. Electron-sensitive plates according to the invention may be made relatively insensitive to light of longer wavelength than about 4500 Angstroms. Inclusion of a dye is, therefore, desirable only when it is desired to render the plate insensitive to short wavelength light such as blue light and ultra-violet light.

What is claimed is:

1. An electron-sensitive photographic plate comprising a metallic base having a coating of an organic material disposed thereon, said material being insolubilizable by electron bombardment, and a semitransparent metallic film disposed over and coextensive with said coating on the opposite surface of said coating from said metallic base for preventing accumulation of electron charges on said coating.

2. A plate according to claim 1 in which said base comprises a transparent material and bears an opaque metal film upon its surface.

3. A plate according to claim 2 in which said transparent material is glass and said metal film is of silver.

4. A plate according to claim 1 in which said insolubilizable material is selected from the group consisting of natural resins, synthetic resins, collodion, gelatin, albumin and gum arabic.

5. A plate according to claim 1 in which said insolubilizable material includes a sensitizing agent thereby to render it more readily insolubilizable by electron bombardment.

6. A plate according to claim 5 in which said sensitizing agent is a dichromate salt.

7. An electron-sensitive photographic plate comprising a base having a metallic surface, a coating of a material insolubilizable by electron bombardment disposed on said surface, a coating of a sizing material superimposed on said insolubilizable material, said sizing being readily soluble in a solvent in which said insolublizable material is relatively insoluble and said sizing being insensitive relative to said insolubilizable material to electron bombardment, and an electron-transparent metal film superimposed on said sizing.

8. A plate according to claim 7 in which said base comprises a transparent material and bears an opaque metal film upon its surface.

9. A plate according to claim 8 in which said transparent material is glass and said opaque metal film is silver.

10. A plate according to claim 7 in which said insolubilizable material is selected from the group consisting of natural resins, synthetic resins, collodion, gelatin, albumen and gum arabic.

11. A plate according to claim 10 in which said insolubilizable material includes a sensitizing agent thereby to render said material more readily insolubilizable by electron bombardment.

12. A photographic plate comprising a base, a film of a material which is insolubilizable by electron bombardment disposed on a surface of said base, a coating of a sizing material superimposed on said insolubilizable material, said sizing being readily soluble in a solvent in which said insolubilizable material is relatively insoluble and said sizing being insensitive relative to said insolubilizable material to electron bombardment, and an electron-transparent metal film superimposed on said sizing.

13. A photographic plate according to claim 12 in which said base is of an insulating material.

14. A photographic plate according to claim 12 in which said base is of a conductive material.

15. A method of making a photographic image comprising treating a film of an insolubilizable, electron-sensitive material by bombarding selected portions of said film with electrons according to a predetermined pattern thereby to insolubilize said selected portions to produce a latent image in said film, and developing said latent image by dissolving non-bombarded portions of said film in a solvent.

16. A method of making a photographic image of relatively high contrast comprising placing an opaque metal film on the surface of a transparent base, superimposing

a film of an insolubilizable electron-sensitive material upon said metal film, insolubilizing selected portions of said electron-sensitive film by bombarding said selected portions with electrons thereby to produce a latent image in said electron-sensitive film, dissolving non-bombarded portions of said film in a solvent to develop said latent image and to expose selected portions of said metal film, and dissolving said selected portions of said metal film in a solvent.

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