

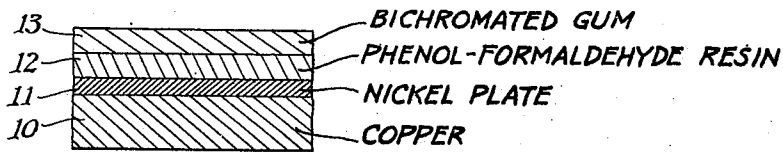
Jan. 11, 1949.

D. C. GRESHAM ET AL

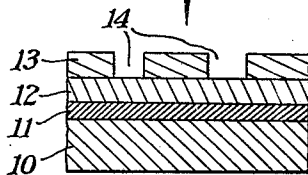
2,459,129

PRODUCTION OF PHOTOGRAPHIC STENCILS

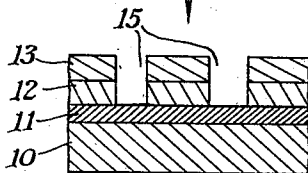
Filed Nov. 30, 1944



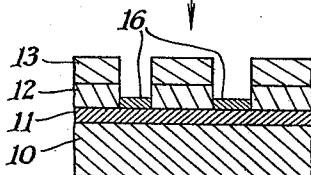
EXPOSED AND WASHED WITH WATER



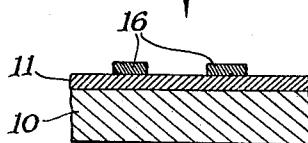
TREATED WITH LACTIC ACID AND ETHYL ACETATE



COPPER PLATED



GUM AND RESIN REMOVED



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PRODUCTION OF PHOTOGRAPHIC
STENCILS

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2 Claims. (Cl. 204—11)

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The present invention relates to the production of stencils of a kind where a photographic relief image is formed in a layer coated on a support which is usually metal and can subsequently be used for photolithographic printing or for metal plating, or glass etching or metal etching, e. g. for making half-tone blocks or graticules.

Various methods have been proposed for producing such stencils. In some such processes a light-sensitive layer is coated directly on to the support of metal or the like, and an image formed in such layer which is then dissolved away image-wise. In such processes, especially when the image consists of fine clear lines in a resistant background, it is well known that difficulties are encountered when a sharp and accurately defined stencil is required. Other processes have been proposed to overcome such difficulties. Thus it has been suggested to use a substratum beneath the light-sensitive layer and after forming an image in the light-sensitive layer and removing it image-wise the parts of the substratum so laid bare are removed by for instance an ether-alcohol mixture if the substratum is collodion. The best known processes of this kind are described in British specifications Nos. 28,415 of 1907, 18,775 of 1908 and 473,446.

The present invention is directed to a method which enables still more sharply defined stencils to be produced whereby details can be reproduced which are finer than those which could be hitherto reproduced.

The accompanying drawing shows in sectional view an element at various stages in our process.

According to the present invention there is provided the method of producing a stencil wherein a light-sensitive layer comprising a colloid which can be hardened, is superimposed on another layer (preferably a hydrophobic layer) the latter being more easily etchable than the former (when hardened) and after exposure of the light-sensitive layer to an object or image it is dissolved away image-wise and the other said layer is dissolved away in the areas so laid bare but not in the protected areas, characterised that image-wise dissolving of the lower layer is performed by treatment with a bath which simultaneously etches the unhardened and less hardened parts of the upper layer but not the hardest parts thereof.

Preferably the lower layer is one which is soluble in acid baths, in which case the said bath is of an acidic character. The viscosity of the bath can be adjusted to obtain the best balance between the rate of the effect on the lower layer and

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that on the upper layer. Usually the more viscous the bath the less is its effect on the upper layer relative to that on the lower layer. For most purposes the viscosity of the bath should be at least 0.10 but preferably 0.25, such viscosity being measured according to Stoke's law. For the best results the viscosity should usually be at least 0.35.

For the best results it is usually desirable that both layers be such as to be removed image-wise by means of an acidic bath. In the preferred form of the invention the image-wise removal of both layers is effected simultaneously by a single treatment in an acidic bath in which the soft parts of the layer which contains the light image and the parts of the other said layer thereunder are both soluble.

When the said other layer is one which is to be dissolved image-wise in acid it may be a resin such as shellac, or a phenolformaldehyde resin which is soluble in lactic acid.

When the layer in which the image has been formed by light exposure is removed image-wise simultaneously with the image-wise removal of the acid soluble layer this can be done by means of lactic acid when the first mentioned layer is gelatine and the acid soluble layer is a phenolformaldehyde resin which is soluble in lactic acid. If pure lactic acid is employed then the rate of penetration of the top layer can be increased if desired by adding small amounts of water, e. g. 5 to 10% to the lactic acid; this addition of water should not be too great or otherwise the solution of the lower layer becomes inconveniently slow. Alternatively, or in addition, small amounts of other liquids can be added, such as ethyl lactate to alter the rate of the image-wise solution.

To obtain the sharpest stencils it is advisable to maintain the lactic acid, or similar solution in a relatively highly viscous state. For instance if an acid such as sulphuric acid is used to remove the said acid soluble layer, then it should be loaded very heavily with, for example glycerine with possibly a trace of water, for example we may use $9\frac{1}{2}$ parts of glycerine and $\frac{1}{2}$ part of sulphuric acid. Alternatively a loading agent such as sodium sulphate can be added.

If desired the stencil may be produced on an electrically conducting support which can be plated in the unprotected areas and then, if necessary, the plated metal stripped from the support. Very fine grids can be made in this manner. It is to be observed that to make an article, such as

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a grid, in this way, the stencil must be a negative (not a positive) image of the desired article.

The invention can be applied to the manufacture of fine metal grids (e. g. electrical resistances) whereby grids as fine as 200 strips or meshes per inch can be produced. An example of the production of such grids is as follows:

A thin sheet of copper is nickel plated and highly polished. It is then coated with a layer of a resin such as phenolformaldehyde resin which is soluble in lactic acid. After the layer has been dried it is then coated with a layer of gum sensitised with potassium dichromate in the manner commonly used in photography. This sensitive gum layer is exposed to a line positive of the desired grid and the unexposed portions washed away in the usual manner. The layer is dried and then treated with a mixture of 90% lactic acid and 10% ethyl acetate until the areas of the phenolformaldehyde resin which are unprotected by the gum have been dissolved. The nickel plated support is then made the anode in a copper plating bath and a current of 40 ma. per square inch is passed for one minute. The plate is then rinsed in water and replaced as the cathode in the copper plating bath and a current of 40 ma. per square inch is passed for 20 minutes. This method of plating gives a thin copper foil which is subsequently stripped without difficulty from the nickel plated support. Before stripping, the gum and phenolformaldehyde resin may with advantage be removed by a solvent therefor.

The present invention can be applied to the production of designs in lead which are suitable for use in contact with sensitive silver halide layers during exposure thereof to X-rays in order to produce an image of the lead design on the sensitive silver halide layer. To give a satisfactory image, the lead forming the design must be sufficiently thick to have a high degree of absorption for X-rays. A design of this kind can be produced as follows.

A thin brass sheet is coated on both sides with a layer of phenolformaldehyde resin which is soluble in lactic acid. After these layers have been dried they are both then coated with a layer of a gum sensitised with potassium dichromate as in the previous example. These sensitive gum layers are both exposed to the design in register and the unexposed portion washed away as before leaving in register images of the design in hardened gum. The phenolformaldehyde resin which is unprotected is, as before, dissolved in a lactic acid bath and the stencils so formed are dried. The plate may then be treated with a bath made of equal parts of lactic acid and water (by volume) to remove any surface stain and then rinsed. The plate is then immersed in a lead-perchlorate plating bath between two lead anodes for 16 hours at a current density of 0.034 ampere per square c. m. These plates lead on to both sides of the plate so that twice the thickness of lead can be obtained than if only one side were treated. If there is any tendency to produce lead trees during plating these can be removed by gentle brushing during interruption of the plating. A thickness of lead of 0.25 mm. on each side of the brass support can be obtained while still maintaining a sharp image of the original design.

The phenolformaldehyde resin layer may, if desired, have a colouring matter incorporated in it when it is first coated, since this facilitates subsequently inspection of the image-wise solution thereof.

The accompanying drawing shows in sectional

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view an element used in our process and the appearance of the element at various stages in our process. As shown in the drawing, a copper plate 10 coated with a layer of nickel 11 is coated with a phenolformaldehyde resin 12 and a bichromated gum or glue layer 13. After exposure of this element, preferably to a line image, it is washed with water to remove portions of the sensitive layer 13 as shown at 14. The element is then treated with a mixture of lactic acid and ethyl acetate to etch out the phenolformaldehyde resin where the bichromated layer has been washed away as shown at 15. The element thus produced is used to form a grid, for example of copper, by electroplating copper on it, the copper adhering only in the unexposed portions as shown at 16. After removal of the resin and gum layers 12 and 13, the copper grid 16 remains as shown in the last step of the drawing and can be stripped from the layer 11 to form the completed grid.

The present invention can be applied to the production of glass-etched graticules. Thus the surface of a piece of glass may be first coated with a layer of a phenolformaldehyde resin as before given, using, for instance, the following mixture containing Sudan Red.

Phenolformaldehyde resin	grams	20
Sudan Red (Rowe's Color Index No. 857)	grams	5
Acetone	cc.	90
Amyl acetate	cc.	10

If desired, this layer can after drying be hardened somewhat by warming it. A layer of gum sensitised with potassium bichromate is coated thereover and dried. After exposure the unhardened gum and the phenolformaldehyde resin thereunder can be removed in a bath of lactic acid. Alternatively, the unhardened gum can be first removed in, for example, glycerine containing a small amount of an acid such as sulphuric acid and then the unprotected areas of the phenolformaldehyde resin removed by lactic acid. The glass bearing the phenolformaldehyde resin stencil so obtained is then treated with an etching solution, such as hydrofluoric acid, in the usual way. If desired, the phenolformaldehyde resin stencil can, before this etching, be hardened by heating.

What we claim is:

1. The method of producing a stencil in an element comprising a support, a first phenolformaldehyde layer carried thereby, and a second light-sensitive bichromated glue layer superimposed thereon comprising the light printing of an image in the second layer and the transformation of said light image to a hardened relief image, characterized by the treatment of said element after formation of said relief image, with an etching bath of 90% lactic acid and 10% ethyl acetate that etches any unhardened portions of the outermost layer and also the portions of the first layer exposed through said relief image.

2. The method of making an electrical resistance consisting of a fine metallic grid that comprises printing an image of fine lines upon an element comprising a nickel-plated copper support and two superimposed layers thereon, the inner layer being a phenolformaldehyde resin composition and the outer layer being light-sensitive bichromated glue, transforming the image in the outer layer into a hardened relief image, treating the element with a bath of 90% lactic acid and 10% ethyl acetate that attacks any unhardened portions of the outer layer and the por-

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tions of the inner layer thus exposed, electro-depositing copper in the spaces thus formed, thus forming a fine copper grid, and stripping the grid from the support.

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