

UNITED STATES PATENT OFFICE.

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PROCESS OF PHOTOGRAPHIC ETCHING AND LIGHT-SENSITIVE RESIST THEREFOR.

No Drawing.

Application filed October 30, 1926. Serial No. 145,373.

This invention pertains to the art of photographic etching. In particular the invention has to do with an improved process of photographic etching and also to an improved and novel light sensitive composition or resist employed in accomplishing the improved process.

One of the well known ways of producing etchings is to apply a light sensitive composition or film to a surface, and subject the film to light with a screen carrying a design interposed. The design carried by the screen then becomes photographed in the film. This film is then subjected to a developer which functions to remove certain portions of the film from the surface. This surface is then subjected to an etching solution which attacks to any desired extent, the surface which is not covered by portions of the film. After the etching operation the portions of the film which remain on the surface are removed in any known manner.

It is well understood in the art of photographic etching that the action of the light on the film renders insoluble the portions of the film which are subjected to the light and it is these portions which are not removed by the developer.

One of the objects of this invention is to produce an improved process of photographic etching and to furnish a novel and improved light sensitive composition which is highly satisfactory for use in process.

A further object of the invention is the provision of a satisfactory process by which a design may be reproduced clearly and in a sharply defined manner, and to provide a highly light sensitive film or coating for use as a resist in an etching process.

Another object of this invention is the provision of new compositions of materials, each constituent of which may be more or less light sensitive but the combination of which produces a materially light sensitive composition which is particularly adaptable as a photographic resist.

A still further object is the provision of a satisfactory water soluble resist which is capable of commercial use in the process herein described or in other processes.

For many years light sensitive films have been made by combining solutions of alkali bichromate with some protein, such as glue or gelatine and then adding thereto certain accelerators or the like. Such light sensitive

films have had extensive use in the photographic etching art, particularly in photolithography, and also for decorative effects upon metals and other materials.

Many types of light sensitive substances suitable for photo-etching have been developed, and these fall in two distinct groups; those which are soluble in water at the outset and which are applied in the form of their aqueous solutions, and those which are insoluble in water but soluble in organic solvents and which are applied in the form of their solution in organic solvents, the film being deposited in a solid state by evaporation of the solvent. Bichromate gelatine combinations are representative of the first class above mentioned, and asphalt, certain metallic resinates and certain gelatinized drying oils are representative of the latter class.

The invention relates particularly to improvements in the class of water soluble combinations and more especially to the character of organic sensitizers which may be combined with proteins such as gelatine or animal glue.

While the proteins such as glue or gelatine are generally slightly light sensitive, it has been found from experience that certain other materials which of themselves are light sensitive to a degree, may be added to the proteins to thereby form a most satisfactory photographic film and resist. Numerous experiments which have been made show that of the many readily obtainable highly active organic sensitizing agents, there are a few which combine with the gelatine or glue in a satisfactory form so as to produce a highly efficient photographic film. The preferred organic sensitizing agents fall within the group of mono-hydroxy aldehydes and include the aliphatic mono-hydroxy aldehydes. It has been found that aldol which comes within this classification is particularly advantageous to be combined with a protein and a bichromate to form a most satisfactory photographic film for etching purposes as more particularly set forth and claimed in my divisional application Serial No. 319,742, filed November 15, 1928. Aldol possesses an aldehyde group and is chemically beta-hydroxy-butyric aldehyde. It is miscible with water and alcohol in all proportions, boils at 83° C. under 20 mms., and when pure is a thick syrupy substance. Aldol under the action of light changes its condition due to more

or less polymerization. It also reacts under the action of light with many organic substances, and particularly those bearing an amino group, such as aniline, toluidine, *a*- and *b*-naphthylamine. Aldol also is particularly responsive to light when combined with proteins and protein degradation products.

Experiments have shown that while aldol alone acts with proteins under the action of light, as also do the alkali bichromates, it has been found that when both are used in combination at the same time, each seems to accelerate the action of the other. Thus, a bichromate glue mixture to which aldol has been added is much more active than the bichromate glue alone, and an aldol gelatine combination is rendered insoluble under the action of light at a far more rapid rate when alkali bichromates have been added to it, and it is this fact that forms an important part of this invention. It has also been found that compositions of the materials above noted give a much better etching result and the lines of the design are more sharply defined and the resist does not tend to scale off.

As an illustration of the advantage of the addition of aldol, I have found that a bichromate glue preparation of certain definite proportions becomes insoluble in water under the action of light in two and one-half minutes, while if a small amount of aldol be added to this same mass, it then becomes insoluble under the action of light in twenty seconds, and I have obtained good resists from films which had been exposed only seven seconds.

As a specific example of how the invention may be carried out, the following will serve:

Nine parts of photo engravers' liquid glue are mixed with five parts of solution of ammonium bichromate of twenty per cent strength by weight. The metal part to be etched or decorated is now coated in any suitable manner with this solution and the excess removed by centrifugal force as on a spinning machine or any other suitable manner. The entire deposited coat of bichromate glue is now moistened over the surface with pure aldol and the excess immediately removed. If the parts to be treated are small, the whole operation may be carried out on a spinning machine, the bichromate glue solution being poured upon the surface, the excess spun off and the aldol immediately applied to the resulting surface. Immediately that the excess aldol has been removed, the surface is ready for exposure to light in any known manner, such as by means of the usual arc projection machines with a condenser attachment for concentrating the light areas, and designs are obtained upon the coated surface by means of an interposed picture which may be either a negative or positive. Exposure for thirty seconds with the composition above mentioned is sufficient to render the resist insoluble, and the picture is developed

by simply washing out the soluble portion with cold water. After the picture has been developed, the article bearing the resist is placed upon a hot plate or in an oven to sufficiently carbonize the remaining gelatine film to render it insoluble in an etching bath. The article is now placed in an etching solution and electrically etched with a suitable current intensity for five to thirty minutes, according to the character of the metal and the concentration of the etching bath. Other well known methods may be employed to coat the desired surface with the mixture of bichromate and glue and to then apply the small amount of aldol. It will also be understood that the bichromated glue and the aldol may be mixed together before they are placed on the surface, and in that case it is desirable to coat the surface within a short time and to expose the same to the projecting light without delay. While it has been described that one form of affixing the resist to the surface after development is by means of the baking step in the process, it will be understood that other operations may be employed to accomplish this end.

It is believed, that a reaction takes place between the mixture of the animal glue and bichromate and the aldol, and that a compound solution is formed therefrom giving a single film.

It will be understood that from the above described composition or compound or film and process that the exact composition of the glue or its source may be varied materially, that the kind of alkali with which the chromic acid is combined may be varied at the will of the operator and that hydroxy aldehydes other than aldol may be used. Such other hydroxy aldehydes are gamma hydroxy butyric aldehyde and glycolic aldehyde. It has been found that other hydroxy aldehydes resulting from the condensation of two molecules of other aldehydes than acetic have yielded products closely related to aldol, which are active in similar manner and which give entirely satisfactory effects. The invention herein is, therefore, regarded as including the use of any aliphatic hydroxy aldehyde in combination with an alkali bichromate and a protein.

It will be seen that the simple composition of the film or resist, and the process of the etching, and the very quick time in which the image or picture may be produced in the film or resist all cooperate to increase the efficiency of the etching process and to thereby permit quick and satisfactory etching which may be accomplished within a commercial cost. Many advantages and uses of this process and the novel resist may readily suggest themselves, and it is to be understood that such advantages and uses are to be considered as being within the scope of the invention herein defined. Also the modification of the amounts

of the materials of the composition may be made. Likewise such modifications are considered as being within the scope of this invention as herein set forth in the claims.

5 What is claimed is:

1. A resist for photographic etching having therein animal glue and an aliphatic monohydroxy aldehyde.

10 2. A resist for photographic etching having therein gelatine and hydroxy butyric aldehyde.

3. A resist for photographic etching being a film consisting of a mixture of a protein and an alkali bichromate, and an aliphatic monohydroxy aldehyde superimposed on said mixture.

4. The process of photographic etching which consists in the depositing upon a surface of an article to be etched, a protein, an alkali bichromate and an aliphatic hydroxy aldehyde, exposing the film to an image projected by light, developing the film to remove portions thereof, rendering the film insoluble to an etching solution, etching the exposed surface with an etching solution, and removing the remaining portions of the film.

5. The process of etching which consists in depositing upon a surface of an article to be etched a light sensitive water soluble compound, exposing the compound to a light projected image, developing the compound, rendering the compound insoluble to an etching solution, etching the exposed surface, and removing that part of the compound which was not removed in the developing.

6. The process of etching which consists in depositing upon a surface of an article to be etched a light sensitive water soluble compound, exposing the compound to a light projected image, developing the compound to re-

move portions thereof, carbonizing the remaining portions of the compound, etching the exposed surface of the article, and removing the remaining portions of the compound.

7. The process of etching which consists in depositing upon a surface of an article to be etched a film including gelatine and ammonium bichromate, superimposing a coating of an additional sensitizer, subjecting the resulting compound film to a light projected image, developing the image, and etching the surface exposed after development.

8. The process of etching which consists in depositing upon a surface of an article to be etched a film including gelatine and ammonium bichromate, superimposing thereon a film of aldol, exposing the resulting compound film to a light projected design, developing the film to remove parts thereof unaffected by the light, rendering the remaining portions of the film insoluble to an etching solution, etching the exposed surface, and removing the remaining portions of the film.

9. The process of etching which consists in depositing upon a surface of an article to be etched a film including animal glue and ammonium bichromate, superimposing a small amount of aldol thereon, exposing the resulting compound film to a light projected design, developing the compound film by means of water to remove portions of said film from surface, carbonizing the remaining portions of the compound film, subjecting the surface and the remaining portions of the film to an etching solution and thereafter removing the remaining portions of the film.

This specification signed this 27th day of October, 1926.

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