Dec. 5, 1933. R. E. HURST ET AL 1,938,291

PHOTOMECHANICAL PRINTING (NEGATIVE COLLOID RELIEF)

Filed May 16, 1932

Fig. 1.

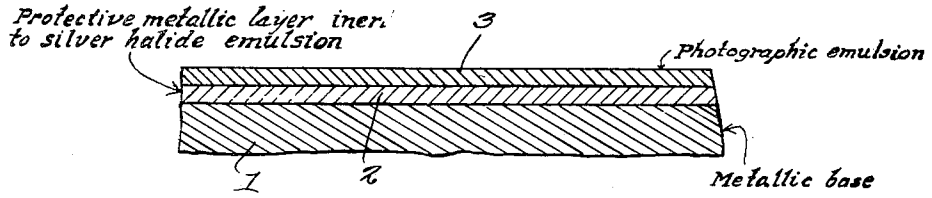


Fig. 2.

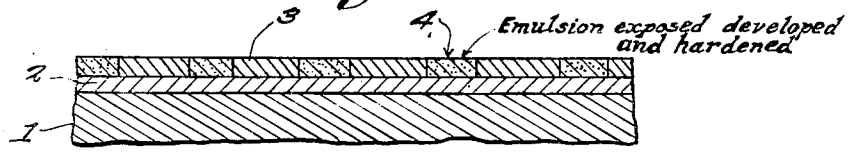


Fig. 3.

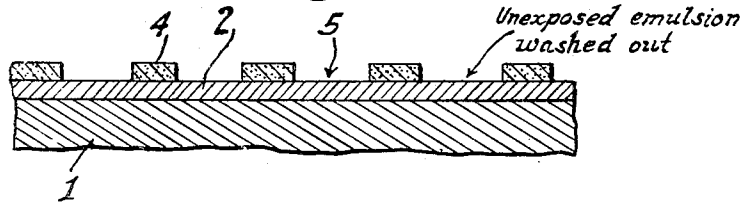


Fig. 4.

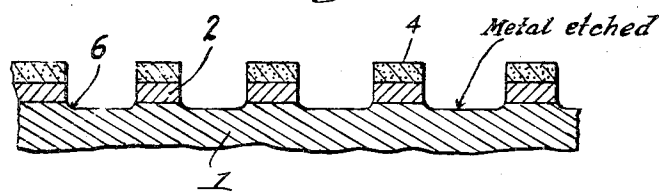
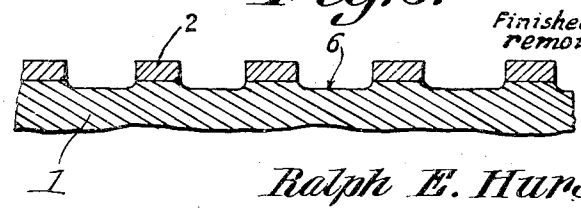


Fig. 5.



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PHOTOMECHANICAL PRINTING (NEGATIVE COLLOID RELIEF)

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Application May 16, 1932. Serial No. 611,646

16 Claims. (Cl. 95—5.7)

This invention relates especially to the preparation of metallic sheets supporting a colloid layer containing a sensitive silver salt with or without an actinic-light restraining agent and to the subsequent processing of such sheets into relief, planographic and intaglio plates for monochrome and polychrome printing.

Within the scope of these improvements and within the art of photo-mechanical printing we intend to include new and useful materials and the processing of the same into relief printing plates as for line and half-tone engraving, intaglio printing plates as for photogravure and rotogravure, and planographic printing plates as for photo-metallography and offset printing.

Generally speaking in the preparation of a photo-mechanical printing plate it is necessary to coat a metallic sheet with a colloid layer containing a light-sensitive salt. In the present state of the art this layer generally consists of a bichromated glue or other colloid. Upon exposure under a photographic negative the glue becomes insoluble where the light penetrates. Upon washing in water the unaffected glue dissolves out leaving a positive colloid relief. This colloid relief can then serve as a resist so that the metal can be etched where unprotected by the resist. The metallic plate so etched when properly inked can serve as a printing plate.

There are objections to a bichromated colloid appreciated by those skilled in the art. A bichromated colloid layer rapidly deteriorates requiring preparation shortly before using. It has too little sensitivity for direct exposure in the camera and even requires several minutes exposure to day light in contact printing. The essentially hand-preparation of metallic plates so sensitized is labor-consuming and time-consuming. A ready-prepared plate of good keeping quality would tend to be cheaper, of better and more uniform printing quality and of greater freedom from defects, derived from the ordinary advantages of quantity-production. Also plates capable of direct exposure in the camera would tend to simplify existing processes. In its favor it may be said that a bichromated colloid can yield an image of high quality and high resolution as evidenced by clean separation of half-tone dots.

It is the purpose of this invention to prepare a metallic sheet supporting a light-sensitive colloid layer of good keeping quality, of sufficient sensitivity for direct exposure in the camera and capable of being directly transformed into a printing plate which in quality can compare most favorably with that afforded by a wet collodion negative printed onto a sheet sensitized with bichromated glue. In referring to a metallic sheet we intend to include metal in the form of a sheet, plate, cylinder, foil, deposition or other form. We will now describe in a general way the steps by which such improvements are accomplished. Later we will show the practicality of such improvements as carried out in a typical branch of the photo-mechanical printing industry.

It is a fact that what is known as a photographic emulsion can be coated on a glass plate and that such coated plate can be made with good keeping quality and with sufficient sensitivity for direct exposure in the camera. A process gelatin dry plate is an example. A photographic emulsion consists of a sensitive silver salt incorporated in a colloid medium which is generally gelatin. In referring to a sensitive salt we intend to include those silver salts capable of exposure and development which are ordinarily coated on photographic plates, films and papers, and in referring to colloid we intend to include not only gelatin but other equivalent colloids.

It is also a fact that a developed silver image in a gelatin layer can be treated with a bichromate in solution to render the gelatin insoluble under the selective control of the silver image, that is to say, the gelatin surrounding the developed silver particles becomes insoluble. Thus a photographic image can be converted into a colloid print of differentially hardened gelatin. If the soluble gelatin is dissolved out a colloid relief is left analogous to that which can be obtained with a layer of bichromated glue which has been exposed and the unaffected glue dissolved out in water. It is apparent that by this process direct exposure in the camera will produce a negative colloid relief. In our companion application filed May 7, 1932, Serial No. 609,997 we propose to use the same materials but process them so that on direct exposure in the camera they yield directly an image which is a positive colloid relief. There are other methods of producing directly a negative colloid relief including the "tanning" developer but we prefer the bichromate method.

The general method which we propose is to coat a metallic sheet with a photographic emulsion of sufficient sensitivity for contact printing or for direct exposure in the camera, to expose and develop the silver image, to render the gelatin insoluble by a suitable agent under the selective

control of the silver image, to dissolve out the soluble gelatin thus forming a colloid resist directly supported by the metal and to subsequently convert to a printing plate by appropriate means. The accomplishment of making and processing metallic sheets directly coated with emulsion presented difficulties to be overcome. A photographic emulsion coated directly upon the ordinary materials of printing plates such as zinc and copper gave rapid deterioration of the emulsion. The well-known types of sensitizing generally employed in photo-mechanical work such as bichromated glue and sensitive bitumen can be coated directly on metallic surfaces without danger of metallic contamination. The particular type of sensitizing which we propose has decided advantages in speed and color sensitivity but its direct coating upon metal has hitherto been associated with metallic contamination. To avoid this it has been proposed to protect such sensitizing by interposing a layer of lacquer or varnish between the sensitizing and the metallic surface and also to treat the metallic surface so as to form a protecting layer of metallic oxides or salts. The first method greatly increases the number of steps and the difficulties of processing. The second method furnishes a very doubtful means of protection and a troublesome layer in processing. We have been successful in plating a basic metallic sheet with a metallic layer which is truly inert to a directly supported emulsion layer. An example is a copper base sheet which is plated with silver, nickel, or chromium, and subsequently coated with emulsion. We have thus produced a metallic sheet which can be directly coated with emulsion without the contamination hitherto associated with directly coated metal. This metallic protecting layer is integral with the metallic base sheet and does not interfere with any subsequent etching of the metal. It has all the advantages of a protecting layer without the disadvantages of the above-mentioned layer of lacquer or varnish. The surface of such protecting metallic layer is preferably slightly grained to promote the adhesion of the sensitizing layer. A well-grained surface is preferable in preparing planographic printing plates by this method. The use of a subbing to promote the adhesion of the sensitizing layer to the metallic surface is preferably to be avoided, but we intend any use of such subbing to be included within the meaning of a metallic surface directly supporting a sensitizing layer. The method of electro-plating is preferably used in the formation of the protecting metallic layer. It is essential that the electro-plated layer shall be of adequate thickness and free from excessive porosity or intercrystalline fracture. It is necessary to guard against metallic and non-metallic contaminations which might be present in the plating-bath and carried down as occlusions or intercrystalline films. Chromium and nickel are preferably used instead of silver. They are cheaper, do not tarnish readily, and afford a harder surface more resistant to wear and abrasion and to the corrosive action of certain metallic inks.

At this point we will describe a manner in which a suitable source of emulsion can be obtained. An emulsion such as is suitable for a process dry plate is suitable for performing the operations herein described. There are various formulas published for making emulsions for transparencies and process plates, but a more convenient source is to remove the emulsion from a ready-prepared plate. However most commercial plates are hardened, that is to say, the gelatin has been rendered insoluble by an agent such as chrome alum, so that the emulsion cannot be readily removed from the plate and readily dissolved. We secured from a manufacturer process plates coated without a hardening agent. By soaking one of these plates in cold water until the emulsion absorbed about ten times its weight in water, then scraping off the emulsion with a knife or straight edge and dissolving at a temperature around 100° Fahrenheit, a convenient source of emulsion was available. Inasmuch as the processing depends upon formation of insolubilized gelatin it is preferable to use an unhardened emulsion.

Up to this point we have described the preparation of metallic sheets which have been plated with metal as a means of protecting the emulsion from deterioration. Also we have described a simple way of securing a source of prepared emulsion.

A convenient method of coating a metallic plate is to take a definite amount of the melted emulsion and pour upon the slightly warmed plate, tilting the plate in different directions until the emulsion has evened out, then placing upon a chilled marble slab to set the emulsion, after which the plate can be dried in a gentle current of air. Another way is to pour on an excess of emulsion and to drain off in the fashion of preparing a wet collodion plate. It is obvious that these operations must be carried on in a photographic dark room.

Assuming that we have coated a metallic plate with an emulsion as described above an exacting and typical method of employing the improvements embodied in this invention is to expose the sheet to suitable copy in the camera behind a half-tone screen. A 60 line screen and a 133 screen afford a practical range. With a coating thickness of emulsion approximating that of a normal dry plate, and treating the normally exposed and developed plate with bichromate solution to obtain dots of insolubilized gelatin, we found that upon treatment with warm water the whole colloid layer was removed from the support. It was evident that if the insolubilized gelatin dots were to adhere to the support that the exposure of both high-lights and shadows must strike through sufficiently so that upon processing there will be no soluble gelatin under the insolubilized dots. On the other hand on coating the emulsion too thinly, the high-lights tended to be over-exposed before the shadows were properly rendered, giving halation and poor resolution of dots. We found that excellent results could be obtained when the thickness of the emulsion layer and the exposure were properly correlated. Further we found that the expedient of adding a light-restraining agent to the emulsion aided the control of the exposing and processing operations. An example of such agent is the yellow dye tartrazin which can be added in the proportion of a trace to .2 gram of dye to 10 grams of the melted emulsion described above. However either with or without addition of the dye we obtained the conditions whereby upon exposure in the camera and processing the insolubilized gelatin dots in both high-lights and shadows were well defined and remained attached to the support, and whereby the spaces between such dots were clean bare metal. In the case of contact printing such as exposing under a half-tone negative somewhat different conditions obtain than for direct exposure through a half-tone

screen in the camera. Due to excessive spreading of the image upon exposure in contact printing we found the use of a light-restraining agent necessary for satisfactory results.

An emulsion such as used above which has not been made color-sensitive is largely sensitive to blue and violet light and a dye such as tartrazin which does not harm the emulsion can be added to it. The yellow color acts as a filter to hold back the penetration of the blue and violet light to which the emulsion is sensitive. The presence of the light-restraining agent prevents halation, holds back the high light exposure to the benefit of the shadows, localizes the developed silver for easier formation of insolubilized gelatin, and gives a print and colloid relief of sharp definition. In the case of an emulsion which has been made sensitive to some other color such as green or red it would of course be necessary to employ dyes which would absorb the green or the red to get an equivalent light-restraining action. For example with red sensitive emulsion, napthol green would tend to absorb red radiation.

There has been previous use of a light-restraining agent in an emulsion layer coated upon a transparent support, notably motion picture film, and a developed relief obtained after exposing through the back of the support. In that case the thickness of the emulsion layer is of little importance and having been exposed through the back of the support, the developed relief naturally adheres to it. There is also no danger of metallic contamination to the emulsion. We believe that we are the first to propose coating a colloid layer containing a sensitive silver salt with or without an actinic-light restraining agent directly upon a metallic sheet consisting of a base sheet plated with a metallic layer truly inert to the emulsion. We believe that we are the first to prepare and to process such a material into a metallic vehicle supporting a colloid relief, and to transform such material into a photo-mechanical printing plate.

In the processing of the exposed sheet any suitable metol-hydroquinone developer can be used, or any developer which does not tend to harden the gelatin. Development should be followed by a thorough rinsing and washing especially to remove all traces of sulfites which might later react with the bichromate to form insolubilized gelatin. The washed sheet with or without drying is then placed in a bichromate bath. A convenient bath consists of 8 grams of potassium bichromate and 8 grams of potassium bromide dissolved in 1 liter of water. In this bath the gelatin corresponding to the developed silver image becomes insoluble while the remaining gelatin retains its original soluble condition. The reaction is complete in about two minutes. It is unnecessary to fix out the residual silver salts or to bleach out the developed silver. By treatment with hot water the soluble gelatin is removed so that we have a metallic sheet supporting a colloid relief. Where bare metal is exposed between the insolubilized gelatin dots the metal can be etched by some suitable agent. Ferric chloride can be used to etch the protecting layer of nickel, dilute hydrochloric acid for etching chromium, and dilute nitric acid for etching silver.

As a specific example of the application of the new and useful improvements embodied in this invention, let us take the case of photogravure. Normally, in the present state of the art the following steps are required:

1. Making of the negative.
2. Making of a laterally reversed positive.
3. Sensitizing of a transfer tissue with bichromate.
4. Exposing the tissue through the positive and through a screen.
5. Transferring the colloid print to metal.
6. Developing (in warm water) the colloid relief.

There is involved in the above a long series of steps. There are three photographic images. There are the difficult and time-consuming steps of preparing the sensitized tissue and making the transfer. There are the long exposures of the tissue. By employing a ready-prepared metallic plate supporting a colloid layer containing a sensitive silver salt, as described in this specification, we can expose the same directly in the camera and behind a gravure screen and directly obtain a negative in correct lateral position. Upon treating the developed image with bichromate the photographic image becomes the colloid image. There is one photographic image instead of three, no hand preparation of materials, no long exposures, and no transfer.

It will thus be seen that we have described materials and processes with all necessary details, embodying the principles and attaining the objects and advantages of the invention. Since many matters of treatment, manipulation, selection and proportion of ingredients, succession of steps and other details may be variously modified without departing from the principles involved, we do not intend any limitation to such details excepting so far as set forth in the appended claims.

For the purpose of illustrating the several steps which can be followed in carrying out the method herein described and at the same time disclosing the article in its several stages of development, attention is called to the accompanying drawing in which:

Figure 1 shows a greatly enlarged section of a metallic base sheet 1, plated with a layer of inert metal 2, directly supporting a silver halide emulsion layer 3.

Figure 2 shows the emulsion layer as exposed under a half-tone screen and developed, exposed areas 4 being subsequently hardened.

Figure 3 shows the emulsion layer with the unexposed soluble areas dissolved out at 5.

Figure 4 shows the plate etched through the inert metallic layer into the base plate corresponding to areas 6 unprotected by the emulsion resist.

Figure 5 shows the completed plate with the emulsion resist removed.

What is claimed is:

1. A material for use in the art of photo-mechanical printing including a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt.

2. A material for use in the art of photo-mechanical printing including a basic metallic sheet whose surface is plated with a metallic silver layer directly supporting a colloid layer containing a sensitive silver salt.

3. A material for use in the art of photo-mechanical printing including a basic metallic sheet whose surface is plated with a metallic nickel layer directly supporting a colloid layer containing a sensitive silver salt.

4. A material for use in the art of photo-mechanical printing including a basic metallic sheet whose surface is plated with a metallic

chromium layer directly supporting a colloid layer containing a sensitive silver salt.

5. A material for use in the art of photo-mechanical printing including a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a silver salt made sensitive to specific radiation by a suitable sensitizing dye.

6. A material for use in the art of photo-mechanical printing including a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt and an actinic-light restraining agent.

7. A material for use in the art of photo-mechanical printing including a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a silver salt made sensitive to specific radiation by a suitable sensitizing dye and containing an actinic-light restraining agent of a color non-actinic to the sensitized silver salt.

8. In the art of photo-mechanical printing, the method of producing a metallic sheet supporting a photographic colloid relief including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt, developing the silver image, rendering the colloid insoluble by a suitable agent under the selective control of the silver image, and dissolving out the soluble colloid.

9. In the art of photo-mechanical printing, the method of producing a metallic sheet supporting a photographic colloid relief including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt, developing the silver image, rendering the colloid insoluble by a suitable agent under the selective control of the silver image, said agent containing a bichromate, and dissolving out the soluble colloid.

10. In the art of photo-mechanical printing, the method of producing a metallic sheet supporting a photographic colloid print including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt, developing the silver image and rendering the colloid insoluble by a suitable agent under the selective control of the silver image.

11. In the art of photo-mechanical printing, the method of producing a metallic sheet supporting a photographic colloid relief including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt and an actinic-light restraining agent, developing the silver image, rendering the colloid insoluble by a suitable agent under the selective control of the silver image, and dissolving out the soluble colloid.

12. In the art of photo-mechanical printing, the method of producing a metallic sheet supporting a photographic colloid print including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt and an actinic-light restraining agent, developing the silver image, and rendering the colloid insoluble by a suitable agent under the selective control of the silver image.

13. In the art of photo-mechanical printing, the method of producing a printing plate including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt, developing the silver image, rendering the colloid insoluble by a suitable agent under the selective control of the silver image, dissolving out the soluble colloid, and etching the metallic surface by a suitable agent under the selective control of the colloid image.

14. In the art of photo-mechanical printing, the method of producing a printing plate including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt, developing the silver image, rendering the colloid insoluble by a suitable agent under the selective control of the silver image, and etching the metallic surface by a suitable agent under the selective control of the colloid image.

15. In the art of photo-mechanical printing, the method of producing a printing plate including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and directly supporting a colloid layer containing a sensitive silver salt and an actinic-light restraining agent, developing the silver image, rendering the colloid insoluble by a suitable agent under the selective control of the silver image, dissolving out the soluble colloid, and etching the metallic surface by a suitable agent under the selective control of the colloid image.

16. In the art of photo-mechanical printing, the method of producing a printing plate including the steps of exposing a basic metallic sheet whose surface is plated with a metallic layer truly inert to and supporting a colloid layer containing a sensitive silver salt and an actinic-light restraining agent, developing the silver image, rendering the colloid insoluble by a suitable agent under the selective control of the silver image, and etching the metallic surface by a suitable agent under the selective control of the colloid image.

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