

UNITED STATES PATENT OFFICE

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LITHOGRAPHIC PLATE AND PROCESS OF PREPARATION

No Drawing.

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This invention relates particularly to plates for use in lithography and a process of preparing the same.

The primary object is to provide plates of the character mentioned with printing portions, such as images, designs, characters, or the like, which are highly resistant to the disintegrating action of lithographic ink, which will, nevertheless, "hold" the ink satisfactorily, and which are also strong and durable and capable of withstanding the mechanical stress to which the plates are subjected in press-printing operations.

Still another important object is to provide an improved process for applying to plates, suitable for lithographing purposes, highly resistant images, designs, or characters, which are capable of taking and holding the ink satisfactorily, and which will withstand the disintegrating action of ink and possess such other resistant qualities as to enable these printing surfaces to be used successfully for producing a very large number of reproductions.

According to the improved process, as preferably practiced, a lacquer comprising a well thinned solution of a highly insoluble and strongly resistant synthetic resinous compound is applied to those areas of a plate which are to serve as a medium for receiving and holding the lithographing ink and printing upon the surface to which the ink is to be transferred. It is preferred to employ a resinous compound which is insoluble in solvents of the order of acetone, benzol (benzene, i. e., the coal-tar product known as benzene), or the like; to dissolve such highly insoluble resinous compound in a special solvent, as for example, furfural, and to mix the solution with suitable thinners and preferably with certain other ingredients, thus producing a highly thinned lacquer. This lacquer then is applied in a thin coating to the "sensitive" areas of the plate, at which areas the resinous compound and certain other ingredients in the coating are caused to become set and strongly adherent to the plate, while the solvent and thinning agents may be largely, or wholly, evaporated therefrom. Those portions of the plate which are not to per-

manently retain the image, design, or characters which function in the printing process may have applied thereto a suitable protective coating, such as a coating of gum arabic, so that the selected areas only will be permanently coated with the resistant coating.

It is preferred to employ in the lacquer a resin which is itself light-sensitive, or which has been rendered light-sensitive by the incorporation therein of suitable sensitizing agents. If desired, accelerators may be employed which comprise halogen-liberating agents. Also, it is preferred to employ a synthetic resin which is rendered highly insoluble in character before it is dissolved in the special solvent, and which can be rendered still more resistant and insoluble after the lacquer has been applied to the plate. Also, it is preferred to employ in the lacquer a highly insoluble resin which can be still further hardened and rendered more insoluble by subjecting the plate to a heating operation after the lacquer has been applied.

As an example, one may take a zinc plate and provide it with "sensitive" areas adapted to permanently receive the coating substance which forms the image, design, or printing characters, may protect the remaining portions of the plate (after first developing, if the "sensitive" area has been produced photographically) by a suitable coating, such as a solution of gum arabic, may then coat the plate with the improved lacquer, may then harden the coating by heating the plate, and may then wash the coating from the protected areas by a suitable developing operation. For example, this may be done by washing with water; or, the plate may be put to use in the press, where the water from the damping roller, which ordinarily precedes the inking roller, will disintegrate the coating throughout the protected areas and leave the strongly attached portions of the coating, forming the image, or the like, in condition to receive and transfer the ink in the printing operation.

The "sensitive" areas of the plate may be provided in any suitable manner. They may, for example, be provided by applying to the plate a light-sensitive coating of albumin,

projecting or transmitting a light image onto this coating, applying a coating of developing ink, washing off the unreacted upon albumin and the overlying developing ink, then
 5 applying a protective coating, such as a solution of gum arabic. After this, the developing ink may be washed off with alcohol, and the improved lacquer may be applied to the plate and hardened. The lacquer strikes into
 10 or permeates the albumin and the resistant coating becomes so strongly set or attached to the sensitive areas of the plate as to remain permanently thereon. The remaining portions of the coating may be washed out, and
 15 the plate may then be used for lithographing purposes.

On the other hand, the zinc plate may be provided with "sensitive" areas by applying transfer ink, in the form of an image, design,
 20 or characters, to the plate in a well known manner; then coating the plate with gum arabic which adheres to those portions of the plate not covered by the transfer ink, and then washing off the transfer ink, leaving the
 25 clean underlying portions of the zinc surface as "sensitive areas". The improved lacquer may then be applied to the plate, may be hardened so that the exposed areas of the plate receive a permanent coating, and the
 30 intervening protective coating may be removed by a developing operation (washing with water, for example), and the plate is then ready for use. It is to be understood that while the lacquer coating may cover the
 35 coating of gum arabic during the period when the plate is being subjected to heat to further harden the resinous coating, nevertheless, the gum arabic prevents the resinous coating from becoming (strongly) adherent to the
 40 plate, and the coating, comprising the resinous compound and the gum arabic, may be readily washed off the plate, leaving the resistant resinous coating at those areas which are to be used to receive and transfer the ink
 45 in the printing operation.

The preferred method of preparing a suitable lacquer for use in accordance with the invention is, as follows:

First, prepare a furfural-acetone resin by
 50 mixing five hundred seventy-five grams of furfural and five hundred seventy-five grams acetone; pouring the mixture slowly into a saturated aqueous solution of sodium hy-
 55 drate, say one thousand grams of such a strong, caustic solution, thus producing a resinous material; draining off the caustic; crushing the remaining resin and washing it with a dilute solution of hydrochloric acid,
 60 say ten percent solution, to free it from the caustic; then heating the resin for a suitable period, say two hours, in an open kettle, at about 300° C. The resin melts and gradually thickens, while giving off fumes. The resin
 65 should be constantly stirred during the heat-

ing period, and, at the end of the heating period, fumes are no longer given off.

The heat treatment preferably is continued to a point where small samples of the resin are shown to be insoluble in benzol (benzene),
 70 and do not even discolor this solvent. The resin is then cooled and crushed.

The lacquer preferably is formed by using the highly insoluble resin prepared in the manner described by dissolving the resin in
 75 a special solvent, such as furfural, and compounding in accordance with the following formula:

Furfural-acetone resin, 400 grams; furfural, 1500 cc.; benzene, 1000 cc.; amyl acetate, or ethyl acetate, 1200 cc.; celluloid, 6
 80 grams; oil of cassia, 10 cc.; oil of lavender, 10 cc.

The benzene and the acetate serve as thinners, or diluents. The essential oils disguise the odor of furfural and also resinify
 85 with heat; and the celluloid improves the ink-holding quality of the coating and tends to toughen the film.

The preferred manner of compounding
 90 the materials is to dissolve 400 grams of the highly insoluble furfural-acetone resin, prepared as described above, in about 1400 cc. of furfural, by heating to the boiling point for about twenty minutes; to add 500 cc. of
 95 an acetate (such as amyl or ethyl) while the solution is warm; to dissolve six grams of celluloid in 100 cc. cold furfural and add same to the solution; then mix 500 cc. of an acetate, such as ethyl acetate and 1000 cc. of
 100 benzene and add to said solution; and finally add the essential oils, i. e. oil of lavender and oil of cassia.

After the developing ink, or the transfer ink, as the case may be, has been washed off
 105 the "sensitive areas", or image, on the gummed plate, the lacquer, prepared as described, is wiped over the entire plate with a rag and rubbed down into a thin and smooth coating. For best results, the plate
 110 is then heated at about 100° C. for about one-half hour. This renders the resinous material even more insoluble. The plates may be sent directly to the press when cooled, in
 115 which case the water from the damping roller of the press, coupled with the operation of the press, will disintegrate and remove the coating between the areas which have received the permanent coating. If
 120 preferred, however, the coating applied over the gum arabic coating may be removed by washing with water before sending the plates to the press. In any case, the lithographing ink will adhere only to the image in the print-
 125 ing operation.

The lacquer prepared, as described above, possesses high penetrating qualities. It will, for example, penetrate the image produced in an albumin coating photographically, and
 130 will form a resistant and practically in-

soluble image on the metal, which image is adapted to receive the ink and transfer it in the printing operation. The improved coating is of such chemical insolubility in inks, and its resistance to mechanical abrasion on the press is such as to render the product far superior to a plate having simply an albumin coating, or a coating of other materials, such as have previously been used, including asphaltum. In fact, the improved lacquer provides an image far superior to that afforded by such coatings as albumin, asphaltum, or the like, even though the plate is not subjected to the heating operation after the lacquer has been applied thereto. On the other hand, when the plate is subjected to the heating operation, the resin in the lacquer, which previously remained potentially reactive in some degree, is transformed into its ultimate insoluble and resistant condition, in which condition it is no longer soluble in furfural.

While it is preferred to employ furfural as a solvent for the furfural-acetone resin, any special solvent which will dissolve the resin in the highly insoluble condition may be employed. Aniline, or nitrobenzene will act as solvents, for example. However, such solvents possess objectionable properties, having bad odors and being of poisonous character. In any event, the solvent should be such that the dissolved resin can be wiped over the picture, or image, formed in the sensitized albumin, or over the "sensitive" area of the plate (where an ink transfer has been used), and afford a thin, smooth coating; also, the solvent should be such as to dry at a reasonably rapid rate after the film of lacquer has been applied.

What has been referred to as "transferring ink" is the colored, greasy compound which is applied to a photo transfer plate and which adheres either to the image produced by light in a coating on the plate, or to the resistant coating applied to "sensitive" areas protected originally by transfer ink, where an ink image has been transferred to the plate and removed, after first covering the intervening spaces with gum. Such an ink contains an oil, or a grease. It may be readily washed off the picture by means of alcohol, benzine, or turpentine.

Synthetic resins which are highly insoluble in oils, inks, or the solvents ordinarily used in lithographic processes are preferable.

In lieu of a sensitized albumin coating, other photo-sensitized coatings may be employed for providing the "sensitive" areas on the plate. For example, one may employ one of the photo-sensitive oil varnishes, such as described in applications hereinafter mentioned, may optically produce an image in such coating, may then develop the coating, protect the non-sensitized areas by gum arabic, and apply the improved resinous lac-

quer in accordance with the invention, and thus provide the plate with a highly resistant image, design, or characters, which will serve for ink transferring purposes in a printing operation.

Examples of light-sensitive varnishes which may be employed in the manner just described are set forth in the following patents:

Patent No. 1,574,358, granted Feb. 23, 1926, Murray C. Beebe; Patent No. 1,574,356, granted Feb. 23, 1926, Murray C. Beebe; Patent No. 1,574,357, granted Feb. 23, 1926, Murray C. Beebe and Alexander Murray.

Other coatings, or varnishes, which will serve the same purpose may be employed.

In place of the furfural-acetone resin employed in the lacquer, one may employ other suitable furfural resins, or other synthetic resins. For example, one may employ furfural resins prepared in accordance with the description given in the patent of Beebe, Murray and Herlinger, Number 1,587,269, granted June 1, 1926, or in the patent of Beebe, Murray and Herlinger, Number 1,587,273, granted June 1, 1926.

As another example, one may employ a phenolic condensation product, or phenol resin, prepared in any suitable manner and having incorporated therein suitable sensitizing agents, or suitable accelerating agents. Thus, one may prepare a phenolic condensation product by any of the well known processes in such manner as to produce a resin closely approaching the infusible stage, may incorporate in such resin suitable sensitizing agents, or accelerators, the resins still being soluble in a special solvent, and still potentially reactive in some degree, may prepare a lacquer from such a resin, and may apply it to the "sensitive" areas of the plate in accordance with the invention, and may then cause the reaction to proceed to render the resin still more resistant and insoluble and produce a permanent resistant coating at the areas which are to serve as the ink-transferring portions of the plate.

In any case, the resin employed in the lacquer preferably should be highly resistant to the solvent action of solvents of the order of benzene, acetone, etc., but should still be soluble in some special solvent; and such special solvent, in connection with suitable thinners, should be of highly penetrating character, especially where the coating is to be applied to a previously sensitized coating, such as an albumin coating. Also, the lacquer should be of such character that it can be applied as a thin, smooth layer.

As has been indicated, it may be desired to incorporate in some of the resinous lacquers, such as a lacquer embodying a phenolic condensation product, a halogen-liberating agent, such as a metallic halide, iodoform, or some ingredient which will liberate halogen

under the action of light, so that the halogen will be free to act as a catalyst to expedite further hardening of the resin. As an illustration, a metallic halide, in colloidal form, may be introduced into a varnish, or a lacquer, by introducing small percentages of drying agents, such as lead resinate, lead oxide, or other metal salts, and introducing also a small percentage of a halogen, such as iodine. The halogen will combine with the metallic salt to form a metallic halide, which remains dispersed in colloidal form throughout the varnish. In the case of a phenolic resin an easier method, and perhaps more satisfactory, is to incorporate in the resinous lacquer about 3% of iodoform.

A light-sensitive varnish, or medium, embodying a phenolic condensation product, is disclosed, for example, in Beebe, Murray and Herlinger Patent Number 1,587,270, granted June 1, 1926.

Natural resins are not adapted to yield the highly resistant, insoluble printing surface desirable, and the artificial resin employed in the lacquer must be potentially reactive and capable of passing, in the final hardening operation, into the infusible and substantially insoluble condition.

The lacquer and process of preparation thereof forms the subject matter of our application, Serial No. 84,775, filed January 29, 1926, said application constituting a division of the present application.

The method of providing the plate with "sensitive" areas by the application of a compound of greasy or oily character such, for example, as a transfer ink, forms the subject matter of our divisional application, Serial No. 313,938, filed October 20, 1928.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, but the appended claims should be construed as broadly as permissible, in view of the prior art.

What we regard as new, and desire to secure by Letters Patent, is:

1. In preparing plates for lithography, the process which comprises: providing a plate with a "sensitive" area, and applying to said area a lacquer comprising a synthetic resin which is substantially insoluble in solvents of the order of acetone and benzene.

2. In preparing plates for lithography, the process which comprises: providing a plate with a "sensitive" area, applying to said area a lacquer comprising a synthetic resin in which the reaction has proceeded to a condition approaching the final stage, and subjecting the lacquer to hardening treatment to render the coating still more insoluble and resistant.

3. In preparing plates for lithography, the process which comprises: providing a plate with a "sensitive" area comprising an image,

design, or character, and applying to said "sensitive" area a lacquer comprising a furfural resin in which reaction has proceeded to such stage as to render said resin substantially insoluble in solvents of the order of acetone and benzene.

4. In preparing plates for lithography, the process which comprises: providing a plate with a "sensitive" area comprising an image, design, or character, applying to said area a lacquer comprising a furfural resin which is highly insoluble but still potentially reactive, and subjecting the lacquer to heat treatment to render the coating more highly insoluble and resistant.

5. In preparing plates for lithography, the process which comprises: providing a plate with a "sensitive" area comprising an image, design, or character, applying to said area a lacquer comprising a furfural resin which is highly insoluble but still potentially reactive, and subjecting the plate to heat treatment to render the coating more highly insoluble and resistant.

6. In preparing plates for lithography, the process which comprises: providing a plate with a "sensitive" area, and applying to such area a lacquer comprising a furfural-acetone resin.

7. In preparing plates for lithography, the process which comprises: providing a plate with a "sensitive" area, applying to said "sensitive" area a lacquer comprising a resin produced by reaction between furfural and acetone, and a special solvent for such resin, and subjecting the coating thus applied to hardening treatment to render the coating still more insoluble and resistant.

8. In preparing plates for lithography, the process which comprises providing a plate with a "sensitive" area, applying to said "sensitive" area a lacquer comprising a resin produced by reaction between furfural and acetone, and a special solvent for such resin, and subjecting the plate to heat treatment to render the coating still more insoluble and resistant.

9. In preparing plates for lithography, the process which comprises: providing a surface of the plate with a coating embodying an image, design, or character, coating the remainder of the surface of the plate with a protecting medium and applying to the plate a lacquer comprising a highly insoluble, potentially reactive, synthetic resin.

10. In preparing plates for lithography, the process which comprises: applying a sensitive coating to a plate, acting thereon selectively with light in accordance with an image, design, or character, developing the plate, applying a protecting coating of gum arabic to exposed areas, and applying a lacquer comprising a synthetic resin in potentially reactive condition, and converting the synthetic resin to the final insoluble condition by heat.

11. In preparing plates for lithography, the process which comprises: providing a plate with a sensitive coating, acting upon said coating with light transmitted thereto in accordance with an image, design, or character, applying to said first-named coating a lacquer comprising a highly insoluble, synthetic resin which is still potentially reactive, and subjecting the plate to heat treatment to render the last-named coating still more insoluble and resistant. 70
12. In preparing plates for lithography, the process which comprises: coating a plate with a sensitive medium, acting upon said medium with light in accordance with an image, design, or character, removing the unreacted portions, applying to said plate a protective coating, then applying a coating of lacquer comprising a potentially reactive synthetic resin, then developing the plate, and finally hardening the synthetic resin by heating the plate. 75
13. In preparing plates for lithography, the process which comprises: applying a sensitive coating to a surface of a plate, acting upon said sensitive coating selectively with light in accordance with an image, design, or character, developing the plate, applying a protective coating and then applying a lacquer coating comprising a furfural resin. 80
14. In preparing plates for lithography, the process which comprises: applying a sensitive coating to a surface of a plate, acting upon said sensitive coating selectively with light in accordance with an image, design, or character, removing the unreacted portions of said coating, applying a protective coating then applying a lacquer coating comprising a furfural resin, and subjecting the plate to heat treatment. 85
15. A plate for lithographic purposes comprising: a metal plate provided with "sensitive" areas, and a coating permanently "set" upon said "sensitive" areas, said coating comprising a synthetic resin in highly insoluble and resistant condition. 90
16. A plate for use in lithography comprising: a metallic plate, and a selectively applied coating "fixed" thereon, said coating comprising furfural resin in highly insoluble and resistant condition. 95
17. A plate for lithographic purposes comprising: a metal plate provided with a coating having "sensitized" areas which have been selectively transformed under the action of light, and a highly resistant and insoluble coating on said "sensitized" areas comprising a synthetic resin. 100
18. A plate for the purpose set forth, comprising: a metal plate having a coating comprising albumin with areas transformed under the action of light, and a coating on the transformed areas comprising a synthetic resin in highly insoluble and resistant condition. 105
19. A plate for the purpose set forth, comprising: a metallic plate, a sensitive coating thereon having selectively transformed areas produced under the action of light, and furfural-acetone resin affording permanent printing surfaces at said areas. 110
20. A plate for the purpose set forth, comprising: a zinc plate, a light-sensitive coating thereon having transformed areas produced under the action of light, and a lacquer coating comprising a synthetic resin, and celluloid, oil of cassia and oil of lavender, in small proportions. 115
21. A plate for the purpose set forth, comprising: a metal plate having "sensitive" areas, and a permanent coating applied directly to the plate at said "sensitive" areas, comprising a synthetic resin in highly insoluble and resistant condition, the remaining portions of the surface of the plate being bare. 120

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