June 9, 1964 G. W. LARSON 3,136,637

PRESENSITIZED LITHOGRAPHIC LIGHT-SENSITIVE SHEET CONSTRUCTION

Filed Nov. 26, 1958

FIG. 1

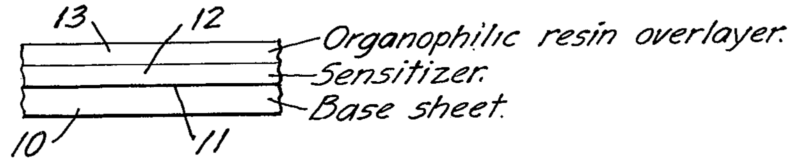


FIG. 2

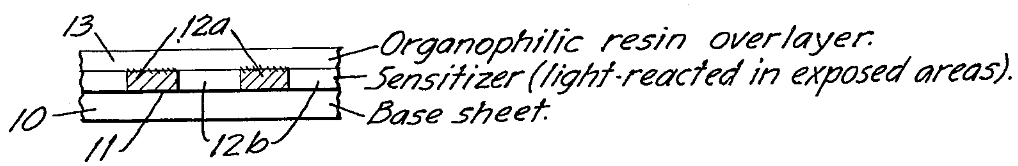
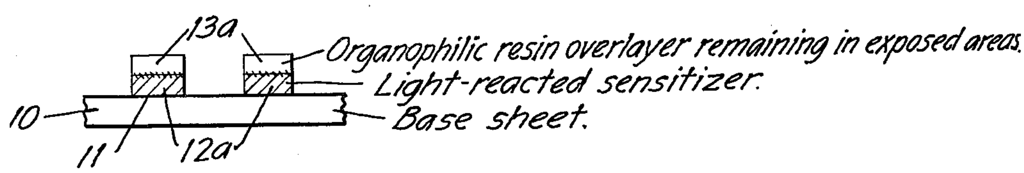


FIG. 3



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PRESENSITIZED LITHOGRAPHIC LIGHT-SENSITIVE SHEET CONSTRUCTION

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The present invention relates to light-sensitive sheet constructions of wide utility upon which can be accurately reproduced images, pictorial representations, messages or the like, by photographic procedures. This invention is particularly concerned with the printing arts, a specific aspect being the provision of a novel presensitized lithographic printing plate.

Commercially successful presensitized metal-backed lithographic printing plates have been available since about 1950. Such plates are the subject of Jewett and Case Patent No. 2,714,066, granted July 26, 1955. In use, the plate is first exposed to actinic light through a negative transparency or stencil to insolubilize the light-sensitive coating in the light-struck areas. Then the plate is washed with water and lightly rubbed to remove the remaining soluble portions of the coating. The plate in this form is ready to be put on the press and is capable of printing satisfactorily. For long press runs, however, it is advantageous to render the image more durable through the addition of an abrasion-resistant cap or coating to the image areas. This has been accomplished by the application of a lacquer to these areas. Thereby press life of the plate can be lengthened materially. The application of such a strengthening material usually involves rubbing onto the plate surface a liquid containing a material which is strongly organophilic, tough and highly adherent to the exposed resin in the light-exposed areas. Said material thus becomes strongly adhered to the image areas. Such a material has sometimes been referred to as an image developer.

Since the advent of the metal-backed presensitized printing plates described in the aforesaid Jewett and Case patent, many have addressed themselves to the provision of materials which would satisfactorily serve as an image strengthener, i.e., the durable cap or coating in the image areas. Hall Patent No. 2,754,279 represents one successful and satisfactory solution.

However, the concept of reinforcing an image after exposure of the plate has inherent difficulties. The manner in which the image strengthener is applied to the plate surface can make a great deal of difference in the press life of the plate. Care is required. For example, when the image strengthener is applied properly, skillfully and uniformly, the plate may be used to reproduce many thousands of copies more than if it is applied poorly. Also, a poorly capped or coated image may not accept ink properly, and be worse than if no strengthener had been applied at all.

Oftentimes, however, the person shouldered with applying the image strengthener is the press operator himself, or someone else other than a highly skilled platemaker. Such persons ordinarily are not adept at applying the image strengthener uniformly so as to obtain consistently good results. Even skilled platemakers have difficulty in attaining consistency. These problems often are further compounded by quality variations in the image strengtheners as supplied by manufacturers.

By and large, in attempting to minimize the difficulties above mentioned, lithographers, manufacturers and suppliers of lithographic supplies, and others concerned have centered their efforts in the direction of attempting to obtain and provide superior image strengtheners which are more effective and easier to apply than those hereto-

fore known. Much time and money have been expended toward this end.

Others, taking a somewhat different avenue of approach, have attempted to alter and improve the strength and durability of light-sensitive resins, e.g., by incorporating or reacting certain resinous materials therewith. Hodgens Patent No. 2,826,501, granted March 11, 1958, is an example. However, the selection of the resinous materials which can be so used is limited. Processing difficulties occur in manufacture of the resulting light-sensitive compositions, e.g., difficulties arise in the selection and use of proper commercial solvents. Moreover, and very significant is the fact that the press life of plates employing such compositions is little, if any greater than plates to which an image developer has been applied with even ordinary care or skill. Moreover, even those suggesting the combination resin and light-sensitive resin mixtures recommend the application of a treatment or coating to the exposed image, such as that disclosed in the aforementioned Hall patent. See the said Hodgens patent in this respect.

Insofar as I am aware, however, no one, prior to this invention has successfully provided a novel stable presensitized printing plate of markedly improved press life wherein there is no need for the addition of any material to the image areas after exposure of the plate, or for any particular skill on the part of the person developing the plate in order to provide a printing plate of extreme long life. The provision of such a structure is a primary objective of the present invention.

In attaining these and many other objects and advantages, many of which will be apparent from the following description, I provide a presensitized plate structure in which, as received from the manufacturer, the entire exterior surface is provided with the ultimate physical characteristics desired of the image areas in the exposed plate. That is, the exterior surface is hard, durable, abrasion-resistant and wear-resistant. It is strongly organophilic so that it will readily accept the oil-based inks used in lithography. When exposed to actinic light in the customary fashion, and then wiped or lightly rubbed with a processing composition involving common solvents, the exterior surface in the non-exposed areas, and the underlying unreacted sensitizer in said areas are quickly, easily and completely removed. An accurate sharp clear image thereby is defined, even in the case of fine half-tone images.

My invention has important utility beyond metal-backed presensitized printing plates, and beyond the printing field. Some of these will be brought out hereinafter in the specific examples which follow.

Generally, the novel plate or sheet structures hereof comprise a base sheet having coated thereover a stable light-sensitive resin layer, e.g., a light-sensitive diazo resin, which upon exposure becomes insolubilized from its initial state. The surface of the base sheet underlying the light-sensitive material is receptive to the formation of a firm bond with the in situ insolubilized light-sensitive material. Coated over and in contact with the light-sensitive material is an actinic light-transmittable film or layer of a hydrophobic water-insoluble solvent-softenable resin. The manner in which the present invention is practiced in overcoming the long-known deficiencies in the prior art, as well as in providing various other advantages will be apparent from the following description of my invention, taken in conjunction with the accompanying drawing.

Referring now to the drawings, FIGURE 1 shows a broken away edge on view of a base sheet **10** having a surface **11** over which is coated a stable initially soluble light-sensitive sensitizer layer **12**. Where necessary, surface **11** may involve a treatment which protects the sensitizer layer **12** from being degraded by any degradative characteristics in the base sheet 10. Overlying said light-sensitive layer 12 is an overcoating or layer of an organophilic hydrophobic water-insoluble substantially continuous solvent-softenable organic resin film or coating 13.

FIGURE 2 shows the sheet construction of FIGURE 1 after it has been exposed to actinic light through a transparency or stencil. During exposure the actinic light passing through the transparency also passes through resin coating 13 and strikes the light-sensitive layer in the image areas 12*a*. In the latter areas the sensitizer reacts to become insolubilized and firmly adhered to the underlying surface 11 of the base sheet 10. Also in said exposed areas the light-reacted resin firmly bonds the overlying resin layer 13. In the non-exposed areas 12*b* the sensitizer remains unreacted and soluble.

Finally, FIGURE 3 shows the sheet construction of FIGURE 2, after it has been wiped or lightly scrubbed with processing solvent selected with respect to the particular material of which layer 13 is composed, and which contains a solvent for the unexposed light-sensitive material. When the plate surface is so treated and lightly scrubbed, the resin layer 13 is softened and breaks away cleanly along the lines of demarcation between the exposed and unexposed areas to leave resin areas 13*a* coinciding with areas 12*a* of exposed reacted sensitizer. The unexposed light-sensitive material in the non-light struck areas is also washed away from the plate baring the underlying surface 11, which, in the case of a printing plate, preferably is hydrophilic in character.

The plate, then, and without necessity of further processing is ready for mounting on the printing press. The image areas are strongly organophilic, firm and wear-resistant.

It is to be noted that the purpose of the drawing is for illustrative purposes only, and it is not intended that the various layers and components of my plate constructions be shown in their true dimensions or proportions.

Having now described an embodiment of my invention in a general way the same will now be illustrated, with the aid of the following non-limiting examples. In the examples the concentrations of all coating solutions or compositions are based on weight of material in grams dissolved or dispersed per 100 milliliters of total volume of solution and/or dispersion.

Example I

A solution is first prepared by dissolving polyvinylformal resin in ethylene chloride solvent to yield approximately an 8 percent solution. A suitable polyvinylformal resin has a polyvinyl alcohol content of from about 7–9 percent and a polyvinyl acetate content of from about 9.5–13 percent, and a 5 percent ethylene chloride solution thereof has a viscosity of about 40–60 cps. at 20° C.

A phthalocyanine pigment, e.g., "Monastral Fast Blue BC" available commercially from the Du Pont Company, is then ball milled into the 8 percent resin solution on the basis of 1 part pigment per 4 parts polyvinylformal resin, by weight. The resulting composition is then diluted with ethylene chloride to a 2½ percent solids concentration, filtered, and transferred to a coating tank. The area around the coating equipment is well vented to exhaust solvent vapors.

A continuously formed presensitized plate construction is then coated under subdued light, e.g., yellow light, with the coating composition previously prepared. The presensitized plate construction is manufactured continuously in accordance with the specific example of Jewett and Case Patent No. 2,714,066. Briefly, such lithographic plate structure is prepared by cleaning a smooth-surfaced aluminum sheet, for example with trisodium phosphate followed by treatment with nitric acid solution and rinsing in water. The sheet is then treated with an aqueous silicate solution and washed clean of any remaining water-soluble materials. An initially water-soluble light-sensitive diazo resin, e.g., a p-diazodiphenylamine-formaldehyde resin, is then coated over the silicate treated surface.

The continuous web of presensitized plate is then flow coated by passing it (sensitized surface outward) around a roller partially immersed in the coating solution at a web speed of about 1.5 feet per minute. The temperature of the coating solution in the tank is maintained at room temperature. A dry coating weight of about 50 mg./ft.^{2} is applied, the exact coating weight applied being determined by the speed of the web, the temperature of the room and viscosity of the coating solution.

The thus coated web, coated side uppermost, is then air dried, the web being passed alongside a vented hood. At normal room temperature the overcoating dries within a very few minutes to its permanently organophilic water-insoluble character.

The web so prepared is then die-cut to standard plate sizes and packaged in light-proof containers in which they are forwarded to customers. The entire operation is conducted under subdued light.

The customer in using the plate removes the same from its package, under subdued light, and then exposes the plate to actinic light through a photographic negative or a stencil. No particular care need be exercised in handling the plate. It matters not, for example if finger prints and/or moisture droplets inadvertently occur on the surface of the yet sensitized plate. If such do occur, the plate simply is wiped clean and processing resumed.

The plate may be exposed in the manner described in the aforesaid Jewett and Case Patent No. 2,714,066. For example, exposure of the plate to a 35 ampere carbon arc at a distance of about 24 inches for a time of from 1 to 2 minutes provides suitable exposure for the light-sensitive diazo resin in the light-struck areas. By the exposure, the sensitizer in the exposed areas is converted to a water-insoluble character. The physical properties of the resin overlayer in said exposed areas do not seem to change.

Following exposure, and still under subdued light, a solvent mixture of 2 parts isopropanol and 1 part water by volume is poured liberally onto the plate surface and spread uniformly thereover by wiping gently with a soft sponge or cloth mounted on a firm backing such as a wood block. After a few seconds a gentle rubbing action removes the polyvinyl-formal resin coating from the unexposed areas while virtually none is removed in the exposed areas. The area being worked should be wet at all times and it may be necessary to add additional solvent mixture. After the resin coating has been removed, which takes only a few seconds, the entire surface of the plate is then treated by wiping it thoroughly with an aqueous desensitizing and gumming solution, for example, a slightly acidified water solution of gum arabic. Thereby any diazo resin remaining in the non-image areas is removed and the underlying silicate treated aluminum surface in these areas is bared.

The image will be clearly visible on the plate, by virtue of the blue color imparted by the pigment, and clearly will contrast with the treated aluminum surface in the non-image areas. It is thus extremely easy to determine when the image is clearly and accurately brought out.

Without further treatment the plate is then mounted on a conventional offset lithographic press for printing.

When optimum adjustments have been made on the press so that the press is adjusted to the least pressure consistent with quality printing, over 200,000 line copies consistently have been produced with a single lithographic plate prepared as described in the present example. So little change and diminution of the image occurs that even a skilled printer can hardly tell the difference between the first few reproductions and the two hundred thousandth copy. Over 50,000 accurate reproductions of fine half-tone originals have been produced from a single plate.

Although the initial abrasion-resistant organophilic nature of the resin overlayer does not seem to change upon exposure of the plate, the resin overcoating nevertheless is bonded extremely well to the underlying in situ insolubilized sensitizer. This is further evidenced by the fact that when the image is being processed with a solvent solution for the resin layer, the resin layer breaks away cleanly and sharply at the line of demarcation between the image and non-image areas and is readily removed from the latter. Although I do not know with exactness just why this occurs, and without intending to be limited by any theories, I hypothesize that there is some physical and/or chemical interaction at the interface of the light-sensitive material and the resin overlayer which occurs when the light-sensitive material is exposed. Then when the solvent, which softens the overlayer, is applied it permeates the thin overlayer film and effectively undermines the overlayer in the non-image areas by the action of the solvent on the unexposed sensitizer.

It is preferable to incorporate a pigment or dye in the resin overlayer. Thereby the image is rendered visible to the eye as the background is removed during the processing. Further, I have found that the presence of a pigment seems to facilitate a clean sharp break at the line of demarcation between the image and non-image areas. Of course, the pigment employed must be such as to transmit the actinic light which must pass through the resin overlayer in order to strike the underlying light-sensitive resin materials. Ordinarily the amount of pigment employed with the resin is maintained at a level sufficient to provide a clear contrast between image and background when the sheet is processed. This amount is usually something less than about 50 percent by weight of the resin, 25 percent being preferred in the printing plates hereof.

In the preceding example, the coating weight of the pigmented polyvinylformal resin overlayer was about 50 mg./ft.^{2}. Although I prefer to maintain a coating weight of from about 50–70 mg./ft.^{2} when employing this overlayer composition, satisfactory plate structures can be prepared where the coating weight varies from about 10–120 mg./ft.^{2}. In general, thinner coatings tend to diminish somewhat the press life of the plate, while very heavy coatings may yield an inferior image structure. This latter effect arises from the fact that a very heavy film may not fracture sharply and clearly at the line of demarcation between the image and non-image areas yielding a distorted printing image. In printing line copies, the perfection of the image structure is not as important as when printing fine half-tones. Thus, particularly where extremely great press life is desired, it may be desirable to employ somewhat heavier coatings in printing operations involving the former than can be satisfactorily used in half-tone work. On the other hand, I have made successful plates in accordance with the present example where the coating weight of the polyvinylformal resin was as low as about 3.6 mg./ft.^{2} while yet providing significant improvement in press life over a corresponding plate wherein the diazo resin image is unreinforced.

Significantly, the thickness of a polyvinylformal resin coating having a weight of about 3–4 mg./ft.^{2} is in the order of only about one millionth of an inch, i.e., 0.001 mil. A rather heavy coating weight of 120 mg./ft.^{2} has a thickness in the order of about four one-hundred-thousandths of an inch, or 0.04 mil. Thus, in any event the resin overcoatings in the structures hereof are quite thin.

While the present example has illustrated the use of polyvinylformal as the resin overlayer, many other organophilic hydrophobic water-insoluble solvent-softenable organic resin compositions are also suitable. These include various vinyl polymers, such as polyvinylbutyral, polymethylmethacrylate, polystyrene, polyvinylchloride-acetate, polyvinyl acetate, polyethylene; epoxy resins; condensation polymers such as polyester resins exemplified by alkyd resins, polyamide resins, phenolaldehyde resins, urea-aldehyde resins; other polymers such as cel-

lulose acetate butyrate, polyalkylene-polysulfide resins, various organic silicon containing resins, etc. Various rubbery compounds such as Buna-N, Buna-S, neoprene and natural crepe are suitable. Natural occurring resinous materials such as shellac can also be used. Various compatible mixtures of the above mentioned and other similar and equivalent resin materials can be used.

The processing solutions to be used in processing the various sheet constructions hereof, after they have been exposed, should have certain characteristics. Preferably the processing solution exerts a slight but not vigorous solvent or swelling action on the overlayer composition, is an active solvent for the unreacted sensitizer, but has little or no effect on the light-reacted sensitizer. Ordinarily a mixture of two or more (preferably miscible) liquids is necessary to provide a processing solution having these desired characteristics. However, an operable processing solution can be found for any combination of sensitizer and resin overlayer employed, although some amount of rudimentary experimentation may be necessary. As a general rule, a suitable processing solution can be obtained by combining a first component which exerts at least a partial solvent or swelling action on the resin composition with a second component, miscible with the first, which is not a solvent for the resin composition, one of the two being a solvent for the unreacted sensitizer. Neither of the two liquids, nor the mixture thereof, should be a solvent for the light-reacted sensitizer. If the first solvent component is an active solvent for the overlayer resin, it should be diluted by the second component to an extent where its solvent action in combination in the mixture is not vigorous.

While suitable processing solutions can be obtained as just indicated, other processing solutions, which can be arrived at by judicious selection, may also be suitable. The isopropanol-water processing solution of Example I is such an instance, neither the water nor isopropanol by itself exerting any substantial solvent action on the polyvinylformal resin.

The following table will further illustrate the solvent from which various resin overcoating compositions are applied, and an appropriate processing solution therefor in a plate construction hereof containing the diazo resin of Example I. Where indicated in processing solutions, ratios are by volume.

Overcoating resin composition	Application solvent	Processing solution
Polyvinylchloride, Buna-N mixture (55:45) (Geon Polyblend 503, B. F. Goodrich).	Methyl ethyl ketone.	Water saturated with methyl ethyl ketone.
Polyvinylchloride-polyvinyl acetate copolymer (91% polyvinyl chloride) ("VAGH," Bakelite Corporation).	do	Acetonitrile-water, 2:1 ratio.
Polyamide resin (nylon) (Zytel 69, E. I. du Pont de Nemours & Co.).	Methanol	Isopropanol-water, 1:10 ratio.
Cellulose acetate butyrate (48% butyryl) (EAB-500-5, Tennessee Eastman Corp.).	Methyl ethyl ketone.	Ethanol-water, 1:2 ratio.
Polytrifluorochloroethylene-vinylidinefluoride copolmer ("Kel-F 800," Minnesota Mining & Mfg. Co.).	do	Acetone-water, 3:1 ratio.
Polychloropene ("Neoprene CG," E. I. du Pont de Nemours & Co.).	Ethylene chloride.	Water alone.
Polyvinylacetate ("AYAT," Bakelite Corporation).	Methyl ethyl ketone.	Isopropanol-water, 1:2 ratio.
Buna-N rubber ("Hycar OR-15," B. F. Goodrich & Co.).	do	Isopropanol-water, 2:1 ratio.
Polyvinylbutyral ("B-72A," Shawinigan Resins Corporation).	Methanol	Do.
Methyl, phenyl polysiloxane silicone resin (Dow-Corning Corporation "DC-840").	Toluene	Isopropanol-water, 1:1 ratio.
Epoxy resin reaction product of bis-phenol A and epichlorohydrin ("EKRD 2003," Bakelite Corporation).	Methyl ethyl ketone.	Acetone-water, 1:1 ratio.

While Example I is directed to a presensitized metal-backed printing plate, printing plates having backings other than metal can also be prepared in accordance with the present invention. The following example illustrates a paper-backed plate.

Example II

A light-sensitive resin, which is initially soluble in an organic solvent, is first prepared. An aqueous solution of the p-diazodiphenylamine-formaldehyde resin utilized in the plate structure of Example I, and described with specificity in Jewett and Case Patent No. 2,714,066 is added to a chemical equivalent, based on the resin content of the solution, of p-toluenesulfonic acid. By a reaction between the resin and the acid the p-toluenesulfonate salt of the resin is formed and oils out of the aqueous medium as a viscous tar-like resinous material. The reaction product is separated by decanting and washed with water. On standing, it dries to a glassy solid amber-colored state. It readily dissolves in methanol, but is only very slightly soluble in most other common organic solvents and in water. Upon exposure en masse to actinic light it becomes insoluble to methanol and turns slightly blue-green from its initial amber color. When exposed in thin films, the characteristic blue-green color is barely visible or in very thin films is not visible at all.

A 2 percent methanol solution of the light-sensitive resinous product just described is prepared.

A sample of 45 lb. vegetable parchment, available from the West Carrollton Parchment Company, of West Carrollton, Ohio, is sensitized with the previously formed light-sensitive resin solution by wiping the surface of the parchment with a cotton cloth saturated with the resin solution. The treated surface is then allowed to air-dry.

The thus sensitized surface of the parchment is then overcoated by coating the surface with the pigmented polyvinylformal-ethylene chloride solution described in Example I, at a dry coating weight of about 30 mg./ft.^{2}, the thickness of the overcoating being about 0.01 mil. The overcoating is then air dried. Upon exposure of the plate through a transparency as outlined in Example I, followed by processing with the isopropanol-water solution in the manner there described, an image results which is a clear, accurate and definite representation of the original. Upon being mounted on a lithographic press, it is found to print clean clear copies.

It will be seen that the light-sensitive material employed in Example II is of different character than the water-soluble light-sensitive resin employed in Example I. A particular advantage in the present invention resides in that virtually any initially soluble light-sensitive material, which insolubilizes upon exposure, can be employed in conjunction with the resin overcoatings hereof so long as the latter are capable of being coated on, i.e., not repelled by, the light-sensitive material. The in situ created adhesion between the light-sensitive layer and the resin overlayer, when the former is exposed and insolubilized, appears to occur largely irrespective of the particular type of light-sensitive material employed. Since the resin overlayer provides the printing surface, light-sensitive materials may now be employed in lithographic plates, even though in and of themselves, they inadequately provide a printing image. Stability of the sensitizer can be high so that the base sheet coated therewith is "presensitized," i.e., the sensitized sheet can be stored for substantial periods of time with the sensitizer remaining stably soluble and light-sensitive. The light-sensitive diazo resins described in the preceding examples are highly stable and serve as preferred sensitizers in the sheet constructions hereof.

It is noted that the various processing solutions noted for the various resin overlayer compositions in the preceding table can also be employed for those respective compositions in plate structures containing the sensitizer of the present example.

Although the previous examples have dealt with the lithographic printing art, the present invention has marked utility in fields diverse from the printing field. In many fields of endeavor it is desired to have some pictorial representation or message adhered on a backing sheet or plate. For example, in the preparation of labels, particularly metal labels, templates, registration tags, signs, etc. a message of some sort is applied to a backing. In so-called "printed circuits" a design, often complex and irregular, formed of conductive metal is adhered to a non-conductive backing. Returning momentarily to the printing field, in the preparation of photoengravings for use in letterpress printing, an image of an acid-resistant material must be adhered to the surface of the plate.

It has long been desired to utilize photographic techniques to bring out a message or pictorial representation on backing structures in the above-mentioned and other fields. However, this has been largely impractical heretofore because the light-sensitive materials which form the image or pictorial representation (the background for such image or representation where the resulting image is negative) have not had suitable physical characteristics for the conditions under which they would be used. By the present invention I am able to provide photographically an image area with any of widely diverse physical qualities appropriately selected with the particular end use in mind. The following examples illustrate a few of these, the next example illustrating the use of my invention in providing a novel "printed circuit" board.

Example III

The copper surface of a construction, consisting of a one mil layer of copper adhered to a non-conducting phenolic resin sheet, was cleaned with scouring powder. Said surface was then coated, by dip-coating techniques, with a diazo-p-toluenesulfonate sensitizer resin described in Example II. Upon air drying, a comparatively heavy diazo resin coating resulted which was clearly visible by its slight yellow tinge. Through dip coating, the light sensitized base was then overcoated at a dry weight of 150 mg./ft.^{2} with a 10 percent toluene solution of homopolymeric polystyrene, "Styron 666" available from the Dow Chemical Co. The coating was air dried. The board then was exposed through a suitable negative of the circuit layout desired. The resin surface was then wiped and lightly rubbed with a cloth wet with methanol, whereupon the resin overlayer and unreacted diazo sensitizer were removed from the non-image areas, the resin overlayer breaking away cleanly at the lines of demarcation between image and non-image areas.

When the resulting sheet was placed in a solution of 40% ferric chloride at 80° C., the copper etched away in the non-image areas from which the polystyrene coating had been removed. However, no undesirable etch of the copper in the image areas, protected by the polystyrene overcoating, occurred. The remaining copper was found to be patterned in the correct form of the original to serve as a printed circuit. On the other hand, when the polystyrene layer is omitted the diazo resin itself does not effectively resist etching in the image areas.

Polystyrene was chosen in the above example because of its insensitivity to water and acid. Similarly, a non-oxygenated resin such as polyvinylchloride or a rubber composition such as Buna-N or neoprene can be used. In other etch resist applications it might be desirable to use a fusible heat curing resin, such as an epoxy resin, which is cured before etching the plate. In employing a curable resin system care should be taken to select a system which will not undesirably degradate the light-sensitizer.

The next example illustrates the preparation of a metal-backed label in accordance with my invention.

Example IV

A coating composition was first prepared by dissolving

5 parts by weight of polyethylmethacrylate resin, available from the Du Pont Company as "Lucite 42," in 100 parts of methyl ethyl ketone following which 1.5 parts of a green phthalocyanine pigment (Du Pont "Monastral Fast Green G Powder") was milled into the solution. The composition was then coated over the diazo resin surface of a presensitized lithographic plate like that employed in Example I, prepared in accordance with Jewett and Case Patent No. 2,714,066. A dry coating weight of 135 mg./ft.^{2} provided good color depth. After the resin overlayer had been air dried the sheet was exposed to actinic light through a transparency of the desired message. The image was then processed with a solution of isopropanol-water (2:1 by volume) to yield a reverse green colored image having pleasant contrast with the aluminum. The image showed excellent durability to weathering.

Thus sheet constructions containing images of a wide variety of colors can be made, in accordance with the procedures hereof, by incorporation of suitably colored actinic-light transmittable pigments into the resin overlayer. Combinations of such pigments can be used, e.g., where a resulting black color is desired. It is to be noted that the exposure time may vary with the color and type of pigment selected. For example, somewhat longer exposure times may be required in the case of yellow and red than with other pigments.

My invention is also valuable in proofing color separation negatives preparatory to color lithography. In color printing, color separation negatives are prepared photographically in three or more colors. Each color separation negative is used to prepare a printing plate from which reproductions are printed in sequence using appropriately colored inks. In proofing the color separation negatives by conventional methods, it is necessary to prepare all of the printing plates, to set up the printing press for operation, and then actually to print all of the colors in the proper sequence and registration. All this is necessary to determine whether the original color separation negatives were true and accurate. Such conventional proofing procedures are extremely costly and time consuming. With each correction, one or more new plates has to be prepared and the entire operation repeated until the desired result is achieved.

In accordance with my invention, it is possible to complete the color proofing to a degree at least equal to that obtained by conventional proofing procedures without having to prepare a printing plate and without having to run a single reproduction. In so doing, I provide a light-sensitive transparent sheet construction in each of the colors to be printed. Each of the sheets is exposed through its respective color negative and then processed, by which the color in the non-image areas is removed. Respectively colored sheets result, each of which is appropriately colored in its image areas and colorless and transparent in the non-image areas. In proofing it is only necessary to superpose the resulting transparencies in registry on a white background, whereupon an accurate color proof of the original negatives results. The entire proofing procedure can be accomplished in a matter of a few minutes. Should a correction of one or more of the color negatives be desired, after viewing the composite proof, a corrected negative can be prepared, a new proof sheet of the negative exposed and processed and then the composite re-proofed. It is thus unnecessary to prepare the plates, to set up presses and actually to print reproductions until the correctness of the negatives has been verified.

In preparing light-sensitive sheet constructions for use in color-proofing, I employ a colorless transparent backing sheet for the light-sensitive layer and resin overcoating, which preferably is dimensionally stable. The overcoating in each sheet contains the same respective pigment, or equivalent thereof, as that contained in the printing ink. The amount of pigment contained per unit area is adjusted to provide the same color-density to be printed from the respective inks. Thus very accurate color proofs result. The following example illustrates the preparation of a color separation proof hereof.

Example V

In accordance with Palmquist Patent No. 2,786,778, a one mil thick film of biaxially-oriented polyethylene terephthalate ("Mylar") is vapor coated to provide thereon a thin, invisible hydrophilic treatment or layer of silicon monoxide. The silicon monoxide surface is then coated with the diazo resin solution described in Example II. The coating weight is quite light so that, upon exposure, no visible blue color will be imparted by the diazo so as to disturb the delicate color balance required in color proofing. Preferably, the amount of diazo applied is just under that which would impart a visible color effect upon exposure.

The diazo surface is then overcoated with a polyvinylformal containing a suitable transparent pigment, in a manner similar to that described in Example I. Since color is of primary importance the pigment loading will be most useful in the range of 30 to 50 percent of total solids in the overlayer. The coating weight required will be dependent upon the color density desired. For use in duplication of 3-color process printing reproductions, reflective optical densities measured through complementary color filters will be in the range of 1.0 to 1.5, and the respective coating weights will be adjusted to attain that range. A coating weight of 60 to 120 mg./ft.^{2} ordinarily is an optimum weight depending upon the specific desired color levels. Suitable pigments for use in each of the three color constructions are: cyan, e.g., "Monastral Fast Blue BC," available from the Du Pont Company; magenta, e.g., "Alkali Resistant Red RT-539-D," available from the Du Pont Company; and yellow, e.g., "Benzidine Yellow Dye D-2840," available from the Sherwin-Williams Company.

Since a transparent backing is employed on the light-sensitive sheet hereof a black backing is required behind the light-sensitive sheet during exposure in order to reduce halation in the exposed image.

In use, each of the three color sheets is exposed through its corresponding color separation negative. The sheet is then processed, as previously described, with a solution of isopropanol-water in a 2:1 ratio to remove the pigmented overlayer from the non-image areas to leave the latter clear and colorless. Thereby an image is defined which corresponds to the single color proof made by mounting the proper plate on a press and printing. When the three proofs are superposed in registry on a white background an accurate proof is obtained of the 3-color print which would result from forming printing plates of the negatives and printing from those plates.

Overlayers which are opaque, i.e., wherein the pigment in the overlayer is opaque, can also be used in structures hereof employing transparent backings. In such construction the sheet is exposed from the reverse side (through the transparent backing sheet). Such a construction is desirable, for example, in providing the black print for proofing 4-color process printing. Carbon black is a suitable opaque pigment in this construction.

A construction of the present example coating, opaque black pigment is also useful in preparing a positive transparency from a negative transparency or vice versa without necessity of employing the usual photographic film.

Although in the previous examples various specific organic hydrophobic organophilic water-insoluble solvent-softenable resin overlayers have been disclosed, it is to be understood that many of the compositions disclosed in the respective examples can be used in the constructions described in other examples. The selection of the appropriate overlayer composition will be governed primarily by the final properties desired of the image-areas, as respects the end use to which the exposed and processed sheet structure hereof will be put.

Herein, I have provided novel means for providing an accurate pictorial representation or message on a backing sheet, wherein the character of the pictorial representation or message, or the background thereof, can be widely varied to suit the particular end use desired of the product. Although the present invention has special significance in connection with metal-backed presensitized lithographic printing plates, it has wide and marked utility elsewhere. Herein my invention has been described with the aid of various illustrative examples. However, my intent is not to be limited thereby. Rather, I intend to be limited only by the disclosure taken as a whole, including the appended claims.

What I claim is:

1. A presensitized lithographic sheet comprising a base sheet, a soluble light-sensitive diazo resin sensitizer layer overlying at least one surface of said sheet in contact therewith, and over and in direct contact with said sensitizer layer a thin continuous hard durable abrasion-resistant and wear-resistant coating composed predominantly of an organophilic hydrophobic water-insoluble solvent-softenable resinous polymer, said coating having a thickness of at least about 0.001 mil and containing not more than about 50 percent by weight of pigment; said sensitizer layer upon exposure of the sheet to actinic light through a transparency reacting in the exposed areas and becoming insolubilized and firmly bonded to said surface of said base sheet; said abrasion-resistant and wear-resistant coating being isolated from bonding contact with said base sheet and being intimately associated with and adherently bonded to said sensitizer layer, and further remaining abrasion-resistant and water-insoluble upon subjection thereof to the products evolved by said sensitizer upon exposure of said sheet to actinic light, and being firmly bonded in said exposed areas, while being readily removable with unexposed sensitizer in areas not light-exposed.

2. The pre-sensitized sheet of claim 1 wherein said abrasion-resistant and wear-resistant coating is composed entirely of said resinous polymer.

3. A presensitized light-sensitive sheet construction comprising an aluminum sheet having a well-bonded treatment on one surface thereof, a soluble light-sensitive diazo resin material over and in contact with said surface treatment, and a thin continuous abrasion-resistant coating composed predominantly of water-insoluble polyvinylformal resin overlying and in contact with said diazo resin layer; said coating of polyvinylformal resin having a thickness of at least about 0.001 mil, being transparent to actinic light, containing not more than about 50 percent by weight of pigment, and being isolated from bonding contact with said aluminum sheet and being intimately associated with and adherently bonded to said diazo resin layer; said coating further remaining abrasion-resistant and water-insoluble upon subjection thereof to the products evolved by said diazo resin upon exposure of said sheet construction to actinic light, said treatment being characterized in that it causes an in situ light-reacted diazo resin firmly to bond to said aluminum sheet.

4. The construction of claim 3 wherein said coating of polyvinylformal resin contains a colored pigment which is transparent to actinic light, said pigment being present in an amount not exceeding about 25 percent by weight of said coating.

5. A plate suitable for use in planographic printing and related uses comprising an aluminum sheet having on at least one surface thereof an extremely thin layer of the reaction product of said aluminum sheet and an aqueous solution of an alkali metal silicate, providing a permanently hydrophilic surface, a thin coating of a water-soluble light-sensitive diazo resin over and in contact with said hydrophilic surface, and over and in contact with said diazo resin coating a thin continuous pigmented coating of water-insoluble polyvinylformal resin in an amount of from about 50-70 mg./ft.^{2}, the amount of pigment in said coating not exceeding about 25 percent by weight thereof; said diazo resin being characterized that, upon exposure of the plate to ultra-violet light through a transparency, it will react in the exposed portions to form an image of water-insoluble, hydrophobic and organophilic material which is tightly bonded to said permanently hydrophilic surface; said polyvinylformal resin coating being transparent to actinic light, being isolated from bonding contact with said aluminum sheet and being intimately associated with said diazo resin and adherently bonded thereto, and further remaining water-insoluble and organophilic upon subjection thereof to the products evolved by said diazo resin upon exposure of said plate to actinic light.

6. A presensitized lithographic plate comprising a metal base sheet, a soluble light-sensitive diazo resin sensitizer layer overlying at least one surface of said sheet in contact therewith, and over and in direct contact with said sensitizer layer a thin continuous hard durable abrasion-resistant and wear-resistant coating composed predominantly of an organophilic hydrophobic water-insoluble solvent-softenable resinous polymer, said coating having a thickness of at least about 0.001 mil, being transparent to actinic light and containing not more than about 50 percent by weight of pigment; said sensitizer layer upon exposure of the sheet to actinic light through a transparency reacting in the exposed areas and becoming insolubilized and firmly bonded to said surface of said base sheet; said abrasion-resistant and wear-resistant coating being isolated from bonding contact with said base sheet and being intimately associated with and adherently bonded to said sensitizer layer, and further remaining abrasion-resistant and water-insoluble upon subjection thereof to the products evolved by said sensitizer upon exposure of said plate to actinic light, and being firmly bonded in said exposed areas, while being readily removable with unexposed sensitizer in areas not light exposed.

7. A presensitized metal lithographic plate comprising an aluminum sheet having on at least one surface thereof an extremely thin layer of the reaction product of said aluminum sheet and an aqueous solution of an alkali metal silicate, providing a permanently hydrophilic surface, a thin coating of a water-soluble light-sensitive diazo resin over and in direct contact with said hydrophilic surface, and over and in contact with said diazo resin a thin continuous hard durable abrasion-resistant and wear-resistant coating of an organophilic hydrophobic water-insoluble solvent-softenable resinous polymer, said coating having a thickness of at least about 0.001 mil, being transparent to actinic light and containing not more than about 50 percent by weight of pigment; said diazo resin being characterized in that, upon exposure of the plate to ultraviolet light through a transparency, it will react in the exposed portions to form an image of water-insoluble material which is tightly bonded to said permanently hydrophilic surface; said abrasion-resistant and wear-resistant coating being transparent to actinic light, being isolated from bonding contact with said aluminum sheet and being intimately associated with said diazo resin and adherently bonded thereto, and further remaining abrasion-resistant water-insoluble and organophilic upon subjection thereof to the products evolved by said diazo resin upon exposure of said plate to actinic light, and being firmly bonded in said exposed areas, while being readily removable with unexposed sensitizer in areas not light-exposed.

8. A presensitized light-sensitive sheet construction comprising a base sheet, a light-sensitive diazo resin sensitizer layer overlying at least one surface of said sheet in contact therewith, and overlying said sensitizer layer in intimate association therewith an in situ formed thin

continuous abrasion-resistant coating composed predominantly of water-insoluble polyvinylformal resin, said coating having a thickness of at least about 0.001 mil, containing not more than about 50 percent by weight of pigment, and being isolated from bonding contact with said base sheet by said coating of diazo resin, said coating further remaining water-insoluble and organophilic upon subjection thereof to the products evolved by said sensitizer upon exposure of said sheet construction to actinic light; said diazo resin layer, upon exposure of the sheet to actinic light through a transparency, reacting in the exposed areas and becoming insolubilized and firmly bonding said resin coating to said base sheet, the portions of said resin coating in the areas not exposed to light being readily separable from the portions thereof in exposed areas and being removable with the remaining unexposed sensitizer upon mild rubbing with an aqueous solvent solution.

9. A presensitized light-sensitive sheet construction comprising a dimensionally-stable transparent and colorless base sheet, a stable soluble light-sensitive diazo resin sensitizer layer overlaying at least one surface of said sheet in contact therewith, said sensitizer layer, upon exposure of the sheet to actinic light through a transparency, reacting in the exposed areas and becoming insolubilized and permanently bonded to said surface of said base sheet and being transparent and essentially colorless in said areas, and said sensitizer having thereover and in

contact therewith a thin continuous abrasion-resistant coating of pigmented water-insoluble polyvinylformal resin, the amount of pigment in said coating not exceeding about 25 percent by weight thereof, said coating having a thickness of at least about 0.001 mil, and further remaining water-insoluble and organophilic upon subjection thereof to the products evolved by said diazo resin upon exposure of said sheet construction to actinic light.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,136,637 June 9, 1964

Gerald W. Larson

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 12, line 1, after "continuous" insert -- abrasion-resistant --.

Signed and sealed this 4th day of May 1965

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents