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J. L. CURTIN

3,682,633

COLOR PROOFING METHOD

Filed May 11, 1970

FIG. 1

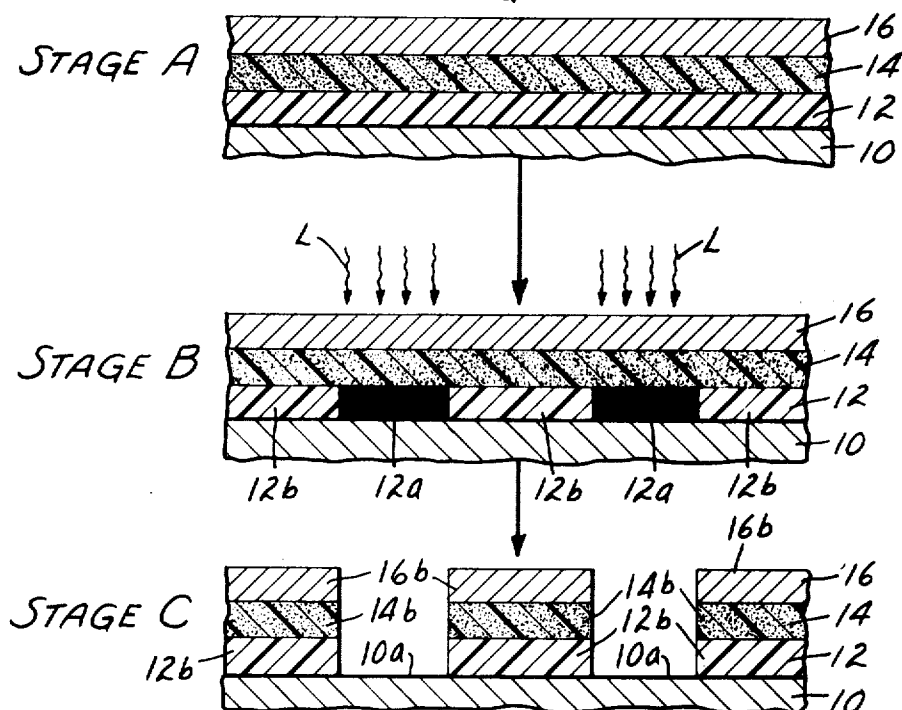


FIG. 2

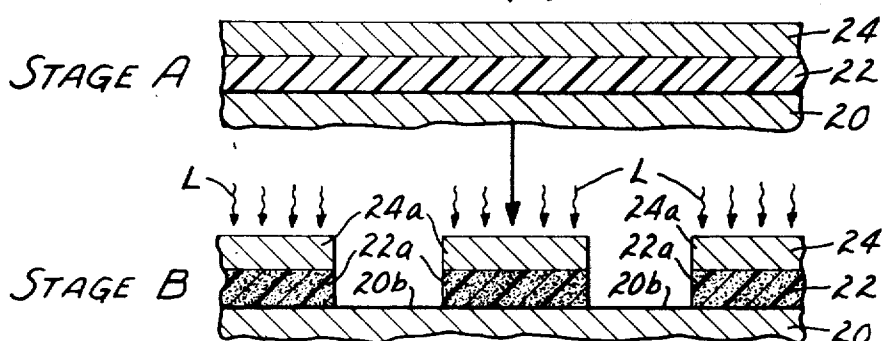
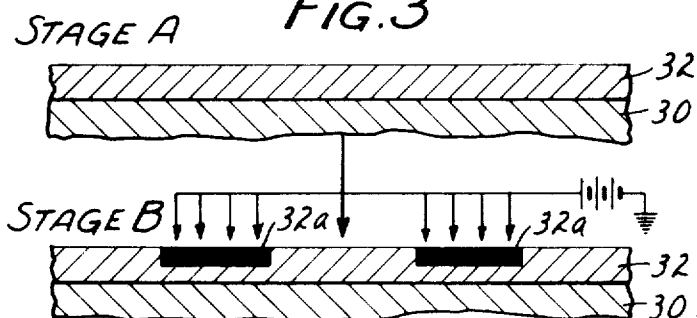


FIG. 3



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1

3,682,633

COLOR PROOFING METHOD

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Continuation-in-part of application Ser. No. 607,728, Jan. 6, 1967. This application May 11, 1970, Ser. No. 36,134

The portion of the term of the patent subsequent to May 12, 1987, has been disclaimed

Int. Cl. G03c 5/04; G03f 7/02; B41m 1/00

U.S. Cl. 96—27 8 Claims

ABSTRACT OF THE DISCLOSURE

A clear, transparent sheet suitable for accepting oleo-ink in image areas and rejecting oleo-ink in non-image areas without the need of dampeners, the non-image areas being a high adhesive layer having an adhesive release value of less than 100 grams/inch, the sheet being useful for color proofing wherein the oleo-ink to be used in the final printing job can be applied to the sheet for pre-press proofing purposes.

This application is a continuation-in-part of application Ser. No. 607,728, filed Jan. 6, 1967, now U.S. Patent 3,511,178.

This invention relates to planographic printing. It particularly concerns novel plates suitable for use in planographic printing, wherein need for conventional dampening with fountain solutions in the printing operation is obviated, so that the only liquid vehicle on the printing press is the conventional printing ink itself. The invention especially is directed to pre-sensitized printing plates of such character, to methods for forming and imaging planographic printing plates, and to methods of printing therefrom.

The basic types of printing in conventional use can be categorized as letter-press printing, gravure printing and planographic printing. In letter-press printing, the plate is provided with areas raised above the plate surface which define the image areas. An ink roller passes over the plate applying ink only to the raised areas, which is then transferred to the copy sheet by direct impression.

In gravure printing, the printing surface of the plate is provided with depressed areas defining the image. Ink is coated over the entire plate surface (both raised and depressed areas) and a doctor blade or wiper is passed over the surface to remove the ink from the raised areas. Ink is thus carried only by the depressed areas of the plate for direct transfer of the image to a copy sheet.

In planographic printing, as the term implies, both the image and non-image areas lie substantially in the same plane. The non-image areas are made ink-repellent so that when ink is applied by roller to the plate surface, only the image areas accept the ink for transfer to a copy sheet. Lithography is the best known form of planography, and has heretofore been the only known practical and successful process of planographic printing. It works on the theory that water and oil are immiscible. The non-image areas are made water-receptive (hydrophilic), and when water-wet they repel the oily ink. The image areas are ink-

2

receptive (organophilic) and water-repellent (hydrophobic). On the press the plate conventionally is first dampened with a fountain solution (which wets the background or non-image areas), after which ink is rolled over the plate. The ink coats the image areas, but is repelled from the dampened non-image areas.

In present times, most lithography is done by "offset," wherein the plate does not itself contact the copy, but instead contacts a rubber-like blanket cylinder during each revolution. The blanket receives the ink image and, in turn, revolves and transfers ("offsets") it to the copy sheet.

Planography, in the form of lithography, was well established as a separate branch of the printing industry in the early 1900's. Because of a number of advantages are realized by the planographic method of printing, lithographic printing has been a well recognized and widely accepted part of the printing art for many years. Despite numerous developments and improvements which have been made over the years, and notwithstanding difficulties inherent therein, lithography has retained its total reliance on the original concept that water which is coated over the non-image areas of a printing surface, being immiscible with oil, will reject an oil-based printing ink.

One of the difficulties inherent in having both ink and fountain or dampening solutions present is that the dampening solution applied to the plates flows back into the train of inking rollers on the press, during the course of the printing run, causing emulsification of the ink.

In addition to back flowing, the fountain solution also tends to flow forward over the offset cylinder, moistening the paper causing it to curl and change dimension. This creates special difficulties in securing accurate registration in color printing where the paper undergoes multiple trips through the presses. Comparatively high quality paper stock must be employed in lithography due to the action of the fountain solution on the cheaper letter press and new print papers.

Control of the delicate balance between ink and fountain solution, which is necessary to image fidelity and uniformity, is difficult to maintain, and must be constantly watched, especially as conditions change on the press during the course of a printing run. This is further complicated by the difficulty in maintaining the chemical consistency of the fountain solution on the press, especially in long press runs.

In an effort to minimize these problems, the proper formulation of fountain solution itself has become a highly complex and demanding art. Typically, a balanced mixture of acids, hydrophilic gums, metal salts, and water, frequently modified to accommodate specific requirements of ink, paper, and plate, the fountain solution in many cases determines the level of artistic and commercially acceptable quality which can be attained in lithographic printing.

While the source of the problems inherent in lithography has long been recognized in the art, in practical commercial printing the remedy heretofore has taken the form of attempts to reduce the amount of water needed, rather than its total elimination. Many worthwhile improvements in the lithographic art have had no other purpose than to reduce the amount of aqueous solution required to maintain the non-image areas in their vital ink-repellent condition. Some attempts have taken the form of eliminating water or fountain solutions as a separate material in the press as by combining it with inking (see

3

U.S. Patents Nos. 1,406,837, 1,817,522 and 2,090,704). Some have attempted to minimize problems associated with dampening by using mechanical dampening means other than rollers and fountain (see U.S. Patents Nos. 2,381,704 and 3,025,789).

During the more than half century in which lithography has been an established commercial form of printing, in which the desirability of eliminating the step of dampening the plate with water has been recognized, no one, insofar as I am aware, has provided a successful planographic printing plate having a printing surface with background areas that are ink-repellent without being pre-wet by an ink-immiscible liquid. The present invention provides for the first time a substantially simplified planographic printing process wherein need for all of the sophisticated dampening systems has been obviated. My invention is accomplished by the recognition of a new concept in ink repellency, which is unrelated to the property of liquid-oil immiscibility.

My approach to ink repellency is based on the properties involving adhesion. In general, my invention comprises a printing plate having a background surface area with a sufficiently low adhesion to the printing ink so that, without pre-wetting the plate, the ink that is applied to the plate in such areas will not split away and transfer from the inking rollers. That is, the adhesion of the ink to the inking roller and the cohesion forces between the ink particles are both greater than the adhesion between the ink and the said surface, and the ink will not transfer to said surface. This property of resisting adhesion is sometimes referred to hereafter as "abhesion," the relative character of such surface being defined in terms of its release value, as hereinafter discussed.

Referring now to the drawing, wherein several forms of my invention are illustrated preliminary to the detailed examples which follow—

FIG. 1 shows a preferred embodiment of my invention in the form of a negatively acting planographic plate, in broken-away edge view, at various stages from its pre-sensitized stage (as it exists in a light-proof package awaiting use), after exposure to light through a negative transparency, and following development of the image-preparatory to use thereof. Thus, under Stage A is shown a metal sheet 10, preferably of aluminum, overlying which is a stable light-sensitive layer 12, of such character that it is water insoluble and firmly bonded to the aluminum in its light-sensitive state, and upon exposure to light becomes broken down and capable of being readily washed or rubbed away from the metal surface. Overlying the light-sensitive material and firmly bonded thereto is an intermediate in situ formed anchoring layer 14, to which is firmly bonded the exterior highly adhesive layer or coating 16. Under Stage B is shown the structure at Stage A after it has been exposed to ultra-violet light through a stencil or negative transparency. During exposure, light passing through the transparent areas of the negative is projected through layers 16 and 14 (which pass actinic light) to light-react and decompose the light-sensitive material in areas 12a. Areas 12b remain shielded from light exposure by the opaque areas of the negative. Under Stage C is shown the structure at Stage B after the areas which were struck by light have been treated with a developing solution and physically rubbed away laying bare the underlying aluminum surface in areas 10a, and leaving the insoluble layers 12b, 14b and 16b, in the areas not light struck, the surface layer 16b forming the highly adhesive ink-repellent non-image areas of the plate. Areas 10a form the ink-receptive or image areas of the plate, corresponding with the transparent areas of the negative.

Interestingly, the surface of the aluminum base sheet, which forms the ink-receptive areas on my novel plate, has been utilized in the prior art lithographic printing plates as the hydrophilic background or non-ink-receiving areas (after being water dampened): see, for example,

4

Ito Patent No. 3,211,553, granted Oct. 12, 1965 on original application filed Oct. 31, 1960.

FIG. 2 shows another pre-sensitized planographic plate of the invention in broken-away edge view, at two stages.

Under Stage A is shown the plate in its pre-sensitized form ready for light exposure and use. A base sheet 20, for example an aluminum sheet having a surface treatment of silicate or equivalent, is overcoated with a soluble diazo light-sensitive resin 22, of such character that it becomes insolubilized, and firmly bonded to the treated metal surface upon being light exposed. Overlying the light-sensitive layer 22, is a coating of highly adhesive material 24. Under Stage B is shown the structure at Stage A after exposure thereof to actinic light through a positive transparency, followed by development of the plate, to remove the non-light struck sensitizer and overlying adhesive material, laying bare the silicate treated aluminum surface in areas 20b. The insolubilized diazo remains in the light struck areas 22a, retaining thereover and firmly bonded thereto the corresponding overlying adhesive material 24a.

Again, the surface defining the image area from which the plate prints, is the treated aluminum surface of the base sheet in the bared areas 20b, which has previously been characterized by its utilization as the non-ink receptive background areas (when wet) in plates of the prior art: see, for example, Jewett and Case Patent No. 2,714,066, granted July 26, 1955 on original application filed Dec. 6, 1950; also, Larson Patent No. 3,136,637, granted June 9, 1964 on original application filed Nov. 26, 1958.

FIG. 3 shows a different embodiment of my invention which does not depend upon photographic imaging techniques. Under Stage A is shown a base sheet 30 over which is coated and firmly bonded the highly adhesive layer 32. Under Stage B is the structure of Stage A after the same has been imaged in the areas 32a, for example, by electrical discharge techniques by which the surface of the adhesive material 32 in these areas is actually converted to an ink-receptive state.

While the thickness of the coatings or layers in the drawing are shown as being generally the same, actually this is not the case. The base sheet is generally much thicker than the coatings thereon, which are quite thin, ordinarily less than .001 inch. The drawing may indicate finite depressions where layers have been removed in certain areas, e.g., after development of the plates, actually the depression left is so slight as not to alter the planar character of the surface, in any practical sense.

Each of the structures illustrated, once it has been imaged, has the common characteristic of being capable of simply being placed on a printing press for printing without the use of any fountain solution or dampening system. Water is not required to create an ink-repellent background surface. When the inking rollers are rolled against the dry imaged plate, the ink does not split away from the rollers in the non-image areas, and will not transfer to the plate in those areas. The image areas do, however, accept the ink, and, accordingly, only the image areas will in turn transfer ink to the printing offset blanket thence to the copy paper.

Not only is a dampening system unnecessary, but such is detrimental, in that if dampened, the plate may then tone or scum in the background areas, and become "blinded" (so as not to print) in the image areas. This is contrary to the hitherto accepted thinking in the printing art, where it has been considered, for over half a century, that a commercially feasible planographic plate must provide a hydrophilic or water-receptive background surface which will (and must) first receive a thin coating of water in order to repel the ink in the background areas.

Having now generally described my invention, the same will be more specifically described with the aid of the following specific, but non-limiting examples.

EXAMPLE I

A web of 5-15 mil aluminum is chemically cleaned and superficially oxidized by several hours exposure to the atmosphere and is then continuously coated with a solution of light-sensitive material, constituted as follows (all operations being conducted under subdued light, such as yellow fluorescent light):

	Parts by weight
Light-sensitive diazonium salt of phosphotungstic acid and para diazo diphenylamine -----	4 10
Resinous copolymer of vinylidene chloride-acrylonitrile (available commercially as "Saran F-220") -----	1
Hydrochloric acid (concentrated) -----	.03
Monomethyl ether of ethylene glycol (available commercially as "Methyl Cellosolve" solvent) --	146.5

The light-sensitive diazonium salt is prepared in the following manner: In one vessel 1342 grams of para diazo diphenylamine sulphate are dissolved in 17 gallons of warm water (approximately 140° F.). This solution is then filtered to remove undissolved material.

In another vessel 4473 grams of 1:12 phosphotungstic acid is dissolved in 3.5 gallons of unheated water. This solution is then added with stirring to the diazo solution. A precipitate is formed, indicating formation of the insoluble complex diazonium salt of the diazo compound and the phosphotungstic acid. The reaction is allowed to go to completion, usually requiring about one hour. The precipitate is recovered by filtration in a filter press, the cake obtained being washed with water until the pH of the wash water becomes constant. The washed filter cake is then dispersed in isopropyl alcohol until the filter cake changes from its yellowish color to an orange color. The dispersion is then filtered, the filtered cake is recovered, and then dried in an oven at 90° F. for about 24 hours. The resultant diazonium salt is light-sensitive, and is insoluble in water and in most common organic solvents. It is one of the useful class of light-sensitive diazonium salts of poly-complex oxygenated anions of at least one metal selected from groups 5A and 6A of the periodic table, disclosed in Ito Pat. No. 3,211,553 aforesaid.

In preparing the light-sensitive coating solution, the "Saran F-220" resin is dissolved in the "Methyl Cellosolve," and to this solution is added the light-sensitive diazonium salt. The mixture is stirred until a fine suspension results, whereupon the hydrochloric acid is added to effect complete solution of the diazonium salt.

The resultant solution is stirred for about 15 minutes, and then is uniformly coated on the aluminum web at a dry coating weight of approximately 30 mg./ft.². The coated web is gradually heated (to avoid boiling of the solvent) over a period of about one minute to approximately 150° F. in an oven to evaporate the solvent. As the solution is coated, the phosphotungstic acid of the diazonium salt forms an inter-action product with the metal, promoting the bond between the metal and the light-sensitive material upon evaporation of the solvent.

An initially water-soluble light-sensitive diazo resin, viz., a p-diazo-diphenylamine-formaldehyde resin, is then coated by squeeze rolls from a solution of 20 parts methanol, 76 parts water, and 4 parts diazo resin, at a dry coating weight of one mg./ft.². Such a resin can be made as described in Jewett and Case Pat. No. 2,714,066, at column 7, line 3 et seq.

A further solution is prepared for coating onto the thus sensitized web by stirring 20 parts by weight of a silicone gum (a high molecular weight linear polysiloxane, such as is available commercially as "G.E. RTV 108"), in 80 parts of heptane, solution being readily effected at room temperature. The coating solution is applied by passing the web (sensitized surface outward) around a back-up roller positioned below a gravity feed extrusion coating head at a web speed of about 7 ft./min., the coating weight on a dry basis being 300 mg./ft.². The

thus coated web is air dried. The silicone gum coating is then cured and converted to a firm tough highly adhesive silicone elastomer, by heating for about 5-10 minutes at 200° F. in an oven situated in a room wherein the air at 72° F. is at a relative humidity in the range of 10-40 percent, preferably being maintained at 30% relative humidity.

The web is then passed through a further oven at 250° F. for about 10 minutes. During this step, wherein the bond of the cured adhesive coating is greatly improved, the second applied diazo immediately underlying the cured adhesive layer is decomposed and polymerized. It is believed that this in situ reaction is what promotes the strong bond (i.e., anchoring layer 14 of FIG. 1) by which the adhesive layer is firmly anchored to the underlying first applied light-sensitive material. The latter being more stable to heat, does not decompose during the heating, and remains light-sensitive. The sole purpose of the second applied diazo forming the in situ in solubilized anchoring layer is to promote the bond of the overlying adhesive layer; and while it can be omitted in the structure of the present example, its presence is greatly preferred.

The resulting plates, which have a shelf-life of weeks or months, can be converted into standard plate sizes, packed in suitable light-proof containers and shipped in commerce.

The above produced dry planographic plate is exposed through a photographic negative for about 2 to 4 minutes using a 35 ampere carbon arc at a distance of about 24 inches. Upon exposure, the diazonium salt of the phosphotungstic acid (layer 12 of FIG. 1) is degraded due to destruction of the light-sensitive groups, the phosphotungstic acid reverting or substantially reverting to its initially water-soluble character. Although the light-decomposed diazo portion of the degraded salt apparently is insoluble, it is believed to be in some way dispersed in the phosphotungstic acid portion of the degraded salt. In any event, following exposure, the light struck portions of the light-sensitive coating, and the adhesive coating overlying these portions, are readily removed upon lightly rubbing the plate with a cloth covered developing pad saturated with a developing solution, to bare the underlying aluminum surface in the light struck areas. The developing solution, in parts by volume, is composed of:

	Parts
n-Butyl acetate -----	2
n-Propyl alcohol -----	5
Water -----	1

The non-light struck areas remain following development. After being thoroughly rinsed with water and air dried, the plate is ready to be mounted on a press for printing without further processing.

A conventional lithographic press is used, with the exception that the entire dampening system is inactivated or removed. Using conventional lithographic ink, and with no dampening or other preparation or treatment of the plate, the press is started and the ink form rollers dropped to contact the plate. In the areas where aluminum has been bared, ink transfers from the form rollers to the dry aluminum surface, providing an ink image for transfer to the offset blanket. In the areas where adhesive coating remains, ink does not transfer from the ink form rollers, thus providing the background (non-image) area of the dry planographic plate.

Hand inking by rubbing with an ink pad may cause the background to appear to take some ink, and thus mislead the operator into thinking the plate is deficient. Application of the ink by rolling (as occurs on the press) will better demonstrate the actual character of the plate.

It will be observed, since the light-exposed areas of the plate of the present example are those removed during development, that the plate as ready for mounting on the press is still light-sensitive in the background areas.

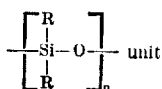
Interestingly, even though during the course of normal handling and printing this still light-sensitive material inevitably becomes light decomposed, this does not seem to present a breakdown problem when the plate is run on the press. Possibly this is due to the total absence of water on the press (which if present would tend to act as a solvent for the light-reacted sensitizer). The fact that the oily ink cannot wet these areas probably also contributes to this advantage, since it thereby cannot penetrate and solvate the underlying decomposed material.

Extremely faithful reproduction of the image areas occurs, even with the finest of half-tone originals. When optimum adjustments have been made on the press so that the press is adjusted to the least pressure consistently with quality printing, over 5,000 copies have been consistently produced with a single planographic plate prepared as described in this example.

Whereas almost all major advances in the planographic art have heretofore been restricted to lithography, it is unexpected that a construction as described above can find utility as a printing plate. It has been universally accepted by the printing art that a commercially feasible planographic plate must provide a hydrophilic background surface which will retain a thin coating of water in order to make it oleophobic. Contrary thereto, the adhesive coating of this example is hydrophobic and, accordingly, will not retain a water coating. Based on all prior teachings, such a construction would thus automatically be rejected as a planographic plate. Moreover, the plate must be used dry. Subjecting it to water or dampening solution on the press ruins the copy. The adhesive material scums (accepting some ink) and the image goes "blend" (refusing to take the ink), until the plate is dried.

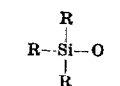
The high degree of adhesiveness required to function as an oleophobic ink repellent surface on my plate without being pre-water wet, has been found to be characteristic of cured, solid, rubbery organopolysiloxanes. These materials as a class are known as "silicone elastomers," formed from the cure or further polymerization of "silicone gums." The G.E. RTV 108 used in the present example is one of a number of commercially available filled silicone gum compositions having as a primary constituent a polysiloxane which, upon curing, under appropriate humidity conditions forms a silicone elastomer.

Depending on the curing mechanism to be used, specific silicone gums are prepared, all having the central, repeating linear.

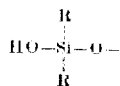


where n may be as small as 2 or as large as 20,000 or more, and where all R's in the chain may be the same, but need not be, each individual R being a monovalent alkyl or aryl group, halogenated alkyl or aryl group or cyano alkyl group, with not more than a few percent of total R being vinyl, phenyl or halogenated vinyl or phenyl, the major proportion of R usually being methyl groups.

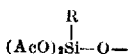
While an internal R may become a cross-linking site, depending somewhat on the curing mechanism, cross-linking more frequently involves the end groups which may be



or



or



where R has the same meaning as above, and where Ac is a saturated aliphatic monoacyl radical.

Silicone elastomers, formed by further polymerizing the gums just referred to, can be characterized generally as the very sparsely cross-linked (cured) dimethyl polysiloxanes of high molecular weight, e.g., 400,000-800,000 average molecular weight. The sparsity of cross-linking is indicated by R/Si ratios very close to 2, generally above 1.95, or even above 1.99, and generally below 2.1 or even below 2.01, there usually being 200-500 dimethyl units between cross-link sites. In contrast, the much more densely cross-linked silicone resins which are considered commercially useful fall in the range of R/Si ratios of 1.2-1.5.

The polymerizable silicone gums preferably are compounded with catalyst as necessary to promote cure, as generally known, also with fillers, e.g., silica fillers, to improve mechanical properties, it being necessary in the plate of Examples I and II (where a metal base sheet is employed) that the resulting adhesive layer be transmissive to the actinic light. Available commercial silicone gum compounds generally provide satisfactory adhesive layers on curing; and I prefer them for their superior mechanical properties which minimize problems of wear, both in physical handling and under the abrasive conditions on the press. It is not vitally necessary that the elastomer be filled. For example, silicone gum SE-76 (General Electric Co.), reported to have an average molecular weight of 400,000-500,000, is an example of an unfilled silicone gum which, after curing to an elastomer, provides a satisfactory adhesive surface.

In evaluating what materials are adequately adhesive, as measured by the characteristic of rejecting ink from an inking form roll, including silicone elastomers as well as other potentially adhesive materials, I have found adhesiveness to increase directly as release agent effectiveness increases. The effectiveness of a release agent surface is measured by a recognized test, by applying a piece of adhesive tape, such as surgical tape, to the surface and thereafter measuring the amount of force required to strip the adhesive tape from the surface.

In determining release values given herein, an "Instron," Model TM was employed, which operates at a crosshead speed of 12 inches per minute and chart speed of 2 inches per minute. One-inch Johnson & Johnson "Red Cross" brand waterproof adhesive tape was used, selecting only a roll having a retention force of about 450 grams (425-475) as measured at 80° F. on a 24-gauge, No. 4 finish stainless steel test panel. In determining either the retention force of the tape to be used or the release value of a sample, a ten-inch strip of tape is applied to a 6-inch by 1½ inch panel by passing a 4½ pound rubber-faced tape roller twice over the tape, using only the weight of the roller. The sample is immediately placed in the Instron and the force in grams necessary to strip the tape at an angle of 180° is determined.

The amount of force required to strip the tape is referred to as the "release value," and the larger the release value, the more adhesion there has been between the adhesive tape and the surface. A small release value indicates a very effective release coating and a large release value indicates a very ineffective release coating. Standard tests for release value as described in TAPPI (Technical Association for the Pulp and Paper Industry), vol. 43, No. 8, pp. 164A and 165A (August 1960) and TAPPI Routine Control Method (not a TAPPI standard) "RC-283 quality of Release Coatings," issued 1960, give results on the order of 300-700 gm./in. as satisfactory for removal of decalcomanias from paper and release values of 5-30 gm./in. as satisfactory for removing frozen foods, asphalt, sticky gums and other adhesive materials from paper.

The G.E. RTV 108 employed in Example I has a release value of 12 gm./in., and the SE 76, referred to above, has a value of 1 gm./in. Many silicone elastomer surfaces have been found to have a release value of only

1 gm./in., and none greater than 30 gm./in. These materials are adequately adhesive, rejecting ink from an inking form roll to serve as non-image background. Silicone resins, on the other hand, have release values in the range 250–550 gm./in., and are unsatisfactory as adhesive materials. Some non-silicone materials recognized as having utility as low adhesion backsizes for pressure-sensitive tapes, and polyethylene films, which are noted for the difficulty with which they are printed upon, have release values in the range 150–500 gm./in., and are generally unsuitable as non-image areas of my dry planographic plate. For quality printing an adhesive material should have a release value of 30 or less. Materials with release values up to about 100 have some utility as adhesive materials, those having a value in excess of 100 being unsatisfactory for even the poorest quality of duplicator copying.

The preceding example illustrates a presensitized dry planographic plate intended for exposure through a photographic negative. A further example of a presensitized dry planographic plate construction intended for exposure through a photographic positive follows.

EXAMPLE II

An adhesive coating solution is prepared by dissolving Dow Corning 780 Building Sealant (an uncured, filled, single component silicone elastomer material, having a release value after cure of 4 grams per inch) in VMP naphtha at room temperature to yield approximately a 20% solution by weight. Five percent (based on solids) of an oxidizing alkyd resin ("Duraplex D65A") is added to the mixture.

A phthalocyanine pigment, e.g., "Monastral Blue BT-284D" available commercially from the Du Pont Company, is then milled into the mixture on the basis of one part pigment by weight per 50 parts of total solids. The resulting pigmented mixture is transferred to an extrusion coating reservoir.

A continuously formed presensitized construction is then coated under subdued light, e.g., yellow light, with the coating composition previously prepared. The presensitized construction is manufactured continuously in accordance with the specific example of Jewett and Case Patent No. 2,714,066, granted July 26, 1955. Briefly, such structure is prepared by cleaning a smooth-surfaced aluminum sheet with, for example, 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 substantially clean of any remaining water-soluble materials. An initially water-soluble light-sensitive diazo resin, e.g., a p-diazo-diphenylamineformaldehyde resin, is then coated over the silicate treated surface. The web is extrusion coated with the adhesive material, in the same manner as in Example I, to a dry coating weight of 300 mg./ft.².

The thus coated web, coated side up, is then air dried and partially cured for about 20–30 minutes at 200° F. in the presence of moisture. Curing continues to completion without further application of heat.

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 positive.

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 silicone elastomer overlayer in the 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 essentially all of the silicone elastomer coating from the unexposed areas, while virtually none is removed in the exposed areas. Especially as a result of the in situ insolubilization of the sensitizer during light exposure the adhesive layer becomes firmly bonded thereto.

The delineated image will be clearly visible on the plate, by virtue of the blue color imparted to the non-image (exposed) areas by the pigment, providing a contrast with the silicated aluminum surface in the image (non-exposed) areas. The point at which the image is clearly and accurately brought out can thus be readily determined.

Following image development, the plate is thoroughly rinsed with water, air dried, and is then mounted on a conventional offset lithographic press for printing, with the dampening system removed or inactivated.

When optimum adjustments have been made on the press so that the press is adjusted to the least pressure consistent with quality printing, over 5,000 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 cannot tell the difference between the first few reproductions and the five-thousandth copy without difficulty.

In the preceding examples, the image is delineated photographically by light exposure through photographic transparencies in a manner well known to the photolithographic art. The plates of these examples are processed after exposure resulting in removal of that portion of the surface and photosensitizer which is exposed (Example I), or not exposed (Example II), to actinic radiation. The following example illustrates a construction imaged by electrical discharge.

EXAMPLE III

An iron oxide filled essentially linear polysiloxane silicone gum, G.E. RTV-60 Potting Compound, is thoroughly dispersed in an equal weight of VMP naphtha. Simple stirring for about an hour is usually sufficient, the red iron oxide filler providing an adequate visual determination as to complete dispersion. When dispersion is complete, 0.5% dibutyl tin dilaurate based on weight of the RTV-60 is added, and stirring continued for 10 minutes to assure thorough dispersion. Dibutyl tin dilaurate is available as "Thermolite-12" from M & T Chemical Corporation, Rahway, N.J. as a curing agent for RTV silicone gums. The thus prepared coating solution is used within 3 hours (preferably sooner).

At or shortly before the coating solution is ready, a backing web of kraft paper having a basic weight of 107 pounds (per 500 25" x 38" sheets), a thickness of .006 inch, one surface being smoothed by super calendering, is prepared. A primer solution of 10% tetrabutyl titanate (TBT) in heptane is applied to the smooth paper surface by roll coating. Dry coating weight of the primer is one mg./ft.², but the primer coating is only partially dried, about 15 minutes at room temperature, before the adhesive layer is applied.

The coating solution is then applied to the primed surface of the paper backing at a wet thickness of .002 inch, using a knife coater. The thus coated web is air dried with a 10 minute pass through an oven at 200° F. and collected on a curing rack so that the coated surface is untouched and available to free passage of air. The coated and racked web is placed in an oven for one

hour at 300° F., resulting in a cured adhesive coating of 1,000 mg./ft.².

The adhesive surfaced planographic plates of this example can be imaged by glow or corona discharge through suitable beam-exposure modifying means. For glow discharge imaging, the planographic plate is placed in a vacuum chamber, covered and in contact with an electron beam modifying mask. I prefer a simple metal foil mask with cut-out image areas which may consist of very finely detailed lines or screens. At a residual air pressure of 10-40 microns, a 10 milliamper 2-5 kv. glow discharge exposure of 2-10 seconds is sufficient to modify and convert the directly exposed adhesive surface to an organophilic nature, while the mask-shielded adhesive surface is not affected. The thus imaged planographic plate can be removed from the vacuum chamber and mounted on a conventional lithographic press, but in which the dampening system is disabled or removed, and used to print as many as 20,000 fine line or screen copies.

For corona discharge imaging I have found a wire discharge from an oscillating high frequency (850 kc.) Tesla Coil to be quite satisfactory, the planographic plate being attached and grounded to a rotating cylinder and the corona discharge wire arranged to traverse the axis of the cylinder. (In this manner, the full surface or any portion of the planographic plate can be scanned and imaged.) Any of the following three systems (and perhaps others) can be utilized.

(1) A master scanning unit, which "reads" the original to be duplicated can be employed to modify and control the corona beam. The discharge wire then traverses the planographic plate directly, no intermediate mask being necessary.

(2) A simpler corona discharge system can be employed, without need of a master scanning unit. A metal cut-out mask (e.g., the same as that used for glow discharge imaging) containing the desired negative image is interposed between the discharge wire and the planographic plate, the corona beam striking the plate through the open areas of the mask.

(3) The intermediate cut-out mask of system 2 above can be eliminated, and replaced by a conventional negative photographic transparency of the image, the beam passing through the transparent portions and being blocked by the opaque silver areas. This system has the virtue that a photographic negative is ordinarily more easily prepared than a metal mask. When this system is used, it is highly desirable to maintain a slight air gap of a few mils, as for example, by the insertion of a fine nylon woven screen, between the planographic plate and the photographic transparency. In connection with this imaging technique, I know of no prior art usage of a photographic transparency to modulate a corona discharge treatment. Regardless of which of the corona discharge techniques is employed, however, the imaged planographic plate is ready, without further treatment, to be mounted on a planographic press without dampening means for the printing of many thousand copies.

While I do not know by what mechanism surface modification takes place in the glow and corona discharge imaging described, I have found that the adhesive silicone elastomers having a release value up to about 30 grams/inch before treatment have a release value of 150-400 grams/inch in the imaged areas. This is sufficient to render the treated surface areas organophilic enough (when dry) to serve as ink-carrying image areas in my dry planographic printing system.

Depending on the specific requirements of their use, even simple mechanical means can be employed in preparing and imaging a dry planographic plate. For example, the sheet illustrated in FIG. 3 Stage A can be used as a dry planographic plate by simply removing the adhesive material for an image area, such as by an artist scribing free-hand or with the use of mechanical instruments. Mechanical systems can be electrically con-

trolled as by various facsimile equipment. The adhesive material can be overcoated in the image areas with an ink-receptive (when dry) material. It is also possible to apply the adhesive material directly to a base in non-image areas only as in an artist's work, followed only by a curing step in preparation for the press.

It will be observed that in the construction described, in each of Examples I and II, the adhesive layer is formed in situ over one or more underlying light-sensitive layers. In preparing this type of embodiment, care should be exercised in selecting a composition which can be cured in place without destroying the sensitivity of the light-sensitive material. RTV (Room Temperature Vulcanizing) silicone gum compositions are generally more suitable for the relatively mild curing conditions desirable with these constructions.

In Example III, the in situ formed adhesive layer does not overlie a light-sensitive layer. Thus, in this construction, the possibility of more drastic curing conditions allows a broader selection of elastomer-forming compositions. Even though the specific material chosen for Example III (G.E. RTV-60 Potting Compound, release value 1 gm./in.) would cure under moderate conditions, an excessive time would be required because of the thickness of coating applied, and, therefore, more aggressive chemical and thermal conditions were selected. Other essentially linear polysiloxane (silicone) gum compositions, requiring the addition of catalysts and/or a heat cure, which are suitable for the construction of Example III include Dow Corning Silastic 432 and G.E. SE-30, SE-52 and SE-76. Each of these materials, when cured, has a release value less than 30 gm./in. Curing temperatures as high as 500° F. can be used, but I find it generally satisfactory to use an hour or less at 300° F. Where the more drastic curing conditions are to be used, it may not be possible to use a paper base.

While coating weights in the adhesive layer ordinarily are not especially critical, sufficient thickness should be present to ensure a complete and thorough coverage and yield usable press life under the abrasive conditions encountered on the press. On the other hand, undue thickness may create difficulties in development of photographically imaged plates (this latter not being a factor in plates imaged otherwise, as in Example III). Uniformity of coating weight is rather important, so that a smooth planar surface is presented and flaws which might cradle or trap pockets of ink on the press (which would cause scumming) are minimized.

Photolithographic plates have been made almost exclusively on metal bases, usually zinc or aluminum, because of the need to convert background areas to a hydrophilic state. There being no such need in my dry planographic plates, the base may conveniently be chosen from metals, plastic films, such as polyesters, or papers. When using an adhesive material which is not adequately transparent (e.g., due to opacity created by fillers) it may be desirable to use a transparent base and perform the light exposure through the base.

A particularly useful construction is obtained when a transparent, colorless film, especially a plastic such as polyester, is used as the base for a presensitized dry planographic plate. In such an embodiment, the printing plate becomes a sheet suitable for use in color proofing. In the printing industry there are many specialized inks used as "corporate identification colors" or for special effects, such as flesh tones, metallic colors, fluorescent colors, etc. Whereas a variety of proofing systems are now available for most standard colors, these specialized colors cannot be adequately reproduced by the usual pigments or dyes of these proofing systems. Additionally, there is a real need to proof, not only the art and photographic work preceding plate making, but, even more critically, the actual ink which will be used for the printing job. Thus in proofing at job which involves a specialized ink it is necessary to prepare a press plate

for that color and actually print a press proof using the specialized ink. This special color press proof can then be combined with the proofing system sheets obtained without printing for the standard colors. Using a clear transparent sheet of my invention, a printing image can be prepared and inked with the specialized ink. This inked sheet can then be used as the proof for this color and combined with other proof sheets, either of the same or a conventional construction, for other colors to provide a complete proof.

In applying the printing images to my sheets for use in proofing, the transparency used for light exposure may be a separation transparency, when process color is being proofed, or a single color transparency, either half-tone for gradation or solid for spot color, when specialized colors are being proofed.

The present invention, involving the concept of adhesion and dry organophobic surfaces, with consequent elimination of dampening, removes a very important factor from consideration of papers and inks suitable for planography. This is of particular importance in the selection and requirements of inks. Compatibility with aqueous films, bleeding of pigments and dyes, water immiscibility of resins, varnishes, and solvents are no longer of concern. Thus, considerably more freedom is permitted in the selection or compounding of inks for dry planography.

The terms "dry lithography" and "dry planography" have occasionally been misapplied to the use of non-planographic plates on modified lithographic presses wherein dampening is not required because relief (non-planographic) printing plates are used. A modern example is the so-called "letterset" process, sometimes called "Shallow Etch" because the degree of relief is much less than required for letter-press printing (but paradoxically much greater than in the Deep Etch process, where the final printing plate is planographic and the lithographic process is used). I am aware of two categories of planographic printing wherein water is not used. In one, a dampening liquid other than water is used with a compatible non-miscible ink (see U.S. Pat. No. 3,167,005). For certain special purposes, such as requirements of a water-soluble or water-sensitive or water-setting ink, this system has definite advantages, but retains most, if not all, the disadvantages of conventional water dampening. The other category is "mercurial lithography." Insofar as I am aware, this never became commercial, but numerous patents did issue in the 1920's and 1930's concerning it: see U.S. Pats. Nos. 1,949,233 and 2,120,416.

What is claimed is as follows:

1. A color proofing process comprising exposing a colorless, transparent light sensitive sheet to a light image corresponding to the color to be proofed to provide a latent image, developing said latent image to provide image areas being oleophilic and oleo ink-receptive when dry, the non-image portions thereof being highly abhesive and oleo ink repellent when dry, and characterized by an

adhesive release value when dry of less than about 100 grams per inch, applying oleo-ink of the color to be proofed to said developed sheet in the absence of dampeners whereby said oleo-ink occupies said image areas and not said non-image areas.

2. The process of claim 1 wherein said non-image portions are cured, solid, essentially linear, elastomeric organopolysiloxane.

3. The process of claim 1 wherein said sheet prior to exposing comprises a base layer, a surface layer of a highly abhesive material which is oleo-ink repellent in the absence of dampeners and characterized by an adhesive release value when dry of less than about 100 grams per inch, and interposed between said base layer and said surface layer a light-sensitive material having one solubility state in relation to developing media before exposure to light and another solubility state in relation to developing media after exposure to light, and being soluble in one of said states and insoluble in its other state.

4. The process of claim 3 wherein said light-sensitive material is a light-sensitive diazo resin characterized in being water-soluble in its light-sensitive state, and becoming water-insoluble in its light-exposed state.

5. The process of claim 3 wherein said light-sensitive material is an insoluble light-sensitive poly-complex oxygenated anion diazonium salt characterized in that it is insoluble prior to light exposure, and upon light exposure is decomposed and readily washed away.

6. The process of claim 3 wherein said abhesive surface layer comprises a solid, cured, linear, elastomeric organopolysiloxane.

7. The process of claim 3 wherein said abhesive surface layer is a solid, cured, linear, elastomeric organopolysiloxane and said light-sensitive material is a light-sensitive diazo resin characterized in being water-soluble in its light-sensitive state, and becoming water-insoluble in its light-exposed state.

8. The process of claim 3 wherein said abhesive surface layer is a solid, cured, linear, elastomeric organopolysiloxane, said light-sensitive material is a light-sensitive diazo resin characterized in being water-insoluble in its light-sensitive state, and becoming water soluble in its light-exposed state, and in which an in situ formed decomposed diazo primer is interposed between the light-sensitive material and the overlying highly abhesive surface layer.

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DAVID KLEIN, Primary Examiner

U.S. Cl. X.R.

96—33; 101—450, 463

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,682,633

Dated August 8, 1972

Inventor(s) John L. Curtin

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 7, line 32 "blend" should read -- "blind" --.

Col. 11, line 59, "known" should read -- know --.

Col. 11, line 61, "adhesive" should read -- abhesive --.

Col. 12, line 74 "at" should read -- a --.

Signed and sealed this 6th day of February 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents