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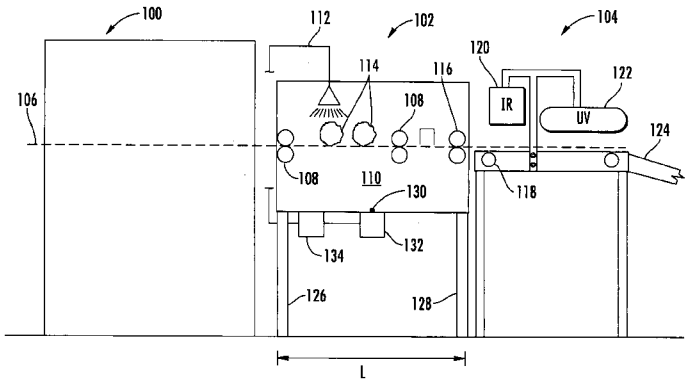

FIG. 1

(57) Abstract: A method for producing a lithographic plate from a negative working, radiation imageable plate having an oleophilic resin coating that reacts to radiation by cross linking and is non-ionically adhered to a hydrophilic substrate. The steps include imagewise radiation exposing the coating to produce an imaged plate having partially reacted image areas including unreacted coating material, and completely unreacted nonimage areas; developing the plate by removing only the unreacted, nonimage areas from the substrate while retaining unreacted material in the image areas; and subjecting the upper surface of the plate to blanket UV while the plate is at an temperature above ambient temperature, which further reacts the retained unreacted material in the image areas.

WO 2013/134395 A1

METHOD OF DEVELOPING A LITHOGRAPHIC PRINTING PLATE INCLUDING DUAL POST TREATMENT

Background

[0001] The present invention relates to lithographic printing plates

[0002] Plates of interest have a solvent-soluble, radiation-polymerizable, oleophilic resin coating on a hydrophilic substrate. In conventional practice, after image-wise exposure at ultraviolet (UV), visible (violet), or infrared (IR) wavelengths, the plates are developed with solvent to remove the unexposed areas of the coating by dissolution, thereby producing a substantially planographic pattern of oleophilic and hydrophilic areas. The developed plates are then ready for mounting on a cylinder of a printing press, where the plates are subjected to fountain fluid and ink for transfer of ink to a target surface according to the pattern of oleophilic and hydrophilic areas on the plate.

[0003] The imaging radiation produces a cross-linking reaction in the imaged areas, which increases the mechanical adhesion of the image areas to the grained surface of the substrate, and also increases the cohesion (hardening) of the image area so that it can withstand the abrasive effect of receiving and transferring ink during the production run on-press.

[0004] Thermally imageable plates are commercially available, which require no pre-heat step prior to development. These plates usually have relatively low resolution and short press lives. The main reason for this is that they need more imaging exposure energy in order to gain integrity for the image. When an image is created in this manner it causes the "dots" or pixels that form the image to gain surface area. This phenomenon is called "dot gain" and causes degradation in the resolution of the plate.

[0005] As an alternative, the plate can be exposed at lower imaging energy and then pre-heated before development, but "dot gain" still occurs. However, in this case it is the excess energy of the heater that is causes the "dot gain". This energy (in the form of heat) forces the polymerization to continue not only in the center of the dots (which is

needed for longer press life) but it also causes the dots to grow out from the edges.

[0006] Yet another alternative for increasing press life while maintaining acceptable resolution, is to "post cure" the plate after development. By applying energy after the non imaged area has been removed during development, "dot gain" cannot occur. At present, the most widely used method of producing plates of high resolution and long run length is by using a post development baking oven. With this method the plate is imaged at a moderate exposure level and then developed. The development not only removes the non image areas, but also dissolves unreacted ingredients in the image areas. After development the plate is run through a baking oven where it is heated to 450 deg. F and held there for one to two minutes.

[0007] This reacts any residual active ingredient and fuses the image areas. Although this produces an extremely long running image with good resolution, this procedure has two problems. By reacting and fusing the image to such a high degree, the dots shrink. Such "dot loss" causes unwanted sharpening of the image. Also, by heating the aluminum substrate to such a high temperature the plate is caused to warp and buckle, causing registration and lock up problems on press.

[0008] There are known advantages to imaging coatings sensitive to violet and ultra-violet (UV) energy. However, a major disadvantage of violet sensitive coatings is the very high sensitivity to low levels of ambient light, thus requiring more complex imaging and processing systems. Also, typical imaging equipment cannot generate high intensity beams, so preheating after imaging is necessary.

[0009] Regardless of how plate manufacturers and end users make this tradeoff, in conventional solvent based development of negative, actinically imageable lithographic plates, no substantial further cross-linking can be achieved in the image areas after development of the plate in the solvent. Any coating material in the image areas that did not react with the radiation, is dissolved and therefore removed from the image areas during the development step.

Summary

[0010] The present invention addresses and minimizes the necessity of such tradeoff. The disclosed method achieves the remarkable combination of significantly reducing the imaging time, increasing the resolution, and increasing the hardness and thus on-press life of the printable plate. The method produces a plate with high resolution, long press life, using low power imaging, and low energy post treatment.

[0011] This method is based on the combination of (i) a coating formulation that yields an image of high resolution when image-wise exposed one of more of IR, visible, or UV energy; (ii) a coating formulation that when exposed to such imaging would have sufficient image integrity to survive the development step with negligible loss of the active ingredients; (iii) a developer that would not leach out or destroy the active ingredients of the image areas; and (iv) a low power post treatment of combined thermal and UV energy to the surface of the plate to further react the active ingredients in the image areas.

[0012] In one aspect, the disclosure is directed to a method for producing a lithographic printing plate from a negative working, radiation imageable plate having an oleophilic resin coating material that reacts to radiation by cross linking and is non-ionically adhered to a hydrophilic substrate, comprising: imagewise radiation exposing the coating to produce an imaged plate having partially reacted image areas including unreacted coating material, and completely unreacted nonimage areas; developing the plate to remove only the unreacted, nonimage areas from the substrate while retaining unreacted material in the image areas; and blanket exposing the developed plate with an external source of UV energy while the plate is heated above ambient temperature, which further reacts the retained unreacted material in the image areas.

[0013] In another aspect, the disclosure is directed to a method for producing a lithographic plate from a negative working, radiation imageable plate having an oleophilic resin coating that reacts to radiation

by cross linking and is non-ionically adhered to a hydrophilic substrate, wherein no active ingredient that participates in a cross linking reaction is soluble in water, said method comprising: imagewise radiation exposing the coating to produce an imaged plate having partially reacted image areas including unreacted coating material, and completely unreacted nonimage areas; without pre-heat, developing the plate with brushes in an aqueous developer by substantially completely removing only the unreacted, nonimage areas from the substrate while retaining all the active ingredients in the image areas; and subjecting the upper surface of the plate to blanket UV while the plate is at an temperature above ambient temperature, which further reacts the retained unreacted material in the image areas.

[0014] These advantages are achieved by shifting a large fraction of the cross-linking, from the imaging step to the post-treating step. Because no nonimage coating material is on the substrate after development, while the imaged areas on the substrate contain a significant unreacted content, there is practically no limit to the intensity of energy that can be beneficially applied to the developed plate.

[0015] Preferably, the imaging radiation is slightly above the minimum level that provides sufficient cross-linking to prevent removal of the imaged areas during mechanical development. Post-treating is then relied on to maximize the cross-linking and thereby achieve improved plate life on-press. For example, conventional infrared (IR) imaging energy is about 125 mj/cm^2, after preheating at 102° C. For a commercial implementation of the present method, imaging can be achieved at up to three or more times the speed, i.e., in the range of about 80-40 mj/cm^2. The per cent of cross linking resulting from the post-heating and UV exposure can be greater than the per cent of cross linking from the imaging radiation.

[0016] Imaging at this much lower energy level has another advantage beyond increased production speed. Imaging at a relatively high but common resolution of 2400 dpi at 200 lines per inch requires that each "dot" or "pixel" of imaged coating have the desired area as imaged and that the surrounding unimaged material be cleaned out. The

use of the common energy level of 125 mj/cm^2, can produce dot gain in which coating material surrounding the nominal area of dot exposed to the radiation, experiences residual or ancillary cross-linking at the edge of the dot, thereby degrading the resolution. At less than 100 mj/cm^2, especially at 70 mj/cm^2, resolution degradation due to dot gain is negligible, if not avoided all together.

[0017] Whereas conventional negative working plates developed via solubilization or dispersion provide up to several hundred thousand impressions on-press, the plates manufactured according to the presently disclosed method easily achieve in excess of 500,000 impressions on-press. This combination of high resolution and high impression capability, permit the present method to compete with lithographic printing using positive working plates.

[0018] The present inventors have recognized the especially suitable applicability of mechanical development for implementing the present invention. Unlike with conventional chemical development, substantially all unreacted material remains in the image areas even after development is complete, so that post-heating produces additional, if not maximum, cross-linking. Development using only mechanical forces, is described in U.S. Pat. No. 8,137,897 "Processless Decelopment of Printing Plate" (the disclosure of which is hereby incorporated by reference). The mechanical development of imaged plates has numerous advantages over known techniques that rely on solubilization or dispersion for removal of the unimaged areas. These advantages include retention of the full integrity of the imaged areas, avoiding the handling of chemical waste product.

[0019] The plate is preferably developed by removing the nonimage areas from the substrate without dissolution or dispersion of any of the nonimage and image areas, but the advantages over previously known techniques are achievable in a practical implementation even if the coating experiences minor, incidental dissolution or dispersion.

[0020] Preferably the plate is developed by application of mechanical force on all the coating to mechanically dislodge only the

nonimage areas as particles from the substrate without dissolution or dispersion of any coating material, such that the integrity of the image areas remains intact. With this preference method, the nominal coating weight is retained in the image areas through completion of the blanket exposure.

[0021] The preferred plate as imaged comprises (i) a substrate with a grained, anodized, hydrophilic surface and (ii) a negative working, organic, polymerizable coating in which all active components for polymerization are not soluble or dispersible in water. In this context, "active" means an ingredient that participates in the radiation induced polymerization in the imaged areas. This generally means the active ingredients are a polymer, a monomer and/or oligomer, at least one polymerization or cross link initiator, and a dye.

[0022] Effective imaging produces no cross linking in the nonimage areas and as little as half of the ultimate cross linking in the image areas. Development removes at least 95 per cent and preferably at least 98 per cent of nonimage material on the plate, while retaining at least about 98 per cent of the initial coating weight in the image areas. Although in some embodiments a small degree of dissolution or dispersion of the binder or stabilizer might occur in image areas, none of the active ingredients in the image areas are dissolved or dispersed. For this reason, the post-treatment can produce the majority of the ultimate cross linking.

[0023] The combined advantages are that (i) plates can be imaged with low intensity radiation; (ii) pre-heating of the imaged plates can be avoided; (iii) development is with an aqueous fluid rather than a solvent; and (iv) low intensity of post-treatment blanket energy exposure produces maximum cross linking.

[0024] The present inventors have discovered that plates imaged with any actinic radiation can be developed without pre-heating and further cross linked in the image areas to achieve finished plates having higher resolution and greater durability than plates that are preheated before development. The disclosed method achieves the remarkable combination of significantly reducing the imaging time, increasing the

resolution, and increasing the integrity and thus on-press life of the printable plate.

[0025] With violet imaging at 40-60 $\mu J/cm^2$ (which is a practical range in the industry) only some of the material in the imaged areas of the PS coating is cross linked-- generally not enough for the subsequently developed plate to be effective as a printing plate. Post treatment of the same imaged plate with UV blanket exposure at 250 mJ/cm^2 after development, produces additional cross linking, and effective plates, but when combined with elevated temperature the UV exposure becomes much more effective.

[0026] This combination of imaging with violet radiation (in the range of 400-450 nm) and post treating with UV radiation (450-750 nm) is possible because the PS coating has a bandwidth of sensitivity outside of the peak or maximum. Thus, a coating formulated for maximum sensitivity to a particular wavelength of a violet imaging laser will have enough sensitivity to a relatively high total blanket exposure of a spectrum of UV wavelengths. Since all the unimaged coating material was removed from the substrate before the post-treatment, no such material remains to be subject to unwanted cross linking adjacent the desired image dots. Combined thermal and UV post-treatment is then relied on to maximize the cross-linking and thereby achieve improved plate life on-press.

Brief Description of the Drawings

[0027] Figure 1 is a schematic of one embodiment of a pre-press water processor

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Description of the Preferred Embodiments

[0028] Figure 1 is a schematic of the operative components of a representative system for implementing the invention, comprising an exposure unit 100, a developing wash out section 102 and a post treatment section 104. An imaged plate having partially cross-linked

image areas and non image (non-cross linked) areas follow process path 106 to upstream conveying rollers 108 and is thereby conveyed through a tank 110 where the plate is subjected to a developing solution or washout solution 112 and heavy brushes 114. The brushes remove the non-image areas from plate while the active ingredients for cross-linking remain intact in the image areas on the plate. The developed plate emerges at 106' from discharge rollers 116 for entering the post treatment station 104, onto an endless belt conveyor 118. The plate is guided at 106", under a heater 120 such as an IR lamp which dries and heats the plate. The plate is continuously conveyed under the immediately adjacent a UV lamp 122. The dual or combined post treatment further cross-links the image areas, thereby producing a finished plate that emerges onto ramp 124 for stacking.

[0029] Although the hardware for implementing the invention can take a variety of forms, it is represented in the figure as elevated on front and rear legs 126, 128 with room between the legs for components to circulate and filter the wash out solution 112. These are shown schematically as a drain conduit 130 leading to a pump 132 which is supported as beneath the tank. The pump delivers flow to a filter 134 which is likewise supported, with the filtered solution returned to spray bar 112 on line 136.

[0030] With the preferred coating of solvent soluble active ingredients for participating in the cross-linking, an aqueous developing fluid alone will not remove material to any significant degree. Rather, removal is entirely or substantially entirely due to the mechanical dislodging of non-imaged coating material by the brushes 114. However, any combination of brushes and developer solution that retains at least 95% of the coating weight of the image areas while removing at least 95% of the nonimage areas from the plate may be suitable, whereas retaining at least 98% of the coating weight of the image areas while removing at least 98% of the nonimage areas from the plate is preferable.

[0031] With IR imaging performed at a relatively low energy, e.g., below 100 mj/cm^2, mechanical development can clean out non-imaged

material to a level approaching 100%, because less than about 50% of the ultimate (post heat) cross linking can be performed during imaging. Even relatively coarse brushes with flushing water can remove unimaged material at the edges of the dots and, furthermore, there is little if any undesirable cross linking of coating material immediately surrounding the nominally exposed pixel due to avoidance of the dot gain effect.

[0032] In one particular embodiment the coating comprises from about 5 to about 30 wt% based on solids content, of a polymer that is generally considered by practitioners of applied chemistry, as insoluble in water. The polymer material may be selected from a wide range of types such as but not limited to acrylates (especially urethane acylates), siloxanes, and styrene maleic anhydrides.

[0033] Advantageously, the coating comprises from about 35 to about 75 wt% based on solids content, of a polymerizable monomer, a polymerizable oligomer, or combination thereof that is similarly insoluble in water. Some suitable radically polymerizable (cross linkable) materials are a multifunctional acrylate such as Sartomer 399 and Sartomer 295 commercially available from Sartomer Co.

[0034] The coating comprises a non-water-soluble initiator system capable of initiating a polymerization reaction upon exposure to imaging radiation. Some suitable initiator systems comprise a free radical generator such as a triazine or an onium salt.

[0035] The coating could include from about 5 to about 15 wt% based on solids content of an organic compound that is soluble in organic solvents and only partially soluble in water. Some suitable compounds include a substituted aromatic compound, such as DTTDA (an allyl amide derived from tartaric acid) and tetra methyl tartaramide. The water solubility must not be so great as to overcome the hardening of the imaged areas and compromise the ability of these areas to remain on the plate without loss of active ingredients.

[0036] Additional optional components include dyes that absorb the imaging radiation (e.g. infrared absorbing dyes) and pigments or dyes that serve as colorants in the coating.

[0037] There are many types of resins, oligomers and monomers that can be used to produce coatings that would have properties suitable for use in the present invention. It is believed that the monomer to polymer ratio in the range of 2-4 and the use of an organo-borate catalyst with an onium salt catalyst are important preferences. A wide mixture of functionalities can be used but dried coatings with better adhesion and cohesion are achieved with multi functional monomers and oligomers (functionality of 3 or higher). It is not necessary to use a resin which contains unsaturated groups but in the majority of the cases the cured film will exhibit better adhesion and integrity. Types of resins can include poly vinyls (poly vinyl acetate, poly vinyl butyral, etc), cellulosic, epoxies, acrylics and others as long as the resin does not produce a strong adhesive bond with the substrate. Monomers and oligomers should be somewhat viscous liquids and can be polyester/polyether, epoxy, urethane acrylates or methacrylates (such as polyether acrylate, polyester acrylate, modified epoxy acrylate, aliphatic urethane methacrylate, aliphatic urethane acrylate oligomers, polyester acrylate oligomers, aromatic urethane acrylate, dipentaerythritol pentaacrylate, pentaacrylate ester, etc.).

TABLE A

Radiation Sensitive Coatings

Formulations

Ingredients	#1	#2	#3
PGME	94.990	94.990	94.990
Poly 123	1.500	------	------
Bayhydrol 2280	-------	1.500	------
ACA Z250	-------	-------	1.500
Sartomer 399	1.750	1.500	2.000
Sartomer 454	0.250	0.250	------
Sartomer 355	-------	0.250	------
IRT thermal Dye	0.150	0.150	0.150
Penn Color	0.350	0.350	0.350
HOINPO2	0.400	0.350	0.050
Showa-Denko P3B	------	0.050	0.350
Phenothiazine	0.010	0.010	0.010
Showa-Denko 2074	0.600	0.600	0.600
TOTAL	100.00	100.00	100.00

[0038] Formulations #1-3 are consistent with the preferred implementation of the present invention, to the effect that a wide range of ingredients can be used in order to produce a lithographic printing that can be developed using only a mechanical force applied to the coating, without reliance on dissolution or dispersion of the coating in water.

[0039] All plates having coating formulations #1-3 are comprised of a substrate with a hydrophilic surface and a very oleophilic radiation sensitive layer, but the mode of development of coating formulations #1-3 relies strictly on the adhesive and cohesive properties of the coating. These coatings as applied and prior to imaging exposure have better cohesive strength than adhesive strength. When the coating is exposed to radiation it undergoes polymerization which greatly amplifies its adhesive and cohesive strengths.

[0040] The following list of representative ingredients will enable practitioners in this field to formulate coating compositions that are adapted to a meet targeted performance that balance cost of ingredients, coating process control, shelf life, range of imaging radiation wavelength, type or types of mechanical forces to be used for development, type of

fountain and ink on press, and ease of achieving target resolution. For commercial purposes additional, non-active water insoluble ingredients can be included such as viscosity agents for facilitating coating of the plate, shelf life stabilizers, and agents for reducing any tendency for removed coating particles to build up in, e.g., a water and rotary brush processor. In variations not shown in Table D, the solvent can be Arcosolve PM, DMF, and MEK; non-active stabilizers, pigments and the like can include Karenz PE1 and 29S1657 as well as the ACA Z 250. Urethane acrylate resins with active ingredients similar to formulation #2 and various water-insoluble inactive ingredients are presently preferred.

[0041] The currently favored prototype coating is shown in Table B.

TABLE B

COMPONENT	% BY WEIGHT
Arcosolv PM(1)	78.0347
DMF(1)	6.8159
MEK(1)	
1% Ciba Geigy UV-10 in DMF(2)	0.1900
Showa Denko P3B(3)	0.0650
HOINTPO2(4)	0.1500
IRT Thermal Dye(5)	0.1152
Secant/Rhodia 2074(6)	0.4116
40% SR-399 in PM(7)	07.2145
29S1657(8)	4.6132
Bayhydrol 2280(9)	2.3900
Total	100.0000
(1) Solvent	
(2) Stabilizer	
(3) Initiator	
(4) Initiator	
(5) IR absorbing dye	
(6) Initiator	
(7) Monomer	
(8) Pigment dispersion	
(9) Polymer Binder (Resin)	

[0042] Mechanical development is preferably achieved with relatively stiff, coarse, rotating brushes in an aqueous environment such as in the Agfa Azura wash out unit or the Proteck XPH 85 HD processor. Both machines use two relatively stiff, coarse brushes supported by a platen and have spray bars that deliver an aqueous wash out solution to the plate. The wash out solution is allowed to flow over the plate and then run back into the sump that is located below the machines. The solution is kept at about 70-100 deg. F in the sump. The basic wash out solution contains anionic surfactants, nonionic surfactants and silica. The components of the wash out solution should be selected to serve three

basic purposes. First, they help prevent the particles of coating that are removed by the brushes from sticking to each other or any surfaces that they encounter. Second, they serve as a finisher on the plates to protect against fingerprints and heat. Third, they increase the hydrophilicity of the substrate.

[0043] Mechanical development for plates IR imaged above 100 mj/cm^2 with brushes and this basic wash out solution will clean out up to about 97% or 98% of unimaged material, which is quite adequate for newspaper printing. However, if the plates are to be used for commercial or other high quality jobs, cleanout should approach 100% before post heating.

[0044] To achieve this level of cleanout, residual unimaged material at the base of the image dots can be removed by the action of one or two additional, non ionic surfactants that have high HLB values. As a practical matter, the surfactant molecule has one end that has an affinity to water and another end that has an affinity to the oleophilic coating, so the action of the brushes and water turbulence removes the residual coating as if by pulling it off the substrate (as distinguished from dissolving the residual coating).

[0045] Increased cleanout can also be achieved only with brushes and tap water if the brush impact duration is extended by decreasing the throughput rate.

[0046] If the coating includes a partially water soluble compound, the water penetrates the unimaged coating to the substrate whereby the coating separates from the substrate in particulate form with less mechanical action than in the preferred embodiment. As in all embodiments, the imaged areas have been exposed to sufficient energy to enhance the adhesion to the substrate and the internal cohesion and thereby resist removal during development. This enhancement in the image areas minimizes the penetration of water due to the presence of the partially water soluble compound. Even if some of the material in the image areas is lost during development, enough partially cross linked material remains such that the additional cross linking reactions during post heating provide the desired advantages.

[0047] Table C shows that over a wide range of IR imaging energy, the hardening of the imaged areas is predominantly dependent on the post heating energy. Even without the UV, one can obtain the advantage of imaging at a low energy/high speed (e.g. 40 to 80- mj), while easily achieving higher durability using post heat temperatures (e.g., 160 C) well above the practical pre-heat limit of 105 deg. C. The table shows that 40 mj imaging with 160 C post heat produces higher cross linking (50% vs. 40%) and much more plate life (1.76% vs. 5.08% color loss) than imaging at 200 mj without pre or post heat. The table also shows that initial radiation imaging at 40 mj or 80 mj, produces 16% and 24% cross linking, respectively. Post heating increases the cross linking to 50% and 52% respectively. As will be shown below, an even higher per cent cross linking can be achieved at a lower post-treatment temperature when combined with UV blanket exposure.

TABLE C

	IR IMAGING INTENSITY				
	200 mj	160 mj	120 mj	80 mj	40 mj
Post Heat @160 C					
% Color Loss	0.04	0.67	1.02	1.37	1.76
% Cross Linked	56	55	55	52	50
No Pre or Post Heat					
% Color Loss	5.08	6.76	9.23	13.93	31.72
% Cross Linked	40	40	35	24	16

The following tables demonstrate either the amount of double bond conversion and/or the resolution of the images when exposed to the various types and amounts of energies. In all examples, the plates were blanket exposed to imaging radiation, development was performed with rotating brushes in an aqueous wash out solution, as described above, and then post-treated.

TABLE D

IR Imaging With Mechanical Development
(Varied Post Exposure Treatments for % conversion)
(All exposures done at 130 mj)

Exposure only ---------- 36% conversion
Exposure + Pre Heat ---------- 44% conversion (+22%)
Exposure + UV Post Cure --------- 46% conversion (+28%)
Exposure + IR Post Cure ---------- 54% conversion (+50%)
Exposure + UV + IR Post Cure --- 66% conversion (+83%)

The numbers in parentheses show the per cent increase in double bond conversion with pre-heat or post treatment, relative to the conversion due to imaging exposure only. Whereas preheating improves the conversion by 22%, all the post-treatment techniques improve the conversion by at least 28% (with UV only) up to 83% (with a combination of UV on an IR heated). Stated differently, at least 20% and up to 45% of the final double bond conversion is achieved in the post-treatment. IR post-treatment alone achieves over 30% of the total conversion.

TABLE E

IR Imaging With Mechanically Development and UV+IR Post Cure
(Varied exposures for % conversion)

30 mj ---------- Exposure too low to obtain reading
50 mj ---------- Exposure too low to obtain reading
70 mj ---------- 66.5% conversion
90 mj ---------- 65.7% conversion
110 mj ---------- 68.3% conversion
130 mj ---------- 67.0% conversion
150 mj ---------- 65.3% conversion
170 mj ---------- 67.5% conversion
190 mj ---------- 68.0% conversion

TABLE F

IR Imaging with Mechanical Development and UV+IR Post Cure (Varied exposures for resolution measurements @ 175 lpi/2400dpi)

Exposure	1 pixel	2 pixel	3 pixel	4 pixel
30 mj	N/A	N/A	N/A	N/A
50 mj	N/A	N/A	N/A	N/A
70 mj	93%	61%	57%	55%
90 mj	97%	68%	60%	58%
110 mj	99%	75%	67%	60%
130 mj	100%	76%	68%	61%
150 mj	100%	78%	69%	62%
170 mj	100%	81%	73%	66%
190 mj	100%	99%	93%	90%

[0048] The following Examples were undertaken for plates having a coating sensitive to violet imaging, development with strong brushes and an aqueous solution, and UV post treatment.

[0049] O-Cl-HABI: 2.2'-bis (2-chlorophenyl)-4,4',5,5'-tetraphenyl 1,1'- biimidazole, CAS7189-82-4, available from Hampford Research, Stratford, CT.

[0050] Ethyl Michler's Ketone: 4,4 –Bis(diethylamino) benzophenone, CAS90-93-7, available from Signa-Aldrich, Milwaukee, WI.

[0051] N-Phenylglycine: CAS 103-01-5. available from Sigma-Aldrich, Milwaukee, WI.

[0052] Joncryl HPD 671: A high molecular weignt styrene acrylic resin available from BASF Corporation, Florham Park, NJ.

[0053] Binder A: A 33% by weight solution of acrylic resin in 2-butanone, supplie by ZA Chemicals, Wiesbaden, Germany.

[0054] Cyclomer Z250: A 45% by weight solution of acrylic resin in diprophylene glycol methyl ether, supplied by Cytec Surface Specialities Inc, Smyrna, GA.

[0055] BYK 344: A silicone surface additive supplied by BYK USA Inc., Wallingtford, CT.

[0056] 29S1657: A pigment dispersion comprising phthalocyanine blue 15-4, (59.5 parts), Cyclomer Z250, (87.8 parts), BYK344 (1 part), 1-methoxy-2propanol, (251.7 parts), prepared by Penn Color, Doylestown, PA.

[0057] SR399: Dispentaerythritol pentaacrylate, available from Sartomer, Exton, PA.

[0058] FST510: A preparation of >82% Diurethanedimethacrylate in 2-butanone, as supplied by AZ Chemicals, Weisbaden, Germany.

[0059] Selvol 107: A 10% by weight solution of polyvinylalcohol in water, as supplied by Sekisui America, Mount Laurel, NJ.

[0060] Selvol 205: A 21% by weight solution of polyvinylacohol in water, as supplied by Sekisui America, Mount Laurel, NJ.

[0061] Capstone FS-30: A 25% solution by weight of an ethoxylated nonionic fluorosurfactant in water, as supplied by DuPont, Wilmington, DE.

[0062] Substrate A: 0.012" x 12'x19' aluminum sheet that has been electro-grained, anodized and post-treated with sodium meta silicate.

[0063] Verti Wash: A non-solvent based processing fluid having a slightly alkaline pH, as supplied by Anocoil Corporation, Rockville, CT.

[0064] N200 developer: A conventional subtractive developer, as supplied by Anocoil Corporation, Rockville, CT.

[0065] NES Opal 850: A cleanout unit used to process and gum plates in a single step, as supplied by NES Worldwide Inc, Westfield, MA.

[0066] Protek XPH85: A conventional plate processor as supplied by Proteck, Sholinganallur, India.

[0067] ECRM Mako 4: A violet computer-to-plate setter as supplied by ECRM, Tewksbury, MA.

[0068] UV Light Frame: As supplied by Thiemer Gmbh, Birstein, Germany, using a THS3007 UV bulb for a time and intensity sufficient to produce radiation of 250 mJ/cm^2, measure using a photometer supplied by International Light of Newburyport, MA.

[0069] Polymerization test: A Prematek flat cloth, as supplied by CCP Industries, Cleveland, Ohio is impregnated with benzyl alcohol. The image on the plate is given 60 hard rubs. The plate is rated on a scale of 1 to 10. If the solvent does not attach the image, the plate receives a score of 10. If the image is completely removed by the solvent, the plate receives a score of 1. Generally plates receiving a score less than 7 do not print with good durability in real world situations.

Coating Solutions

Component	Coating A Amount (g)	Coating B Amount (g)
1-methoxy-2-propanol	261.58	261.58
2-butanone	175.00	165.54
Dimethylformamide	28.26	28.26
o-cl-HABI	0.81	0.81
Ethyl Michler's Ketone	1.20	1.20
N-phenylglycine	0.93	0.93
Joncryl HPD 671	4.66	
Binder A		14.12
29S1657	13.52	13.52
SR399	9.30	9.30
FST510	4.69	4.69
BYK344	0.05	0.05
Total	500.00	500.00

Topcoat A:

Component	Topcoat A Amount (g)
Selvol 107	122.50
Selvol 205	59.52
FS-30	1.00
Propan-2-ol	20.00
water	196.98

[0070] Coatings A and B were applied to Substrate A with a 0.0012" wire- wound bar. The resulting plates were dried in an oven at 90°C for 120 sec. The weight of the dry coating was approximately 1.0gm^{-2}.

[0071] Topcoat A was applied to both coatings A and B with a 0.008" wire-wound bar. The topcoat was dried for 120 sec at 90°C. The weight of the dry topcoat was approximately 0.80gm^{-2}.

[0072] The resulting plates were exposed with a test pattern using an ECRM Mako4 set to 100mW laser power (approximately 62 $\mu J/cm^2$ exposure on coating).

[0073] Example 1: After laser exposure, a plate comprising Coating A was processed through an NES Opal processing unit containing Verti wash at 72°F. The processing speed was set at 2 feet per minute. Any coating not addressed by the laser was easily removed by the wash and brushes to produce a high definition image. This plate received a score of 4 for the polymerization test.

[0074] Example 2: After laser exposure, a plate comprising Coating B was processed through an NES Opal processing unit containing Verti wash at 72°F. The processing speed was set at 2 feet per minute. Any coating not addressed by the laser was easily removed by the wash and brushes to produce a high definition image. This plate received a score of 2 for the polymerization test.

[0075] Example 3: After laser exposure, a plate comprising Coating A was processed through an NES Opal processing unit containing Verti wash at 72°F. The processing speed was set at 2 feet per minute. Any coating not addressed by the laser was easily removed by the wash and brushes to produce a high definition image. The plate was the subject to 250 mJ/cm^2 post development UV exposure. This plate received a score of 10 for the polymerization test.

[0076] Example 4: After laser exposure, a plate comprising Coating B was processed through a NES Opal processing unit containing Verti wash at 72°F. The processing speed was set at 2 feet per minute. Any coating not addressed by the laser was easily removed by the Verti wash and brushes to produce a high definition image. The plate was then subject to the 250 mJ/cm^2 post development UV exposure. This plate received a score of 10 for the polymerization test.

[0077] Comparative Example 5: After laser exposure, a plate comprising Coating A was pre-heated at 105°C for 40 seconds, then processed through a NES Opal processing unit containing Verti wash 72°F. The processing speed was set at 2 feet per minute. Any coating not addressed by the laser was easily removed by the wash and brushes

to produce a high definition image. This plate received a score of 7 for the polymerization test.

[0078] Comparative Example 6: After laser exposure, a plate comprising Coating A was pre-heated at 105°C for 40 seconds, then processed through a NES Opal processing unit containing Verti wash at 72°F. The processing speed was set at 2 feet per minute. Any coating not addressed by the laser was easily removed by the wash and brushes to produce a high definition image. The plate was then subject to the 250 mJ/cm^2 post development UV exposure. This plate received a score of 10 for the polymerization test.

[0079] Comparative Example 7: After laser exposure, a plate comprising Coating A was processed through a Protek XPH85 processor containing N200 developer at 78°F. The processing speed was set at 4 feet per minute. Any coating not addressed by the laser was easily removed by the developer to produce a high definition image. This plate received a score of 4 or the polymerization test.

[0080] Comparative Example 8: After laser exposure, a plate comprising Coating A was processed through a Protek XPH85 processor containing N200 developer at 78°F. The processing speed was set at 4 feet per minute. Any coating not addressed by the laser was easily removed by the developer to produce a high definition image. The plate was then subject to 250 mJ/cm^2 post development UV exposure. This plate received a score of 4 for the polymerization test.

[0081] Comparative Example 9: After laser exposure, a plate comprising Coating A was pre-heated at 105°C for 40 seconds, then processed through a Protek XPH85 processor containing N200 developer at 78°F. The processing speed was set at 4 feet per minute. Any coating not addressed by the laser was easily removed by the developer to produce a high definition image. This plate received a score of 6 for the polymerization test.

[0082] Comparative Example 10: After laser exposure, a plate comprising Coating A was pre-heated at 105°C for 40 seconds, then processed through a Protek XPH85 processor containing N200 developer at 78°F. The processing speed was set at 4 feet per minute.

Any coating not addressed by the laser was easily removed by the developer. The plate was then subject to the 250 mJ/cm^2 post development UV exposure. This plate received a score of 6 for the polymerization test.

[0083] Comparing Example 1 with Example 3: A UV post-development exposure clearly increased the polymerization and therefore the durability of the coating.

[0084] Comparing Example 2 with Example 4: A UV post-development exposure clearly increased the polymerization and therefore the durability of the coating.

[0085] Comparing Example 5 with Example 6: A UV post-development exposure clearly increased the polymerization and therefore the durability of the coating.

[0086] Comparing Example 3 with Example 6: A pre-heat step is unnecessary for satisfactory practice of the present invention. Conventional violet plates utilize a pre-heat step, which is an energy intensive process.

[0087] Comparing Example 7 with Example 8: When the plate is processed in strong chemical developer, the image becomes much less susceptible to post UV exposure.

[0088] Comparing Examples 1, 3, 9 and 10: When the plate is processed in a strong chemical developer, the image becomes much less susceptible to post UV exposure.

[0089] It should be appreciated that as used herein, "reactions" refer to cross linking. The invention can be practiced even if the coating resin is partially dissolved during development, as long as enough unreacted material remains so that the post treatment increases the cross linking The additional cross linking is achieved after all the unimaged coating areas have been removed from the substrate.

[0090] In the foregoing examples, the unimaged coating areas are removed in part by a chemical effect, such as dispersion or dissolution. The reason for this is that the Verti wash has a mildly alkaline pH. The binder resin is a highly carboxylated styrene/acrylic resin that is soluble at the pH of the Verti wash . When the coating is exposed the violet imaging

radiation, there is enough cross linking of the monomer to prevent dissolution of the imaged coating. The binder resin is not changed; it (and all the other components) are held in place by the matrix formed by the partially cross linked monomer. Since the binder resin is the only component that is alkali soluble (and it is being prevented from solubilizing due to the matrix formed by the partially cross linked monomer) all of the reactive ingredients remain to undergo further cross linking by the post exposure to violet radiation.

[0091] In a similar vein, the coating could have an adhesive promoter to help keep the coating on the substrate before imaging, and the wash could have a surfactant or similar agent for emulsifying the adhesive promoter and thereby helping the mechanical action of the brushes remove the unimaged areas during development. This is in essence, a modified mechanical development. Imaging enables the cross linking of the material in the image areas to become entangled with the rough surface of the substrate and thereby prevent the surfactant from undermining the integrity and active ingredients in the imaged areas. Any loss in coating weight was found to be no more than about one percent, i.e., at least 98% of coating weight is retained.

[0092] According to the present invention, the UV post treatment described above is enhanced by combining it with elevating the temperature of the surface of the plate. Table

TABLE G

Violet Imaging With Modified Mechanical Development
(Varied Post Exposure Treatments for % Conversion)
(All exposures were done at 40 micro joules)

Exposure only ---------- 66%
Exposure + Pre Heat ---------- 69% (+5%)
Exposure + Post UV Cure ---------- 70% (+6%)
Exposure + Post IR Cure ---------- 72% (+9%)
Exposure + Post UV&IR Cure ---------- 80% (+21%)

The numbers in parentheses in Table G show the per cent increase in double bond conversion with pre-heat or post treatment, relative to the

conversion due to imaging exposure only. The dual post treatment of violet imaged plates increases the conversion by at least 20%.

TABLE H

Performed under same conditions as in Table G on AGFA – N94 Violet Plate

Exposure only ---------- 60%
Exposure + Pre Heat ---------- 64%
Exposure + Post UV Cure---------- N/A*
Exposure + Post IR Cure ---------- N/A*
Exposure + Post UV&IR Cure --------- N/A*

The asterisk (*) in Table H indicates that none of the post energy tests could be performed because the N-94 plate lost 90% of its image when developed without a pre-heat treatment.

CLAIMS

1. A method for producing a lithographic printing plate from a negative working, radiation imageable plate having an oleophilic resin coating material that reacts to radiation by cross linking and is non-ionically adhered to a hydrophilic substrate, comprising:

imagewise radiation exposing the coating to produce an imaged plate having partially reacted image areas including unreacted coating material, and completely unreacted nonimage areas;

developing the plate to remove only the unreacted, nonimage areas from the substrate while retaining unreacted material in the image areas; and

blanket exposing the developed plate with an external source of UV energy while the plate is heated above ambient temperature, which further reacts the retained unreacted material in the image areas.

2. The method of claim 1, wherein the plate is developed by removing only the nonimage areas from the substrate without solubilization or dispersion of any of the material in the nonimage and image areas.

3. The method of claim 1, wherein the plate has a nominal coating weight before developing and the image areas substantially retain the nominal coating weight through completion of the blanket exposure.

4. The method of claim 1, wherein the plate is developed by application of mechanical force on all the coating to mechanically dislodge only the nonimage areas as particles from the substrate while the image areas remain intact.

5. The method of claim 1, wherein the blanket exposing at elevated temperature increases the cross linking by at least about 20% above the cross linking from the imaging radiation.

6. The method of claim 1, wherein at least about 30% of the total cross linking after said blanket exposure, was achieved during said blanket exposure at elevated temperature.

7. The method of claim 1, wherein developing removes at least 98% of the coating material in the unreacted, nonimage areas from the substrate while none of the coating material in the image areas is removed.

8. The method of claim 1, wherein the plate is developed in an aqueous wash including anionic surfactants, nonionic surfactants and silica.

9. The method of claim 1, wherein no ingredient in the coating that participates in cross linking is soluble in water.

10. The method of claim 9, wherein no ingredient in the coating is soluble in water.

11. The method of claim 1, wherein the coating is sensitive to infra-red radiation, the initial exposure is with infra-red radiation at an energy level in the range of 50-150 mj/cm2, and the blanket exposure is with thermal energy at a temperature above 120 deg. C.

12. The method of claim 11, wherein the plate is developed in an aqueous wash including anionic surfactants, nonionic surfactants and silica.

13. The method of claim 1, wherein the plate is imaged with violet radiation and the temperature of the plate during blanket exposure is above 120 deg. C, preferably above 140 deg. C.

14. The method of claim 13, wherein the plate is imaged with violet radiation within the range of about 40 - 65 $\mu J/cm^2$

15. The method of claim 1, wherein the UV blanket exposure is about 250 mJ/cm^2.

16. The method of claim 1, wherein after developing, the plate is conveyed under an IR lamp to elevate the plate temperature and while the temperature is elevated the plate is conveyed under a UV lamp.

17. The methods of claim 16, wherein the plate is conveyed continuously from under the IR lamp to under an immediately adjacent UV lamp.

18. A method for producing a printable lithographic plate from a negative working, radiation imageable plate having a hydrophilic substrate covered at an initial coating weight with an oleophilic resin coating material having active ingredients that react to radiation to produce cross linking, comprising:

imagewise radiation exposing the coating to produce an imaged plate having partially reacted image areas and completely unreacted nonimage areas;

without pre-heat, developing the imaged plate to remove at least 98 per cent of the nonimage areas from the substrate while retaining the image areas at a coating weight of at least about 98 per cent of the initial coating weight without loss of active ingredients; and

subjecting the upper surface of the plate to blanket UV while the plate is at an temperature above ambient temperature, which further reacts the retained unreacted material in the image areas.

19. The method of claim 18, wherein the elevated temperature is above about 120 deg. C., preferably above about 140 deg. C.

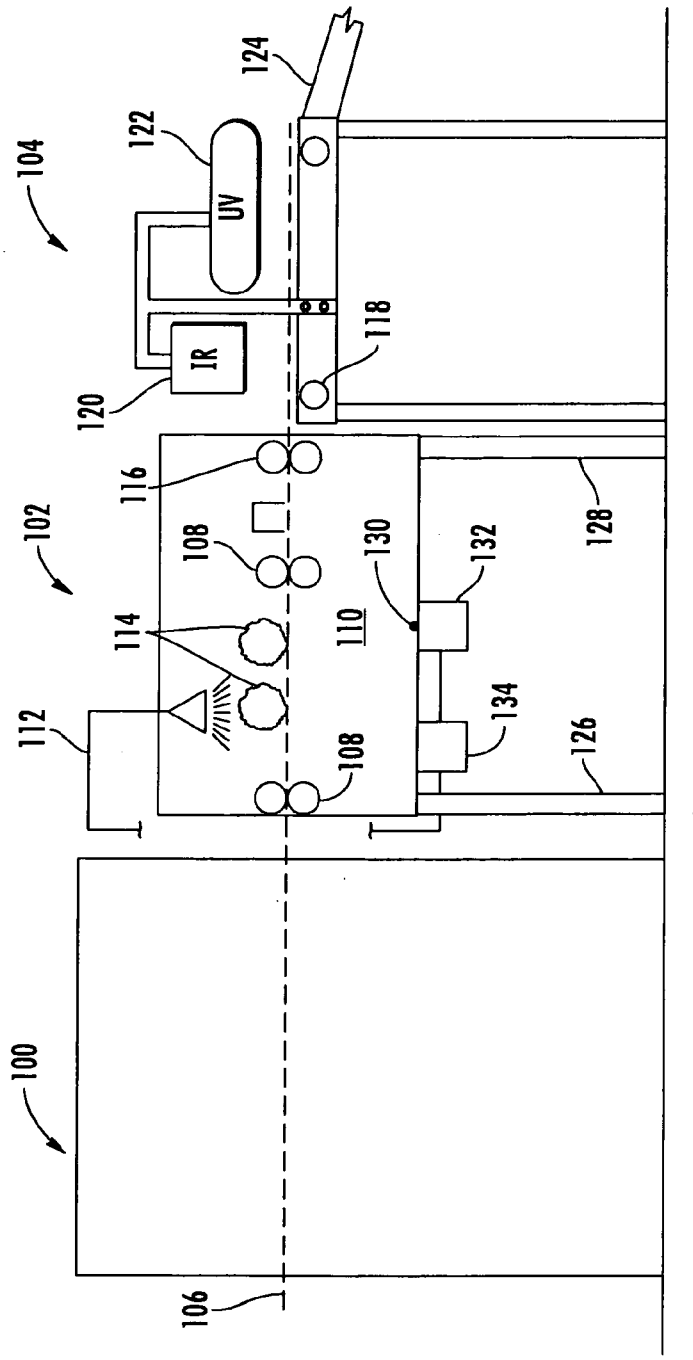
20. A method for producing a lithographic plate from a negative working, radiation imageable plate having an oleophilic resin coating that reacts to radiation by cross linking and is non-ionically adhered to a

hydrophilic substrate, wherein no active ingredient that participates in a cross linking reaction is soluble in water, said method comprising:

imagewise radiation exposing the coating to produce an imaged plate having partially reacted image areas including unreacted coating material, and completely unreacted nonimage areas;

without pre-heat, developing the plate with brushes in an aqueous developer by substantially completely removing only the unreacted, nonimage areas from the substrate while retaining all the active ingredients in the image areas; and

subjecting the upper surface of the plate to blanket UV while the plate is at an temperature above ambient temperature, which further reacts the retained unreacted material in the image areas.


124
122
UV
104
118
IR
120
116
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108
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132
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114
110
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126
100
106

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/029387

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - G03F 7/40 (2013.01)
USPC - 101/467
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - G03F 7/26, 7/26B, 7/26DO, 7/38, 7/40 (2013.01)
USPC - 101/456, 457, 463.1, 465, 466, 467; 430/302

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - G03F 7/26, 7/26B, 7/26DO, 7/38, 7/40 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patent, Google

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,091,287 A (DUSTIN) 25 February 1992 (25.02.1992) entire document	1-20
Y	US 2010/0212522 A1 (FROMSON et al) 26 August 2010 (26.08.2010) entire document	1-20
Y	US 5,223,041 A (CERNEY) 29 June 1993 (29.06.1993) entire document	1-20
Y	US 2010/0015556 A1 (BAUMANN et al) 21 January 2010 (21.01.2010) entire document	8, 12

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 April 2013	09 MAY 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)