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(54) **Printing plate for raised printing and method of making the same.**

(57) A printing plate formed by transferring a toned electrostatically formed image to a thin coating (10') of one reactive component of a two-part thermosetting epoxy resin system bonded to a sheet metal substrate (12). The toner includes the second reactive component of said epoxy system. The coating can include a heat softenable material and also can

include the hardener reactive component while the toner can be formed of the second or epoxy component either with or without a small amount of hardener. Heat (32) after transfer can be employed to complete polymerization of the two components.

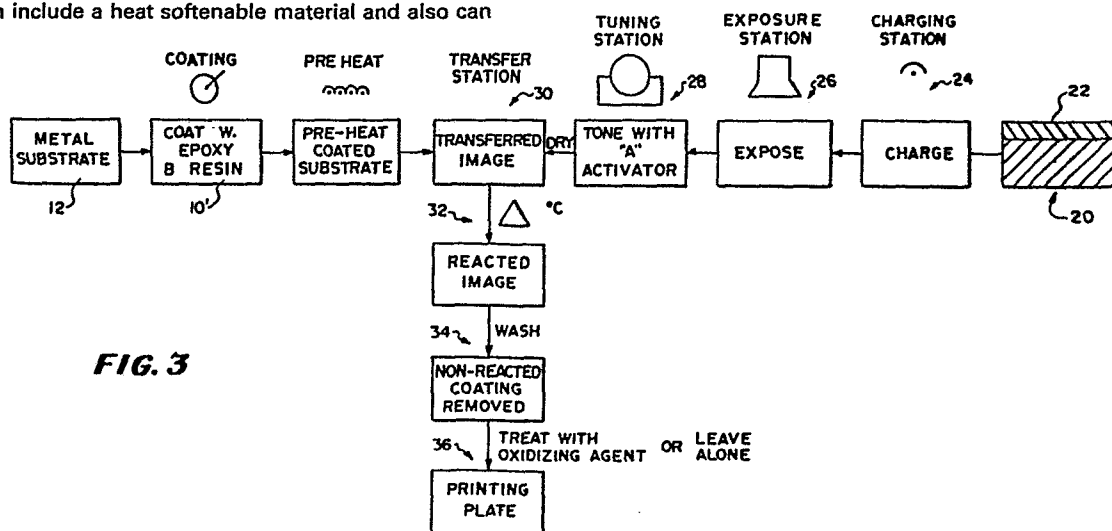


FIG. 3

The field of the invention comprises printing plates primarily for offset type printing and provides two component electrostatic methods of forming such a printing plate and the printing plate resulting therefrom.

5 One of the well-known type of printing plates available to the art is characterized by formation of a raised relief image on a substrate, usually formed of metal, the ink rollers touching only the raised areas with the inked image being transferred to the paper or similar
10 printing media. These printing methods are widely used for printing of reading matter such as price lists, directories, timetables, letterheads, announcements, books, newspapers, magazines, packaging, etc. Advantages of these printing plates include the capability readily to effect changes, direct
15 printing from raised or "embossed" surfaces, speed of operation and a resultant crisp, sharp printed image.

 Offset lithography has achieved rapid and expanding acceptance in the printing arts and generally uses a planographic method wherein the image areas and the
20 nonprinting areas are essentially on the same plane of the surface of substrate (primarily metal), the definition therebetween being effected chemically. Printing is effected from a planar surface which is neither raised or depressed. The lithographic process differs primarily from
25 the other processes in that it is based on the principle that grease and water do not mix and that the ink is offset first from the plate to a rubber blanket and then from the blanket to a print receiving medium, generally paper. The

image areas are oleophilic in nature while the nonprinting areas are hydrophilic (having an affinity for water). In the printing process, the printing plate surface is bathed in water which wets the hydrophilic parts of the surface but is repelled by the oleophobic parts. When the oily ink is applied to the plate by an ink roller or the like which engages over the entire surface of the plate, such ink is picked up and adhered to the oleophilic parts which have an affinity for such ink but the ink is repelled by the hydrophilic parts which carry the water so that no ink is deposited on the latter parts.

As will become apparent with the detailed description, the imaged parts on the printing plate of the invention normally will comprise toner that is adhered to the surface of the plate. It is feasible to make reverse images, however, in which case the image will comprise the parts which carry no toner. In the course of this description, the toned parts will be referred to as oleophilic or printing parts (areas) while the untuned parts or increments will be referred to as oleophobic or nonprinting parts (areas) rather than referring to them respectively as imaged and nonimaged.

The basic technique of lithographic printing is to cause ink to adhere to areas of a surface which is receptive to the ink while the remainder of the surface is bathed in water and does not accept ink and has been known for over a hundred years. Today it is practiced on high speed printing presses, but the technique is basically the same - the treated surface is bathed in water as an ink roller is applied thereto.

In modern lithography the imaging is done photographically upon flexible metal sheeting such as aluminum, stainless steel and the like which can withstand considerable rough handling and will wear well in a printing press. The sheeting is made up into rectangular plates punched with holes and/or slots on their ends to enable securement to the printing roller or rollers of a printing press and are flexible sufficiently to be accommodated on such printing roller. Plates suitable for so-called flat bed printing need not be very flexible.

There is universal use of these metal printing plates in lithography at the present time notwithstanding their shortcomings which are many, because, until the advent of the invention, there has been no practical alternative.

This invention seeks to overcome shortcomings and provide a wholly new type of sheet metal printing plate particularly for offset type printing which effectively opens a completely new field for high quality and economical printing.

Conventional printing plates based upon substrates of aluminum must be imaged photographically. They are carried through multiple step processes which involve applying an ultra-violet sensitive (diaz) coating to the aluminum surface after a prior treatment, exposing the coating through a negative by means of UV light, fixing the image onto the plate by means of chemical treatment, dissolving parts which were not exposed to the UV light by etchants to remove the coating at these parts down to

the aluminum surface. The etched surface of the lithographic plates readily lose its hydrophilic nature, hence, if the plate is removed from the press and stored or shipped it must be protected by treating the plate with gum arabic and various other materials to preserve the differential hydrophobic-hydrophilic character of the plate surface. The unexposed plate must be kept in darkness and the fixing of the image must also be carried out in darkness to prevent chemical changes which will ruin the plate and render it incapable of being used to acquire an image of varying density. Many corrosive and light-sensitive chemicals are required to handle the processing which places stringent specifications on the apparatus needed to achieve a lithographic plate.

Some of the most expensive processes to which conventional aluminum plates must be subjected, aside from their chemical treatments, are brush graining and anodizing. The brush graining is a roughening of the surface so that the photosensitive coating applied to the plate will adhere. The anodizing is to ensure that the aluminum surface will be hydrophilic after the plate has been made. Anodizing prevents degradation (corrosion and oxidation) of the aluminum surface.

When the conventional process of making a printing plate has been completed, the image is carried on the plate surface chemically and it is barely visible to the naked eye. Accordingly, in order to inspect the plate ink must be applied to it and a proof made. The plate then must be cleaned if it is to be handled again as for example in storing or shipping. It is very expensive and time consuming to proof directly upon the press.

If there are any errors in the plate, the conventional printing plate must be made all over again because the changes wrought by the imaging process and the chemical processing upon the UV sensitive coating are irreversible. It is not practical to attempt to remove the photosensitive coating from the aluminum surface and start all over again because these aluminum plates are normally sold in lightproof packages with the photosensitive material already coated thereon and it is not common for a printer of high quality graphics to have the equipment needed to apply the photosensitive coating.

One of the greatest of shortcomings of the conventional plate, i.e., one made using photographic technique, is that it is sensitive to light of a very narrow part of the spectrum. Regardless of the material which it is desired to print, such material must be converted into a projected ultraviolet image. The production of color in photolithographic technique is most difficult. Obtaining the needed color separations and working out the process so that the projected light for each color to be ultraviolet is timeconsuming, expensive and complicated. The range is narrow and exposure requires critical parameters of time and intensity to prevent overexposure or underexposure.

Electrostatic methods for formation and transfer of images to a substrate surface for later use as printing plates generally are known. These methods may involve formation of a latent charge image upon a charged photoconductive surface carried by a suitable substrate, developing the electrostatic latent charged image using particulate toner and fusing the toner to the photoconductive surface. Conversion of the nontoned areas from a normal

oleophilic property to a hydrophilic property is effected to produce a printing plate using the electrophotographic member as the "base". Of course, these members are expensive. Preferably, they should be used merely as image carriers and be reuseable if possible.

U.S. Patent 4,025,339 discloses and claims a novel photoconductive coating which comprises an inorganic, microcrystalline material that is produced by r.f. sputtering, the characteristics of which are set forth in said patent, reference being made thereto for details.

Accordingly the invention provides an electrophotographic method of making a printing plate comprising the steps of providing a metal sheet substrate, coating the metal sheet substrate with a thin layer bonded thereto and including one reactive component of a two-component thermosetting epoxy resin system forming a receptor, providing an electrophotographic medium having a photoconductive surface capable of accepting a rapid charge and retaining the same sufficient to enable toning, charging the surface of the photoconductive surface in darkness and exposing same to a light pattern forming a latent charge image of the pattern on the photoconductive surface, toning said latent charge image with a toner which includes as a part thereof the second reactive component of said two component thermosetting epoxy system to form a toner image, transferring said toner image to said receptor, interacting said two reactive components only at the imaged areas to form an infusible thermoset epoxy polymer to define printing parts and the unreacted areas forming the nonprinting parts and thereafter removing the unreacted areas.

The invention further provides a printing plate resulting from the practice of the method formed of a metal sheet having raised oleophillic image printing areas bonded to the surface of said metal sheet surface and nonprinting areas characterized in that said printing areas comprise a two-component epoxy polymer that is polymerized in situ.

The preferred embodiments of this invention now will be described, by way of example, with reference to the drawings accompanying this specification in which:

FIGURE 1 is a fragmentary sectional view on a greatly enlarged scale through a printing plate according to the invention;

FIGURE 2 is a fragmentary sectional view on a greatly enlarged scale through the coated metal substrate employed as the base for the printing plate according to the invention, and

FIGURE 3 is a diagrammatic view generally illustrating the process of producing the printing plate of the invention.

Briefly, there will be described the formation of a toner image receptor by coating of a sheet of thin metal such as aluminum, steel or other metal with a generally uniform, softenable thin coating including one component of a two-component thermosetting epoxy resin system. The photconductive coating of electrophotographic member such as described in U.S. Patent 4,025,339, is charged, exposed to a light image of the subject matter to be printed and then toned to render the latent charge image visible. The toner includes the other component of said two-component epoxy resin system.

The toner particles are attracted to the charged surface areas and adhere to these surfaces because of the electrostatic attraction between the charged areas and the fine toner particles. The toner image receptor is heated to tackify the coating sufficiently to hold the image defining toner particles. The temperature usually reached to make the coating tacky is about 40°C. The receptor then is brought into engagement with the toner image carrier and laminating the two, the toner image transferred to the coating and thereafter, same are separated, the toner image being retained on the softened coating. Little, if any, residue is left on the photoconductive coating. The electrophotographic member may be re-used. After separation of image receptor, further heating is effected, causing the two reactive components to interreact completing the formation of the thermosetting epoxy polymer but only at those locations where both components are present.

Only the imaged or printing areas will have both reactive components of said thermosetting resin/hardener epoxy system, and hence, when further heated, the polymerization of those image areas is permitted to reach completion. The remaining nonimaged (nonprinting) portion of the image receptor unable to polymerize due to the absence of the hardener and resin combination, is removed from the image receptor surface, as by washing, etc.

It is contemplated that a manufacturer can produce the metal substrate having the coating bonded thereto including the one component (the hardener) of the two-component thermosetting epoxy resin system. The purchaser of the coated sheets can be either the printer

or an intermediate processor who makes the printing plate from the coated sheet. It also is contemplated that the hardener component can be applied to the metal substrate just prior to bringing same together with the toner image carrier, say using relatively simple roller coaster apparatus, for example. A peelable protective sheet can be applied to the coated metal substrate and removed just prior to effecting the transfer process.

Generally, after heating, the raised polymer produced at the imaged area is oleophilic with the with the nonprinting parts comprising the surface of the metal substrate, the unreacted coating being removed.

Referring to the drawings, Figure 1 illustrates (in cross-section) a completed printing plate 10 that is based upon a substrate 12 of aluminum sheet. Other materials such as tin plated cold rolled steel and stainless steel also are suitable. The substrate has a thickness of 13 mils and is hardened by working and is dimensionally stable. The sheets can be easily punched or slotted along their edges so that they can be engaged upon pins or other projections that may be carried by a painting roller of a printing press. These punches or slots will retain their integrity even though the aluminum plate is subjected to considerable tension. Plates can even be clamped to rollers without using holes or slots or in the case of steel, held in plate magnetically. Preferably, the aluminum sheet is about 13 mils thick, the imaged or printing area comprising a thermosetting epoxy type polymer. One component here called the resin or A component is part of the toner employed and a second component called the B or hardener component is employed as the coating medium (FIGURE 2), generally with

a material that can be softened to a tacky state at an elevated temperature. 0104625

The B component preferably is coated as a thin layer coating 16 or film onto the one surface 18 of the aluminum sheeting substrate forming a bonded coating 2 to 5 microns thick on said surface. The bonded film coating is generally uniform and nontacky at room temperature. The B component can comprise a polyamide resin such as Versamid 115 (VERSAMID is a trademark of General Mills Chemicals, Inc., Minneapolis, Mn.). The B component, where coated on the metal substrate may include a carrier or binder resin in which the hardener is dispersed. Coating is performed employing accepted conventional coating technique and likely will be applied just prior to the transfer thereto of the toner image. It is also feasible to apply the B component to the aluminum substrate by coating using a simple roller or wiper just prior to use.

The A or epoxy resin component is included preferably as a component of the toner particles and can comprise an epoxy resin composition such as Epon 10007, EPON being a trademark of Shell Chemical Corp., Houston, Texas.

An example of a suitable two-component thermosetting epoxy resin system and the individual properties of each are set forth below.

"A"		"B"	
<u>EPON 1007 (EPOXY RESIN)</u>		<u>VERSAMID 115 (HARDENER)</u>	
25	Epoxy Equivalent wt.	1550-2000	Amine Value..... 210
	Hydroxyl Equivalent Wt....	200	Amine Equivalent Wt.. 250
	Average Molecular Wt.....	2625	Amine Equivalents
	Hydroxyl Functionality.....	13.0	Per 100 g..... 0.40
	Calculated Epoxies Per		Viscosity, poises
	Molecule.....	1.3-1.7	23°C.....Solid
	Melting Point.....	127,-133	40°C.....500-700
			Specific Gravity..... 0.99

An electrophotographic member 20 carries a photoconductive coating 22 bonded thereto. The photoconductive coating has charge acceptance and retention characteristics

that change with thickness as explained in some detail in the said U.S. Patent No. 4,025,339. The voltage achieved during charge and remaining after imaging is proportional to the thickness of the coating and should be chosen on the basis of the type of toner which is to be used. Since the voltages which are involved are substantially lower than those of photoconductive materials such as selenium and zinc oxide, toners which give good results at lower voltages are required to be used, but should be related to thickness of the coating and the voltages achieved. However, members whose photoconductive coatings comprise selenium or zinc oxide are nevertheless useful for the practice of the invention.

The electrophotographic member has a photoconductive coating which is very dense and resists abrasion; it has high photon quantum efficiency compared to known photoconductors; it is microcrystalline with all the crystals being oriented vertically relative to the substrate; it is electrically anisotropic with respect to its surface and provides extremely high resolution; the resistivity in darkness and during charge of the surface is of the order of 10^{20} ohms per square and it has a light resistivity which is substantially lower so that it can be discharged to practically zero charge and thereby will provide a wide grey scale range extending from practically zero density to almost maximum for black; it is wholly inorganic and hence not affected by moisture, temperature, fungus and the like and is flexible and transparent per se.

Photoconductive materials other than cadmium sulfide are taught in the said referenced patent, but the cadmium sulfide of the preferred electrophotographic member gives panchromaticity making this type of member superior

in producing printing plates for color reproductions, for example.

The "B" component coating 16 in a suitable binder resin is applied to the metal substrate 12 which has a thickness between about 2 and 5 microns; the printing plate 10 resulting therefrom is quite flexible. The coating 16 is nonblocking, quite coherent and will not crack, craze, chip or adhere to itself so that it may be stored in rolls subsequent to its manufacture, until intended for use to receive the toned image from the electrophotographic member. A protective sheet 15 is applied to shield the coating until peeled off just before use to expose the surface coating.

A modified embodiment of the subject process consists of the photoconductive surface of the electrophotographic member being charged by means of corona at station 24, this being the negative type since the photoconductive material is n-type material. Further, the charging can be effected through a liquid layer of isoparaffinic hydrocarbon which keeps the surface clean by preventing fog during toning. The charged surface then is exposed to a pattern of light as explained in the referenced patent at station 26, a latent image of the pattern resulting on the photoconductive surface in the form of charged and uncharged parts. After charging, the surface can be engaged by mechanical means in order to transport the plate without losing the latent image. The plate surface is then bathed in liquid toner at station 28, the toner particles being electroscopic but here including the hardener, B component, of the thermosetting epoxy resin/hardener system and which carry positive charges which are capable of discharging the electrons on the latent image carrying

surface, which combine therewith. Where there is no charge or there are no electrons, the particles are not attracted. As a result, the toner particles will adhere to the charged parts and will not adhere to the uncharged parts. The substrate may be connected to suitable polarity voltages to aid in the toning, if desired. When the toner has been applied, there result islands of toner and areas which are not toned.

The toning thus preferably is performed electrophoretically and thereafter, the resulting toner image is dried with the suspending medium being evaporated.

The metal substrate here carries a coating including the "A" (resin) component of the thermosetting epoxy resin/hardener system and is fed to a transfer station to which the electrophotographic member bearing the dry toner image is brought. The coated substrate preferably is preheated to 40°C just prior to reaching the transfer station, making the coating tacky.

The member 20 and the coated surface of the image receptor 10' are brought into engagement at the transfer station 30. The toner particles adhere to the tacky coating so that the toner image is transferred in its entirety to the coating surface 18.

The receptor carrying the coated surface and having the toner image adhered thereto is further heated, say by passing through a drying or heating station 32. Here the A and B components react chemically to form a cross-linked polymer solid only at the printing portions. The remaining B component of the coating at the nonprinting portions is unreacted and thus can be easily removed by

washing at station 34 with a suitable solvent such as isopropyl alcohol.

The epoxy resin part A can be compounded and processed to produce a concentrated mixture of micron-to-submicron size toner particles bearing a positive charge. The toner mixture is diluted with a nonpolar hydrocarbon liquid such as Isopar G to give a stable suspension suitable for imaging a negatively charged photoconductor.

A negative charge potential was applied to the photoconductive surface of the electrophotographic member of a corona generating device, exposed to an original document to produce a latent image which is made visible by development with the liquid suspension of the epoxy toner. The said wet image again is allowed to dry by evaporation of the fluid dispersant before transfer to the coated aluminum plate described below.

A brush-grained or etched aluminum plate was coated with a thin layer of an epoxy resin cross-linking (hardener) compound (Part B). The member containing the image is then brought into intimate contact with the coated aluminum plate. Pressure and heat then are applied simultaneously to the plate/member laminate using a heated roller. The purpose of the applied heat and pressure is to soften and thereby increase the tack of the hardener (Part B) to achieve complete transfer by encapsulation of the resin (Part A) and simultaneously allow penetration of Part A through the hardener (Part B) layer to the aluminum surface to accelerate the cure rate and conversion of the resin, and produce a strong adhesive bond of resin to the aluminum plate surface. The laminate then is separated and the

surfaces of the two sheets are scrubbed with a solvent to remove the excess hardener. The clean electrophotographic member thereby was available for immediate reuse (reimaging).

A similar related composition involves

- 5 compounding the epoxy resin (Part A) as described above except that in addition a calculated quantity of hardener (Part B) is incorporated by weight as an ingredient. The prescribed amount of Part B is determined insufficient to correspond to the number of active groups available for
10 cross-linking. This expedient would help to assure the subsequent penetration of the hardener into the bulk of the softened toner particles during the heating following the image transfer to the hardener coated metal sheet.

- Another example of the practice of the invention
15 involved the coating of a superficially roughened aluminum sheet of about 8 mil thickness with a solution of 5g. polyamide resin (Versamid 115) in 45g. cyclohexanone or isopropyl alcohol and dried to give a 1-4 μ thick layer. The preferred thickness is 2 μ .

- 20 The epoxy toner was prepared by adding 30g. epoxy resin (Epon 1007, m.p. 127-133°C, Shell Chemical Corp.) to 125 ml methyl acetate in a 400 ml beaker. The mixture was stirred with Cowles dissolver and heated to 60-65°C for 10 min., or until the epoxy resin is completely dissolved.
25 A solution of 4.0g dispersing agent (FOA-2, Dupont) in 200 ml Isopar was added to the resin solution under rapid stirring. After complete addition, the mixture is heated to 80°C for about 30 min. to boil off the methyl acetate. The mixture was cooled to about 30°C, treated with a mixture 7.0g Calco
30 SSB dye. CALCO is a trademark of American Cyanamid Co. and 1.4g zirconium octoate 18 percent solids (Witco Chemical Corp.) and reheated under a moderate rate of stirring to 80°C.

The mixture was cooled to ambient temperature under continuous stirring and strained through a paint filter to give a toner concentrate, that is, a stock solution, containing approximately 16.2 percent nonvolatiles. The
5 working concentration of the toner for use in imaging is prepared by diluting about 100g concentrate with 1 liter Isopar G.

The photoconductive coating is charged to an average surface voltage (ASV) of 25-30 volts with a corona
10 operated at -350 microamps and a charging rate of 4 inches per second. The plate was exposed for 15 sec. to an original document located at a distance of 5 feet from the charged electrophotographic member using a 100 watt tungsten lamp and a lens aperture of f8. The latent image was made
15 visible by developing with the resin hardener toner. The Isopar G dispersant liquid is evaporated to give a dry image. The coated aluminum sheet is superimposed face-to-face on the member carrying the toner image. A pressure of 40-50 pounds per linear inch is applied across
20 the entire area of the aluminum by use of a 1.5 inch diameter stainless steel roller, heated to a temperature in the range of 140-160°C and in one continuous, uniform pass. The resulting laminate is separated with the result that the toner image was on the aluminum substrate and well
25 adhered to the surface of said aluminum sheet. Any excess coating is then removed from the electrophotographic member and from the aluminum sheet by scrubbing with a cotton pad moistened with a solvent such as isopropyl alcohol.

The image defining polymerized epoxy resin
30 composition is a hard, infusible raised solid printing area on the metal substrate. The resulting printing plate can be used for printing directly after the nonreacted

coating portions are washed from the surface.

Other metals additional to aluminum and steel could be used as suitable substrates if capable of being manufactured in thin flexible sheets with economy. Such metals are titanium, nickel, nickel-chromium and the like.

WHAT WE CLAIM IS:

1. An electrophotographic method of making a printing plate comprising the steps of providing a metal sheet substrate, coating the metal sheet substrate with a thin layer bonded thereto and including the reactive component of a two-component thermosetting epoxy resin system forming a receptor, providing an electrophotographic medium having a photoconductive surface capable of accepting a rapid charge and retaining the same sufficient to enable toning, charging the surface of the photoconductive surface in darkness and exposing same to a light pattern forming a latent charge image of the pattern on the photoconductive surface, toning said latent charge image with a toner which includes as a part thereof the second reactive component of said two component thermosetting epoxy system to form a toner image, transferring said toner image to said receptor, interacting said two reactive components where present only at the imaged areas to form an infusible thermoset epoxy polymer to define printing parts and the unreacted areas forming the nonprinting parts and thereafter removing the unreacted areas.

2. The method according to claim 1 in which the said receptor is preheated to soften the coating prior to transfer of the toner image thereto.

3. The method according to claims 1 or 2 in which said receptor is heated subsequent to receipt of the toner image thereon whereby to effect the polymerization.

4. The method according to any one of claims 1, 2 or 3 wherein the toning is effected electrophoretically and the resulting toner image is dried before transfer.

5. The method according to any one of claims 1 to 4 in which the toner particles include the resin component and the receptor coating carries the hardener component.

6. The method according to any one of claims 1 to 4 in which the toner includes both the epoxy resin and a hardener component but in an amount insufficient to effect full cross-linking with the remaining amount of hardener carried by the receptor coating.

7. The method according to any one of claims 1 to 6 wherein the receptor substrate is formed of one of aluminum, cold rolled steel or stainless steel.

8. A printing plate resulting from the practice of the method according to any one of claims 1 to 7 formed of a metal sheet and raised oleophillic image printing areas bonded to the surface of said metal sheet surface and non-printing areas; said printing areas comprising a two-component epoxy polymer that is polymerized in situ.

9. The printing plate according to claim 8 in which said metal sheet is formed of one of aluminum, stainless steel or cold-rolled steel.

10. The printing plate according to claims 8 or 9 in which said metal sheet surface has roughened or brushed finish.

FIG. 1

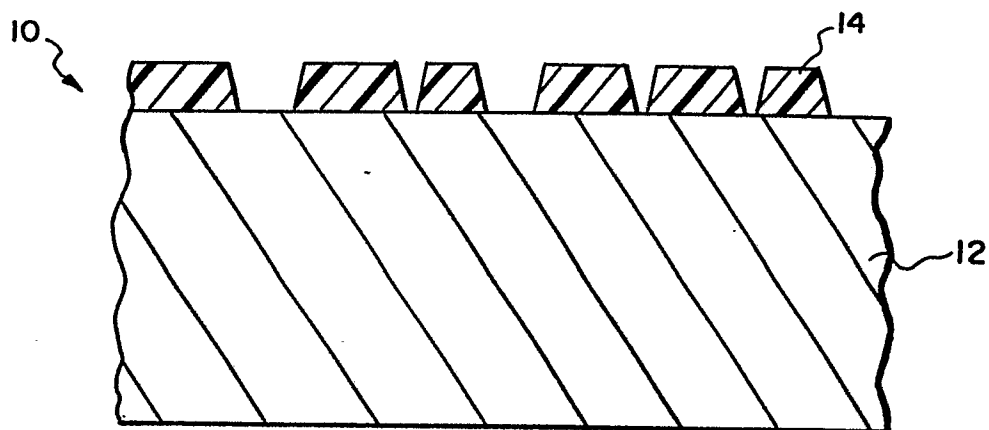


FIG. 2

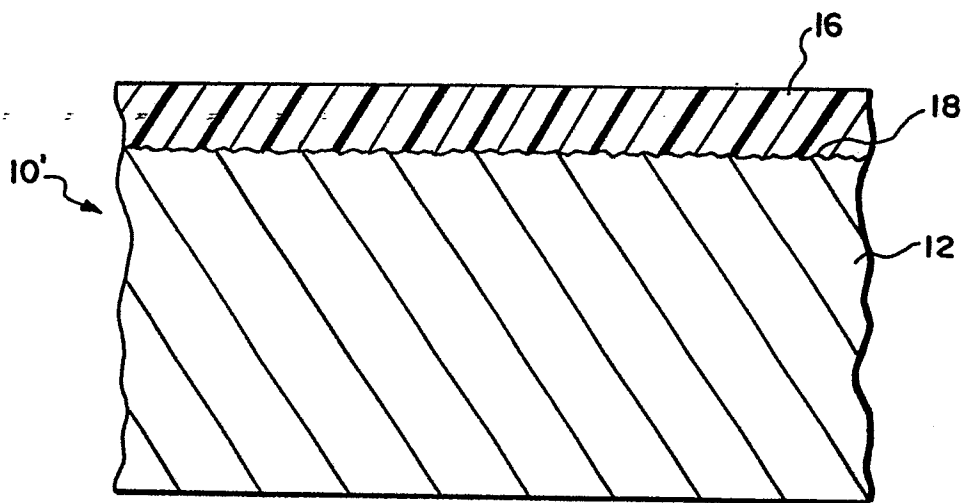
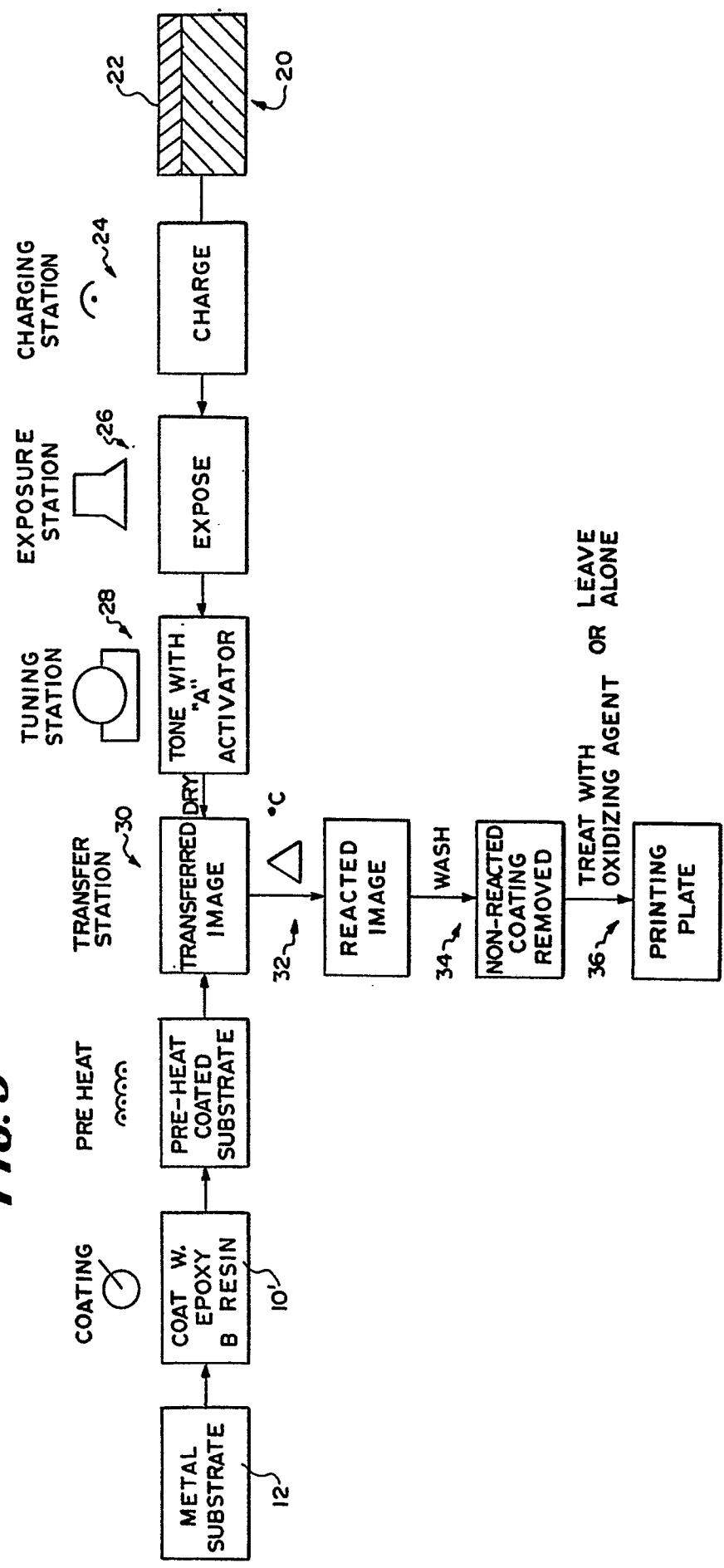


FIG. 3





European Patent
Office

EUROPEAN SEARCH REPORT

0104625

Application number

EP 83109493.3

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	<u>GB - A - 1 314 109 (FUJI)</u> * Claims 1,2,8 * --	1-3,7	G 03 G 13/26 G 03 G 13/16 B 41 N 1/04
A	<u>DE - A - 2 226 292 (KABUSHIKI KAISHA RICOH)</u> * Claims 1,5 * --	1-3	
A,D	<u>US - A - 4 025 339 (KUÉHNLE)</u> * Abstract * ----	1-3,7	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			G 03 G G 03 F B 41 N
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 29-12-1983	Examiner SCHÄFER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			