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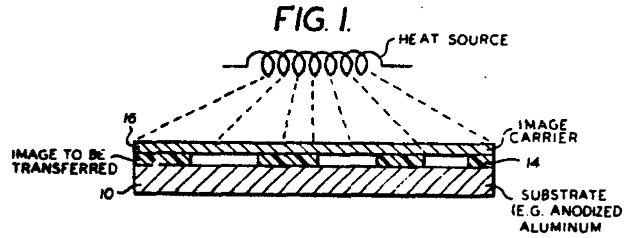
(54) **Lithographic printing plate with oleophilic sublimated image, process for its manufacture and electrostatic toner composition comprising a sublimatable material.**

(57) Lithographic printing plate having an aluminium substrate (10) with a hydrophilic, porous anodic oxide layer thereon and an oleophilic image (14) deposited by sublimation from a carrier (16) in and on the anodic oxide layer.

The sublimation can be performed using a laser irradiation. The image on the carrier can be obtained using electrostatic techniques. Use of electrostatic toners comprising a sublimatable material.

FIG. I.



EP 0 001 068 A2

Croydon Printing Company Ltd.

BACKGROUND

This invention relates to aluminum base lithographic printing plates and to the preparation of such plates.

Albuminum base lithographic printing plates such as described in US Pat. No. 3,181,461, issued May 4, 1965, have come into wide use in the printing industry and especially in offset printing and direct lithographic printing by newspapers using converted letterpress printing presses.

Time is often a factor in making lithographic printing plates and this is especially critical in the case of newspapers. The present day technique involves making a full size photographic negative of a paste-up of each page for the newspaper, exposing a wipe-on or pre-sensitized lithographic plate through the negative, developing the plate 1 and mounting it on the printing press. This process is time consuming and becomes even less efficient where duplicate plates are required for a multiple press operation which is common in the newspaper industry.

In order to improve the time element, it has been proposed to eliminate the use of a light-sensitive substrate, and, instead, to directly reproduce the printing surface on the substrate via electrostatics or laser transfer. US Pat. No. 2,862,815 issued

December 2, 1958, describes an electrostatic reproduction process and US Pat. No. 3,962,513 issued June 8, 1976, and US Pat. No. 3,964,389 issued June 22, 1976, describe forming the printing surface via laser transfer. However, these proposals have not met with much success because the images formed using these direct reproduction techniques lacks the integrity and durability required for good quality, dependable lithographic printing.

It has also been proposed to print on anodized aluminum surfaces by heat transferring a minor image from a pre-printed carrier sheet followed by sealing of the anodized surface by prolonged immersion in boiling water (cf. US Pat. No. 3,484,342, issued Dec. 16, 1969). This transfer of a pre-printed image is for decorative purposes and sealing closes the pores over the transferred image for light fastness.

SUMMARY

The present invention provides a high quality, dependable aluminum base lithographic printing plate and method. The printing plate comprises an aluminum substrate having a hydrophilic porous anodic oxide layer thereon and a durable and reinforceable oleophilic sublimated image in and on the porous anodic oxide layer. Heat transferable dyes are preferred and the use of wet photochemical and wet photographic processing is eliminated.

The process of the invention for making a lithographic printing plate includes the steps of providing an aluminum substrate with a hydrophilic, porous

anodic oxide layer and depositing or transferring an oleophilic image in and on the porous layer by sublimation. The second step can be carried out in a number of ways. For example, a carrier with a sublimatable oleophilic image can be placed face down on the aluminum substrate and heated to sublimate the image in and onto the porous layer. The image can be formed on the carrier using electrostatic techniques such as xerography, zinc oxide imaging and charge transfer imaging (electrostatography) and an electrostatic toner composition containing a sublimatable material such as a disperse dye.

Another way of carrying out the second step of the process is to place a carrier which is transparent to laser radiation having a laser responsive coating containing a sublimatable oleophilic material thereon face down on the lithographic substrate and depositing the oleophilic image by selected irradiation with a laser.

Another approach involves coating the substrate with a sublimatable material such as a dispersion of a disperse dye in a water soluble film former such as polyvinyl alcohol, carboxymethyl cellulose, gelatin and the like. A solution of a sublimatable material such as a disperse dye dissolved in acetone or other suitable solvent can be used in the same fashion for coating the substrate. With his approach, two techniques are available to transfer an image to the underlying substrate via sublimation. The first involves selected irradiation of the coated substrate followed by removal of the unirradiated non-image portions. If a water soluble film former is used in the coating this can be done simply by washing the laser imaged plate with water. The second technique involves using a mask such as a black image on white paper. The latter is placed image up on the coated substrate and flasher with infrared. This causes the material in the coating under the image to sublimate onto the substrate. The process is completed by removing the non-image portions.

DESCRIPTION OF THE DRAWING

The present invention will be more fully understood from the following description taken in conjunction with the accompanying drawing wherein:

Fig. 1 is a cross-sectional diagrammatic view illustrating one embodiment of the present invention;

Fig. 2 is a cross-sectional diagrammatic representation of a lithographic printing plate formed according to the embodiment illustrated in Fig. 2;

Figs.3 and 4 are cross-sectional diagrammatic representations illustrating another embodiment of the invention utilizing laser transfer techniques;

Figs.5 a and 5 b are cross-sectional diagrammatic views illustrating a further embodiment using a coated substrate and laser image for the transfer; and

Figs. 6 a and 6 b are cross-sectional diagrammatic views illustrating another embodiment using a coated substrate and a mask.

DESCRIPTION

Fig. 1 of the drawing provides a simple illustration of the present invention wherein an anodized aluminum substrate 10 is in contact with a carrier 12 having a sublimatable image 14 thereon. Heat from the source causes the image 14 to sublimate in and onto the pores of the substrate 10 producing oleophilic image 14' thereon (Fig. 2). The image 14 for transfer to the substrate 10 is preferably formed on the carrier 12 using direct imaging such as electrostatic copying of an original or composite using a toner containing, for example, a sublimatable disperse dye. The image 14 can also be formed by incorporating a sublimatable material into ribbons used in typewriters, telexes, teletypes and other mechanical and automatic typing devices. Normal typing will transfer the sublimatable material from the ribbon to paper which can then be used as the imaged carrier 12 in the manner described herein. There are also known image transmission systems that employ electrostatics or other means to convert sound or electrical impulses into visible images. These can be employed in the invention by incorporating a sublimatable material such as disperse dye into the toner or toner medium used to produce a visible image on a carrier such as paper. The imaged paper can then be used as the imaged carrier 12 in the manner described herein.

Figs. 3 and 4 illustrate another embodiment of the invention wherein a laser transfer technique is employed. A laser transparent film 16 having thereon a laser responsive sublimatable coating 18 is placed face down on the substrate 10. A laser is employed to transfer portions of the sublimatable coating 18 from the film 16 onto the substrate 10. Using known techniques, a "reading" laser causes the "writing" laser to transfer the laser coating 18 in the image areas illustrated by reference numeral 14'. If desired the film 16 can have a dark or black coating on the side facing the laser to facilitate heat transfer through to the coating 18.

The laser transparent film 16 with the portions 15 (Fig. 4) remaining after the laser transfer operation can be used as a negative itself to produce duplicate lithographic printing plates using conventional sensitized substrates.

Figs. 5 and 6 show a coating 50 on the substrate 10. The coating 50 is or can contain a sublimatable material such as a disperse dye. The coating can be a disperse dye in a water soluble film former or it can be deposited from a solution of a disperse dye, as described above.

Direct imaging with a laser forms image portions 52 and non-image portions 54. The portions 54 are removed, for example by dissolving with water leaving the plate shown in Fig. 5 b.

Imaging through a paper mask 60 with black (or dark) image 62 via an IR flash or exposure is shown in Fig. 6. The image 62 readily transmits heat to the underlying coating 50 while the non-image portions of paper 60 reflect the heat. In both Figs. 5 and 6 a transparent cover such as glass and/or a vacuum can be used to assist in the sublimation transfer.

In all of the embodiments shown in Figs. 1 - 6, a heated platten can be used in contact with the back or underside of the substrate 10 to approach (but not exceed) the sublimation temperature. This means that the transferring heat source need only add a small increment of heat energy to cause sublimation rather than having to bring the temperature up from ambient.

An essential feature of the invention involves the transfer by sublimation of a material placed in contact with (Figs. 1 - 4) or coated on an aluminum substrate (Figs. 5 and 6). In the transfer process, the image becomes firmly affixed in and on the porous anodic layer on the substrate via sublimation through most likely a combination of physical and chemical forces although this is not fully understood.

The aluminum substrate must be capable of holding a sublimated image and is provided with a porous anodic oxide layer for this purpose. The aluminum substrate can be pretreated (e. g. grained) bevore anodizing and/or posttreated such as described in US Pat. No. 3,181,461 with sodium silicate, provided the substrate retains sufficient residual porosity so as to be substantive toward the sublimatable material. The term "porous" thus includes anodized and unsealed aluminum as well as anodized aluminum that has been posttreated in such a way that it retains sufficient residual porosity.

Tempered aluminum is generally used to make anodized substrates which are suitable for use in the present invention. Tempered aluminum generally has a temper rating of between H-12 and H-19 where direct cold reduction is employed or between H-22 and H-27 where a combination of cold reduction and back annealling are employed. See the American Aluminum Association publication entitled Aluminum Standards and Data.

Unlike decorative printing on anodized aluminum, the porous anodic layer of the substrate of the invention must remain unsealed after image transfer via sublimation in order for the image to form the oleophilic printing area which itself comes in contact with the printing ink or is reinforced with known lacquers which do the printing.

The oleophilic sublimatable image 14 can be deposited on the carrier 11 using known electrostatic techniques such as xerography, zinc oxide imaging and charge transfer imaging. US Patent 2,862,815 referred to previously and US Patents 3,671,119 and 3,671,230 both issued June 20, 1972, are examples of such electrostatic techniques and are incorporated herein by way of reference. Charge transfer imaging (e. g. Minolta Camera Co.) is preferred because of the character of the image formed.

Basically, what is involved in using a laser transfer technique to form the image 14' (Fig. 4) is to employ a laser transparent film such as a polyester film coated with a material 18 that can be sublimated by laser energy. If necessary or desired, oxidizable or explosive constituents may be used to encourage transfer or increase sensitivity of the coating 18. Nitrocellulose, peroxides, azides and nitrates are examples of these constituents. To transfer selected portions of coating to form image 14' on the substrate, a beam of energy from a laser which produces wave lengths in the infrared region such as a YAG (Yttrium-Aluminum-Garnet) laser which has an effective wave length of about 1.06 microns, or an Argon laser which has an effective wave length in the range of from about 0.48 to about 0.52 microns, is focused by means known in the art through the laser transparent film to the interface between the coating and the film. The energy provided by the laser beam causes sublimation leaving a clear area on the laser transparent film 16 (see Fig. 4).

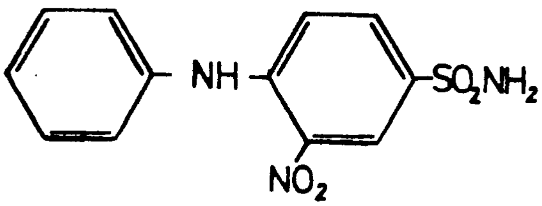
Imaging with a laser as described herein can also be used to advantage for making nameplates, dials and signs on unsealed or porous anodized aluminum which can be sealed, if desired or necessary, after image transfer. This has real advantages over current systems since it eliminates preprinting prior to image transfer and permits one-step, direct imaging.

The plate of the invention (e. g. as shown in Figs. 2, 4, 5 b and 6 b) can be treated using conventional techniques to reinforce the image 14' for example by applying a lacquer composition containing gum arabic.

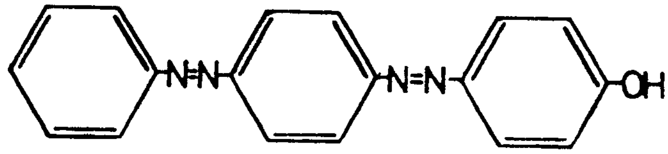
A sublimatable material is one that will under proper conditions of temperature and pressure) pass directly from the solid state without ever going through the liquid state. Temperatures will generally be in the range of 60^{o} C to 260^{o} C and pressures in the range of 1 to 10 psi, depending on the character of the material being worked with. Suitable materials have a sublimation half-life (the time required for one-half of a given amount of material to pass from the solid to the vapor state) in this temperature range of from 0.5 to 75 seconds. The preferred temperature range is 82^{o} C to 232^{o} C and the more preferred range is 121^{o} C to 219^{o} C. Suitable sublimation materials are described in US Patents 3,484,342, 3,707,346, 3,792,968 and 3,829,286 and need not produce a visible image so long as it is oleophilic and will accept ink or a reinforcing lacquer.

Heat transfer dyes commonly used in dry heat transfer printing of textiles can be used to form sublimated oleophilic images according to the invention. Many of these Materials are known as disperse dyes examples of which are as follows:

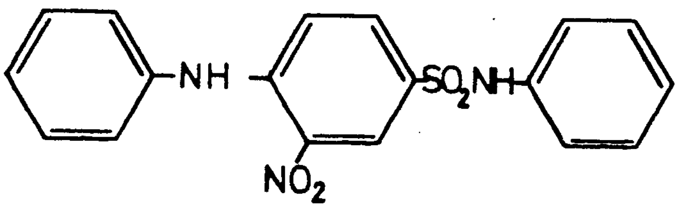
YELLOW



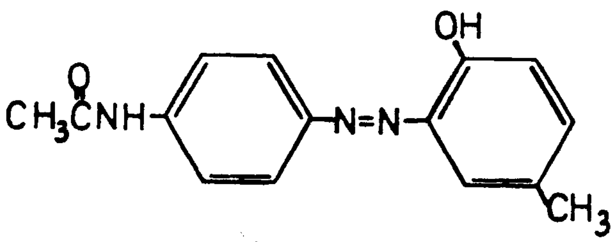
Yellow 33



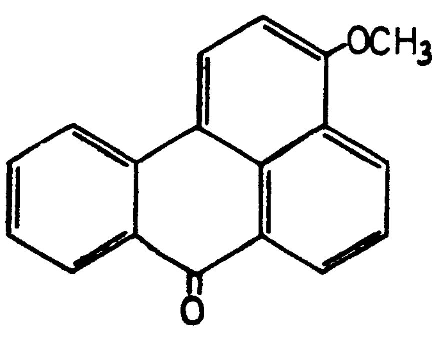
Yellow 23



Yellow 42

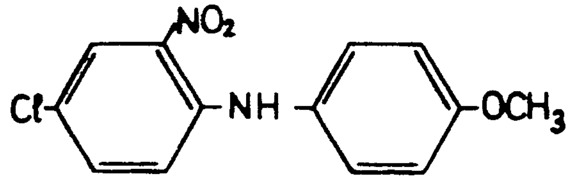


Yellow 3

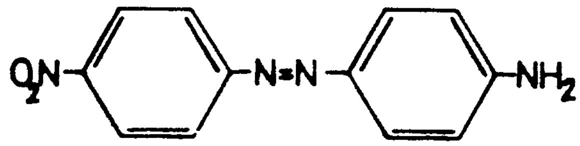


Yellow 13

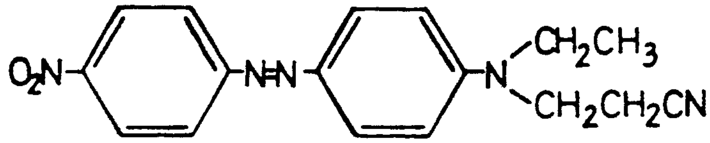
ORANGE



Orange 15

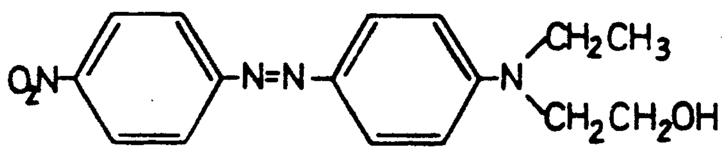


Orange 3

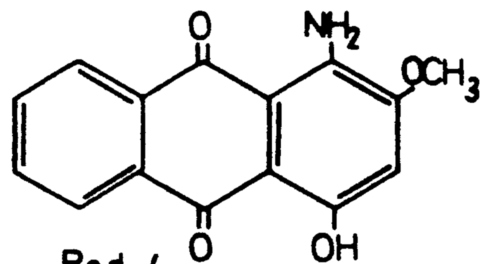


Orange 25

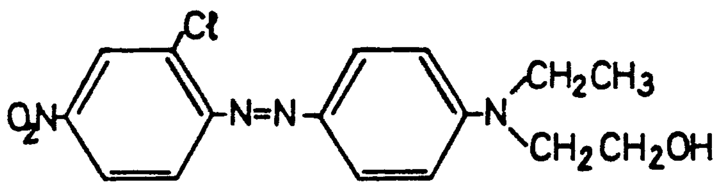
RED



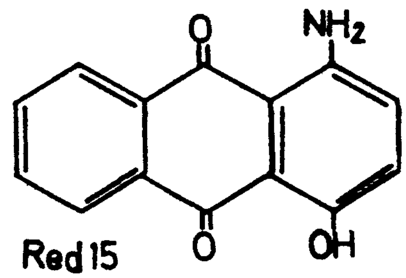
Red 1



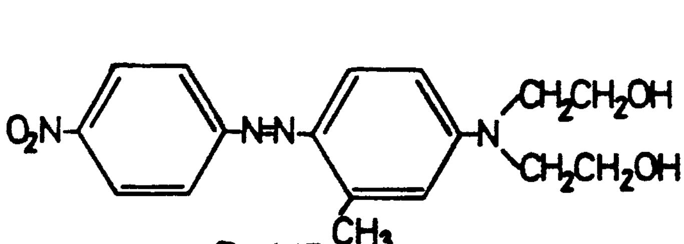
Red 4



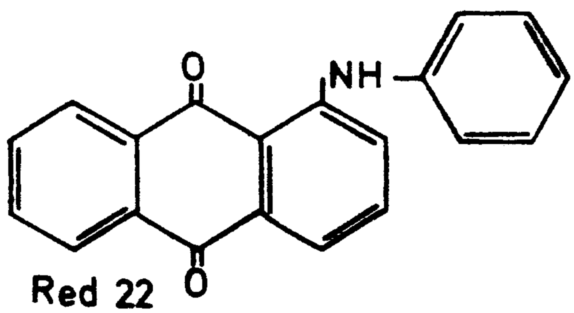
Red 13



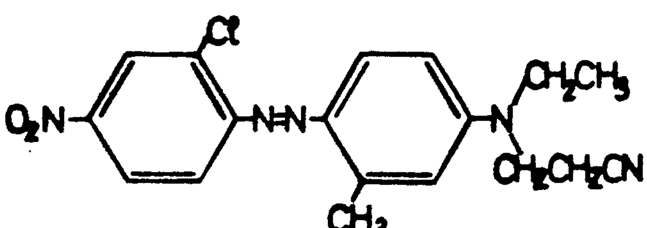
Red 15



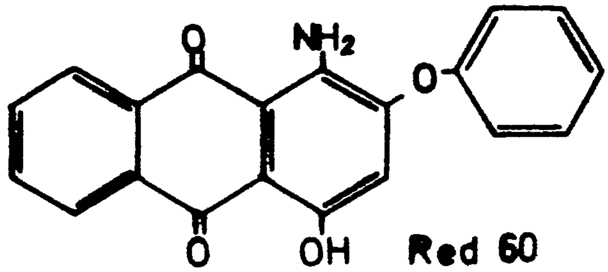
Red 17



Red 22

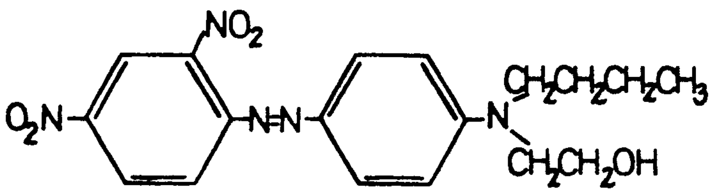


Red 65

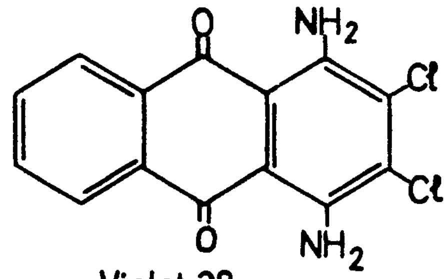


Red 60

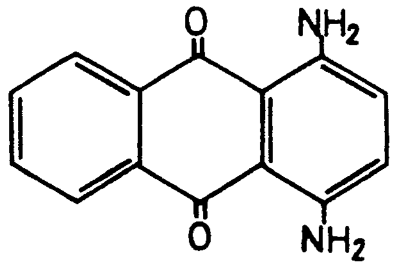
VIOLET



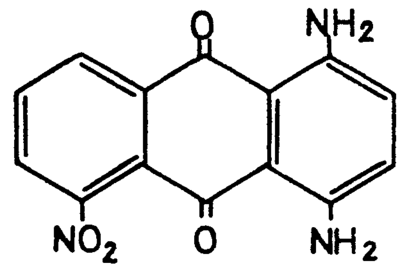
Violet 12



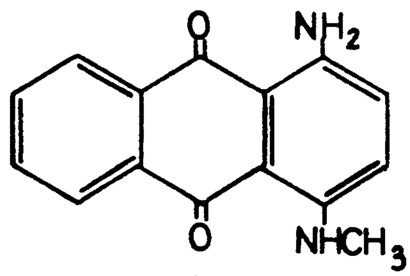
Violet 28



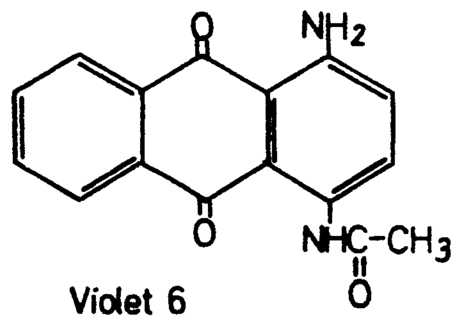
Violet 1



Violet 8

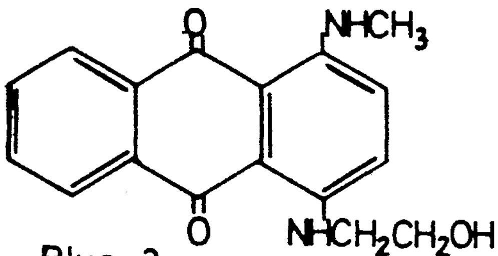


Violet 4

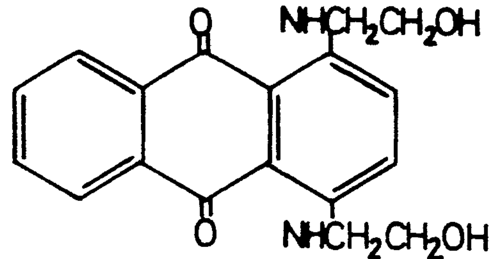


Violet 6

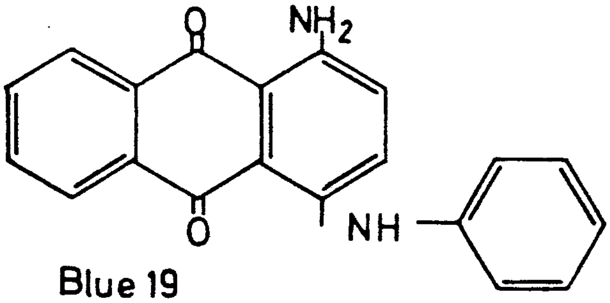
BLUE



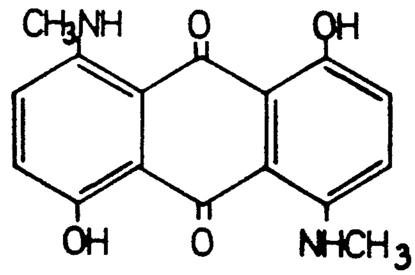
Blue 3



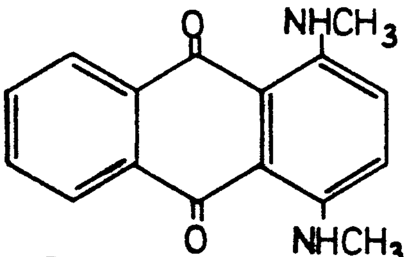
Blue 23



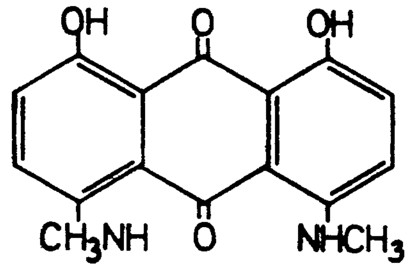
Blue 19



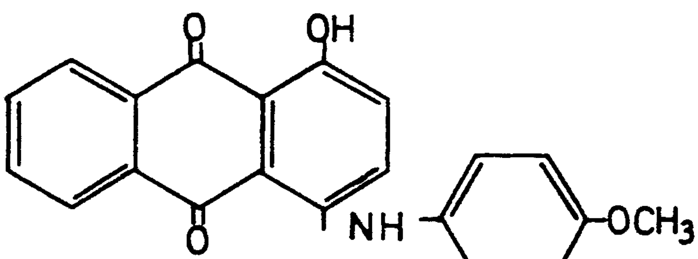
Blue 26



Blue 14



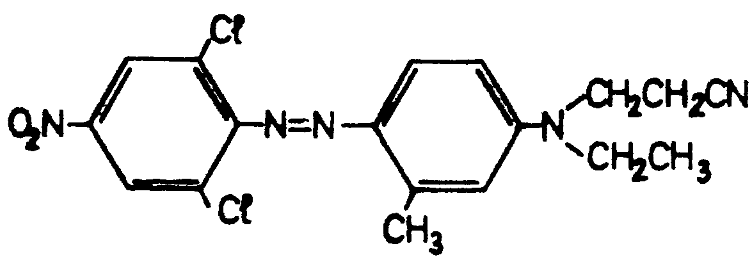
Blue 35



Blue 64

BROWN

Brown 2



Disperse type inks generally contain from 5 - 20 % by weight disperse dye, preferably about 10 % such inks are commercially available and the following (Manufactured by Crompton and Knowles Corp. of Fair Lawn, New Jersey) are useful in practicing the invention:

Intratherm Yellow P-345 NT
Intratherm Yellow P-340 NT
Intratherm Yellow P-342
Intratherm Yellow P-343 NT
Intratherm Yellow P-346
Intratherm Brilliant Yellow P-348
Intratherm Brilliant Orange P-365
Intratherm Orange P-367
Intratherm Orang P-368
Intratherm Pink P-335 NT
Intratherm Brilliant Red P-314 NT
Intratherm Red P-334
Intratherm Red P-336
Intratherm Red P-339
Intratherm Scarlet P-355
Intratherm Scarlet P-358
Intratherm Violet P-344 NT
Intratherm Blue P-304 NT
Intratherm Blue P-305 NT
Intratherm Blue P-306 NT
Intratherm Brilliant Blue P-308
Intratherm Blue P-310 NT New
Intratherm Dark Blue P-311 NT
Intratherm Brown P-301
Intratherm Dark Brown P-303
Transfer Black XB-6
Transfer Black XB-8

Heat transfer dyes can be formulated into coating containing from 5 - 20 % by weight (preferably about 10 % by weight) disperse dye and applied to a carrier such as paper, plastic or the like for later transfer to a lithographic substrate using a laser transfer technique. Formulations based on conventional wet or dry toners can be used to form an image on a carrier using electrostatic copying techniques such as xerography, zinc oxide or charge transfer imaging. Toners containing 5 - 60 % weight disperse dye, preferably 10 - 40 % by weight, can be employed.

The following examples are intended to illustrate the invention without limiting same:

Example 1:

Sublimable dyes such as the disperse dyes mentioned above may be incorporated into inks, one example being Black NY 83779, sold by Sinclair and Valentine Co. for heat transfer textile printing. The ink is coated onto a film substrate with a Meyer rod or Bird applicator. Suitable films for this are Mylar (tm, DuPont), acetate and polystyrene. After drying, the coated film is put coated-side down in contact with an anodized aluminum offset plate which, in turn, is placed on a curved stepping platen. Esposure of the film is via an Argon laser (5 W., Spectra-Physics 165) using the 4800 line only. Scanning is achieved by means of a single-facet, rotating 45° mirror. Input is provided via magnetic tape. After imaging, the film which is lifted from the aluminum substrate retains a negative dye image, while the high density, positive, dye image, which had transferred (sublimated) to the aluminum plate, readily accepts lacquer and ink. Abrasion tests, made on a Gardner Abrasion Machine, indicate that the sublimed dye image is capable of long runs on an offset press.

Example 2:

Inks normally used for heat transfer printing of textiles containing red, blue and yellow sublimable dyes as described above are obtained from Sinclair and Valentine Co. and coatet on Mylar film (TM DyPont). These inks are designated Red NY 83983, Blue NY 83982, and Yellow NY 83777. Films made with these inks are exposed as in Example 1, with similar results of dye image transfer and retention, and abrasion testing.

Example 3:

Crompton & Knowles' 8 % intratherm Red P-399, incorporated into a gravure ink, is printed onto conventional paper. The paper is placed printed-side down onto a rained anodized aluminum substrate, which is then placed in a Simplex, Slide-O-Mat, Transfer Press sold by Archie Solomon & Associates. Heat (204^{o} C) cand pressure are applied for 10 seconds. Upon separation a dense image of the print was on the plate. This transferred (sublimated) image accepted ink and lacquer readily.

Example 4:

40 % Intratherm Red P-339 is incorporated into a conventional liquid toner for electrostatic imaging. The toner is placed in a Minolta electrostatic copier. The copy produced is placed face-down on an aluminum anodized surface. Transfer is accomplished as in Example 3. The transferred sublimated image is a perfect facsimile which accepted lacquer and ink readily.

Example 5:

A coating is formulated as follows (Parts by weight):

57	- Water
5	- Pluronic F-38 (non-ionic sufucant)
38	- Intratherm Red P-339
100	Total Slurry

These are mixed for 5 minutes in a blender.

Coating (Parts by Weight)

26.3	- slurry as above
73.7	- (5 %) Polyvinyl Alcohol (Monsanto 40-20)

This is mixed for 5 minutes in a blender.

The coating is applied to an anodized aluminum plate. The coated plate is then imaged with a YAG Laser as in Example 1. After exposure, the plate is washed in water to remove the non-image area leaving asublimated disperse dye image on the anodized plate.

Example 6:

A coated plate, prepared as in Example 5, is covered with a mask (black image upon an opaque, white background). The masked plate is exposed to a source of infrared radiation. The image areas absorb the radiation, heating the coated plate image-wise underneath. The dye sublimates into the substrate forming an image. Water was removed from the non-image area leaving a sublimated image on the anodized plate.

Example 7:

A film of polyester is sub-coated with a 5 % solution of nitrocellulose (RS 1/2 sec. Hercules Corp.). The subbed film is then coated with a disperse dye coating as in Example 5. The coated film is the used to image an anodized aluminum plate as in Example 1.

Example 8:

Intratherm Red P-339 is incorporated into a 5 % solution of nitrocellulose (RS 1/2 sec. Hercules Corp.). This material is coated onto a polyester film and coated film is used to image an anodized plate as in Example 1.

Other sublimable materials that are of use in this invention are naphthalene, iodine, anthracene, adipic acid, anthraquinone, benzophenone, caprolactam, lauric acid, sebacic acid and other componds as listed in Handbook of Cem. & Physics, page C-716, Ed. 52, 1971 - 1972.

WHAT IS CLAIMED IS:

1. Lithographic printing plate comprising an aluminum substrate having a hydrophilic, porous anodic oxide layer thereon and an oleophilic sublimated image in and on said layer of anodic oxide.

2. Plate of claim 1 wherein the image area is reinforced.

3. Plate of claim 1 wherein the sublimated material comprises a disperse type heat transfer dye.

4. Process for making a lithographic printing plate which comprises:
   (a) providing an aluminum substrate having a hydrophilic, porous anodic oxide layer thereon; and
   (b) depositing an oleophilic image in and on the porous lyer by sublimation.

5. Process of claim 4 wherein an oleophilic image comprising a sublimatable material is formed on a carrier, said carrier is placed face down on said lithographic substrate and said oleophilic image is transferred to said substrate by sublimation.

6. Process of claim 5 wherein the image is formed on the carrier electrostatically.

7. Process of claim 6 wherein the image is formed on the carrier by charge transfer imaging.

8. Process for making a lithographic printing plate

which comprises:

(a) providing an aluminum substrate having a hydrophilic porous anodic oxide layer thereon;

(b) forming an oleophilic image on an carrier by charge transfer imaging using a toner comprising a sublimatable material; and

(c) contacting the imaged carrier with the porous layer and transferring the image in and onto the porous layer by sublimation.

9. Process of claim 8 wherein the toner contains a disperse type heat transfer dye.

10. Process of claim 4 wherein a laser responsive coating containing a sublimatable oleophilic material is applied to a carrier which is transparent to laser radiation and said oleophilic image is transferred to said porous layer via sublimation by selected irradiation with a laser.

11. Process of claim 4 wherein a laser responsive coating containing a sublimatable oleophilic material is applied to said substrate, an oleophilic image is transferred in and onto said porous layer via sublimation by selected irradiation with a laser and the non-image portion of the coating is removed.

12. Process of claim 4 wherein a coating containing a sublimatable oleophilic material is applied to said substrate, an oleophilic image is transferred in and onto said porous layer via sublimation by the application of heat through a mask and the non-image portion of the coating is removed.

13. Electrostatic toner composition comprising a sublimatable material.

14. Composition of claim 13 wherein the composition is oleophilic.

15. Composition of claim 13 wherein the sublimatable material is a disperse type heat transfer dye.

16. Process for imaging aluminum having a porous anodic oxide layer thereon which comprises contacting said layer with a laser responsive material containing a sublimatible material and selectively irradiating said aluminum with a laser to transfer the desired image by sublimation in and onto said porous layer.

17. Process of claim 16 wherein the laser responsive material is applied to a carrier that is transparent to laser radiation.

18. Process of claim 16 wherein the laser responsive material is coated onto the aluminum.

ABSTRACT OF THE DISCLOSURE

Lithographic printing plate having an aluminum substrate with a hydrophilic, porous anodic oxide layer thereon and an oleophilic sublimated image in and on the anodic oxide layer.

FIG. 1.

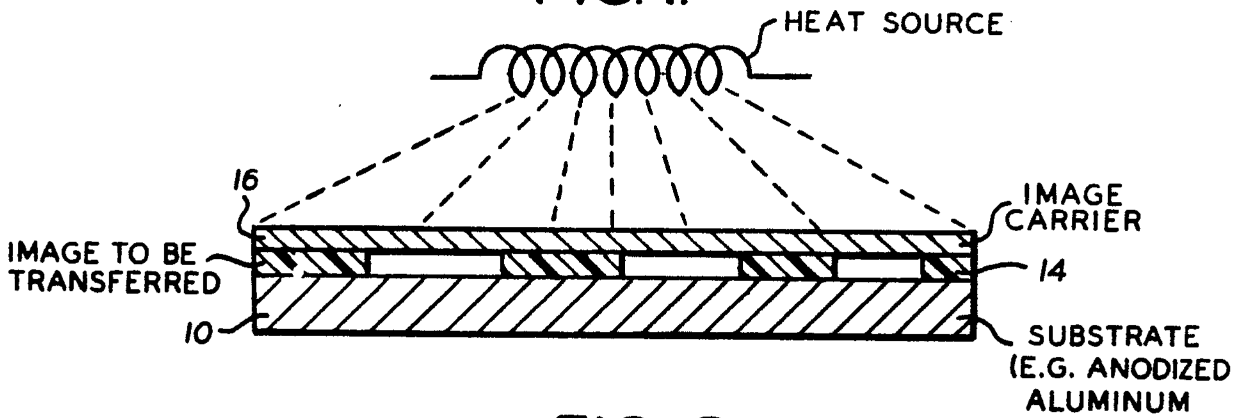


FIG. 2.

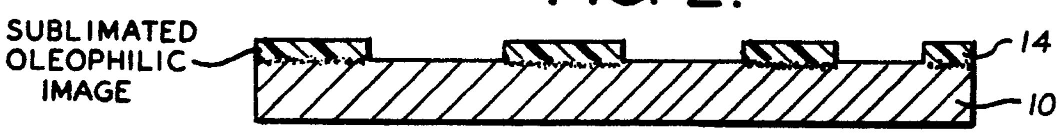


FIG. 3.

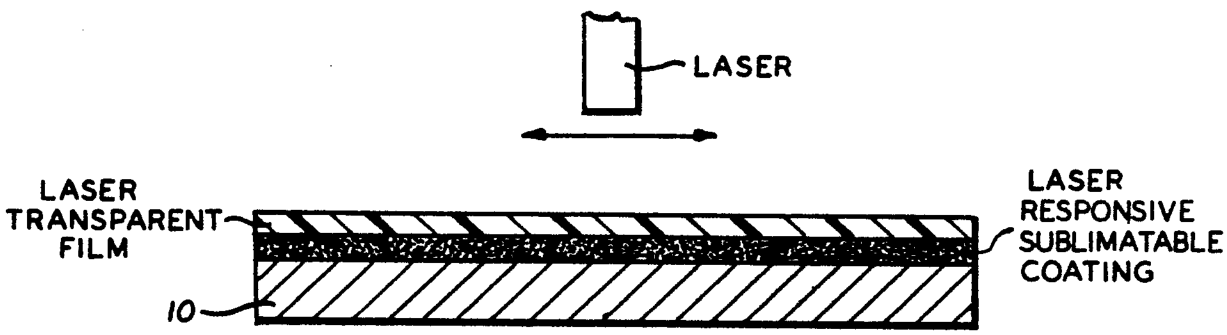


FIG. 4.

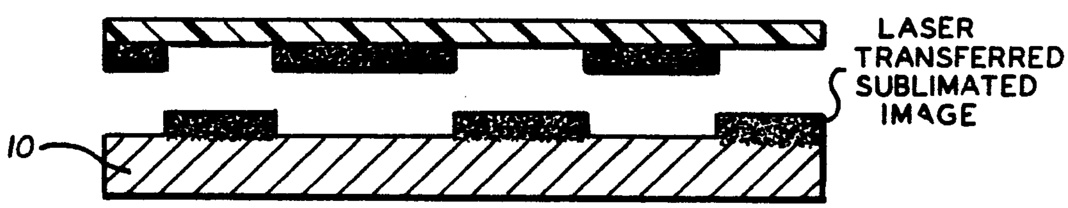


FIG. 5.

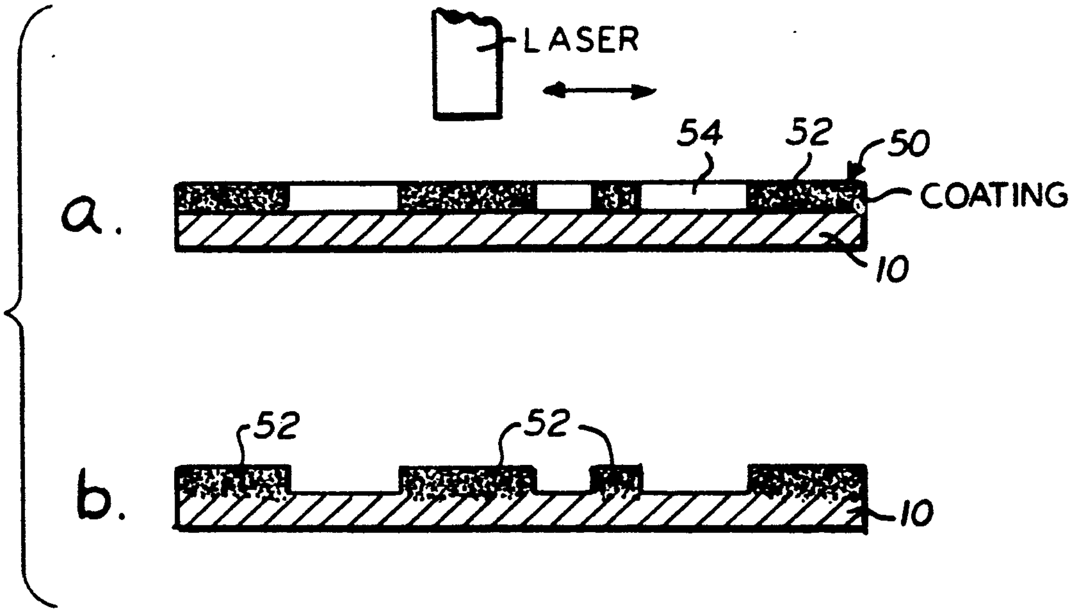
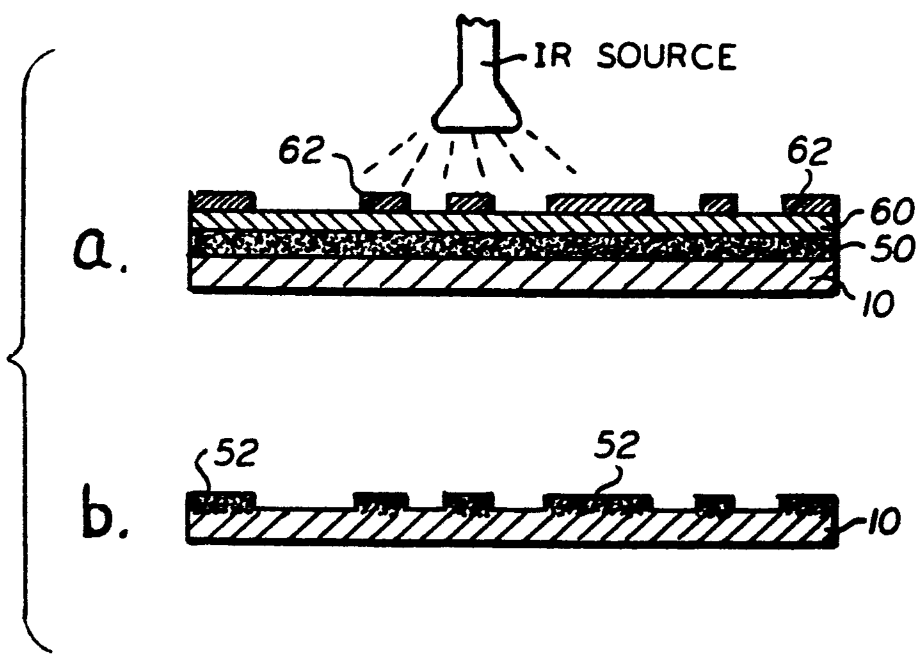

LASER
54
52
50
COATING
a.
10
52
52
b.
10

FIG. 6.


IR SOURCE
62
62
60
50
a.
10
52
52
b.
10