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(54) Magnetic printing plate with protective coating.

(57) A printing plate useful for printing a magnetic toner resist comprising a support substrate, a layer of a magnetic material, and a top layer of fluoropolymer with a critical surface tension not greater than 24 dynes/cm and a hardness greater than 5.1 Adjusted Vickers. The printing plate has good release properties, minimizes or avoids premature build-up of toner in the background areas, provides an extended temperature window for transfer, and has an extended life.

EP 0 083 935 A1

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TITLE

MAGNETIC PRINTING PLATE WITH PROTECTIVE COATING

TECHNICAL FIELD

The present invention relates to magnetic printing, and more specifically to an improved magnetic printing plate with a hard protective coating over the magnetizable layer.

BACKGROUND OF THE INVENTION

The prior art teaches the use of a magnetic printing plate comprising a flexible film coated with magnetic material to prepare resist images. The magnetic printing plate is imaged, toned, and the toner transferred to a substrate such as a heated copper panel. However, these plates are found to have limited thermal transfer latitude and poor background cleaning.

Coatings for magnetic printing plates have also been taught in the prior art. However, the coatings disclosed in the prior art constitute soft coatings used to lubricate the substrate coated. They tend to have high background stain due to the toner becoming embedded in the soft coating.

The magnetic printing plates of the invention, having a hard protective coating have good release properties at operating temperatures, avoid premature build-up of toner in the background areas, provide an extended temperature window for transfer, i.e., raise the maximum temperature at which toner will not adhere to the master, and have extended life.

SUMMARY OF THE INVENTION

The present invention provides a printing plate useful for printing a magnetic toner resist comprising a support substrate, a layer of magnetic material in contact with said substrate, and a layer of fluoropolymer in contact with the magnetic

PD-1912

material, said fluoropolymer having a critical surface tension not greater than 24 dynes/cm and a hardness greater than 5.1 Adjusted Vickers. The printing plate has good release properties at standard temperature settings, minimizes or avoids premature build-up of toner in background areas, provides an extended temperature window for transfer, and has an extended life.

DETAILED DESCRIPTION OF THE INVENTION

The process of using the printing plate of the present invention involves forming a magnetically held image of toner on the plate and transferring this image to a substrate by means of heat and pressure. The heat is preferably supplied by preheating the substrate receiving the toner. The transferred toner forms an image on said substrate which is useful as a resist in such processes as making printed circuit boards, printing plates or in chemical milling, i.e., the process can involve the steps of (a) transferring a magnetically held image of colescible magnetic particles from a magnetic member to a suitable surface to form a coalesced resist image, (b) modifying the exposed areas of the surface which are unprotected by the resist image, and (c) optionally removing the resist image from the surface-modified product. The modification can be to make the exposed surface hydrophilic or hydrophobic, opposite to the characteristic of the resist image, in which case the resultant product could be used as a lithographic printing plate. The modification can be to etch or deposit a metal on the exposed surface of the substrate to form the desired electrical circuit as a network of metallic conductors on an insulating background of suitable dimensions. In chemical milling (etching), the interconnecting metallic network is either selfsupporting or it may be attached to a suitable substrate. The process and apparatus except for the improved printing plate are described in published European Patent application 79 100 892.3.

The magnetic printing plate comprises a support substrate which is provided with a layer having a surface capable of containing a magnetic image over which is coated a top layer of a fluoropolymer. The support substrate can be in the form of an endless belt, flexible film or platen. The magnetic material forming the surface capable of containing a magnetic image generally will be a particulate hard magnetic material in a binder. Suitable hard magnetic materials include the permanent magnetic materials such as the "Alnicos", the "Lodexes" (acicular iron-cobalt alloys encased in lead or plastic; manufactured by General Electric Company), the "Indox" barium ferrite compositions, and materials used in tape recording, magnetic discs, and magnetic printing inks. These latter materials include γ-iron oxide (Fe_2O_3), magnetite (black Fe_3O_4), x-iron carbide and chromium dioxide. Acicular chromium dioxide is generally preferred because of its magnetic properties. The magnetic member preferably is a drum in which case the imaging surface may be an integral part of the drum or it may be a flexible film coated with the magnetic material and mounted on the drum.

The top coating comprises a hard fluoropolymer which has a critical surface tension not greater than 24 dynes/cm and hardness greater than 5.1 Adjusted Vickers. Preferably the critical surface tension is not greater than 18 dynes/cm and more preferably 11 dynes/cm. Preferably the hardness is greater than 9.0 Adjusted Vickers and more preferably greater than 12.0 Adjusted Vickers.

Examples of useful fluoropolymers are:

Poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane/vinylidene fluoride) (ca. 75/25 mole %)

Poly(hexafluoroisopropyl methacrylate)

Poly(perfluoro 2,2-dimethyl-1,3-dioxole/-tetrafluoroethylene) (ca. 21/79 mole %)

Poly(perfluoro-2,methyl-1,3-dioxole/tetra-fluoroethylene) (ca. 75/25 mole %)

Poly(perfluoro-1,3-dioxole/tetrafluoroethylene) (ca. 75/25/ mole %)

Poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane/tetrafluoroethylene) (ca. 75/25 mole %)

Critical surface tension (γc) is determined in accordance with the following: Zisman, "Advances in Chemistry Series", 43, provides "a rectilinear relationship between the cosine of the contact angle, θ, and the surface tension, γ LV° for each homologous series of organic liquids. The critical surface tension for wetting by each homologous series is defined by the intercept of the horizontal line cos θ = 1 with the extrapolated straight-line plot cos θ vs $\gamma_{LV°}$, and is denoted by γ_C. When cos θ is plotted against $\gamma_{LV°}$ for a variety of nonhomologous liquids, the graphical points fall close to a straight line or collected around it in a narrow rectilinear band. In general, the graph of cos θ vs $\gamma_{LV°}$ for any low-energy surface is always a straight line (or a narrow rectilinear band) unless the molecules in the solid surface form hydrogen bonds."

Based on the above information and the following relationship, γ_C values for various fluoropolymer were determined:

$$\cos \theta - 1 + m (\gamma_{LV} - \gamma_c)$$

where: θ = receding contact angles (degrees) - with n-hexadecane

m = slope = -0.034 as determined by Zisman for fluorinated surfaces

γ_{LV} = surface tension of n-hexadecane = 27.6 dynes/cm.

The Adjusted Vickers Hardness was determined using the method described in U.S. Patent 3,923,715 issued Dec. 2, 1975, col. 5, lines 15 et seq.

Critical surface tension and hardness values for polymers both within and outside the scope of the present invention are as follows

TABLE I

Fluoropolymer	Critical Surface Tension, γc	Vickers Hardness
poly(PMD/VF_2)	11.1	15.9
poly(PMD/TFE)	10.1	19.1
poly(PDD/TFE)	11.5	6.2
poly(PD/TFE)	15.5	12.4
poly(PMMD/TFE)	10.1	7.4
poly(HIM)	12.9	11.5
poly(HM-1)	8.2	5.1
SYL-OFF Coating 7044 (Dow Corning)	24 (1)	1.9
VYDAX®AR	22.3	2.6
Zepel® Fluoropolymer	4.2	1.1
poly(MMA)	39 (2)	12.3

(1) From "Advances in Chemistry Series" 43, page 44

(2) From "Advances in Chemistry Series" 43, page 20

- poly(PMD/VF_2) = (perfluoro-2-methylene-4-methyl-1,3 dioxolane/vinylidene fluoride)
- poly(PMD/TFE) = (perfluoro-2-methylene-4-methyl-1,3 dioxolane/tetrafluoroethylene)
- poly(PDD/TFE) = (perfluoro-2,2-dimethyl-1,3 dioxole/tetrafluoroethylene)
- poly(PD/TFE) = (perfluoro-1,3-dioxole/tetrafluoro-ethylene)
- poly(PMMD/TFE) = perfluoro-2-methyl-1,3 dioxole/tetrafluoroethylene)
- poly(HIM) = (hexafluoroisopropyl methacrylate)
- poly(HM-1) - (fluoroalkylethyl methacrylate/methyl methacrylate) (80/20 wt %)
- SYL-OFF® 7044 Coating - Solvent-free silicone (Dow Corning)
- VYDAX® Du Pont = Fluorocarbon telomers

The fluoropolymer top coat of the present invention has the following basic requirements. It should act as a good release coating for the toners used at temperatures from 160°F (71.1°C) to 260°F (126.7°C). At these temperatures, the toners used are designed to be very tacky so that they will have good adhesion to the surface to which they are transferred e.g. the surface of a copper-clad laminate used in the printed circuit industry. However, for good quality printing it is important that all the toner on the magnetic recording member tape or master be transferred, i.e., adhere preferentially to the surface to be printed, and that whatever toner remains on the master be easily removed by light brushing. Using a fluoropolymer having a low critical surface tension good release properties are obtained.

This fluoropolymer coating must also adhere well to the layer below which is capable of containing a magnetic image or has a surface capable of containing a magnetic image. This is needed to prevent the fluoropolymer layer from being pulled off by the toner during transfer or printing. This hard top coating also provides wear resistance and it must not be worn away even after several hundred boards have been printed. The top coating should be applied as a very thin layer, preferably, less than 0.0001 inch (0.000254 cm). If this coating is too thick it will act as a mechanical barrier holding the toner away from the magnetic surface, thus reducing the magnetic field strength seen by the toner. The fluoropolymer coating should also have a low tendency for electrostatic charge build-up or the electrostatic charges must be easily discharged by use of coronas or other charge dissipating devices. If the toner is held on the master by electrostatic forces, "background", i.e., toner in the nonimage areas; will be unacceptably high. The top coating, should not be damaged by the radiant energy to which it is exposed during imaging of the master.

The top fluoropolymer coating may be applied by any known methods such as liquid extrusion coating using a doctor knife, dip coating, spraying, swabbing the surface with a cheesecloth containing the solution, etc.

Some suitable support materials include films composed of high polymers, which are cast as films from molten polymer, such as polyamides, e.g., polyhexamethylene sebacamide, polyhexamethylene adipamide; polyolefins, e.g., polypropylene; polyesters, e.g., polyethylene terephthalate/isophthalate; vinyl polymers; e.g., vinyl acetals, vinylidene chloride/vinyl chloride copolymers, polystyrene, polyacrylonitrile; and cellulosics, e.g., cellulose acetate, cellulose acetate/butyrate, cellophane. A particularly preferred support material is polyethylene terephthalate film of the kind described in Alles et al., U.S. Patent 2,627,088, and Alles, U.S. Patent 2,779,684, with or without the surface coating described in the former patent. The support may have a resin sublayer or other layer thereon which for purposes of this invention is considered part of the support. However, the total thickness of the contiguous layer and any soluble sublayer or underlayer should not exceed 0.0006 inch (0.015 nm). Preferably the support substrate is flexible.

Where the particular application does not require that the base support be transparent, the contiguous composition may usefully be coated on an opaque support, such as paper, especially water-proof photographic paper; thin metal sheets, especially aluminum and copper sheets, cardboard and the like.

Any method for forming a latent magnetic image in the magnetic member is useful in the present invention. The image is latent in the sense that it is generally not visible to the naked eye until decorated with magnetic toner which develops the image.

When using thermal imaging to create the latent magnetic image, the surface is magnetically structured by one of several methods with from about 100 to 1000 magnetic lines per inch (39.4 to 393.7 per cm) and preferably from 150 to 600 magnetic lines per inch (59.1 to 236.2 per cm). As used herein, a magnetic line contains one north pole and one south pole. The technique of roll-in magnetization can be used to structure the surface of the magnetic member, wherein a high permeability material such as nickel, which has been physically discretely structured to the desired width is placed in contact with the surface of the magnetic member, which previously has been magnetized in one direction by a permanent magnet or a DC electromagnet, and a DC electromagnet or permanent magnet with the polarity reversed is placed on the backside of the permeable material. As the structured high permeability material is brought into contact with the magnetic member, the nickel or other permeable material concentrates the magnetic flux lines at the points or contact causing polarity reversal at these points and resulting in a structured magnetization of the magnetic member.

The surface of the magnetic member can also be a thermoremanently structured by placing the magnetic member having a continuously coated surface of magnetic material on top of a magnetic master recording of the desired periodic pattern. An external energy source then heats the surface of the magnetic member above its Curie temperature. As the surface of the magnetic member cools below its Curie temperature, the periodic magnetic signal from the magnetic master recording thermoremanently magnetizes it. When acicular chromium dioxide is used as the magnetic material in the surface of the magnetic member, as little as 20 oersteds can be used to structure the surface of the magnetic member when passing through the Curie temperature whereas over 200 oersteds are needed to apply detectable magnetism to acicular chromium dioxide at room temperature.

Alternatively, the latent magnetic image can be created in the magnetic member by means of a magnetic write head. The magnetic write head can provide the requisite magnetic structuring in the latent magnetic image directly.

The magnetic member used in the examples is a layer of acicular chromium dioxide particles in a binder coated on a polyester film which may, or may not be aluminum-backed or aluminized.

The thickness of the CrO_2 layer on the film is limited only by the ability of the layer to absorb sufficient thermal energy to effectively demagnetize the CrO_2 layer by raising a given thickness of the said layer above the Curie point of 118°C during the thermal imaging process. Thicker layers are preferred to enhance magnetic field strength. Practically, the thickness of the CrO_2 layer on the imaging member is from 50 to 2000 micro inches (1.27 to 50.8 micrometers), and is preferably from 150 to 500 micro inches (3.81 to 12.7 micrometers).

The magnetic member can be used either mounted in the form of an endless belt supported by a plurality of rolls or mounted to the curved printing roll. The imaging and toning steps are separate entities which do not need to be done consecutively. However, the imaging step must precede the toning step. For instance, it may be desired to mount a preimaged magnetic member on the printing roll.

The magnetic member can be imaged in a variety of ways, either held flat or attached to the curved printing roll. One form of the master image is a silver photographic image transparency of a printed circuit diagram. This is held in contact with a prestructured magnetic member and flashed with a Xenon flash tube. The energy transmitted through the transparent parts of the master raises the CrO_2 above its Curie temperature of 118°C and demagnetizes it; the opaque parts of the design minimize energy transmission and the design remains as a latent image on the CrO_2 film if excessive flash energy is avoided. Alternative procedures are to scan the desired circuit designs onto the printing member having no prestructure with electromagnetic recording heads, or to selectively demagnetize prestructured areas of the magnetic member with point sources of radiation, e.g., lasers, which heat selected areas of the magnetic member to above the Curie temperature of the magnetic material in the magnetic member. These devices may be designed to respond in an on-off fashion to a computer-stored or computer-aided design.

Precise image registration is important when the process of the present invention is used to form both single-sided and double-sided circuit boards or to chemically mill double-sided patterns or shapes on metal.

The toning and transfer steps are carried out using the process and equipment described in published European Patent Application 79 100 892.3 except for the printing plate described herein with its improved fluoropolymer layer. The imaged master is (1) mounted on the print roll and rotated past the corona unit (2) toned with a finely divided magnetic toner (3) passed near an AC corona discharge device to reduce static electricity (4) passed under a combination air knife/vacuum knife to remove background toner from the demagnetized areas of the imaged magnetic film (5) contacted momentarily with a preheated circuit board blank to tackify, transfer and adhere the toner to the copper surface simultaneously. An example of a suitable circuit board temperature, i.e., substrate, is in the range of 110°C to 125°C and preferably 112°C to 120°C.

The invention will now be further illustrated, but it is not intended to be limited by the following examples. All parts and percentages are by weight unless otherwise indicated.

Example 1

A portion of a Cirtrak® printing plate which comprises an acicular chromium dioxide binder matrix on polyester film was coated with an approximately 6.8% solution of poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane/Vinylidene fluoride) in trichlorotrifluorethane. A draw-down on the tape was made using a 2.5 mil draw-down knife. The partially coated printing plate was then placed in a hot air oven at 100°C for 2 hours. The tape was imaged with a permanent magnet, and then treated on a thermal transfer unit similar to that described in published European Patent Application 79 100 8923 by (1) mounting it on the print roll; (2) toning it with a finely divided magnetic toner (3) passing the toned image under a vacuum knife to remove background toner from the demagnetized areas of the imaged magnetic film and (4) contacting the toner image momentarily with a preheat circuit board blank to tackify, transfer, and adhere the toner to the copper surface simultaneously.

The binder system of the toner consisted of 43.2 parts by weight ATlac 382 ES, triphenyl phosphate plasticizer and pressure sensitive additive. The ATlac 382 ES polyester resin from ICI, Ltd. (a propoxylated bisphenol-A, fumaric acid polyester having a tack point of 70°C and a liquid point of 199°C) has a molecular weight of 2500-3000 and a Tg of 58°C. The remaining portion of the tonr (50 parts by wt.) is composed of Magnetic Pigment 345 from BASF having an average particle size of 08. μm. Tack point and liquid point are manufacturer's tests involving temperature at which resin particles will stick to a heated bar and the temperature measured in a melting point tube, respectively. The average particle size of this toner was 12-14 μm. The toner was placed in the toner applicator. The applicator was activated and moved close to the printing roll so that fluidized toner contacted printing roll. The printing roll drive was activated to move the preimaged magnetic film through the standing wave of toner and cause magnetic toner to adhere to the magnetic parts of the image. The toned film was then rotated past the corona discharge and the vacuum knife. The knife was placed approximately 10 mils (0.254 mm) from the film surface. The vacuum was 0.5 inch (1.27 cm of water).

To effect transfer of the toned image, the film was rotated into position. The circuit board blank preheated to 245°F (118.3°C) by hot plates was pushed into the nip and contacted with the toned image rotating through the nip at a speed of 20 ft/min (10.2 cm/sec and a pressure of 30 pounds per inch^2 gauge. The circuit board with the printed resist was deposited beyond the nip.

Another similarly coated plate was tested as above with the following exception: the circuit board was preheated to 270°F (132.2°C).

No toner adhesion was noted on the fluoropolymer coated areas of the tape at 245°F (118.3°C) or 270°F (132.2°C), although severe toner adhesion was noted on the uncoated areas of the tape.

Example 2

A Cirtrak® Printing Plate was coated and tested as described in Example 1 at several copper panel surface temperatures ranging from 196°F (91.1°C) to 236°F (113.3°C).

No toner adhesion was noted in the coated areas even at a surface temperature of 236°F (113.3°C). Adhesion in the uncoated areas was evident at panel surface temperatures of 214°F (101°C) - 218°F (103.3°C).

Example 3

An 18" x 27" (45.7 cm X 68.6 cm) Cirtrak® printing plate was coated in separate areas with concentration of 3%, 4% and 5% by weight of poly(hexafluoroisopropyl methacrylate) in Freon F-113 (trichlorotrifluoro ethane) and in other areas with a 3%, 4%, 590 6.8% by weight solution of poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane/vinyldene fluoride) in Freon® F-113 solvent.

The coated plate was then tested as described in Example 1 with the following exception: the heating of the copper panel was done in a dynamic mode where the panel was high-speed contact heated. The poly(hexafluorosopropyl methacrylate) coatings gave an ~10°F (4.7°C) increase in panel preheat temperatures vs. the uncoated areas of the plate. The poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane/vinylidene fluoride coatings gave an increase of approximately 60°F (~28°C) increase in panel preheat temperatures.

The increases in panel preheat temperatures indicated above are obtained by subtracting the maximum panel preheat temperature attained before physical damage occurred in the coated areas of the plate from that attained in the uncoated areas.

Approximately 25 panels were processed with no unusual effects. Background areas were very clean with both fluoropolymers.

Example 4

One half of Cirtrak® printing plate was coated with a 5% solution of polysilicic acid, similar to that described in U.S. 3,698,005 using a 0.0025 inch (0.0064 cm) draw-down knife followed by drying for approximately 2 hours.

One half of another Cirtrak® printing plate was swabbed with a cheesecloth containing a 5% solution of polysilicic acid and the plate was dried for approximately 2 hours.

The coated and dried plates were then tested as described in Example 1. Both coatings appear very nonuniform. The polysilicic acid coating appeared to attack the CrO_2 surface. Further, toner was found to adhere very strongly to the coated area.

Another Cirtrak® printing plate coated with a 5% by weight solution of poly(perfluoro-2-methylene-4-methyl-1,3 dioxolane/vinylidene fluoride) in 3:2 Fluorinert® FC-72/Fluorinert® FC-75 (3M Co.) solvent and tested as in Example 1, had very good release properties with no toner adhesion to the background.

Example 5

Several Cirtrak® printing plates were treated as follows: one half of each plate was dip coated in one of the solutions indicated in Table II below at 70 inches/minute (2.963 cm/sec.) followed by heat treating at 180°F (82.2°C) for approximately 2 hours. Solution concentration is by weight.

TABLE II

Solution 1: 1%	Soln. of fluoroalkyl methyl methacrylate/2 ethyl hexyl methacrylate (75/25) in trichlorotrifluoroethane, bpt. 117.6°F (47.6°C)

Solution 2:	2%	Soln. of fluoroalkyl methyl methacrylate/2 ethyl hexyl methacrylate (75/25) in trichlorotrifluoroethane, bpt. 117.6°F (47.6°C)
Solution 3:	0.5%	Soln. of fluoroalkyl methyl methacrylate/2 ethyl hexyl methacrylate (75/25) in trichlorotrifluoroethane, bpt. 117.6°F (47.6°C)
Solution 4:	1%	Soln. of fluoroalkyl methyl methacrylate/butyl acrylate (98/2) in trichlorotrifluoroethane, bpt. 116.6°F (47.6°C)
Solution 5:	2%	Soln. of fluoroalkyl methyl methacrylate/butyl acrylate (98/2) in trichlorotrifluoroethane, bpt. 116.6°F (47.6°C)
Solution 6:	0.5%	Soln. of fluoroalkyl methyl methacrylate/butyl acrylate (98/2) in trichlorotrifluoroethane, bpt. 116.6°F (47.6°C)
Solution 7:	1%	Soln. of fluoroalkyl methyl methacrylate/lauryl methacrylate (65/35) in trichlorotrifluoroethane, bpt. 117.6°F (47.6°C)
Solution 8:	2%	Soln. of fluoroalkyl methyl methacrylate/lauryl methacrylate (65/35) in trichlorotrifluoroethane, bpt. 117.6°F (47.6°C)
Solution 9:	0.5%	Soln. of fluoroalkyl methyl methacrylate/lauryl methacrylate (65/35) in trichlorotrifluoroethane, bpt. 117.6°F (47.6°C)

One half of an additional Cirtrak® printing plate was coated with polydimethyl siloxane by rubbing the surface of the same with it, and continuously wiping to remove or reduce tackiness.

The plates were then tested as described in Example 1. The plates treated with Solutions 1-9 were unacceptable. The 2% treatments resulted in greater adhesion of toner to the plate because the toner becomes embedded in the thick soft fluoropolymer surface. The 0.5% solution treated areas of the plate appeared comparable to the untreated areas. The fluoropolymers used were relatively soft, low Tg polymers.

The polydimethylsiloxane treated half of the plate had far less adhesion to toner than the untreated half of the plate, however, adhesion in the background areas of the treated half was somewhat higher.

One half of another Cirtrak® printing plate was coated with a 4% solution by weight of methyl methacrylate in toluene to give a 0.0025 inch (0.00635 cm) wet coating followed by drying in a hot air oven for 30 minutes at 100°C. The plate was then tested as in Example 1. The coated areas had greater or comparable adhesion to toner than the uncoated areas.

Example 6

One half of a Cirtrak® printing plate was sprayed with "Slip Spray Dry Lubricant" (Du Pont) until the surface of the plate was wetted, and left with a white haze residue. The excess was wiped off, and the plate was then tested as described in Example 1 at various panel surface temperatures. The coated plate had unacceptable electrostatic properties, and at a panel surface temperature of 207°F (97.2°C) it had poor release characteristics, i.e., toner adheres to the plate.

What is claimed:

1. A printing plate useful for printing a magnetic toner resist comprising a support substrate, a layer of magnetic material in contact with said substrate, and a layer of fluoropolymer in contact with the magnetic material, said fluoropolymer having a critical surface tension not greater than 24 dynes/cm and a hardness greater than 5.1 Adjusted Vickers.

2. The printing plate of claim 1 wherein the critical surface tension is not greater than 18 dynes/cm.

3. The printing plate of claim 1 wherein the critical surface tension is not greater than 11 dynes/cm.

4. The printing plate of claim 1 wherein the hardness is greater than 9.0 Adjusted Vickers.

5. The printing plate of claim 1 wherein the hardness is greater than 12 Adjusted Vickers.

6. The printing plate of claim 1 wherein the critical surface energy is not greater than 18 dynes/cm and the hardness is greater than 9.0 Adjusted Vickers.

7. The printing plate of claim 1 wherein the critical surface tension is not greater than 11 dynes/cm and the hardness is greater than 12 Adjusted Vickers.

8. The printing plate of claim 1 wherein the fluoropolymer is selected from the group consisting of

Poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane/vinylidene fluoride)

Poly(hexafluoroisopropyl methacrylate)

Poly(perfluoro 2,2-dimethyl-1,3-dioxole/-tetrafluoroethylene)

Poly(perfluoro-2,methyl-1,3-dioxole/tetrafluoroethylene)

Poly(perfluoro-1,3-dioxole/tetrafluoroethylene) and

Poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane/tetrafluoroethylene)

9. The printing plate of claims 1 or 7 wherein the magnetic material comprises acicular chromium dioxide.

10. A process for transferring a toner resist image from a surface with a surface tension not greater than 24 dynes/cm. and a hardness greater than 5.1 Adjusted Vickers to a preheated substrate.

European Patent Office

EUROPEAN SEARCH REPORT

0083935

Application number

EP 83 10 0102

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	US-A-4 074 276 (W.E.L. HAAS et al.) * Column 3, lines 54-68 *	1	G 03 G 19/00

A	US-A-4 273 797 (G. AKASHI et al.) * Column 3, lines 59-68 *	1	

A	US-A-4 096 294 (T.J. PACANSKY) * Column 3, lines 40-58 *	1,8	

A	US-A-4 103 616 (J.Y. CHU et al.) * Column 2, lines 22-33 *	1,8	

			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			G 03 G 19/00 G 03 G 13/00 G 11 B 5/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-04-1983	GRASSELLI P.

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