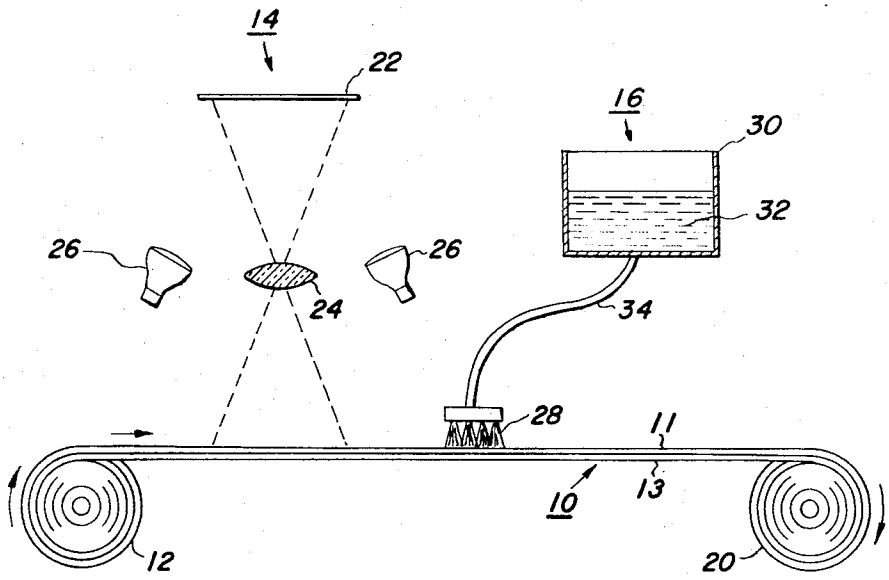
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METHOD OF IMAGE REPRODUCTION BY PHOTOPOLYMERIZATION AND BLUSHING

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METHOD OF IMAGE REPRODUCTION BY PHOTOPOLYMERIZATION AND BLUSHING

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ABSTRACT OF THE DISCLOSURE

The latent image on a photohardenable material which has been exposed to a light and shadow pattern of actinic light is rendered visible by contacting the material with a liquid developer which is a nonsolvent for the photohardenable material and which is selectively absorbed in the unexposed nonphotohardened portions of the material to create two phases therein; one dispersed in the other to produce a light scattering visible lightened effect in unexposed, unphotohardened portions.

This invention relates in general to an imaging process and more specifically to an imaging system capable of producing blush-like images.

Blushing or blooming (the two terms are somewhat synonymous; blushing will hereafter be used to include both terms) has been defined as a surface coating defect, sometimes associated with lacquers, and is generally characterized by the formation of a milky opalescence which develops as the lacquer dries in a humid atmosphere. The Science of Surface Coatings, edited by H. W. Chatfield, D. Van Nostrand Company, Inc., pp. 465–466 (1962).

It has recently been discovered as described in copending application Ser. No. 522,759, filed Jan. 24, 1966, that blushing rather than being considered as a troublesome defect associated with surface coatings may be used to advantage to improve the properties of certain electrophotographic plates useful in the process of xerography. In the basic xerographic process, for example, as described in Carlson Pat. 2,297,691, a xerographic plate comprising a layer of photoconductive insulating material on a conductive backing is given a uniform electric charge over its surface and is then exposed to the subject matter to be reproduced usually by conventional projection techniques. This exposure discharges the plate areas in accordance with the radiation intensity that reaches them and thereby creates an electrostatic latent image on or in the photoconductive layer. Development of the latent image is effected with an electrostatically charged finely divided material such as an electroscopic powder that is brought into surface contact with the photoconductive layer and is held thereon electrostatically in a pattern corresponding to the electrostatic latent image. The developed image may be fixed to the plate or the unfixed image may be transferred to a support surface, for example, paper to which it may be affixed by heat, solvent vapors or other means known in the art.

Xerography has found extensive commercial success especially in the office copying field and the aforementioned copending application improves the characteristics of certain imaging materials employed in the xerographic process. However, that application is concerned with xerography and as advantageous a process as xerography is, it does entail the use of xerographic plates which generally comprise at least a two-layer system of a photoconductive insulating material overlying a conductive backing layer and generally calls for a charging step wherein the xerographic plate is brought to a certain surface potential followed by an image exposure step and a developing step and a subsequent fixing step to permanentize the image. Charging usually requires high voltages which introduces the danger of sparking and requires that the xerographic plate be sensitized or charged in the dark or in the absence of activating electromagnetic radiation. Additionally, the xerographic plate configuration is limited by the electrical characteristics it must possess in order to accept and retain charge from a charging device. Also fixing is a separate required step if the marking particle image is rendered to be in a form for normal handling. All these factors and others add additional steps and complexity to the xerographic process.

It has also recently been discovered as described in copending application Ser. No. 362,982, filed Apr. 27, 1964, now U.S. Pat. 3,350,205, entitled "Blushed Images" that blushing may be employed to form images by drying a surface coating of a photopolymerizable material in a humid ambient atmosphere to blush the surface of the material which, when followed by exposure and a heat or solvent softening step, selectively erases the blushed surface in image configuration in non-light struck areas. Alternative methods are to expose the photopolymerizable material, soften it, dry it in a humid ambient atmosphere and soften, or to expose, soften and dry it in a humid ambient atmosphere to form blushing in non-light struck areas.

While advantageous, this concept in each of its embodiments calls for a three and four step process which adds to the complexity of the process and in every embodiment calls for drying of a photopolymerizable surface coating in a humid ambient atmosphere to produce blushing which is somewhat limiting because of the difficulty of obtaining and maintaining a suitable supply of water vapor during drying of the photopolymerizable material.

It is therefore an object of this invention to provide an imaging process which overcomes the above-noted disadvantages.

It is a further object of this invention to provide an imaging process which requires no charging step.

It is a further object of this invention to provide an imaging system wherein the imaging member need not be of xerographic plate configuration.

It is a still further object of this invention to provide an imaging process capable of producing good continuous tone and solid area images as well as line copy images.

It is a still further object of this invention to provide an imaging system which is clean and which employs reusable, non-toxic developer liquids.

It is a still further object of this invention to provide an imaging system to produce fixed images with no separate fixing step being required.

It is a still further object of this invention to provide an imaging process which for certain imaging materials may be carried out in normal room light.

It is a still further object of this invention to provide an imaging process capable of producing blush-like images which process is simpler than prior art image blushing methods.

It is a still further object of this invention to provide an imaging process which employs liquid development to produce a blush-like image effect rather than by drying a surface coating in water vapor.

The foregoing objects and others are accomplished in accordance with this invention by providing an imaging member comprising a layer of photohardenable material which is exposed to actinic radiation for example in imagewise pattern to selectively photoharden said material to create a latent image of photohardened and non-photohardened portions.

The latent image is rendered visible by contacting the material with a non-solvent, developer liquid which when selectively absorbed in the unexposed, non-photohardened,

more soluble portions of the material, creates two phases in the material, one dispersed in the other to produce a light scattering, visible, lightened effect in unexposed, non-photohardened portions.

Some non-solvent developer liquids may be absorbed into the photohardenable material in sufficient quantities by their own action to produce images by this invention.

Alternatively, the non-photohardened portions of the member may be rendered more receptive to the non-solvent developer liquid by contacting the imaging member with a relatively active solvent for the photohardenable material either prior to or simultaneous with the application of the non-solvent developer liquid.

For a better understanding of the invention as well as other objects and further features thereof, reference is made to the following detailed disclosure of the invention taken in conjunction with the accompanying figure wherein:

A schematic representation of an exemplary selective blush imaging system according to one aspect of the invention is illustrated.

Referring now to the figure, there is seen continuous web imaging member **10** passing from supply roll **12** and progressively through exposure station **14** and development station **16** to take up roll **20**.

Imaging member **10** may comprise almost any photohardenable material **11** conventionally used in photomechanical applications in the printing, photoengraving and related arts. A wide variety of photohardenable materials are found to be incompatible with various non-solvent, developer liquids which when absorbed into the photohardenable material, create two phases in the member one dispersed in the other to produce a light scattering, visible, lightened effect in two phase portions of the member.

It is understood that the photohardenable material **11** will in most applications be coated on a suitable rigid or flexible support **13** such as metal, glass, paper, plastic film or other substrate to lend mechanical support to the photohardenable layer. An alternative approach is to mix the photohardenable material with a binder type material, this layer optionally supported by a support layer. If the support is transparent the resultant image will not only be directly viewable but may be used as a transparency in conventional projectors.

The cinnamate esters of polyvinyl alcohol and/or cellulose which may be further sensitized by the presence of anthrones and their derivatives, polynuclear quinone derivatives and certain ketones such as Michler's Ketone and which are commercially available under the trademarks Kodak Photoresist (KPR), KMER and KOR from the Eastman Kodak Co. are found to be preferred photohardenable materials for use herein because of the excellent light reflecting images obtained from the process of this invention.

However, any suitable photohardenable material may be used. Typical photohardenable materials are systems comprising a non-photosensitive polymer and a photosensitive low molecular-weight compound with which it is capable of reacting on exposure to produce insolubility typified by polymeric materials such as casein and rubber, in combination with photosensitive azidostilbene sulfonate derivatives; systems comprising a monomer, a dimer and/or a low-molecular weight polymer with a filler and one or more polymerization catalysts typified by materials as described in Plambeck Pats. 2,760,863 and 2,791,504; systems comprising a non-photosensitive polymer and photosensitive low-molecular weight compounds wherein the photosensitive agent reacts with itself on exposure to create insolubility in exposed portions typified by ethylcellulose, polymethyl methacrylate and numerous other commercial plastics containing photosensitive chalcone or unsaturated ketone derivatives typified by materials as described in Murray Pat. 1,965,710 and Van Deusen Pat. 2,544,905; systems of chromate compounds in colloids such as gelatin, albumen and glue or protein colloids sensitized for example with potassium bichromate or cellulose derivatives sensitized for example with ammonium dichromate or other polyvinyls such as polyvinylalcohol, polyvinylacetal, polyvinyl methyl ether and polyvinylpyrrolidone sensitized for example with ammonium dichromate or polyamides sensitized by dichromates; diazo-sensitized materials, and others.

As the imaging member is unwound from supply roll **12** it passes exposure station generally designated **14** whereat an original **22** to be reproduced is projected onto the image surface by means of lens **24** operating in conjunction with the lighting means, for example, light bulbs **26**, the lens, original and lighting means synchronized by apparatus well known in the art (not shown) to the motion of member **10**. Exposure causes the photohardenable material to become photohardened in latent image pattern configuration corresponding to the projected image of original **22**. For example, if original **22** is a piece of hard copy such as a typewritten letter, than the latent photohardened pattern on the imaging member after exposure will be a negative image of the image on the original the typewritten or dark image portions being non-exposed on the member to be devoloped by the process of this invention to form a light scattering visible dispersed phase in such non-exposed areas, and the background or white portions of the original corresponding to exposed and photohardened portions of the imaging member which appear after development by the process hereof as non-light scattering, relatively dark portions of member **10**.

It will be understood by those versed in the art that original **22** may be a transparency such as a conventional photographic negative whereupon exposure of the imaging member may take place by positioning a light source above the negative and directing light through it in transparent areas to impinge on the imaging member and photoharden it in image configuration to produce a positive right reading image.

It will be understood that many photohardenable materials are most sensitive to ultraviolet light which permits the process of this invention to be completely carried out in room light without unduly effecting the sensitivity of the imaging member.

Exposure times may vary over rather wide ranges and generally are in the order of times as would be used if the photohardenable material were to be used in a conventional photomechanical process. Underexposed images usually appear as somewhat lighter and more light scattering with slightly lower resolutions than optimumly exposed images. Over-exposed images usually appear as somewhat darker and less light scattering with slightly lower resolutions than optimumly exposed images.

After exposure the image member is then developed at development station **16** whereat brush **28** contacts the member with a quantity of a liquid **32** comprising a non-solvent developer liquid supplied from liquid reservoir **30** by connecting tube **34**. It will be appreciated that this method of applying the liquid to the image member is exemplary and that many other suitable means exist.

As will be seen the non-solvent developer liquid may be recycled and used many times. For example, a chamber surrounding the imaging member in the region of brush **28** with ingress and egress ports for member **10** would permit evaporation and collection of the liquid **32** used to develop the member. It is found that very little, if any, liquid used in development may not be reclaimed for further use in this or some similar manner.

For the single treatment development illustrated by the figure, liquid **32** may comprise a non-solvent, developer liquid which may be absorbed into the non-photohardened portions of material **11** in sufficient quantity to produce a two phase, light scattering effect in said portions. This absorption will generally result because of the inherent permeability of the photohardenable material itself, even for a non-solvent, to cause the liquid to be absorbed to

cause the film whitening effect hereof. This mode of development is illustrated in Example XIV.

Alternatively, for single treatment development, liquid **32** may be a liquid mixture comprising a non-solvent developer liquid and an active solvent for material **11**, the solvent to serve as a vehicle to carry the developer liquid into material **11** in non-photohardened portions. In this aspect of the invention the active solvent component of the liquid mixture should preferably be more volatile than the developer liquid, so that after absorption of the mixture into the material the solvent is evaporated off first to leave the developer liquid behind in the material to create the two phase, visible, light scattering effect in portions where the developer liquid is absorbed.

Preferred volatile, active solvents for use herein may comprise any fairly volatile, active solvent for the particular photohardenable film being used which is preferably also miscible with or a solvent for the less volatile, developer liquid. A preferred solvent for use herein has been found to be methylene chloride which is a volatile, active solvent for the preferred photohardenable materials described herein and also is compatible with the less volatile, developer liquids used herein.

Any suitable volatile, active solvent for the particular photohardenable material may be used. Typical such solvents for the preferred photohardenable films described herein include acetone, methanol and mixtures thereof.

The less volatile, non-solvent developer liquid may comprise any liquid compatible with the volatile, active solvent for the imaging member and which being incompatible with the photohardenable material creates two phases in the material, one dispersed in the other, to produce a light scattering, visible, lightened effect in areas where the developer liquid is absorbed.

Preferred developer liquids for this aspect of the invention are Freon 113, a trichlorotrifluorethane liquid available from E. I. du Pont de Nemours & Co., hexamethyl disiloxane, a silicone oil and mixtures thereof. Any suitable liquid which causes a two phase light scattering effect in absorbed portions and is a non-solvent for material **11** and preferably less volatile than the volatile, active solvent component of the liquid mixture **32** may be used herein. Typical such liquids may include water, methanol and other aliphatic hydrocarbons and mixtures thereof. The particular liquid chosen will of course depend on the type of photohardenable material being used and on the properties of the volatile, active solvent component of the liquid mixture.

It is found that the ratio of components in the liquid mixture for liquid mixtures of preferred solvents and developer liquids to develop preferred photohardenable materials may be varied over a wide range. Parts by volume of the volatile, active, component/less volatile, developer liquid may vary from 4/1 to 1/4 and still produce viewable images in accordance with the invention.

As an alternative to simultaneously contacting a liquid mixture comprising an active solvent and a developer liquid to the imaging member a sequential process may be employed to permit use of developer liquids which evaporate at nearly the same rate or even faster than the active solvents for a particular photohardenable material. In this alternative, the latent image is developed by first treating the member with an active solvent and then with a suitable developer liquid. The active solvent softens the material and makes it receptive to the developer liquid which is then contacted with the member and absorbed in non-photohardened portions to create a two phase, light scattering effect in said portions. This alternative is illustrated in Examples XII and XIII.

It may be desirable for particular liquids and photohardenable materials to follow the developing with a rinsing step to wash any liquids from the developed member but such a step is not necessary to produce prints with the preferred materials listed herein.

Also, depending on the volatility of the liquids used in development and on development times, it might be found desirable to follow the developing step or the optional rinsing step with a drying step utilizing, for example, heated air blowers. Such a step is not required for preferred liquid mixtures used herein since even the less volatile, developer liquids are sufficiently volatile to evaporate readily by mere air drying at room temperatures.

It should be noted that while "blush-like" is used herein, because of the lack of a more descriptive term to describe the resultant effect and image appearance produced by the liquid development process herein, the creation of two phases in the imaging member in areas of absorption of the non-solvent, developer liquid, one phase dispersed in the other to produce a light scattering, visible, lightened effect in said portions, although somewhat similar in appearance to the "blushing" produced when certain lacquers are dried in a humid atmosphere is thought to be caused by different factors, at least in some instances.

The causes of blushing in lacquers and the blush-like effect in photohardenable materials by this invention are not completely understood but it is thoughtful that the reason why a two phase system is created by the process as disclosed herein may be that the long chain polymers comprising many photohardenable materials are caused to assume a coil form in non-photohardened portions by reaction with non-solvent developer liquid, thus causing the light scattering effect dispersed within the remainder of the material producing a visible, white or light effect in said portions. It is also thought that the blush-like effect produced by this invention in non-photohardened portions may be caused because the developer liquid being incompatible with the material because of its non-solvency may cause the liquid upon being absorbed into the material to separate in the form of many bubbles to create a bubbled or pocketed effect after all liquids are evaporated.

The following examples further specifically define the invention with respect to the imaging process hereof. Parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the selective blush-like image process of this invention.

EXAMPLE I

The liquid photohardenable material KPR from Eastman Kodak Co. is coated on about a 5 mil aluminum substrate and allowed to dry to form about a ¼ mil layer of KPR.

The imaging member thus formed is exposed to a photographic negative by focusing on the member an image produced by a 100 watt Hanovia Utility Model Quartz Lamp positioned about 7 inches above the member transmitting light through the translucent portions of the negative for about 5 minutes.

The imaging member is then dipped into a liquid mixture of about three parts by volume of methylene chloride as the more volatile active solvent and about two parts by volume of about 0.65 centistoke hexamethyl disiloxane as the less volatile non-solvent, developer liquid, for about three seconds.

A faithful right reading, positive, high resolution reproduction of the original appears on the image member with faithful image reproduction of continuous tone and solid area portions of the original.

EXAMPLE II

Example I is followed except that the imaging member is dipped after exposure into a liquid mixture of about one part by volume of methylene chloride as the more volatile active solvent and about two parts by volume of Freon 113 as the less volatile, non-solvent, developer liquid, for about three seconds.

An image reproduction comparable in quality to the image of Example I is produced.

EXAMPLE III

An imaging member is made and exposed as in Example I except that exposure is for a period of about 2½ minutes.

The member is developed and dried as in Example I to produce a somewhat lighter and more light scattering image with somewhat lower resolution than the image produced in Example I.

EXAMPLE IV

An imaging member is made and exposed as in Example I except that exposure is for a period of about 30 minutes.

The member is developed and dried as in Example I to produce a somewhat darker and less light scattering image with somewhat lower resolution than the image produced in Example I.

EXAMPLE V

Example I is followed except that the KPR is coated on black paper.

An image is produced with more contrast than the image of Example I because of the darker background areas.

EXAMPLE VI

Example I is followed except that the member is dipped into the liquid mixture for about 20 seconds.

An image is produced with somewhat less contrast than the image produced in Example I resulting from some light scattering even from exposed photohardened portions of the imaging member.

EXAMPLE VII

Example I is followed except that the liquid mixture comprises about 4 parts by volume of methylene chloride, about 1 part by volume of about 0.65 centistoke hexamethyl disiloxane and about 1 part by volume of Freon 113.

An image reproduction comparable in quality to the image of Example I is produced.

EXAMPLE VIII

Example I is followed except that the liquid photohardenable material KOR available from Eastman Kodak Co. is coated to form the imaging member.

An image results with slightly less contrast, density and resolution that the image of Example I.

EXAMPLE IX

Example I is followed except that the liquid photohardenable material KMER available from Eastman Kodak Co. is coated to form the imaging member.

An image results with slightly less contrast, density and resolution than the image of Example VIII.

EXAMPLE X

A solution of about 5 parts RS, 600–1,000 second nitrocellulose in about 100 parts ethyl alcohol is saturated with ammonium dichromate and coated on an aluminum substrate and allowed to dry to form about a 0.1 mil layer of photohardenable material.

The member is exposed as in Example I.

The imaging member is then dipped into a liquid mixture of about 1 part by volume of acetone as the more active, volatile solvent and about 1 part by volume of water as the less volatile, non-solvent developer liquid, for about 15 seconds. An image is produced.

EXAMPLE XI

Example X is followed except that the imaging member after exposure is dipped into a liquid mixture of about 4 parts by volume of acetone and about 1 part by volume of water for about 10 seconds. An image is produced.

EXAMPLE XII

About 50 parts of a solution of about 200 parts by volume water and about 10 parts by volume of polyvinyl methyl ether/maleic anhydride copolymer available from General Aniline and Film Corp. under the trademark Gantrez 139 is doped with about 1 part ammonium dichromate, coated on an aluminum substrate and allowed to dry to form about a 0.2 mil layer of photohardenable material.

The member is exposed as in Example I.

The imaging member is then dipped in methanol for about 1 second and then dipped in Freon 113 for about 15 seconds.

An image is produced.

EXAMPLE XIII

About 50 parts of a solution of about 100 parts of water and about 10 parts of polyvinyl pyrrolidone is doped with about 1 part ammonium dichromate, coated on an aluminum substrate and allowed to dry to form about a 0.5 mil layer of photohardenable material.

The member is exposed as in Example I.

The imaging member is then dipped in a liquid mixture of about equal parts by volume of methanol and acetone for about 1 second and then dipped in acetone for about 15 seconds.

An image is produced.

EXAMPLE XIV

About 4 parts of Polectron 450, an emulsion copolymer of vinyl pyrrolidone-styrene available from General Aniline and Film Corp. is doped with about 1 part ammonium dichromate, coated on Cronar polyester film available from the E. I. du Pont de Nemours & Co. and allowed to dry to form about a 0.2 mil layer of photohardenable material.

The member is exposed as in Example I except that exposure is for a period of about 1 hour.

The imaging member is then dipped into water for about three seconds.

An image is produced which appears to fade upon drying but which may be regenerated by rewetting.

Although specific components and proportions have been stated in the above description of preferred embodiments of the blush imaging system herein, other suitable materials as listed herein may be used with similar results. In addition other materials may be added to the mixture and variations may be made in the various processing steps to synergize, enhance or otherwise modify the resultant image. For example, dark pigments or dyes may be added to the photohardenable material to enhance resultant image contrast by decreasing the amount of light scattering from photohardened light struck portions of the imaging member. Also photohardenable material support **13** may be darkened or may comprise a black material to add contrast to the resultant image.

In addition, although the blush-like images produced herein are customarily milky or white in color when colorless developer liquids are used, colored developer liquids may be utilized to give colored images.

It will be understood that various other changes in the details, materials, steps and arrangements of parts which have been herein described and illustrated in order to explain the nature of the invention will occur to and may be made by those skilled in the art upon a reading of this disclosure and such changes are intended to be included within the principle and scope of this invention.

What is claimed is:

1. An imaging process comprising the steps of:

(a) providing an imaging member comprising a layer of photohardenable material;

(b) exposing said material to a light and shadow pattern of actinic light to selectively photoharden light struck portions of said material relative to the non-light struck portions of said material; and

(c) developing said exposed member, said developing step consisting essentially of contacting said layer of exposed photohardenable material with a developer liquid which is a nonsolvent for said photohardenable material and which upon being absorbed into the nonlight struck portions of said layer creates in said portions at least two phases, one dispersed in the other thereby creating a light scattering visible effect in said portions.

2. An imaging process comprising the steps of:

(a) providing an imaging member comprising a layer of photohardenable material;

(b) exposing said material to a light and shadow pattern of actinic light to selectively photoharden light struck portions of said material relative to the nonlight struck portions of said material; and

(c) developing said exposed member by simultaneously contacting said exposed layer of photohardenable material with:

(i) a developer liquid which is a nonsolvent for said photohardenable material and which upon being absorbed into the nonlight struck portions of said layer creates in said portions at least two phases, one dispersed in the other thereby creating a light scattering visible effect in said portions; and

(ii) an active solvent for said nonlight struck portions of said material.

3. An imaging process according to claim 2 wherein said active solvent and said developer liquid comprise a liquid mixture.

4. An imaging process according to claim 3 wherein said active solvent is more volatile than said developer liquid.

5. An imaging process according to claim 4 wherein said photohardenable material comprises a polyvinyl cinnamate.

6. An imaging process according to claim 5 wherein said photohardenable material includes a light sensitizer for said polyvinyl cinnamate whereby the photographic speed of said photohardenable material is substantially increased.

7. An imaging process according to claim 4 wherein said more volatile, active solvent is selected from the group consisting of methylene chloride, acetone, methanol and mixtures thereof.

8. An imaging process according to claim 7 wherein said developer liquid is selected from the group consisting of hexamethyl disiloxane, trichlortrifluorethane, water and mixtures thereof.

9. An imaging process according to claim 1 wherein said developer liquid comprises water.

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