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[54] MULTIPLE COPY PHOTOGRAPHIC SYSTEM
11 Claims, No Drawings

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[50]	Field of Search.....	101/453- —473

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ABSTRACT: This disclosure relates to new offset printing masters which contain a supply of printing fluid thus permitting their use in multiple copying. The new masters obviate the need of frequent replenishment of the printing fluid. The new masters of this invention comprise crazed thermoplastic layers in which the extent of crazing permits retention of a supply of printing liquid in the thermoplastic layer. Various such masters are described in which the printing liquid is added from an external source or is present in the offset master and available for printing after crazing of the thermoplastic layer. Also described are masters which are especially suitable for use with oleophilic or hydrophilic printing liquids by virtue of the content therein of a layer of oleophilic or hydrophilic material made available to the crazed areas of the thermoplastic layer by the extent of crazing. Processes of multiple copying using the new offset printing masters are also described.

MULTIPLE COPY PHOTOGRAPHIC SYSTEM

FIELD OF THE INVENTION

This invention relates to novel offset printing masters, and their use in multiple-copying processes.

DESCRIPTION OF PRIOR ART

Surface-deformation is a well-known phenomenon which has been described in the patent and scientific literature. A comprehensive article on surface deformation appeared in RCA Review, June, 1964, p. 209 in which this phenomenon is described at great length with reference to fundamental aspects and considerations, and this article is incorporated herein, by reference, therefore. Various U.S. Patents describe this phenomenon and modifications thereof in commercial application, such as U.S. Pat. Nos. 3,196,011; 3,317,315; 3,258,336; 3,333,958; 3,318,698; 3,329,500.

As disclosed in the aforementioned RCA Review article, surface deformation involves imagewise charging the surface of a thermoplastic layer and thereafter heating the charged layer to deform the surface. The surface deformation occurs only when the thermoplastic layer is coated with a layer of certain materials, and only occurs where the surface of the thermoplastic layer is charged and coated with the aforesaid layer. The thickness of the coating layer is of a degree of criticality in that it cannot be too thin since the result is nonuniform and blotchy, nor too thick since it forms a homogeneous smooth surface that is sufficient to prevent any development of surface deformation. In general, the tolerable as well as preferable thickness for any cover layer can be easily determined for any specific system by a minimum of experimentation. Practical and generally accepted thicknesses lie in the range of from about one-thousandth of a monolayer up to about 100 millimicrons. The top layer materials can vary widely and include a large variety ranging from good insulating materials to metals at the other extreme. Organic surface layers, e.g. polyvinyl alcohol, can be used, as well as oxides, such as silica, and finally, metals, such as gold, aluminum and tungsten. The metal layers should be discontinuous to permit retention of charge which is essential.

The thermoplastic material must be a good insulator at room temperature and remain so, at least for a short time, when heated to the softening point. Polystyrene is quite satisfactory, either in the low-melting form or in the higher melting form which is usually available in the form of sheets and solid stock. The material dissolves readily in toluene as well as other solvents, e.g. methylene chloride or tetrahydrofuran in which state it is readily applicable as a coating to suitable substrates, such as glass, by dipping and draining. The thickness of coatings thus obtained is a function of the concentration of polystyrene in the solution and the rate of withdrawal from the solution.

Charging of the thermoplastic layer surface is accomplished most effectively with corona discharge which is usually preferred since uniform charge is thereby attained. For example, one or more fine wires stretched inside a grounded metal shield open on one side can be used by passing the open side over the thermoplastic surface without contacting the surface while the wires are maintained at the desired voltage. Patterns of charge can be formed on the surface by use of a stencil, e.g. a metal or plastic mask.

Heat development of the image pattern is effected by means of hot air or infrared radiation. Usually it is simpler to heat the image pattern by contact with a hot plate, e.g. maintained at a temperature to permit softening of the thermoplastic layer, usually about 80° C. and up to temperatures of about 180° C. The crazed pattern develops on heating, the pattern scattering white light while the smooth regions do not. The images can be viewed with suitable optics, especially schlieren optics when the crazing is only slight, with which the crazed regions appear white and smooth areas dark.

In the aforementioned Review Article, as well as the deformations of the aforementioned U.S. Patents, the degree of

deformation is not substantial with respect to penetration of the thermoplastic layer, the deformation being principally confined to the surface of the thermoplastic layer. Such deformed layers can sometimes be inked but only with considerable difficulty and serve, however ineffectively, as an offset master for production of prints. Since the extent of deformation only affects the surface, i.e. surface deformation, and does not constitute any appreciable penetration of the thermoplastic surface, the deformed thermoplastic layers must be inked usually after each printing which additionally limits the use thereof as offset printing masters.

SUMMARY OF THE INVENTION

It has now been surprisingly discovered that versatile offset printing masters can be prepared by effecting a greater degree of deformation of the thermoplastic layer thus creating in the thermoplastic layer voids in which printing fluids, e.g. inks or dyes, can be stored so that the inked master can be used a substantial number of times without replenishment of the printing fluid. For the purposes of this disclosure, this type of surface deformation is referred to as crazing and the image thus obtained is called a crazed image, as distinguished from the aforesaid surface deformation and surface deformed images. Especially preferred masters are those in which the crazing extends through the thickness of the thermoplastic layer, penetrating to the layer on which the thermoplastic layer is supported, i.e. the substrate, or any intermediate layer interposed therebetween. In such masters can be included layers of useful materials and, with the intermediate layer being in surface contact with the thermoplastic layer, the crazed portions can be exposed to materials contained in this layer. For example, the intermediate layer can comprise a printing ink or dye solution which can be forced into the crazed areas, e.g. by pressure contact with printing paper, thus provided a printed image corresponding to the crazed image pattern. The intermediate layer can also contain reagents to improve printing fluid reception by the crazed areas. For example, the intermediate layer can contain oleophilic or hydrophilic materials and when passed into the crazed portions improve the receptivity for oleophilic or hydrophilic printing fluids. As recognized by those skilled in this art, the intermediate layer must be conductive.

Thus, the improved masters of this invention permit multiple copying without the need of replenishment, the number of copies being determined by the amount of ink in the intermediate layer or in the crazed portions of the thermoplastic layer, whichever modification is employed.

DESCRIPTION OF PREFERRED EMBODIMENTS

In forming the novel and useful masters of the present invention, the extent of crazing should be sufficient to at least substantially penetrate the thermoplastic layer to permit retention of a supply of printing liquid in the crazed layer. Such extent of crazing is principally dependent on the thickness of the crazable layer, but also on the amount of heating as well as the charge of the layer. These variables should be taken into account with any given system. For example, with a polystyrene layer of about 10 microns thickness, a corona discharge of about 6,000—7,000 volts for a few seconds followed by heating on a hot plate at a surface temperature of about 80° C., usually at 125° C., for a few seconds gives quite satisfactory results. In view of the simplicity of this procedure, little, if any, improvement can be obtained by altering the heating temperature or time of heating, for which reason the said conditions are preferred. Obviously, the use of lower effective temperatures of crazing will necessitate longer periods of heating, but the time periods would still be measurable in seconds since crazing does occur quite rapidly as long as an effective crazing temperature is employed. For any given system, a simple test procedure can be employed to determine optimum crazing conditions. This procedure merely involves inking the crazed areas, printing on a suitable receptor and

then determining whether ink remains on the crazed master by visual inspection. In general, the crazing temperature will be found in the range of from about 80° to about 180° C.

The thermoplastic layer of the master is preferably polystyrene which, at present, gives the best results. Any of the available available forms of polystyrene can be employed, as hereinbefore described. In addition, acrylic polymers are also well suited for use in the present masters, the results therewith being comparable to those obtained with polystyrene. The thermoplastic layer is formed on the substrate by usual methods of dipping, hand or machine coating, brushing or spraying. For best results, dipping the substrate into a solution of the thermoplastic material, e.g. polystyrene, in a suitable solvent, e.g. toluene, is preferred since control of the layer thickness is best accomplished thereby. As is known in the art, the concentration of thermoplastic material in the solvent will be the principal determinant of layer thickness. Since the thermoplastic layer is desirably of a thickness in the range of from about 2.0 to about 12.0 microns, it is preferred to dip the substrate into a solution which is from about 8 percent to about 20 percent by weight of thermoplastic material. The use of such concentration permits relatively rapid, efficient coating for which reason it is preferred. Solutions of higher or lower concentration can be employed but are less efficient in the formation of layers of the desired thickness.

As mentioned, the thickness of the thermoplastic layer should be from about 2 to about 12 microns. The use of thinner films is avoided since there is a tendency for the surface charge to leak off. The thicker films, though operable are somewhat difficult to craze to the extent required since they have a tendency to yield only a deformed image rather than the degree of crazing required in the present masters. Since no appreciable advantage can be obtained using thicker films, they are not preferred because of the extreme conditions which would be required to attain practical crazing to permit retention of sufficient printing fluid.

In a preferred embodiment of the invention the thermoplastic layer contains at least one photoconductor, i.e. a radiation-activatable compound, which permits the use of the present masters in positive image formation. With such layers, the imaging is much the same as that used in xerography. The master is uniformly charged and then imagewise exposed with radiation by which the photoconductor is activated, thus removing the initial charge on the surface in the image areas. Heating of the master leads to crazing in the nonimage areas, i.e. a positive image is obtained.

The photoconductors contemplated are known to those skilled in the art and need not be enumerated particularly since the literature on such compounds is voluminous and well known. Although various types of photoconductors may be used, including inorganic photoconductors such as titanium dioxide, zinc oxide, selenium and the like, it is preferred to use organic photoconductors since these are more compatible in the organic thermoplastic layer and are more readily incorporated into the thermoplastic layer.

Suitable organic photoconductors are described in the patent literature, e.g. in U.S. Pat. Nos. 3,250,615; 3,163,530; 3,163,531; 3,163,532; 3,169,060; 3,174,854; 3,180,729; 3,180,730; 3,189,447; 3,215,528; 3,231,500; 3,232,755; 3,240,594; 3,240,595; 3,240,597; 3,250,615; 2,738,272; 2,952,538; 2,954,291; 2,997,387; 2,999,750; 3,037,861; 3,041,165; 3,066,023 and many other U.S. and foreign patents.

The photoconductors can be dye-sensitized or otherwise treated to alter the spectral sensitivity. For example, the photoconductor, if not sensitive to visible light, can be so sensitized with certain dyes as is recognized by those skilled in the art.

The new crazed masters of this invention are particularly adaptable for multiple copying by virtue of their ability to hold a supply of printing liquid in the crazed portions. Modification of the masters to improve their printing liquid retention is contemplated by incorporation therein of materials designed for

this purpose. In view of the degree of crazing in the thermoplastic layer called for in the present masters, the inclusion of a layer of the said materials between the thermoplastic layer and the support and in surface contact with the thermoplastic layer permits release of the said materials into the thermoplastic layer in the crazed areas. If the crazing is sufficient to penetrate the full thickness of the thermoplastic layer, it allows for adequate diffusion of the said materials into the thermoplastic layer. As should be obvious, it is not necessary for all of the crazing to completely penetrate the thermoplastic layer but a substantial degree of complete penetration in the crazed areas should occur for practical considerations.

In a preferred embodiment, the material of the said intermediate layer comprises a printing fluid, preferably in a pressure-releasable form such as in microencapsulated form. When the master is used for printing after the crazed image is formed, the pressure contact of the printing medium on the master releases the printing fluid and thus the printed copy is formed. Alternatively, the printing fluid may be formed in situ by use of the dry components thereof in the intermediate layer and the printing medium wetted with a solvent for the dry components.

In another embodiment, the intermediate layer comprises a hydrophilic or oleophilic substance which on penetration of the crazed areas of the thermoplastic layer renders it more receptive to oleophilic or hydrophilic printing fluids. Especially preferred are oleophilic substances which are volatilized on heating. During or after the crazing step, the oleophilic substances will distill into and form ink receptive areas in the crazed areas of the thermoplastic layer. With a coating layer of hydrophilic substance, such as polyvinyl alcohol, the non-crazed areas will be hydrophilic and the crazed areas printable with oleophilic ink.

The various materials, such as printing fluids, oleophilic or hydrophilic substances, are well known to the art and can be incorporated into the said intermediate layer by recognized methods. Generally, it is preferred to incorporate these materials into a binder such as gelatin or polyvinyl alcohol, although other such binders can be used as are commonly employed in the art. The width of the intermediate layer is not critical and is determined by the amount of the said materials required for the intended use. For practical purposes, the said layer can assume any thickness as long as it remains conductive.

The surface layer which coats the thermoplastic layer is preferably gelatin or polyvinylalcohol, and especially gelatin which has been hardened, e.g. with an aldehyde hardener, conveniently formaldehyde, which is readily available and economical. Other aldehydes can also be employed, e.g. succinaldehyde or glutaraldehyde or derivatives thereof. The hardened gelatin layer usually yields the most uniform crazing and is more suitable for use with the normal printing fluids, e.g. ink.

Other materials which may be applied on top of the thermoplastic layer includes among others, carboxylic acids, such as acetic acid, oleic acid, myristic acid, stearic acid, caproic acid, adipic acid, ethylenediaminetetraacetic acid, lactic acid, decanoic acid, acid salts, such as calcium stearate, ethylenediaminetetraacetic acid disodium salt, alcohols, such as ethyl alcohol, n-propyl alcohol, iso-propyl alcohol, n-butyl alcohol, tert-butyl alcohol, iso-butyl alcohol, n-amyl alcohol, iso-amyl alcohol, n-hexyl alcohol, n-octyl alcohol, cyclo hexanol alcohol, furfuryl alcohol, benzyl alcohol, hydrocarbons, such as n-pentane, hexane, benzene, toluene, kerosene, halogenated hydrocarbons, such as 1-4 dichlorobutane, sec-butyl bromide, benzo trifluoride, carbonyl compounds, such as acetone, methyl ethyl ketone, paraldehyde, amines, such as n-butylamine, triethylamine, heptylamine, ethylene-diamine, dibenzyl amine, n-amylamine, decylamine, ethers, such as n-hexyl, phenyl ether, 1-4 dioxane, esters, such as ethyl orthosilicate, diethyl phthalate, tri-ethyl ortho formate, dyes such as methylene blue, quinaldine red, and others, and polymers, such as polyvinyl alcohol, polyvinylacetate and others.

The substrate of the present masters can be any of those commonly employed in the art such as glass, metal foil, paper, plastic sheets, and the like as long as they are conductive and remain stable under the conditions of the process.

The surface charging of the masters of this invention is by the art-recognized methods, preferably by corona discharge, as described hereinbefore. The voltage employed is conveniently in the range from about 5000 to 7000 volts for periods of but a few seconds. In view of the efficiency from the viewpoint of time, this range is preferred, although it is possible to attain surface charge at other voltages as recognized in the art. The charge, either positive or negative, is normally applied to the surface of the formed master, prior to heating although it is sometimes desirable to apply the charge after or during the heating step.

On heating, as hereinbefore described, the crazed image appears. If heating is conducted for too long, the thermoplastic layer can melt sufficiently to erase the image. Therefore, care should be exercised in the heating step to obtain maximum effect without permitting excessive melting and concomitant erasure of the image. In addition to hotplate heating as described herein, infrared heat, electrical resistance heat, or the like can be used, for which purpose, it is advantageous to include infrared absorbers in the aforementioned intermediate layer to improve the heating efficiency.

The crazed areas of the present media are thought to constitute capillarylike penetrations which vary in total volume individually. In general, it is probably more accurate to consider the crazed areas as consisting of "capillary areas—" which function as reservoirs for treating materials, e.g. printing inks in the crazed layer. Of course, applicants do not wish to be bound to any specific explanation of the observed phenomenon and merely proffer such a possible explanation to permit understanding of the function of the crazed layers in the various embodiments of this invention. In all probability, the crazed areas are composed of small pockets and capillaries which would explain the unusual results obtained.

The application of printing fluid to the surface of the crazed masters of the invention can be accomplished by any of the methods employed in the art. For example, the ink is applied with an ink roller by rolling across the surface of the master. The master may be inked automatically, as in an offset printer, when it is being used in a multiple-copying apparatus. Preferably, the ink is incorporated in the photographic master prior to exposure. In view of the aforesaid explanation, the type of ink used for direct application to the crazed surface should exclude extremely viscous inks which could not penetrate the crazed areas to any appreciable extent. Thus, it is preferable to use liquid inks which are free flowing and can readily penetrate the crazed areas by displacing the air therein. Either water or oil-base inks can be employed as long as they are liquids that can displace the air in the crazed areas. Obviously, where viscous inks are used, the present crazed masters can be inked for copy-making but the number of copies obtainable per individual inking is limited since the crazed areas cannot be fully saturated therewith due to entrapped air.

Once inked, the master can be used for preparing multiple copies without replenishing the ink supply. Thus the present masters are not only useful in automated printing apparatus but also in simple handprinting. The aforementioned masters containing an intermediate layer of printing material, either fluid, including viscous inks, or dry composition, are especially useful for handprinting, as for example, in a simple, hand operated office copy machine for production of a limited number of copies, and are disposable. Alternatively, these masters, after the printing material is spent, can additionally be inked, e.g. by hand rolling, and reused as additional copies are required.

The type of image formed on printing will be determined by the nature of the printing fluid used and the nature of the crazed and noncrazed surface of the master, i.e. whether hydrophilic or oleophilic. For example, the crazed areas of a gelatin coated master can be made hydrophilic by etching with

dilute alkali and the noncrazed areas remain oleophilic, thus producing a positive-working offset master. Similarly, alteration of the surface properties of the master will yield any desired result with respect to the type of print obtained. If the etching by alkali, preferably alkali metal hydroxides, is allowed to continue until a relief image is obtained, the resulting master is useful for lithographic-type printing.

The following examples are given to further illustrate the invention.

EXAMPLE 1

Fifteen g. of Dow PS-2 polystyrene is dissolved in 100 ml. of toluene. Clean conductive glass slides 1 inch $\times$ 3 inch are coated by mechanically lowering into this solution at the rate of 0.3 inches per second and immediately raising at this same rate. This coating is allowed to dry for 10 minutes. A second solution consisting of 1 g. of gelatin dissolved in 400 ml. H_2O is coated onto the polystyrene layer in the same procedure as above. The gelatin coated layer is immediately immersed into a 3 percent formaldehyde solution for 3 seconds. Three washings with distilled water for 2 seconds each follow the latter step. The prepared slide is allowed to air dry for one hour.

The dry slide is covered with a metal stencil and subjected to a 6,000 Volt positive Corona charger for 3 seconds. The slide is immediately placed onto a hot plate with a surface temperature of 125° C. for a period of 2 seconds in which time crazing appears. The slide is then removed and allowed to cool.

A rubber roller coated with Speed-O-Print duplicator ink by rolling back and forth on a glass plate containing some ink is rolled back and forth over the crazed slide until a uniform coating on ink is applied. Pressing the inked slide against plain bond paper transferred the ink to the paper only in the non-crazed areas. Ink in the crazed areas remained on the slide; and the slide can be used to make additional prints without re-inking.

EXAMPLE 2

Aluminum foil is coated with polystyrene as in Example 1. By contacting a finger upon this plate for an instant a sufficient amount of essential human oil is transferred to cause crazing when the slide is heated for several seconds on a hot plate, with a surface temperature of above about 125° C. The crazed areas are sharp outline of the finger print with much detail.

EXAMPLE 3

An acrylic ester polymer is coated onto clean glass slides from a solution consisting of 15 gms. of polymer to 100 ml. of toluene as in Example 1 and are allowed to dry. The coated slide is heated for several seconds on a hot plate with a surface temperature of 125° C. Upon immediate application of a positive corona charge of 6,000 volts through a metal stencil, crazed areas corresponding to the cut out areas of the stencil are produced.

EXAMPLE 4

One g. of 1-phenyl-3,5-bis-(p-methoxyphenyl) pyrazoline plus 5 g. of Dow PS-2 polystyrene are dissolved in 100 ml. of toluene. This solution is coated onto clean conductive slides (Nesa glass) in the procedure described in Example 1. A top coat of the disodium salt of ethylenediamine tetraacetic acid is applied from a 0.01 percent aqueous solution as described in Example 1 for top coats. The slide is then rinsed in distilled water and allowed to dry. The coated conductive slide is uniformly charged via either a positive or negative corona charger at a potential of 6,000 volts. The charged slide is imagewise exposed by a low pressure mercury Hanovia lamp through a photographic negative for 2 minutes. The exposed slide is then heated for several seconds on a hot plate with sur-

face temperature greater than 160° C. Crazing occurs in the nonlight struck areas to yield a positive picture.

EXAMPLE 5

Three layers, A, B and C are coated on a conductive substrate using the following solutions:

Solution A

4 g. of gelatin are dissolved in 100 ml. of warm water to which is added 0.100 g. of methylene blue.

Solution B

12 g. of Dow PS-2 polystyrene are dissolved in 100 of toluene.

Solution C

0.1 of gelatin is dissolved in 100 ml. of water.

Solution A is dip-coated onto a clean glass slide and allowed to dry. Solution B is then dip-coated and air-dried to form layer B. After drying, Solution C is coated on top of layer B. Immediately after dipping into solution C the slide is dipped into a 3 percent formaldehyde solution for 5 seconds followed by two water washes of —5 seconds each. The slide is allowed to dry.

The slide is then subjected to a +7,000 volt Corona charging apparatus through a stencil for several seconds. Upon heating the charged slide on a hot plate, with a surface temperature of about 125° C., a crazed image is produced.

The crazed slide is brought in intimate contact with a moist piece of paper for several seconds. Upon removal, the paper contains a methylene blue dye image corresponding to the pattern of the crazed areas.

EXAMPLE 6

Solution B of Example 5 is dip coated onto commercially available aluminum foil. This foil contains an organic polymer coating which provides good adhesion for the polystyrene coating. Solution C of Example 5 is applied and again the coatings are dipped into a 5 percent formaldehyde solution for 5 seconds followed by two water washes of 5 seconds each. The coatings are allowed to dry.

The layers are then subjected to a +7,000 volt Corona charging apparatus through a stencil for several seconds. Upon heating the charged layers on a hot plate with a surface temperature of about 140° C., a crazed image is produced.

The crazed foil is immersed in a warm 5 percent sodium hydroxide solution. The crazed areas etched within 60 seconds, while the noncrazed areas did not.

Since the etched areas become hydrophilic and nonetched areas are oleophilic, a positive working offset plate is produced.

EXAMPLE 7

The procedure of Example 6 is repeated except that the etching is allowed to proceed until a relief image is obtained. This plate is used for relief type printing.

EXAMPLE 8

The procedure of Example 5 is repeated using a black printing ink in lieu of methylene blue in layer B with the same results, the print being black.

EXAMPLE 9

The procedure of Example 5 is repeated using a printing ink in microencapsulated form in lieu of methylene blue. Printing is accomplished by pressure-contacting a sheet of paper with the surface of the master to obtain a print corresponding to the crazed areas of the master.

In the procedure of Example 5, substitution of an oleophilic material, e.g. an oil, for methylene blue in layer B results in the

crazed areas becoming oleophilic due to penetration of the crazed areas by the oil. If the top layer is polyvinyl alcohol (hydrophilic) the noncrazed areas are hydrophilic. Thus the master produces a direct positive print when oleophilic ink is used.

Oleophilic distillable liquids include such substances as hydrocarbon solvents, mineral oils, paraffin waxes, chlorinated polyphenyls, and natural occurring waxes and oils. Exemplary substances for use in this invention are illustrated in British Specification 943,401 and Belgian Patent 639,795, which are incorporated herein by reference for such illustration.

EXAMPLE 10

A mixture of 1 g. of polyvinyl carbazole and 10 g. of polystyrene are dissolved in 100 ml. of methylene chloride and the solution coated onto aluminum foil as described in Example 1. A top coat of gelatin is applied from a (0.1 g. in 100 ml.) aqueous gelatin solution in similar manner. Immediately the foil is dipped into a 3 percent formaldehyde solution for 5 seconds followed by two water washes of 5 seconds each.

The dried foil is subjected to a negative 7,000 volt corona charge for several seconds, and the charged foil is exposed imagewise in a photographic enlarger for 30 seconds. The exposed foil is then heated on a hot plate (surface temperature of 125° C.) until crazing occurs. A positive copy of the image is obtained.

EXAMPLE 11

One gram of dimethylaminostilbene and 10 g. polystyrene are dissolved in 100 ml. of tetrahydrofuran and coated as in Example 1, followed by a gelatin coating as in Example 10. The coating is then subjected to a negative 7,000 volt corona charge for several seconds and then is exposed imagewise through a negative for 30 seconds. On heating as in Example 10, a crazed image is obtained.

The crazed image of Examples 10 and 11 are suitable for inking and making copies as described in the preceding examples.

We claim:

1. A printing master comprising an image-wise crazed thermoplastic layer on a substrate therefor, to provide crazed portions of said layer wherein the extent of crazing is sufficient to permit retention of a supply of printing liquid and noncrazed portions of said layer which do not permit retention of a supply of printing liquid to permit multiple printing without replenishment.
2. Master as in claim 1 wherein the thermoplastic layer comprises polystyrene.
3. Master as in claim 2 wherein the thermoplastic layer is top coated with a layer of gelatin.
4. Master as in claim 2 wherein the thermoplastic layer is coated with a layer of polyvinyl alcohol.
5. Master as in claim 1 wherein the thermoplastic layer includes a photoconductor.
6. Master as in claim 1 wherein the thermoplastic layer includes an organic photoconductor.
7. A printing master comprising an image-wise crazed thermoplastic layer having both crazed and uncrazed portions, on a substrate therefor, including a layer of printing material intermediate of said thermoplastic layer and of said substrate and in surface contact with said thermoplastic layer, the extent of crazing in said thermoplastic layer being sufficient to penetrate the surface thereof adjacent to said printing fluid layer and to permit penetration by the printing fluid of the crazed areas of the thermoplastic layer.
8. A printing master comprising an outer layer capable of repelling greasy ink and an image-wise crazed thermoplastic layer having both crazed and uncrazed portions, on a substrate therefor, including a layer comprising a volatilizable oleophilic material intermediate of said thermoplastic layer and of said substrate and in surface contact with said thermoplastic layer,

the extent of crazing in said thermoplastic layer being sufficient to permit penetration of said thermoplastic layer by the said oleophilic material from the said intermediate layer.

9. A positive printing master comprising an image-wise crazed thermoplastic layer having both crazed and uncrazed portions on a substrate therefor, the extent of crazing being sufficient to permit retention of a supply of printing fluid in said layer to permit multiple printing without replenishment; the crazed areas being capable of repelling greasy ink and the noncrazed areas being oleophilic.

10. A printing master comprising an oleophilic outer layer and an image-wise crazed thermoplastic layer having both crazed and noncrazed portions on a substrate therefor, including a layer comprising a volatilizable hydrophilic material in-

termediate of said thermoplastic layer and of said substrate and in surface contact with said thermoplastic layer, the extent of crazing in said thermoplastic layer being sufficient to permit penetration of said thermoplastic layer by the said hydrophilic material from the said intermediate layer.

11. A positive printing master comprising an image-wise crazed thermoplastic layer having both crazed and noncrazed portions on a substrate therefor, the extent of crazing being sufficient to permit retention of a supply of printing fluid in said layer to permit multiple printing without replenishment; the crazed areas being oleophilic and the noncrazed areas being hydrophilic.

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