Feb. 21, 1967 J. T. LEONE 3,305,360

METHOD OF PREPARING LITHOGRAPHIC PLATES

Filed Sept. 20, 1963

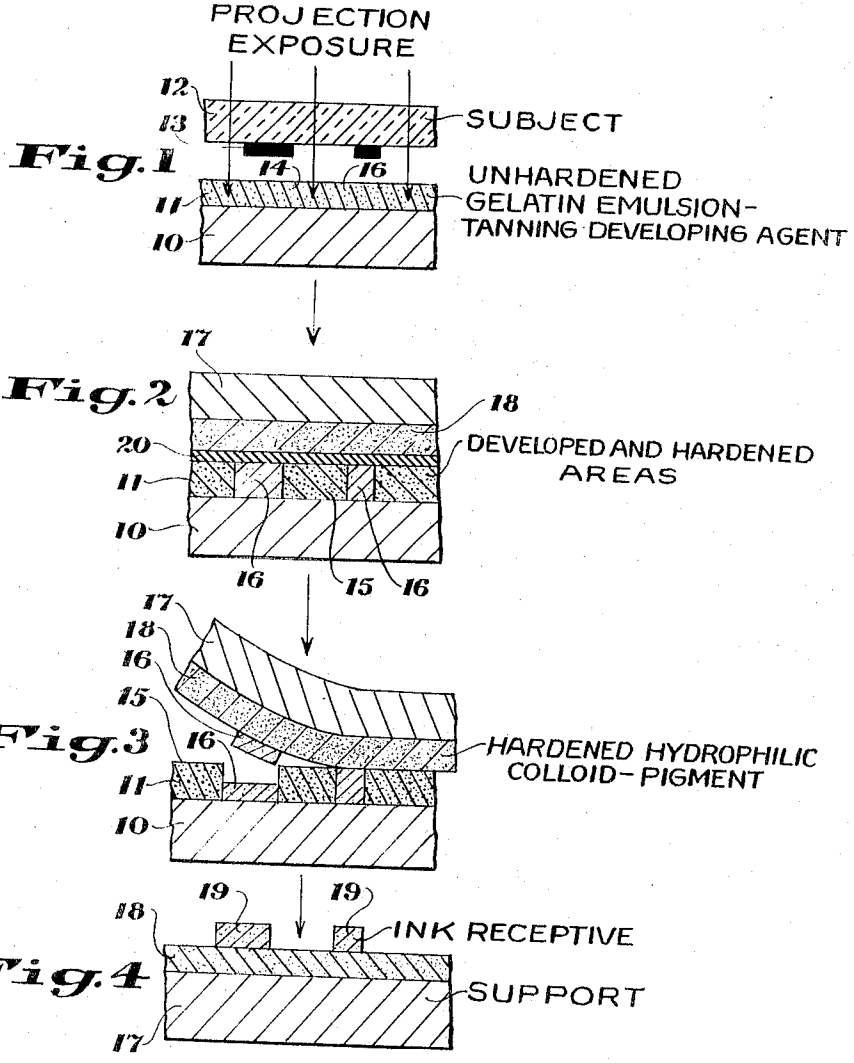


Fig. 1

Fig. 2

Fig. 3

Fig. 4

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United States Patent Office 3,305,360 Patented Feb. 21, 1967

3,305,360

METHOD OF PREPARING LITHOGRAPHIC PLATES

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Filed Sept. 20, 1963, Ser. No. 310,416
9 Claims. (Cl. 96—28)

This invention relates to methods for preparing lithographic offset printing plates, and particularly methods for preparing such plates having a paper base.

Various methods are known for photographically preparing lithographic offset printing plates, such as those wherein the printing plate has a paper support. For instance, a paper sheet provided with a hydrophilic surface, is coated with an unhardened silver halide photographic emulsion and after exposure to an image, developed with a tanning silver halide developer. The unexposed, and therefore, unhardened areas, are removed by washing in warm water. It is necessary that the unhardened colloid be completely removed in order to avoid any attraction by the unwanted colloid to the greasy printing ink used in lithographic printing. This has been found difficult to do and a method has been proposed employing a colloid transfer system of preparing a lithographic printing plate, as described in U.S. Patent 2,763,553, issued September 18, 1956, to Clark et al.

In carrying out the Clark et al. process, a substantially unhardened gelatino-silver halide emulsion layer is exposed to an image and developed under light-safe conditions with a tanning developer which forms a hardened image in the areas corresponding to the highlights of the subject and leaves other coplanar areas which are not hardened and which correspond to the shadows of the subject. A stratum of the unhardened areas is then transferred to a hydrophilic surface which will repel greasy printing inks when wetted during lithographic printing operations.

The light-sensitive unhardened silver halide emulsion preferably contains a tanning developing agent and is developed under conditions of tanning development prior to transferring the unhardened areas to a suitable hydrophilic surface. It is customary to use an alkaline activator solution in order to institute development and a dye is incorporated in the activator in order to render the transferred colloid image visible. The tanning developer does not result in a visible image of sufficient density for satisfactory use. However, this dye stains clothing, surroundings, hands, etc., so that it has been desirable to find a way of obtaining a visible transferred image without employing a dye in the activator solution.

Many other factors are involved in the preparation of a suitable photographic element for making lithographic plates by the colloid transfer process. For instance, the emulsion should be projection speed, so that the emulsion can be exposed by a process camera, whereas the emulsions normally associated with colloid transfer office copying processes are exposed by reflex means through the emulsion. Incorporation of a non-tanning developer in the emulsion along with the tanning developer results in adversely affecting the photographic properties such as speed, stability, etc. of the projection type emulsion as well as creating internal competition between the developers during the development step. For instance, the

non-tanning developers would develop faster and relatively little tanning would result. This, in turn, would increase the total amount of silver halide which is transferred to the support, and the image areas would not be sharply delineated. Still other developers have staining characteristics so that they are not suitable for use. Applying a non-tanning developer in the activator solution results in a similar competition between the developers for the exposed silver halide grains and adversely affects the quality of the image transferred to the receiving support.

In view of the small amount of moisture in the transferred layer, the development time after transfer is relatively short. Therefore, any developer intended to make this transferred image visible must operate before the transferred layer has dried.

I have discovered that prepared lithographic plates can be provided which have been tub-sized with a solution of developing agents which, when used with the colloid transfer type emulsions disclosed in U.S. Patent 2,763,553, result in obtaining a visible image on the photographic plate.

One object of this invention is to provide an improvement for the colloid transfer process of preparing a paper lithographic printing plate. An additional object is to obtain a visible image using a colloid transfer process on a lithographic printing plate without using an activator solution containing a dye. Another object is to provide a method of obtaining a visible image on a lithographic printing plate using a colloid transfer system. Additional objects will be apparent from the following disclosure.

A lithographic printing plate which is to be used in my invention preferably has a paper base which has been rendered water repellent and which has been coated with a mixture of hardened hydrophilic organic colloid material and inert (i.e. non-silver halide reducing) material. Suitable for this purpose is a paper which has been coated with a mixture of well-hardened casein and a pigment or filter such as clay, barium sulfate, etc. In some instances, a casein coated paper may be provided with a layer containing gelatin and pigment. Various hydrophilic surfaces may be suitable in addition to the above, including cellulosic surfaces such as wood, paper, cloth and the like, grained zinc, anodized aluminum, surfaces of hydrophilic organic colloids such as surface hydrolyzed cellulose ester, e.g. a surface hydrolyzed cellulose acetate sheet, surface hydrolyzed synthetic resins, such as surface hydrolyzed polyvinyl acetate, polyvinyl alcohol, proteins such as gelatin, casein, etc.

The lithographic plate is tub-sized with a non-tanning developer solution preferably containing ascorbic acid and 1 - phenyl - 3 - pyrazolidone. When this tub-sized lithographic plate is used with a colloid transfer emulsion containing therein a tanning developer, all that is required is that the surface of the photographic emulsion be suitably developed by imbibing an alkaline fluid when the exposed photographic emulsion is contacted against the lithographic plate so that the colloid in the unhardened areas can be transferred to the hydrophilic surface of the lithographic plate.

Non-tanning silver halide developing agents which can be used in this process include pyrazolidone developers, for example, 1-phenyl-3-pyrazolidone, 1-phenyl-4-dimethyl-3-pyrazolidone, etc., Elon (p-methylaminophenol), and ascorbic acid. Mixtures of these can be used to enhance

development. Kodak D–52, for instance, is a useful developer containing Elon and hydroquinone.

Although we prefer to use a tub-sizing process to apply the developer solution to the printing plate, other methods of applying the developer may be used, such as surface coating and the like. Known methods of surface coatings may be used including wick, knife, hopper, and the like. One useful concentration range of the coating solution is 0.1 percent to 1 percent pyrazolidone and 0.2 percent to 1.8 percent ascorbic acid for both the surface coating and the tub-size applications. Preferably, the coverage ranges are 1 to 10 milligrams per square foot for the pyrazolidones and 2 to 18 milligrams per square foot for ascorbic acid. When other known developing agents are used, such as Elon, etc., a useful coverage is from 1 to 18 milligrams per square foot.

The exposure procedure is illustrated in FIG. 1 of the drawings, wherein the silver halide sensitized element having the paper, film, or other support **10** carrying the unhardened emulsion layer **11** is shown undergoing exposure to light through a lens system in a process camera to reflection copy **12** carrying a line or halftone image **13**. Exposure produces latent images principally in areas **14** of emulsion **11**, the remaining areas receiving little or no exposure.

The exposed emulsion **11** is then developed in the presence of a tanning silver halide developer and pressed against a hydrophilic surface **18** on which has been coated a silver halide developer **20**, taking reasonable care to prevent excessive light exposure of the emulsion layer, for about 20 to 45 seconds at room temperature. The result, as shown in FIG. 2 of the drawings, is to develop the exposed silver halide and tan or harden the gelatin in areas **15** of the emulsion layer **11**, the remaining unexposed areas **16** containing unhardened emulsion.

The emulsion layer **11** contains the hardened image areas **15** which will not adhere to the pigmented hardened hydrophilic surface of layer **18**, and other coplanar unhardened areas **16** which will adhere to layer **18**. When the layer **18** is peeled off, as shown in FIG. 3 of the drawings, a stratum of area **16** adheres to the pigmented hardened hydrophilic colloid surface of the baryta-coated paper. This stratum develops to form a visible image. After treatment with a conventional image conditioning solution as, for example, that described in Lake U.S. Patent 2,794,388, the printing element carrying the adhered area **16** is useful as a lithographic printing plate.

If the printing element is dried down before use, it is found that while areas **16** are still more hydrophilic than desired, these areas will selectively attract printing inks when run on a lithographic printing press and prints can be obtained therefrom. Accordingly, at this stage in order to render the printing areas more fully ink-receptive, the printing element may be subjected to dry heat sufficient to improve ink-receptivity and preferably at a temperature below the charring point of the transferred colloid stratum; that is, a temperature of the order of 150 to 275° C. for ten seconds to three minutes, depending upon the temperature used and the extent to which the element has been dried before heating. At 230 to 250° C., 20 seconds is satisfactory for a previously dried element or 30 seconds if the element is moist from the transfer operation. At 150° C., three minutes and at 275° C., 10 seconds heating are required.

The final printing plate is then obtained having the structure shown in FIG. 4 of the drawings wherein areas **19** are the ink-receptive portions of the printing plate and the remaining surface of layer **18** is hydrophilic and will absorb sufficient moisture in the lithographic printing press to repel the greasy printing ink. The printing plate may then be used directly in a lithographic printing press. However improved results are obtained, if, prior to inking, the plate is next treated with a solution of a bi-valent metal salt such as zinc acetate and/or application of an aqueous solution of glycerin and phosphoric acid. Other metal salts which are satisfactory are disclosed in the Worthen U.S. Patent 2,534,650, issued December 19, 1950, and suitable acidic glycerin solutions are disclosed in the Van Dusen U.S. Patent 2,515,536, issued July 18, 1950.

The addition of softening agents, e.g. citric acid, sulfite, urea, etc., to the activator solution used for treating the lithographic plate improves the quality of the transfer.

The following examples are provided to illustrate representative methods for carrying out my invention.

Example 1

A lithographic printing element having a hydrophilic surface is prepared by coating a melamine-formaldehyde sized paper stock of medium weight with a mixture of gelatin and baryta containing a gelatin hardening agent such as formaldehyde or aluminum chloride. The baryta coating is then hardened by application of 1.7 grams of the following solution per square foot of surface followed by drying:

Water	cc..	295
Hydrochloric acid (0.05 grm. per cc.)	cc..	64
Potassium dichromate	g..	4
Tannic acid (0.05 g./cc.)	cc..	32
Saponin (7.5% aqueous solution)	cc..	5

The printing element is then tub-sized with a developer comprising a mixture of ascorbic acid and 1-phenyl-3-pyrazolidone and dried.

An unhardened paper stock is coated with a substantially unhardened gelatino-silver chloride emulsion preferably containing a substantially water-insoluble gelatin tanning developing agent such as 3,4-dihydroxy diphenyl, 2,5-dihydroxy diphenyl or 2,3-dihydroxy diphenyl and prepared by the methods described in the Yackel U.S. Patent 2,592,368 issued April 8, 1952. Water-soluble tanning developing agents such as hydroquinone or pyrocatechol are less preferred but can be utilized in the emulsion. The emulsion is not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated. The silver halide sensitized sheet is then exposed by projection printing methods under a two-tone or high-contrast subject such as a line or halftone transparency or printed matter.

The exposed element is developed by imbibing into the exposed emulsion a minimum amount of alkaline solution such as 3 percent aqueous sodium carbonate solution which may contain a softening agent such as urea, etc., for about 20 to 45 seconds at room temperature. The excess alkaline solution is then squeegeed from the surface of the emulsion layer.

The pigmented hardened hydrophilic colloid surface of the baryta-coated paper prepared as above is pressed against the surface of the wet developed emulsion layer, taking reasonable care to prevent excessive light exposure of the emulsion layer, and very soon thereafter is peeled off. A good visible image is formed. After treatment with image conditioners described above, the printing element carrying the adhered area is useful as a lithographic plate.

Example 2

A sized paper stock of medium weight is rendered water-repellent by coating a casein solution on the face side so as to obtain about .15–.6 gram of casein per square foot of surface as follows:

To 800 grams casein in water is added sufficient aqueous ammonia solution to obtain a pH of 9.0. After filtering, the solution is neutralized to a pH of 6.5 with citric acid. This solution is then diluted with 120° F. water to a 7 percent casein solution. Spreading agent and 11 cc. of 20 percent formaldehyde solution per 100 grams of casein are then added and coatings are made directly from this solution. A normal baryta coating is then applied to the casein coating from a composition containing one

part of gelatin per 10 parts of barium sulfate and formaldehyde as the hardener for the gelatin. The coating is applied so as to obtain three grams of solid per square foot. Subsequently, the baryta coating is further hardened by treatment with the acid dichromate solution of Example 1 using 1.7 grams of solution per square foot of surface.

This sheet is then swabbed with Kodak Developer D–52 containing hydroquinone and Elon.

An unhardened paper stock is coated with a substantially unhardened gelatino-silver chloride emulsion layer containing a silver halide tanning developing agent as described in Example 1. This sensitive element is then exposed to the desired subject and developed in alkaline solution.

The casein and baryta-coated printing element prepared above is then pressed against the wet developed emulsion layer under reduced illumination and quickly peeled off. As in Example 1, the hardened image areas do not adhere to the baryta-coated surface whereas the unexposed, undeveloped and unhardened areas adhere, and a stratum thereof comes off on to the pigmented hydrophilic surface of the printing element. A good visible image is obtained.

The printing plate, now carrying the adhered stratum is then heated under dry heat at a temperature of 200° C. for about two minutes. Prior to inking the printing plate in the lithographic printing press, it is treated with a zinc acetate and glycerin solution as described in Worthen U.S. Patent 2,534,650. As a result of using the casein coated paper stock as a support for the baryta layer, the printing plate shows little distortion in the printing press in the presence of moisture. Therefore, press endurance is high since the printing areas adhere well to the baryta coating.

Example 3

As the hydrophilic lithographic printing element, a sized paper support is provided carrying a layer of a mixture of hardened casein and clay. It is then immersed in a solution of zinc acetate before application to the casein-pigment coat of a thin coating of sodium alginate as described in U.S. Patent 2,534,650, issued December 19, 1950.

The dried coated surface of the plate is then pressed against the moist surface of the sensitive element which has been exposed and processed as described in Example 1, followed by separation of the two sheets and heating the printing element carrying the adhered emulsion stratum.

The resulting printing plate is used directly in a lithographic printing press after treating with the solution described in Example 1 prior to inking the plate.

Example 4

The transfer of the unhardened emulsion stratum, as described in Example 3 is made to the hydrophilic surface, then treated with an alkali solution. Since the stratum contains undeveloped silver halide, developing agent and gelatin, the result is to develop the silver halide and at the same time tan the gelatin with the oxidation products of the developing agent. For this purpose a 5–20 percent sodium carbonate solution is used, for about 30 seconds at about 70–85° F., followed by an acid rinse of 1–2 percent acetic acid. The plate is dried and used on a lithographic press with good results. Similar results are obtained by using other alkaline solutions such as those containing trisodium phosphate, alkali metal hydroxide, sodium metaborate, etc.

A number of other variations may be made in my methods for preparing printing plates which fall within the scope of my invention. I may use light-sensitive elements described in the Clark et al. patent referred to above, containing the developing agent in the emulsion. If the developing agent is not contained in the emulsion,

a soluble silver halide tanning developing agent is employed in the alkaline developing solution used to effect tanning development. The silver halide emulsion may be of the usual negative type or may be a direct positive emulsion.

The pigment used in the coating of the hydrophilic printing element may be any of the well known inert pigments, particularly inert mineral pigments such as clay, barium sulfate, titanium oxide, etc., and carbon black, although it is preferred to use light-colored pigments to obtain maximum contrast to light between the inked image and the hydrophilic surface of the printing plate.

The hydrophilic colloid of the pigmented printing element can be gelatin or casein, as indicated, or other organic colloids such as polyvinyl alcohol, gum arabic, starch, albumin, methyl cellulose, cellulose sulfate, partially hydrolyzed polyvinyl acetate, zein, etc., particularly those materials which can be insolubilized and hardened most readily especially with the bi-valent metal salts and yet retain hydrophilic properties. As mentioned above, the hydrophilic surfaces to which the emulsion transfer is made can be any of the metal surfaces such as of grained zinc and anodized aluminum.

The organic colloid material used as in Example 3 to render the paper support moisture-repellent may consist of any of the well known water-resistant materials such as synthetic resins, cellulose esters, rubber, etc., applied from solvent or aqueous dispersions, such as methyl methacrylate resin, cellulose acetate, natural or artificial rubber latex. The organic colloid component of the pigmented layer should be selected so as to obtain optimum adherence to the water-repellent layer and to this end subbing layers may be interposed between the pigmented hydrophilic colloid layer and the moisture-repellent layer. It is not necessary, but may be advisable in some cases to coat the paper base on both sides with the water-repellent organic colloid material such as hardened casein.

Although we prefer to use a silver chloride light-sensitive emulsion, it will be clear to one skilled in the art that other known light-sensitive silver halide emulsions can be used, such as silver bromide, silver chlorobromide, silver chlorobromoiodide, and the like.

Fogging agents may also be incorporated in the developers on the plate to obtain a visible image without requiring exposure to light.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A method for preparing a lithographic printing plate which comprises pressing the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

2. A method for preparing a lithographic printing plate which comprises the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer comprising a hydroquinone silver

halide developing agent, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

3. A method for preparing a lithographic printing plate which comprises pressing the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer comprising a pyrazolidone silver halide developing agent, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

4. A method for preparing a lithographic printing plate which comprises pressing the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer comprising a hydroquinone silver halide developing agent and p-methylaminophenol sulfate, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

5. A method for preparing a lithographic printing plate which comprises pressing the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer comprising hydroquinone and p-methylaminophenol sulfate, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

6. A method for preparing a lithographic printing plate which comprises pressing the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer comprising 1-phenyl-4-dimethyl-3-pyrazolidone, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

7. A method for preparing a lithographic printing plate which comprises pressing the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer comprising 1-phenyl-3-pyrazolidone, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

8. A method for preparing a lithographic printing plate which comprises pressing the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer, comprising ascorbic acid and 1-phenyl-3-pyrazolidone, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

9. A method for preparing a lithographic printing plate which comprises the hydrophilic surface of a supported layer containing a mixture of hardened colloid and an inert pigment and having thereon a coating of non-tanning silver halide developer comprising hydroquinone, against a moist supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a high-contrast subject and developed in the

presence of a gelatin tanning silver halide developing agent producing hardened image areas which will not adhere to said hydrophilic surface and other coplanar areas corresponding to the shadows of the subject which adhere to said hydrophilic surface, said emulsion layer being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, mechanically removing the support of said emulsion layer

together with the hardened image areas from the hydrophilic surface to leave a stratum of only said coplanar emulsion areas containing gelatin tanning silver halide developing agent adhered to said surface.

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