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Martens et al.

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[54] LITHOGRAPHIC PRINTING PLATE AND PROCESS

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[52] **U.S. Cl.** ....**101/462,** 96/29 L

[51] **Int. Cl.** **B41n 3/00**

[58] **Field of Search**.............................96/29, 84, 114; 101/457, 462

[56] **References Cited**

UNITED STATES PATENTS

3,557,696	1/1971	Hoover	96/29 X
3,532,315	1/1971	Ormsbee	96/29 X

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[57] ABSTRACT

A printing plate is prepared by coating on a support a lithographic layer comprising a self-hardening copolymer such as a copolymer of acrylamide and 2-acetoacetoxyethyl methacrylate, colloidal silica and titanium dioxide. Over the lithographic coating can be located a silver precipitating layer preferably comprising nickel sulfide and silver iodide. An image is provided in the silver precipitating layer by diffusion transfer and treated with a thiol or similar sulfur containing material to improve the ink-water balance of the plate. In an integral product the nucleated lithographic layer is coated with a silver halide layer and processed to provide a silver image after which the silver halide layer is removed.

12 Claims, No Drawings

LITHOGRAPHIC PRINTING PLATE AND PROCESS

BACKGROUND OF THE INVENTION

This invention is concerned with the preparation of printing plates and their use. In one aspect, the invention relates to the formation of a lithographic surface using a self-hardening polymer and a mixture of pigments. In another aspect this invention relates to the formation by diffusion transfer of lithographic plates.

It is known to obtain lithographic printing plates by using various light sensitive materials to prepare an image on a hydrophilic support. Typical light sensitive materials include diazo resins, light sensitive silver halide emulsions, cinnamic acid esters, etc. However, for many purposes lithographic plates using these light sensitive materials to print from are unsatisfactory. For example, such plates exhibit relatively short press life and require methods of preparation which are quite complex.

For lithographic plates which are intended for a relatively short press life, where only a few hundred copies are required, or even up to about 1,000 copies, it is quite common to use a paper printing plate. However, it has been desirable to improve the lithographic coating used on the paper surface in order to increase the ink-water differential between the image areas and the background, improve wearability on the press, freedom from blinding, etc.

Perkins U.S. Pat. No. 3,055,295 issued Sept. 25, 1962 describes a planographic printing plate having thereon a lithographic coating comprising a polymeric material and a mixture of pigments. The polymeric material requires a cross-linking agent such as dimethylol urea in order to provide a satisfactory lithographic layer. However, it has been desirable to obtain a lithographic surface which is self-hardening.

One method of making a lithographic plate is to coat an unhardened silver halide emulsion on a suitable support. The emulsion is developed using a tanning developer which hardens the emulsion image wise after which the remaining unhardened emulsion is removed by using warm water. However, when using a surface which contains a crosslinking agent such as formaldehyde, dimethylol urea or similar hardening material, there has been a problem with migration of the hardener or crosslinking agent from the surface of the lithographic layer into the unhardened emulsion so that the emulsion becomes hardened and cannot be readily removed. Therefore, it has been desirable to have a hydrophilic lithographic surface which does not require the presence of a crosslinking or hardening agent in the lithographic surface itself.

In a particularly useful printing plate in which the image is obtained by diffusion transfer, a silver precipitating or nucleated surface is provided on a lithographic surface which is suitable for forming a silver image by diffusion transfer. Hepher et al. U.S. Pat. No. 3,161,508 describes preparing an aluminum lithographic printing plate by diffusion transfer. However, the formation of a paper lithographic plate using conventional paper plates such as a crosslinked polymeric binder as described in the prior art has not been entirely satisfactory due to problems of slow inkup, blinding, etc.

Accordingly, it has been desirable to provide an improved lithographic surface for preparation of lithographic plates especially by diffusion transfer, which would be hydrophilic with respect to an oleophilic image area, have good reproducibility, and which can be used as a surface for various types of oleophilic images.

SUMMARY OF THE INVENTION

We have found that a lithographic layer which is particularly useful comprises a self-hardenable polymeric material containing at least about 0.1 percent by weight of active methylene groups in aliphatic side chains, which contains a hydrophilic pigment mixture. A particularly useful hydrophilic self-hardening polymer is a copolymer of acrylamide and 2-acetoacetoxyethyl methacrylate, containing a pigment mixture of colloidal silica and titanium dioxide. This coating composition is coated on a suitable support such as, for example, paper having thereon a polyethylene coating which has been electron bombarded. Over the coating is located a silver precipitating layer such as a gelatin description of nickel sulfide and silver iodide or the like. An image is obtained on the precipitating layer by diffusion transfer by contacting against the silver precipitating surface an exposed silver halide emulsion in the presence of a silver halide developing agent and a silver halide solvent. The resulting image is preferrably treated with a solution of an organic compound containing an oleophilic group in the molecule and being a compound which when brought into contact with the silver at ordinary room temperature becomes integrated to the surface of and only in the region of the silver and thereby renders the surface of the silver oleophilic by virtue of the oleophilic groups so that greasy printing inks adhere thereto.

PREFERRED EMBODIMENTS

Various supports may be used under the lithographic coating of this invention. However, a paper support is preferred. The paper can be any conventional cellulosic paper support including those prepared from cotton, linen and wood (sulfate and sulfite pulp) and which supports are typical 5–60 pounds per 1,000 square foot papers. The paper is preferably coated with a polymeric material in order to make it more resistant to wear on the press and also to prevent processing chemicals from being absorbed by the paper. Particularly useful polymeric materials are polyolefins such as polyethylene which is employed as a coating on the paper support. A polyolefin material which forms the surface can be coated over any support, typically on a thickness of about 0.3 to 5 mils. For instance, particularly useful polyolefin materials include the olefin homo- or copolymers prepared from alpha-olefins having two to 10 carbon atoms. A coating may be applied by extrusion or hot melt coating techniques, as latexes, as solvent coatings, etc. When the polyolefin is self-supporting, it can be of any convenient thickness.

In some instances it is desirable to incorporate in the polyolefin at least one pigment or dye, especially where a white background is required, but this is not required. In a particularly useful embodiment, titanium dioxide is incorporated as a pigment in an amount of up to 25 percent, preferably 10–15 percent by weight of the resin. Other pigments or dyes which may be useful include those commonly known as pigments or dyes for polymeric materials.

The polyolefin surface can be given an additional treatment when the polyolefin material such as polyethylene is extruded but this is not necessary to this invention. Shortly after extrusion, the polymeric material is contacted against a chilled roll which may be glossy, preferably, or matte depending upon the desired finish. In another embodiment, the coating is placed on the support as a latex or solvent coating and then contacted against a hot glossy roll in order to provide a glossy or matte finish. This is particularly suitable when a latex coating has been applied or when the polymeric surface has been softened on the surface by contacting with a semisolvent solution which softens the surface of the coating. In still another embodiment a latex coating may be applied to a support after which the coated support is subjected to heat such as by hot air impinging on the surface or from infrared lamps directed to the surface.

The polymeric surface may be given a treatment to improve the hydrophilic character of the surface to improve adhesion, but this is not necessary. Typical treatments which are particularly suitable for use with hydrophobic polyolefin polymers, such as polyethylene, include electron bombardment, radiation by ultraviolet light, etc.

Electron bombardment of polymeric surfaces is conveniently carried out by means of a corona discharge. The level of electron bombardment or similar surface treatment of the polymeric surface can be measured by the contact angle obtained when a drop of distilled water is placed on a level sample of the polymeric coating. By projecting the image of the drop and sample on a suitable screen, and measuring the angle of a line tangent to the drop image at the point of the drop touches the polymeric sample, a contact angle is obtained which can be measured and utilized to determine the degree of hydrophilicity. Generally untreated polyethylene coated paper gives a contact angle of about 90°. A contact angle of preferably from about 40° to about 75° improves the adhesion of hydrophilic coatings and is highly desirable for coatings such as cellulose ester coatings, subbing coatings or the like. With polypropylene, the preferred contact angle is preferably less than 54° for subsequent coatings.

Typical methods of treating polyethylene by electron bombardment are disclosed in Traver U.S. Pat. No. 3,018,189 directed to methods for treating the surface of polyethylene with electrostatic discharges to change the surface properties of the polyethylene with respect to adhesion of materials coated thereon. British Patent Specification 715,915 issued to the Visking Corp., published Sept. 22, 1954 also discloses a method and apparatus for treating plastic structures with a corona discharge.

Another method of improving adhesion to a polyolefin coated surface is illustrated by Alsup U.S. Pat. No. 3,161,519 issued Dec. 15, 1964 in which colloidal silica is employed in a coating over the polyolefin surface. In the particular disclosure therein, a coating mixture containing colloidal silica is coated on untreated polyethylene coated paper and dried with hot air at about 150° F. A particularly useful coating composition is disclosed in Example 6 in which an acrylic resin is employed in the coating composition.

It will be appreciated that various layers of polymer may be coated on a support such as paper. In one embodiment, glasine paper is employed with polyolefin coated on each side followed by another sheet of glasine paper and an additional coat of polyolefin. The polyolefin may be coated on both sides of the paper support in order to improve the durability of the support and reduce the processing chemical absorption.

Cellulose esters may also be used for coating on a support such as paper and include cellulose esters which are obtained from organic acids having two to four carbon atoms including mixed esters such as cellulose acetate butyrate, cellulose acetate propionate and the like. Particularly useful esters are those of lower aliphatic, preferably monocarboxylic acids, such as cellulose acetate, cellulose triacetate, cellulose butyrate and the like. Typical cellulose ester formulations are described in Fordyce et al. U.S. Pat. Nos. 2,492,977 and 2,492,978 issued Jan. 3, 1950, Fordyce et al. U.S. Pat. No. 2,739,070 issued Mar. 20, 1965 and Fordyce et al. U.S. Pat. No. 2,607,704 issued Aug. 19, 1952.

It will be appreciated that other suitable supports may be used.

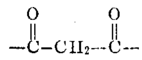
The lithographic coating of this invention contains colloidal silica having a particle size between 7 to about 30 millimicrons. The colloidal silica which can be used to form the pigment mixture of this invention contain silica particles of very small size. The mean average size of the silica particles can be within a range of from about 7 millimicrons to about 30 millimicrons. Although colloidal silica of less than about 7 millimicrons has not been commercially available, it is believed that the coating composition of this invention may be advantageously prepared from colloidal silica containing silica particles of a size even less than 7 millimicrons.

The most advantageous colloidal silicas are those which contain silica particles ranging in size from about 7 to 17 millimicrons. Such colloidal silicas are generally marked as a 30 percent silicon dioxide dispersion but the colloidal silica can be prepared containing a higher or lower percent silica. The silica preferably comprises about 10 percent to about 50 percent by weight of the pigment mixture. The pigment mixture comprises about 25 percent to about 90 percent by weight of the total layer, solids basis.

The titanium dioxide is of pigment size and preferably has an average mean diameter of 0.3 μ and a range of about 0.1 μ to 0.6 μ. It is preferably the anatase type since the anatase pigment provides a desirable white appearance to the lithographic layer.

Clays may be used in place of titanium dioxide provided they are of small size such as kaolin or china clays. Other pigments which may be used with silica include calcium silicate, barium sulfate, etc. Mixtures may be used.

The self-hardening polymers which are particularly useful as the binder in the lithographic coating according to our invention are film-forming polymers containing at least about 0.1 percent by weight of active methylene groups in aliphatic side chains. A particularly effective class of copolymers useful for this invention is prepared by copolymerizing an acrylamide with an acrylic type ester having active methylene groups in the ester moiety in a substituent alpha to the carbonyl group. Such compounds preferably contain the group:



$$-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-$$

The ethylenically unsaturated polymerizable monomers having the above formula can be prepared using any procedure suitable for this purpose. Polymers of this type are disclosed in Smith U.S. Pat. No. 3,488,708 issued Jan. 6, 1970. The preferred copolymers contain from about 80 to 98 percent by weight acrylamide of a unit such as acrylamide, methacrylamide or the like and from about 20 to 2 percent by weight of the monomeric unit containing an active methylene group such as 2-acetoacetoxyethyl methacrylate. The molecular weights of the copolymers are generally in the range of 5,000 to 500,000.

The coating composition is coated using any satisfactory coating method and has a contact angle as measured by water of less than 65°.

Precipitating agents which are particularly useful for use in the receiving sheet for use in a black and white diffusion transfer process include nuclei which are useful as precipitating agents with a silver halide complex, including all of those which are commonly useful in the diffusion transfer process. Nuclei which can be employed include silver precipitating agents known in the art such as sulfides, selenides, polysulfides, polyselenides, heavy metals, thiourea, stannous halides, heavy metal salts, fogged silver halide, Carey Lea silver, and complex salts of heavy metals with a compound such as thioacetamide, dithiooxamide and dithiobiuret. As examples of suitable silver precipitating agents and of image-receiving elements containing such silver precipitating agents, reference may be made to U.S. Pat. Nos. 2,698,237, 2,698,238 and 2,698,245 issued to Edwin H. Land on Dec. 28, 1954, U.S. Pat. No. 2,774,667 issued to Edwin H. Land and Meroe M. Morse on Dec. 18, 1956, U.S. Pat. No. 2,823,122 issued to Edwin H. Land on Feb. 11, 1958, U.S. Pat. No. 3,396,018 issued to Beavers et al. Aug. 6, 1968 also U.S. Pat. No. 3,369,901 issued to Fogg et al. Feb. 20, 1968 and U.S. Pat. No. 3,532,497 issued to Goffe Oct. 6, 1970. The noble metals, silver, gold, platinum, palladium, etc., in the colloidal form are particularly useful.

Noble metal nuclei are particularly active and useful when formed by reducing a noble metal salt using a borohydride or hypophosphite in the presence of a colloid. The metal nuclei can be prepared in the presence of a proteinaceous colloid such as gelatin and coated on the receiving sheet. The same or a different colloid may be added if desired. It will be appreciated that the coating composition generally contains not only nuclei, but also reaction products which are obtained from reducing the metal salt.

It will also be appreciated that the nuclei or silver precipitating agent may be incorporated in the lithographic layer itself by adding a suitable silver precipitant to the coating composition including the silica, titanium dioxide, polymeric material, etc. By incorporating the silver precipitating agent in the coating composition itself, a lithographic layer and silver precipitating material can be coated in one operation.

Various colloids can be used as dispersing agents or as binders for the precipitating agents in the receiving layer. Any suitable colloids can be used. Particularly useful colloids are hydrophilic colloids which are used for binders in silver halide emulsions. Advantageously, they are coated in a range of about 5–5,000 mg/ft^2. Included among suitable colloids are gelatin, preferably coated at a level in the range of about 7–100 mg/ft^2, polymeric latices such as copoly(2-chloroethyl-methacrylate-acrylic acid) preferably coated in the range of 15–350 mg/ft^2 in a polymeric vehicle containing two components (1) polyvinyl alcohol, and (2) interpolymer of n-butylacrylate, 3-acryloyloxypropane-1-sulfonic acid, sodium salt and 2-acetoacetoxyethyl methacrylate, in a preferred range of about 10–300 mg/ft^2.

It will also be appreciated that the precipitating agents can be formed in situ or can be applied by precipitating or evaporating a suitable precipitating agent on the surface.

The receiving layers of our invention may also have therein particles such as silica, bentonite, diatomaceous earth such as kieselguhr, powdered glass, micro crystalline asbestos and fuller's earth. In addition, colloids and colloidal particles of metal oxides such as titanium dioxide, colloidal alumina, coarse aluminum oxide, zirconium oxide and the like may be used with the nuclei in the receiving layers.

In carrying out the diffusion transfer process, conventionally a silver halide emulsion is exposed to a light image after which it is contacted with a silver halide developing agent containing a silver halide complexing agent. The exposed emulsion is developed in the light struck areas and the unexposed silver halide is complexed with the silver halide complexing agent after which the emulsion is contacted against a receiving sheet and the complex silver halide diffuses imagewise to the receiving sheet containing a silver precipitant.

Silver images produced photographically are customarily treated with an oleophilic compound which absorbs itself to the silver of the image area and improves greasy printing ink-water differential. Particularly useful compounds are disclosed in Hepher et al U.S. Pat. No. 3,161,508 which specify various sulfur containing compounds which are particularly useful. In U.S. Pat. No. 3,099,209 issued July 30, 1963 to Damschroder et al. certain specific sulfur containing compounds are also disclosed. In U.S. Pat. No. 3,083,097 issued Mar. 26, 1963 to Lassig et al., it is disclosed that silver images produced photographically can be converted by means of a bleaching or coating process or by reducers or intensifiers with the aid of oxidation baths into sparingly soluble heavy metal and/or silver salt images. In this process potassium ferricyanide is used, for example, for oxidizing the silver, whereby the silver image is converted into a ferricyanide which is precipitated partly as insoluble silver ferricyanide and partly as insoluble ferricyanide of other metals which are added to the baths in the form of salts.

Silver halide developing agents used for initiating development of the exposed sensitive element can be conventional types used for developing films or papers with the exception that a silver halide solvent or complexing agent such as sodium thiosulfate, sodium thiocyanate, ammonia or the like is present in the quantity required to form a soluble silver complex which diffuses imagewise to the receiving support. Usually, the concentration of developing agent and/or developing agent precursor employed is about 3 to about 320 mg/ft^2 of support.

Developing agents and/or developing agents precursors can be employed in a viscous processing composition containing a thickener such as carboxymethyl cellulose or hydroxyethyl cellulose. A typical developer composition is disclosed in U.S. Pat. No. 3,120,795 of Land et al. issued Feb. 11, 1964.

Developing agents and/or developing agent precursors can be employed alone or in combination with each other, as well as with auxiliary developing agents.

Suitable silver halide developing agents and developing agent precursors which can be employed include, for example, polyhydroxybenzenes, alkyl substituted hydroquinones, as exemplified by t-butyl hydroquinone, methyl hydroquinone and 2,5-dimethylhydroquinone, catechol and pyrogallol; chloro substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy substituted hydroquinones such as methoxy hydroquinone or ethoxy hydroquinone; aminophenol developing agents such as 2,4-diaminophenols and methylaminophenols.

Silver halide emulsions employed with lithographic layers and elements of this invention either in integral products or on separate supports can contain incorporated addenda, including chemical sensitizing and spectral sensitizing agents, coating agents, antifoggants and the like. They can also contain processing agents such as silver halide developing agents and/or developing agent precursors. Of course, the processing agents can be incorporated in a layer adjacent to the silver halide emulsion if desired.

The photographic emulsions employed can also be x-ray or other non-spectrally sensitized emulsions or they can contain spectral sensitizing dyes such as described in U.S. Pat. No. 2,526,632 of Brooker et al. issued Oct. 24, 1950 and U.S. Pat. No. 2,503,776 of Sprague issued Apr. 11, 1950. Spectral sensitizers which can be used include cyanines, merocyanines, styryls and hemicyanines.

The photographic emulsions can contain various photographic addenda, particularly those known to be beneficial in photographic compositions. Various addenda and concentrations to be employed can be determined by those skilled in the art. Suitable photographic addenda include hardeners, e.g., those set forth in British Pat. 974,317; buffers which maintain the desired developing activity and/or pH level; coating aids; plasticizers, speed increasing addenda, such as amines, quaternary ammonium salts, sulfonium salts and alkylene oxide polymers; and various stabilizing agents, such as sodium sulfite. The photographic silver salt emulsions can be chemically sensitized with compounds of the sulfur group such as sulfur, selenium and tellurium sensitizers, noble metal salts such as gold, or reduction sensitized with reducing agents or combinations of such materials.

Various photographic silver salts can be used in the practice of the invention. These include photographic silver halides such as silver iodide, silver bromide, silver chloride, as well as mixed halides such as silver bromoiodide, silver chloroiodide, silver chlorobromide and silver bromochloroiodide. Photographic silver salts which are not silver halides can also be employed such a silver salts of certain organic acids silver-dye salts or complexes, etc.

The photographic silver salts are typically contained in an emulsion layer comprising any binding materials suitable for photographic purposes. These include natural and synthetic binding materials generally employed for this purpose, for example, gelatin, colloidal albumin, water-soluble vinyl polymers, mono and polysaccharides, cellulose derivatives, proteins, water-soluble polyacrylamides, polyvinyl pyrrolidone and the like, as well as mixtures of such binding agents. The elements can also contain releasing layers and/or antistatic layers (i.e., conducting layers).

Integral elements may be prepared by coating a silver halide emulsion over the nucleated layer or over the lithographic layer containing the silver precipitating agent. The silver halide emulsion is coated over the layer comprising a colloid material which can be easily removed from the lithographic layer after a silver image has been formed on the lithographic layer or in the lithographic layer. Typical diffusion transfer integral processes and products are described in U.S. Pat. No. 3,020,155 issued Feb. 6, 1962 to Yackel et al., U.S. Pat. No. 2,563,342 issued to Land, Aug. 7, 1951, U.S. Pat. No. 2,692,830 issued Oct. 26, 1954 to Land, British Patent 746,948 issued to Levenson et al., published Mar. 21, 1956, British Patent 878,064 issued to Ilford, published Sept. 27, 1961 and U.S. Pat. No. 3,186,842 issued to DeHaes et al. June 1, 1965.

The following examples are included for a further understanding of the invention:

EXAMPLE 1

The following coating composition is coated in an amount of 15 grams per square meter on a dry basis and drying is accomplished at 180° F on polyethylene coated paper which has been electron bombarded for preparing element I.

Component	Parts per dry Weight
Anatase titanium dioxide	65.77
Nonionic dispersant	.05
Colloidal silica, 15 mμ aluminum modified	32.08
Copolymer of 90% acrylamide, 10% 2-acetoacetoxyethyl methacrylate	2.10

A nucleating layer is then coated over the lithographic layer comprising a mixture of nickel sulfide and silver iodide dispersed in 0.25 percent gelatin as described in U.S. Pat. No. 3,532,497 issued Oct. 6, 1970 to Goffe.

A lithographic element II is prepared using a styrene-butadiene copolymer latex coated paper employing a lithographic layer having the following composition, dry basis:

II.

Component	Parts by weight
Titanium dioxide	70.3
Surfactant	0.6
Colloidal silica	20.4
Polyvinyl alcohol	7.0
Dihydroxy dioxane	1.5
Tannic acid	0.2
t	100.0

The resulting lithographic layer is nucleated using the same nucleating composition as element I and coated at the same rate.

A lithographic element III is prepared having the following composition:

III.

Component	AMOUNT
Water	100 g.
30% colloidal silica (Ludox LS)	450 g.
0.5% Na_2S	88 cc.
0.5% $AgNO_3$	60 cc.
60% polyvinylidene chloride latex	30 cc.
40% acrylic emulsion polymer (Rhoplex A.C. 33-Rohm & Haas Co.)	5 cc.
10% Saponin	0.5 cc.
	733.5

The coating is made on the same type of support as element I after electron bombardment of the polyethylene surface at the same rate. No additional nuclei coating is applied.

Tests are made by contacting the lithographic elements I, II and III against an exposed developing silver halide emulsion having a silver halide solvent in the processing solution. Samples of each element are evaluated on a lithographic printing press. At this time the hardener free base (coating F, below) exhibits good inking characteristics and acceptable press run of more than 1000 impressions. Element II containing the hardener has very poor inking and is unacceptable for mottle.

Element III has slow ink-up and shows blinding after 200 copies.

Another nucleating variation is identified by coatings A–G. A, B and C represent silver iodide-nickel sulfide nuclei (1:1) (as disclosed in U.S. Pat. No. 3,532,497) applied to hardener free lithographic base with an extrusion hopper at various coverages. D through G are the same nuclei in gelatin applied with a gravure roll. H represents element III with no additional nuclei coat. Results are given below in Table I.

TABLE I

Coatings	Ag Cov mg/ft²	Fresh press test	Press Test after 8 days 120°F	Run Length
A	0.26	Very slow inkup	Not run	Satisfactory 2000
B	0.17	Very slow inkup	Not run	Satisfactory 300
C	0.18	Very slow inkup	Not run	
D	0.04	Slightly Slow inkup	Slow inkup	
E	0.05	Good	Satisfactory inkup	
F	0.06–0.11	Good	Satisfactory inkup	Satisfactory 3000
G	0.4	Good	Satisfactory inkup	
H	—	Very slow inkup	Very slow inkup	Blinding at 200

The results indicate that the various nuclei coverages can be used but a preferred coverage is between 0.04 and 0.17 milligram per square foot, the lower coverage appearing better for inking (nuclei expressed in terms of silver). Satisfactory inkup is obtained even after incubations at 120° F for 8 days and coating F provides over 3,000 impressions of good quality.

EXAMPLE 2

An example similar to that of Example 1 is carried out in coatings A–D using two separate coating operations and in E–H using a dual slide coater in which both the lithographic layer and the nuclei layer are coated in the same coating pass under the hoppers. The following data indicate the effectiveness of the resulting plates.

Coating	Nuclei pptd in	No. of Operations	Fresh Press Results	8 Day Inc. Press Results
A	gelatin (0.5%)	two	good	good
B	gelatin (.05%)	two	good	good
C	*Polymer (1.0%)	two	good	good
D	*Polymer (1.0%)	two	good	good
E	Gelatin (.05%)	one	fair-good	good
F	*Polymer (1.0%)	one	fair	good
G	*Polymer (1.0%)	one	good	good
H	Gelatin (.05%)	one	good	good

*Polymer of 90% acrylamide and 10% 2 acetoacetoxyethyl methacrylate.

The coatings exhibit good inking characteristics on all phases single operation material (dual slide coated) and slightly better for startup inking than the two operation plates.

EXAMPLE 3

Integral elements are prepared by coating an unhardened silver chloride emulsion over the nucleated layer of each of the elements described in Example 1 indicated as elements I and II. After processing in a developer bath containing sodium thiosulfate, the unhardened emulsion is removed. However, in element II after one week at room temperature the emulsion is hardened so that it cannot be removed with warm water. The emulsion on element I, without the hardener, is removed after 5 months at room temperature. After treatment with a bleach containing potassium ferricyanide, the surface is treated with a solution of 1-amino-2-mercapto-5-heptadecyl-1,3,4-triazole, NaOH and propanol.

EXAMPLE 4

A lithographic element I, as described in Example 1, without a nuclei coating is coated with a camera speed silver halide emulsion of the type described in Example 1 in U.S. Pat. No. 2,596,756. The plate is exposed in a reversing camera to a line image for a short exposure period. The exposed plate is activated in a caustic solution for 1½ minutes rinsed with a water spray at 110° F and air dried. At this stage, the plate contains a dense silver image in slight relief on top of the lithographic layer. The plate is run on a lithographic press producing satisfactory copies.

EXAMPLE 5

A lithographic element I, as described in Example 1, has a gelatin image placed on the unnucleated surface thereof by a silver gelatin transfer process as described in U.S. Pat. No. 2,596,756, wherein unhardened gelatin is transferred from a light sensitive sheet to a lithographic receiving sheet, after the emulsion layer is exposed and developed. The image areas are transferred under pressure to a lithographic layer as described above. The image is then treated with an image conditioner as disclosed in British Patent 934,691 to improve ink receptivity of the colloidal image portions and placed on a lithographic press to make satisfactory prints.

EXAMPLE 6

A lithographic element I without a nuclei layer, as described in Example 1, is placed in a typewriter employing a ribbon which provides an oleophilic typed image. Copy is typed employing the ribbon on the lithographic surface, after which the printing plate is used on a lithographic press. Satisfactory copies are provided.

EXAMPLE 7

A lithographic element I as described in Example 1 is coated with a hardened high-contrast silver chlorobromide negative emulsion having a melting point of 250° F coated to yield a silver coverage of 165 mg. of silver per square foot.

The element is exposed in a standard copy camera fitted with an image-reversing prism. It is processed in a hydroquinone type silver halide developer for two minutes at 68° F. After development, the plate is etch-bleached in a solution of the following composition for 60 seconds:

5 g. cupric chloride
75 g. citric acid
75 g. urea

all dissolved in one liter of 1½ percent hydrogen peroxide.

The plate is then rinsed with water, swabbed with an image conditioner and run on a lithographic printing press.

In some instances it is desirable to obtain negatives from letterpress printing plates in order to use these negatives to form printing plates by the offset process. Typically a light sensitive silver halide emulsion is overcoated with an ink receptive layer which is then contacted against the inked letter-press printing plate and subsequently exposed. The overcoat is removed during the processing of the silver halide emulsion providing a negative which can then be used for preparing offset printing plates. According to U.S. Pat. No. 3,473,926 issued to Abbott et al. Oct. 21, 1969, ink receptive binders such as alkyl acrylate-acrylic acid copolymers, cellulose ether phthalate or cellulose acetate phthalate may incorporate such preferred ink absorbing pigments as barium sulfite, silica, calcium carbonite or zinc oxide. In addition to the above, such binders as polyvinyl alcohol containing titanium dioxide may be used.

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.

We claim:

1. A lithographic element for use in diffusion transfer comprising a support having thereon a lithographic layer consisting essentially of an acrylamide copolymer having at least 0.1 percent by weight active methylene groups in aliphatic side chains, colloidal silica and a pigment.

2. An element of claim **1** in which said support is polyolefin coated paper.

3. An element of claim **1** in which said support is polyethylene coated paper.

4. An element of claim **1** having over the lithographic layer a silver precipitating layer.

5. An element of claim **4** in which said silver precipitating layer comprises a mixture of nickel sulfide and silver iodide.

6. An element of claim **1** having in said layer an oleophilic image area.

7. A lithographic element of claim **1** having over said layer a silver halide emulsion layer.

8. A photographic element of claim **4** having over said layer a silver halide emulsion layer.

9. An element of claim **1** including a silver precipitating agent.

10. An element of claim **1** having a silver precipitating layer comprising a mixture of nickel sulfide and silver iodide.

11. An element of claim **1** in which said lithographic layer comprises a copolymer of an acrylamide and 2-acetoacetoxyethyl methacrylate, colloidal silica and titanium dioxide.

12. An element of claim **11** in which said copolymer comprises 80 to 98 percent by weight acrylamide and about 20 to about 2 percent by weight 2-acetoacetoxyethyl methacrylate.

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