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LITHOGRAPHIC OFFSET PRINTING PROCESS

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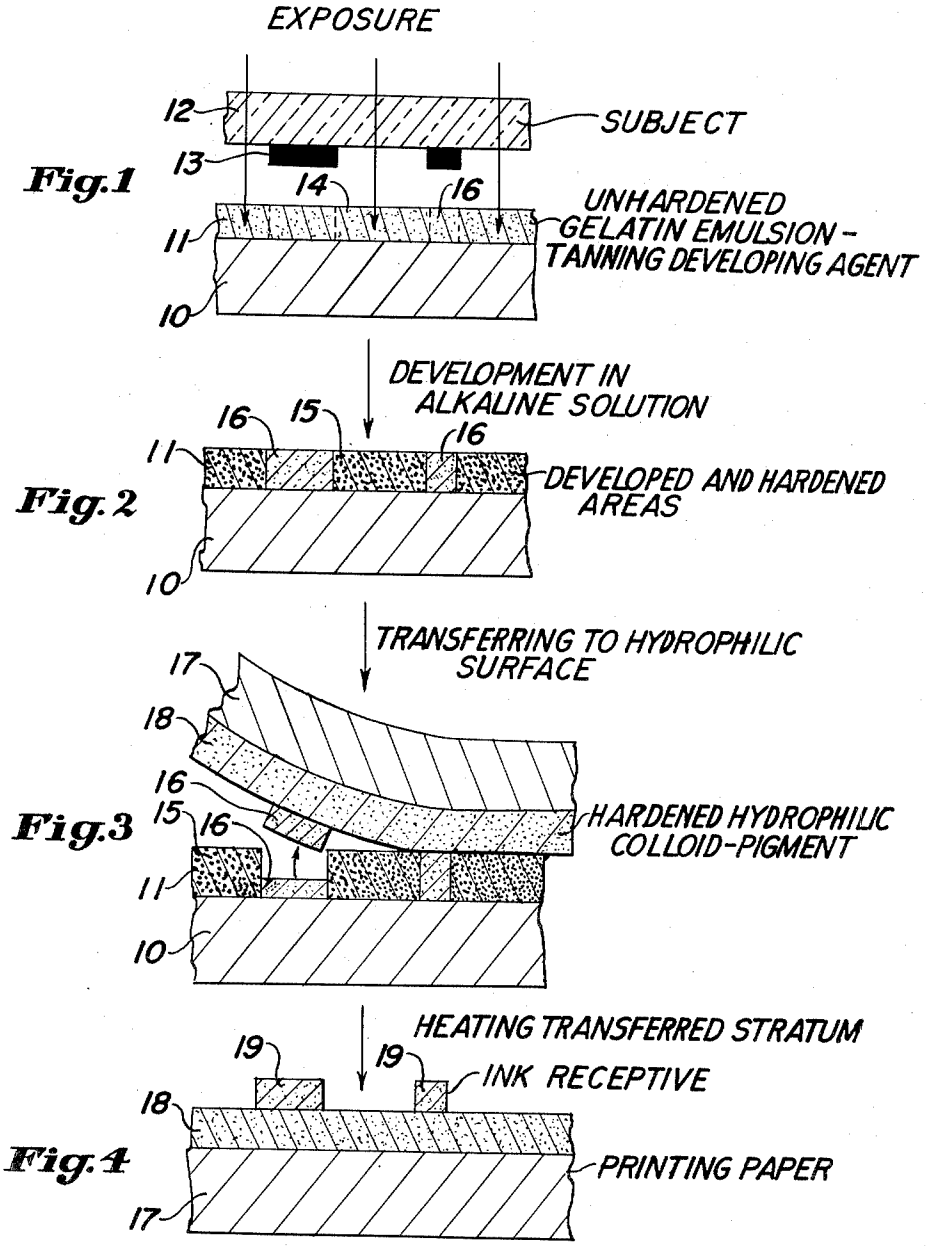

Fig. 1

Fig. 2

Fig. 3

Fig. 4

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LITHOGRAPHIC OFFSET PRINTING PROCESS

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1 Claim. (Cl. 95—5.4)

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

There are a number of well-known methods for preparing lithographic offset printing plates. Perhaps the most common method involves sensitizing a metal plate, such as a zinc plate which has been grained, with a light-sensitive coating such as bichromated albumin following which the plate is exposed usually to a line or halftone negative and before developing the plate a coating of lithographic developing ink is applied. Subsequently the plate is developed in water to remove the albumin in the unexposed areas leaving the hardened albumin covered with ink in the exposed regions. When the plate is moistened and then inked with a greasy printing ink in the lithographic printing press, the ink is taken up only in the areas occupied by the hardened albumin image. If it is necessary to reverse the image, actually this can be accomplished in the usual manner by first transferring the ink image to a rubber offset blanket and thence to the paper, otherwise the ink image can be transferred directly from the printing plate to the receiving paper.

Lithographic paper printing plates have been prepared and used in a similar manner. That is, a paper sheet may be provided with a hydrophilic surface and the ink-receptive image is applied to the surface in a well-known manner. For example, the ink-receptive image can be developed in a light-sensitive colloid layer on the treated surface of the paper plate as described above. These methods possess the obvious disadvantages that during the development of the ink-receptive image, it is difficult to remove all of the unhardened colloid in the unexposed region which is intended to repel the greasy printing ink when moistened. Moreover, in the development of such paper plates with aqueous solutions, a certain amount of distortion of the plate occurs which is obviously undesirable.

We have discovered a process which overcomes the disadvantages of previously known methods for preparing lithographic printing plates. Our process involves exposure to a subject, of a substantially unhardened silver halide emulsion layer, followed by tanning development of the emulsion and transfer of the unexposed areas to a suitably prepared absorbent hydrophilic surface. Subsequently the transferred colloid image is heated or given other treatment to render it more fully receptive of greasy printing inks, and the resultant product used directly in a lithographic printing press in the usual manner.

In the Yutzy and Yackel U. S. patent application Serial No. 783,914, filed November 4, 1947, now U. S. patent 2,596,756, granted May 13, 1952, is described a photographic reproduction method which involves the steps of exposing a substantially unhardened silver halide emulsion layer, preferably containing a tanning developing agent, followed by development of the emulsion layer under conditions of tanning development and then transferring a stratum only of the unhardened areas of the emulsion layer to a suitable absorbent hydrophilic surface such as paper, cloth or wood.

We have discovered that the basic principles of that process can be utilized for forming a lithographic printing plate. That is, we have found that the stratum of emulsion which has been transferred to the absorbent hydrophilic surface can be inked with greasy printing inks and used for making lithographic prints, particularly if the stratum is further treated to render it more fully selectively receptive of printing ink when the element is moistened and inked in the press. Accordingly, our invention contemplates forming in a substantially unhardened gelatino-silver halide emulsion layer, hardened image areas corresponding to the highlights of a subject and other coplanar areas which are not hardened and which correspond to the shadows of the subject, then transferring a stratum of the unhardened areas to a hydrophilic surface which will repel greasy printing inks when wetted during lithographic printing operations. As examples of suitable hydrophilic surfaces to which the stratum adheres in preference to the hardened areas of the emulsion, can be mentioned fibrous cellulosic surfaces such as present on wood, paper and cloth; grained zinc, anodized aluminum, surfaces of hydrophilic organic colloid 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, gelatin, casein, pigmented gelatin or casein etc.

The balance of our process includes treating the transferred stratum of gelatin emulsion on the hydrophilic surface so as to increase its ink receptivity and decrease its moisture absorbing properties, and then using the resulting printing plate in a lithographic printing press to obtain lithographic prints.

Several methods are available for treating the transferred stratum of emulsion to increase its ink receptivity as will be apparent from consideration of the examples thereinafter, such as drying and heating.

Preferred embodiments of our invention involve making the transfer of the stratum unhardened emulsion to the surface of pigmented hydrophilic colloid layers. We have found that useful results are obtained if we make the transfer of the unhardened colloid image to dry pigment-coated paper such as a paper coated with a mixture of gelatin and baryta, for example, ordinary baryta-coated photographic paper, and after heating the transferred colloid image, or other treatment to render the transferred colloid ink-receptive, a moderately durable printing plate results. In order to obtain a printing plate of better quality, it is desirable to decrease the moisture absorption properties of the pigment-coated paper. This can be accomplished by moistening the pigmented surface prior to making the transfer but this operation increases the transfer time and the image tends to smear. Alternately, the pigmented paper can be coated with a thin layer of organic colloid material such as gum arabic and the transfer made to the dried sheet. However, in this case press endurance is reduced since the transferred image adheres less readily to the unpigmented organic colloid surface. Further improvement is obtained if the pigment-colloid coated sheet is hardened more than is normally possible during the pigment-colloid coating operation, by treatment of the pigmented paper with an oxidizing solution such as an acid dichromate solution containing tannic acid.

In a preferred method a lithographic printing element is provided which includes 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 pigment. Suitable for this purpose is a paper which has been coated with a mixture of well-hardened

casein and a pigment such as clay, barium sulfate, etc. If the casein-coated paper is provided with a layer containing gelatin and pigment, it may be treated as above to render the surface less absorptive.

In the accompanying drawings, Figs. 1 to 4 illustrate in greatly enlarged cross-sectional view representative materials and methods used in preparing a lithographic printing plate according to our invention.

The following examples are provided to illustrate representative methods for carrying out our 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 gm. per cc.)	cc.	64
Potassium dichromate	grams	4
Tannic acid (0.05 gram per cc.)	cc.	32
Saponin (7.5% aqueous sol.)	cc.	5

The printing element prepared as just described has the structure of the element shown in Fig. 3 of the accompanying drawings wherein layer **17** is the paper support to which is attached the hardened baryta coating **18**.

An unhardened paper stock is coated with a substantially unhardened gelatino-silver halide 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 application Serial No. 783,912, filed November 4, 1947, now U. S. Patent 2,592,368, granted 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 or contact printing methods under a two-tone subject such as a line or halftone transparency or printed matter. If desired, reflex exposure methods may be used for making the exposure. 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 under the subject comprising a transparent or semi-transparent support **12** carrying a line or halftone image **13** such as present on printed matter on paper. Exposure produces latent images principally in areas **14** of emulsion **11**, the remaining areas receiving little or no exposure unless it is desired to impart optical density to those areas to facilitate inspection of those areas subsequently.

The exposed element is then developed as described in the Yutzy et al invention by treating the exposed emulsion with a minimum 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 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 excess alkaline solution is then squeegeed from the surface of the emulsion layer.

As shown in Fig. 3 of the drawings, the pigmented hardened hydrophilic colloid surface of the baryta-coated paper prepared as above is then pressed against the surface of the developed emulsion layer **11**, taking reasonable care to prevent excessive light exposure of the emulsion layer, and very soon thereafter is peeled off. Since the emulsion layer **11** contains the hardened image areas **15** which will not adhere to the 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 a stratum of area **16** adheres to it. Even at this stage the printing element carrying the adhered area **16** is useful as a lithographic printing plate. If it is dried down before use in the printing press, it is found that while areas **16** are still more hydrophilic than desired, these areas will selectively attract printing inks when moistened and prints can be obtained therefrom. Accordingly, at this stage in order to render those areas more fully ink-receptive, we subject the printing element 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 granted December 19, 1950, and suitable acidic glycerin solutions are disclosed in the Van Dusen U. S. Patent 2,515,536, granted July 18, 1950.

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 gms. casein in water is added sufficient aqueous ammonia solution to obtain pH=9.0. After filtering, the solution is neutralized to pH=6.5 with citric acid. This solution is then diluted with 120° F. water to a 7% casein solution. Spreading agent and 11 cc. of 20% formaldehyde solution per 100 gms. 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.

An unhardened paper stock is then coated with a substantially unhardened gelatino-silver halide emulsion layer preferably 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 developed emulsion layer under reduced illumination and quickly peeled off. As before, 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. The element now carrying the adhered stratum is then heated under

the conditions set forth in Example 1. Prior to inking the printing plate in the lithographic printing press, it may be treated with the mentioned salt and glycerin solutions if desired. 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 and 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 a hardened organic colloid such as casein and an inert pigment such as clay or baryta, and if desired, treated with a cuprammonium solution or a salt solution such as zinc acetate before, after, or during application to the casein-pigment coat of a thin coating of a hydrophilic colloid such as sodium alginate as described in U. S. Patent 2,534,650 granted December 19, 1950. The coated surface of this element is then pressed against the moistened surface of the sensitive element which has been exposed and processed as mentioned in the previous examples, 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, treating it if desired with the solutons indicated in Example 1 prior to inking the plate.

Our invention contemplates the use of other treatments besides heat, zinc salts, etc. set forth in Example 1, for increasing the ink-receptivity of the transferred colloid image on the hydrophilic surface. To this end we can obtain very satisfactory results by treating the gelatin emulsion image with a hardening agent for gelatin such as formaldehyde, alum, etc. Another very convenient and useful method involves making the transfer of the unhardened emulsion stratum, as above described, to the hydrophilic surfaces mentioned, then merely (further exposure is not necessary) treating it with an alkali solution. Since the stratum contains undeveloped silver halide, developing agent and gelatin, apparently 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% sodium carbonate solution is satisfactory, employed for about 30 seconds at about 70–85° F., followed by an acid rinse such as 1–2% acetic acid, or rinsing with water. Other alkaline solutions may be used with similar results such as those containing trisodium phosphate, alkali metal hydroxides, sodium metaborate etc.

A number of other variations may be made in our methods for preparing printing plates which fall within the scope of our invention. We may use light-sensitive elements disclosed in the Yackel invention mentioned, containing the developing agent in the emulsion or not. In the latter case a soluble silver halide tanning developing agent is employed in the alkaline developing solution used to effect tanning development. Also, as described in the Yutzy et al. U. S. patent application Serial No. 267,447, filed concurrently herewith, now U. S. Patent 2,716,059, granted August 23, 1955, we may employ a mixture of gelatin tanning and non-tanning developing agents in the emulsion layer such as a mixture of preferably 35–40% of one of the indicated dihydroxy diphenyl tanning developing agents, and 4-methoxy-1-naphthol or p-hydroxyanilino-methane sulfonic acid, etc., non-tanning developing agents. 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, particularly with the bi-valent metal salts and yet retain hydrophilic properties. As mentioned, the hydrophilic surfaces to which the emulsion transfer is made can be any of the grained 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-repellant 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.

What we claim is:

A method for preparing a lithographic printing plate which comprises pressing the hydrophilic surface of a supported layer containing a mixture of hardened gelatin and an inert pigment, against a moistened supported substantially unhardened gelatino-silver halide emulsion layer which has been exposed to a two-tone subject and developed in the presence of a mixture of gelatin tanning and non-tanning silver halide developing agents 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, and then treating said hydrophilic surface with an alkaline solution to develop the silver halide of the adhered stratum and at the same time tan the gelatin thereof with the oxidation products of the developing agent.

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