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2,570,262

PHOTOSENSITIVE PLANOGRAPHIC PLATE

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Fig. 1

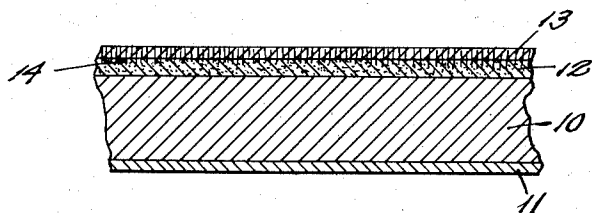


Fig. 2

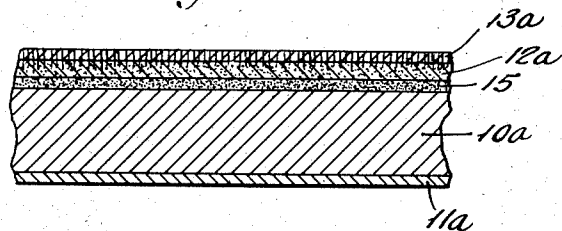
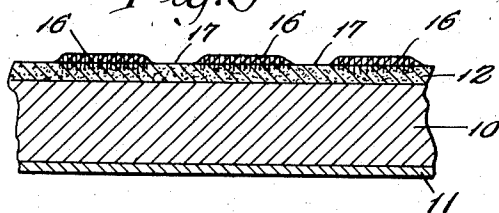


Fig. 3



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UNITED STATES PATENT OFFICE

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PHOTOSENSITIVE PLANOGRAPHIC PLATE

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13 Claims. (Cl. 95—8)

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This invention relates to the art of planographic plates, and particularly, to the manufacture of photosensitive planographic plates adapted for the formation of a printing image by photographic processes.

Planographic printing involves the provision of a printing plate having a water-repellent ink-receptive image on its printing surface and water-receptive non-print background areas surrounding the image which repel printing ink when moistened with an aqueous fountain fluid, moistening the plate with an aqueous fountain fluid to render the non-print background areas ink-repellent, and inking the plate with printing ink which adheres only to the image portions, and transferring the ink thus deposited to a copy sheet, usually by way of an offset blanket, or if desired, by direct impression; the aforesaid moistening, inking and transferring steps being repeated successively to yield a series of copies.

For the production of a planographic image on a plate by photographic processes, a photosensitive layer, adapted when exposed to actinic light to form an ink-receptive image, is applied to a plate having a surface adapted to form water-receptive, non-print background areas. The photosensitive layer commonly employed is a water-soluble film of glue, gelatine or egg albumen (hereinafter called albumins) sensitized with a bichromate. Such a film when exposed locally to actinic light under a photographic negative, usually with interposition of a half-tone screen, is locally hardened by the light to a water-insoluble ink-receptive state, while the unexposed portions remain water-soluble. The resulting surface is developed for printing, usually by coating with an asphalt solution or other greasy ink-receptive developer to enhance the ink-receptive nature of the light-exposed portions, and is washed with water to remove the unexposed portions and any asphalt deposited thereon. The printing plate, thus prepared, can be used in the usual way in a planographic printing press for reproduction of the photographic image carried thereby.

A serious problem in photoplanographic printing lies in the provision of a plate which will retain the hardened albumin image unchanged during numerous printing operations, so that a large number of faithful copies can be obtained. Numerous proposals have been made to solve this problem. In the case of metal plates, commonly used heretofore for planographic printing, of which the surface is of such metals as zinc, or aluminum, grained or etched to impart the re-

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quired water-receptive properties, hardened albumin images are relatively sensitive to undermining by the aqueous fountain fluid used for moistening the plate, so that the number of satisfactory copies which can be produced is exceedingly limited. Some improvement results from special preparation of the metal surface, but in general, successful operation depends upon careful control by the operator of the ink and fountain compositions applied to the plate during printing, great skill being required to obtain satisfactory results.

More recently, planographic plates have been made of paper and allied materials, having a surface adapted to constitute the non-print background areas of the plate and at the same time to retain an ink-receptive image applied thereto.

Sheets having a surface of amyloid cellulose or other forms of regenerated cellulose (e. g. parchmentized paper) have been found suitable in some respects for this purpose; but for the reproduction of photographic images, parchment and similar surfaces are unsuitable in that they fail to retain a hardened albumin image with sufficient tenacity to permit production of a substantial number of copies.

Other non-metallic plates have been made by applying to the surface of a high wet-strength paper foundation, a composition forming a film or surface coating having the desired planographic properties. Thus, a number of colloidal materials have been used for making such coatings, for example, casein-formaldehyde, polyvinyl alcohols, and (as disclosed in my co-pending applications Serial No. 586,825 of April 5, 1945, and Serial No. 637,088, of December 22, 1945) carboxymethyl cellulose compounds. The term "carboxymethyl cellulose" refers to carboxymethyl ethers of cellulose, sometimes called cellulose glycolic acid. Such materials are generally applied to the paper foundation in such a manner as to yield a film or coating which is hydrophilic, but insoluble in the aqueous fountain solution employed. Often a mineral filler is employed therewith, lending tooth or grain to the surface.

Most of the aforesaid colloidal coating compositions yield surfaces which are not adapted to retain photographic images of chromate hardened albumin. Thus, casein coatings containing a filler, fail to retain hardened albumin images for a sufficient length of time to render their use satisfactory in planographic printing. Polyvinyl alcohol films required special treatment to yield satisfactory results. In addition, coated

surfaces proposed prior to my discovery of the suitability of carboxymethyl cellulose compounds for the manufacture of planographic surfaces were subject to deterioration through aging, as well as during the printing operation, whereby their ink-repellent image-retaining properties were seriously impaired.

It is an object of this invention to provide a planographic plate having a paper foundation, a photosensitive layer of bichromated albumin suitable for the production of photographic images, and an underlying coating of colloidal material adapted to form a non-print background, wherein the latter coating retains its planographic properties unchanged during storage, as well as during the use for planographic printing, and tenaciously retains photographic images of hardened albumin produced thereon during the printing operation, so that a greatly increased number of faithful copies of the photographic image can be produced.

These objects are accomplished by providing on a plate having a water-resistant paper foundation and a printing surface coating of an insolubilized carboxymethyl cellulose compound as disclosed in my aforesaid co-pending applications, a photo-sensitive coating of bichromated albumin applied to the surface of the carboxymethyl cellulose. Such plates when exposed to light under a negative yield images of hardened albumin which penetrate sufficiently into the carboxymethyl cellulose coating to remain firmly bonded thereto during the ensuing printing operations. The resulting plate is practically insensitive to variations in the fountain solution employed, and can be used with any of the standard fountain solutions in ordinary use, no special skill being required to use the plate to the best advantage. The copies produced are characterized by excellent clarity and sharpness; reproducing every detail of the negative with utmost fidelity, and permitting the use of the finest half-tone screens.

Advantageously, a photoplanographic plate in accordance with this invention is prepared by making a plate in the manner disclosed in my co-pending application, Serial No. 637,088. Thus, the plate includes, as a foundation, a sheet of paper, preferably originally manufactured or subsequently treated to render it resistant to swelling or deformation when the plate is subjected to moisture during the printing operation. The foundation can be made, for example, by incorporating a wet strength-imparting resin, such as melamine-formaldehyde or urea-formaldehyde resins, in the pulp used for making the paper, or by impregnation of the paper with such materials after the paper has been formed. The rear surface of the foundation is advantageously coated with waterproof lacquer, such as a solution of a polystyrene resin in a volatile solvent. If desired, a water barrier can be formed on the front surface of the foundation, adapted to receive and retain thereon a coating of the carboxymethyl cellulose composition, said water barrier being, for example, a film of casein-formaldehyde, which can be formed by coating the foundation with an ammoniacal solution of casein containing a small amount of formaldehyde, and drying the coating.

The front surface of the foundation is then provided with a film of insolubilized carboxymethyl cellulose, constituting a surface which is adapted to receive the photosensitive albumin coating, to retain the hardened image produced therefrom. Thus, in accordance with my pre-

ferred procedure, I coat the front surface of the foundation with an aqueous composition containing a water-soluble carboxymethyl cellulose compound (e. g. an alkali metal salt, or an ammoniacal solution of the aluminum salt thereof) dissolved therein, and preferably containing a finely divided inert mineral filler to produce a fine tooth or grain in the coating. A small amount of a plasticizer for the carboxymethyl cellulose compound, such as glycerin, can also be included to lend added flexibility to the coating. The coating film is preferably formed by several coating operations to insure complete coverage of the foundation and elimination of pinholes which might be left in a single coating operation. The resulting carboxymethyl cellulose layer is insolubilized, preferably by treatment with a solution of a coagulant metal salt, or mixture of such salts, such metal salt solutions preferably include a copper salt, advantageously mixed with an aluminum salt and/or a ferric salt, with or without a small amount of chromic acid. The resulting insolubilized carboxymethyl cellulose layer is dried and calendered.

Other methods for forming an insolubilized carboxymethyl cellulose layer can also be used. For example, the foundation can be coated with an ammoniacal solution of the aluminum salt of carboxymethyl cellulose, and the resulting layer can be insolubilized by heating at a sufficiently high temperature and for a sufficient length of time to drive off the ammonia. Another method involves acidifying a solution of a soluble salt of carboxymethyl cellulose with a mineral acid or a strong organic acid, and then drying to form a film of carboxymethyl cellulose which is insoluble in water. A similar film is obtained by coating the foundation with an aqueous solution of carboxymethyl cellulose or its water-soluble salts, and after drying to form a film, treating the film with dilute aqueous mineral acid or dilute strong organic acid to insolubilize the film.

In forming the carboxymethyl cellulose layer, a minor proportion of the carboxymethyl cellulose compound can be replaced by another gelatinous colloid, compatible with carboxymethyl cellulose and susceptible to insolubilization along with the carboxymethyl cellulose. Such colloids are added preferably in amounts equal to about 10% of the quantity of carboxymethyl cellulose employed, and should not exceed 20% of the carboxymethyl cellulose. For example, colloids such as sodium alginate, alkali casein, zein, or the like, can be incorporated in the aforesaid proportions with the carboxymethyl cellulose to make the coating composition.

The resulting plate is then provided with a photo-sensitive layer by coating the carboxymethyl cellulose layer with an aqueous solution of glue, gelatin, or albumen (or mixtures of such albumins) mixed with an aqueous solution of ammonium bichromate, and drying the plate to form a bichromate-albumin film thereon. The bichromated coating is then exposed to actinic light under a negative, and if desired, with interposition of a half-tone screen.

Development of the resulting image can be carried out by applying a solution of asphalt, such as gilsonite, in a suitable organic solvent, to the surface of the albumin layer, and then washing with distilled water, or dilute aqueous ammonia to remove the unexposed portions of the albumin layer. If desired, application of the asphalt solution can be omitted, the exposed plate being washed with water to remove the unexposed

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portions of the albumin, and then dried. In this case, the oleous printing ink applied to the plate during printing performs the function of the asphalt in developing the ink-receptive properties of the image.

If the plate is to be stored prior to its use for printing, it is preferably gummed with a gumming composition of the type ordinarily employed, usually containing gum arabic, or a similar water-soluble colloid, forming a protective film on the surface of the plate. If it is to be used immediately, the plate is coated with the usual etching composition, placed on the cylinder of the printing press, and successively moistened with fountain solution, inked with printing ink, and the ink transferred from the image to a copy sheet in the usual manner.

The resulting copies are of excellent sharpness and the image is reproduced in every detail. The printing plates retain the image tenaciously, yielding a greatly increased number of copies. Moreover, the plates have no tendency to alter their properties due to aging during storage.

A number of preferred methods for making planographic plates in accordance with my invention are described in the following examples, wherein parts and percentages are by weight, unless otherwise specified.

Example 1

Heavy calendered water-leaf paper, prepared from long fibre pulp to which a melamine formaldehyde resin is added to increase the wet strength of the resulting paper, is brush-coated with a composition made by dissolving the aluminum salt of carboxymethyl cellulose in aqueous ammonia, adding a lower alcohol, and mixing colloidal clay with the resulting solution until a uniform slurry is obtained. The mixture has the following composition:

180 parts of the aluminum salt carboxymethyl cellulose
463 parts of methyl alcohol
90 parts of aqueous ammonia (containing about 28½% of NH_3)
5238 parts of water
180 parts of colloidal clay

After coating the paper with the foregoing composition, it is dried and calendered. The paper is brush-coated a second time with the same composition and again dried and calendered. The paper is then tub-sized with an aqueous solution of metal salts containing—

3% of copper sulphate (CuSO_4)
1% of aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3$)
½% of ferric chloride (FeCl_3)
½% of chromium trioxide (CrO_3)

The paper is again dried and calendered, and the back of the sheet is advantageously coated with a 20% solution of polystyrene resin in ethyl-acetate to form a water-proof coating.

A photosensitizing composition is then prepared as follows: a solution of 7 parts of egg albumen in 32 parts of water, is mixed with a solution of 1 part of gelatine (photoengraver's glue) in 8 parts of water. 2 parts of aqueous ammonium bichromate solution (containing 1 mol per liter of ammonium bichromate) is diluted with 15 parts of water, and mixed with ½ part of 28% aqueous ammonia, diluted with 3 parts of water. The albumin solution is mixed with the aforesaid ammonium bichromate solution. The resulting mixture is applied to the insolubilized

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carboxymethyl cellulose coating on the surface of the foundation, in such a manner as to obtain a uniform thin coating, e. g. by means of a whirler, and the plate is dried.

To produce a photographic image, the plate is exposed under a photographic negative for 3 to 4½ minutes, to the light of a 35 ampere arc lamp at a distance of 30" (for a 17" x 22" plate).

The exposed plate is then coated with a developer constituted by a solution of asphalt or gilsonite in a volatile organic solvent. The plate is then submerged in dilute aqueous ammonia, made for example by adding 1 oz. of 28% ammonia to 1 gal. of water; or if desired, the plate can be simply washed with distilled water to remove the unexposed portions of the bichromated albumin layer. The plate can then be gummed for storage with the usual gum arabic compositions, or coated with an etching solution and used in the press for making copies.

Alternatively, application of the asphaltum solution can be omitted, and the plate is merely washed with water to dissolve the unexposed bichromated albumin. After drying, the plate is used directly for printing, the ink initially deposited on the hardened albumin image performing the function of the asphaltum.

Some of the albumin layer is superficially absorbed by the carboxymethyl cellulose coating, preventing undermining of the image by the fountain solution, and thus greatly increasing the life of the plate during the printing operation. Sharp, clear prints are obtained even when the finest half-tone screens are employed.

Example 2

Paper of the type employed in Example 1 is brush-coated with a uniform slurry composed of

100 parts of a 5% aqueous solution of low viscosity sodium carboxymethyl cellulose
20 parts of china clay
3 parts of glycerin

After drying and calendering the paper, it is again brush-coated with the same composition and again dried and calendered. The resulting coating is then tub-sized with a 5% aqueous solution of copper sulphate to insolubilize the carboxymethyl cellulose, and the plate is dried and calendered. The rear of the foundation is advantageously coated, as in Example 1, with water-proof polystyrene resin lacquer.

The insolubilized carboxymethyl cellulose layer on the surface of the foundation is coated with a sensitizing composition containing ammonium bichromate, gelatine and albumin, prepared in the same manner as that described in Example 1. The resulting plate has properties similar to those of the plate of Example 1 and can be used in the same manner for reproduction of a photographic image.

Instead of using a copper sulphate solution as aforesaid for insolubilizing the carboxymethyl cellulose, a mixture of metal compounds like that used in Example 1 can be similarly used to insolubilize the carboxymethyl cellulose; or, if desired, a solution of aluminum sulphate or ferric chloride having a concentration of about 5% can be used instead of the copper sulphate mentioned above. Similarly, solutions containing 5% of copper sulphate together with ½% of chromium trioxide, or 2½% of copper sulphate and 2½% of aluminum sulphate are also satisfactory for this purpose.

Other standard formulas for photosensitive albumin bichromate layers can be substituted for the composition disclosed in the foregoing example.

Example 3

180 parts of the aluminum salt of carboxymethyl cellulose is suspended in 1200 parts of water, and dissolved therein by adding thereto 36 parts of aqueous ammonia (containing 28½% NH₃), diluted with 120 parts of water, 16 parts of glycerin and about 180 parts of china clay are added to the solution, and the mixture stirred to form a uniform slurry. The resulting composition is applied to a paper foundation as described in Example 1, by brush-coating, and the paper is dried and calendered. A second application of the coating composition is made in the same manner. The coated paper is then heated at 120° C. for ½ hour to drive off ammonia, and thereby insolubilize the aluminum salt of carboxymethyl cellulose. The rear surface of the paper foundation is then coated as in the preceding examples with a water-repellent polystyrene resin lacquer.

The surface of the plate is then sensitized by application thereto of a bichromate-albumin sensitizing mixture, as disclosed in Example 1, or an equivalent mixture. The resulting plate can be used in the same manner as the plate of Example 1 for reproduction of the image of a photographic negative.

Example 4

Heavy calendered paper, weighing about 100 lbs. per ream (500 sheets) of 25" x 38" sheets, made from pulp to which a melamin-formaldehyde resin has been added to impart wet strength to the paper, is coated with a composition adapted to form a water barrier, said coating composition being prepared by mixing 50 parts of casein with 200 parts of water, heating the dispersion to 50° C. and adding 7.5 parts of 26% aqueous ammonia. The resulting solution is maintained at 55° C. and stirred for about 1 hr. to dissolve the casein completely. 100 parts of the resulting solution is diluted with 100 parts of water, and 1.2 parts of 39% aqueous formaldehyde diluted with 100 parts of water is added to the casein solution. The resulting mixture, containing about 6.25% of casein and about 0.15% of formaldehyde is brush-coated on the front surface of the heavy paper stock in sufficient amount to yield when dry a casein-formaldehyde coating amounting to about 3 lbs. per ream of the aforesaid sheets. Instead of employing 7.5 parts of 26% ammonia to prepare the casein solution, a mixture of 3.75 parts of 26% ammonia with 3 parts of sodium carbonate can be used.

After drying, the casein-formaldehyde water barrier is coated with a composition prepared as disclosed in Example 1, containing an aluminum salt of carboxymethyl cellulose dissolved in dilute ammonia and containing colloidal clay as a filler. The resulting coating is dried and calendered. The coating operation and the drying and calendering thereof is then repeated a second and a third time, to produce a carboxymethyl cellulose layer of greater weight than that of the preceding examples. The carboxymethyl cellulose layer is tub-sized with an aqueous solution of coagulant metal salts as disclosed in Example 1, and the paper is again dried and calendered. The rear surface of the foundation is coated with a 20% solution of polystyrene resin in ethyl acetate.

The resulting plate material is coated with a sensitizing composition containing albumen, gelatin and ammonium bichromate as disclosed in the preceding examples. After drying, it is ready for exposure under a photographic negative, and the resulting plate is used for printing as described in Example 1.

Variations and modifications can be made in the foregoing examples without departing from the scope of this invention, as will be obvious to those skilled in the art. Thus, other soluble salts of carboxymethyl cellulose, such as the ammonium, calcium or magnesium salt can be used in place of the sodium or ammonium-aluminum salt in preparing the surface of the foundation which is subsequently insolubilized and to which the bichromated albumin composition is applied. Water-proof lacquer can be applied either before or after the coating operations performed on the front surface of the foundation. The concentration of the carboxymethyl cellulose compound is between 1 and 5% in the coating composition. To increase the durability of the coating, a modifying colloid, such as sodium alginate, zein or casein can be incorporated with the carboxymethyl cellulose in amounts up to about 20% of the amount of carboxymethyl cellulose employed.

Coagulant reagents, other than metal salts disclosed in the foregoing examples, can be used for insolubilizing the carboxymethyl cellulose coatings, as for example, dilute aqueous solutions of strong mineral acids, such as hydrochloric, sulfuric, phosphoric or phosphorous acids, or of strong organic acids such as citric, tartaric, lactic or tannic acids. Such solutions are applied to the carboxymethyl cellulose coatings after the latter have been dried to yield a film. Dialdehydes, such as glyoxal are also effective as coagulants for treatment of water-soluble carboxymethyl cellulose films as produced in the foregoing examples.

The high wet strength paper used as a foundation for the plates of my invention may contain a melamine- or urea-formaldehyde resin as the wet strength-imparting material, or such resins can be used in conjunction with carboxymethyl cellulose in the pulp or as impregnants in manufacturing the paper.

The structure of the plates prepared in accordance with the foregoing examples is illustrated in the accompanying drawing wherein—

Figure 1 is a cross-section of a plate as prepared in accordance with the Examples 1 to 3 above.

Fig. 2 is a similar view of a plate prepared according to Example 4; and

Fig. 3 is a cross-sectional view of the plate of Fig. 1 after exposure and development.

Thus, as shown in Fig. 1, the plate includes a high wet strength paper foundation 10, having on its rear surface a coating 11 of a water-proof lacquer, and on its front surface a coating 12 of insolubilized carboxymethyl cellulose. A photosensitive layer 13 of bichromated albumin is applied to the surface of the carboxymethyl cellulose and superficially penetrates the surface thereof, as indicated by the vertical cross-sectioning 14 at the interface. The plate of Fig. 2 represents a plate prepared according to Example 4, and is similar to that of Fig. 1, except that it includes a water barrier 15 of casein-formaldehyde interposed between the paper foundation 10a and the carboxymethyl cellulose layer 12a, the rear surface of the foun-

dation bearing a water-proof lacquer coating 11a and the photosensitive layer 13a being applied as in Fig. 1 to the surface of the carboxymethyl cellulose layer.

After exposure to light and development, as described in Example 1, the plate of Fig. 1 has the form shown in Fig. 3, wherein portions 16 of the bichromated albumin layer 13, which have been hardened by exposure to light, remain attached to the carboxymethyl cellulose layer 12 and constitute an ink-receptive image thereon; while intermediate portions 17 of the carboxymethyl cellulose surface are exposed by washing away the unexposed portions of the layer 13, and are adapted to form ink-repellent background areas upon moistening with aqueous fountain fluid.

Variations and modifications can be made within the scope of this invention, and portions of the improvements can be used without others.

I claim:

1. A planographic plate having a paper foundation, an insolubilized coating of a carboxymethyl cellulose compound overlying the front surface of said foundation, and a photosensitive layer of bichromated albumin adhering to the surface of said carboxymethyl cellulose coating.
2. A planographic plate having a paper foundation, a coating of an insoluble metal salt of carboxymethyl cellulose overlying the front surface of said foundation, and a photosensitive layer of bichromated albumin adhering to the surface of said carboxymethyl cellulose coating.
3. A planographic plate having a paper foundation, a coating of an insoluble copper salt of carboxymethyl cellulose overlying the front surface of said foundation, and a photosensitive layer of bichromated albumin adhering to the surface of said carboxymethyl cellulose coating.
4. A planographic plate having a paper foundation, a coating of an insoluble aluminum salt of carboxymethyl cellulose overlying the front surface of said foundation, and a photosensitive layer of bichromated albumin adhering to the surface of said carboxymethyl cellulose coating.
5. A planographic plate having a paper foundation, a coating of an insoluble ferric salt of carboxymethyl cellulose overlying the front surface of said foundation, and a photosensitive layer of bichromated albumin adhering to the surface of said carboxymethyl cellulose coating.
6. A planographic plate having a paper foundation, a coating of casein-formaldehyde on the surface of said foundation to form a water barrier, an insolubilized coating of a carboxymethyl cellulose compound on the surface of said casein-formaldehyde coating, and a photosensitive layer of bichromated albumin adhering to the surface of said carboxymethyl cellulose coating.
7. A planographic plate having a paper foundation, an insolubilized coating of a carboxymethyl cellulose compound containing another gelatinous hydrophilic colloid compatible therewith and insolubilized with the carboxymethyl cellulose compound, in an amount not exceeding 20% of the weight of the carboxymethyl cellulose compound, said coating overlying the front surface of said foundation, and a photosensitive layer of bichromated albumin adhering to the surface of said carboxymethyl cellulose coating.
8. The process of making a planographic plate which comprises coating a foundation of paper

with a water soluble carboxymethyl cellulose compound, treating the resulting coating with a solution of a coagulant metal salt to insolubilize said coating, and applying a photosensitive film-forming solution of bichromated albumin to the surface of the insolubilized carboxymethyl cellulose coating to form a photosensitive layer.

9. The process of making a planographic plate which comprises coating a foundation of paper with a water-soluble carboxymethyl cellulose compound, treating the resulting coating with a solution of a copper salt to insolubilize said coating, and applying a photosensitive film-forming solution of bichromated albumin to the surface of the insolubilized carboxymethyl cellulose coating to form a photosensitive layer.

10. The process of making a planographic plate which comprises coating a foundation of paper with a water soluble carboxymethyl cellulose compound, treating the resulting coating with a solution of an aluminum salt to insolubilize said coating, and applying a photosensitive film-forming solution of bichromated albumin to the surface of said insolubilized carboxymethyl cellulose coating to form a photosensitive layer.

11. The process of making a planographic plate which comprises coating a foundation of paper with a water-soluble carboxymethyl cellulose compound, treating the resulting coating with a solution of a ferric salt to insolubilize said coating, and applying a photosensitive film-forming solution of bichromated albumin to the surface of the insolubilized carboxymethyl cellulose coating to form a photosensitive layer.

12. The process of making a planographic plate which comprises coating a foundation of paper with casein-formaldehyde to form a water barrier thereon, coating the casein-formaldehyde coating with a water-soluble carboxymethyl cellulose compound, insolubilizing said carboxymethyl cellulose coating, and applying a photosensitive film-forming solution of bichromated albumin to the surface of the insolubilized carboxymethyl cellulose coating to form a photosensitive layer.

13. The method of making a planographic plate which comprises repeatedly coating a paper foundation with a 1 to 5% solution of a water-soluble carboxymethyl cellulose compound, containing an inert filler suspended therein, coagulating the resulting coating with a solution containing a copper salt, an aluminum salt, a ferric salt and chromic acid, having a total concentration of these compounds amounting to about 5%; and applying a photosensitive film-forming solution of bichromated albumin to the surface of the resulting carboxymethyl cellulose coating to form a photosensitive layer.

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