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PHOTOSENSITIVE PRINTING PLATE HAVING A LIGHT-SENSITIVE COATING CONSISTING OF A COLLOID, A PHOSPHATE, AND A CHROMIUM COMPOUND

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This invention relates to the art of photolithography and more particularly to a sensitizing composition and to a photosensitive plate comprising a surface coating of said composition.

The invention resides primarily in the incorporation of certain water-soluble phosphate salts in sensitizing compositions consisting essentially of a protein and a chromate or dichromate as will be more fully described hereinafter.

The usual preparation of plates for photolithography may be described as follows. A suitable base or support such as a grained metal plate or a coated paper surface is coated or "sensitized" with a light-sensitive film of an aqueous solution containing a protein such as egg albumin and a "sensitizing" chemical such as ammonium dichromate. In place of egg albumin other proteins such as animal glue, casein and blood albumin may be used and the ammonium dichromate may be replaced by other soluble dichromates or chromates such as those of sodium and potassium. The sensitized plate, after being dried, is placed under a mask or negative having a transparent pattern in an opaque field, and it is exposed through the mask to strong light such as an arc-light. The action of the light on the photo-sensitive film, while not wholly understood, is said to "tan" the film, and the film becomes water-insoluble in the exposed or tanned areas. In the unexposed areas under the opaque portions of the mask or negative the film is not affected by the light and remains water-soluble. The exposed plate is next wiped over with greasy developing ink which coats the entire surface. Finally the plate is washed with gentle rubbing in water which loosens the water-soluble areas of film and removes them together wtih the ink overlying those areas, but leaves on the plate the exposed, water-insoluble areas together with the ink overlying them. After the preceding treatment the plate is ready to use for printing. The unexposed areas are kept wet with aqueous solution and an inking roller coated with lithographic printing ink is rolled across the entire surface. Ink is taken up by the greasy image but is repelled by the water on the non-imaged areas. When the inked plate is brought into contact with another surface it transfers the ink thereto in a pattern reverse to that on the plate. The surface so printed upon may be a paper sheet, but in most cases is an offset blanket which in turn transfers the print to a paper sheet to complete the printing operation in a pattern identical with that of the original plate. The plate is then repeatedly dampened, inked, and printed from until the desired number of copies have been made.

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There are several objectionable features in the present-day art. In the first place the treatment with developing ink and the subsequent washing operation together constitute troublesome and time-consuming procedure. Even when metal plates are used great care must be exercised to ensure both that all the unexposed film is removed from the plate and that the developing ink does not soil the bare non-printing areas of the plate. On the other hand, if the application of developing ink is omitted and the unexposed areas are washed off directly the image is liable to be very slow in taking sufficient ink for good printing, and in some cases the image may actually be obliterated in the washing process while the unexposed areas are being washed off. Moreover, if the film is not washed completely off the unexposed areas the plate is liable to scum or become dirty while it is being used, so that unsatisfactory prints will be obtained therefrom. Complete removal of unexposed film and overlying ink is difficult enough even when metal plates are used; it is doubly difficult in the case of paper-base plates which have a more or less porous surface.

The practice of the present invention avoids some of the difficulties previously met with in the art of sensitizing plates for photolithography. For instance, the invention makes entirely feasible the omission of the customary development of the image by the application of developing ink prior to removal of the film in unexposed areas although the customary development with ink may be carried out as usual if desired. Whether or not developing ink is used on the plate prior to removal of the unexposed film, the invention greatly facilitates removal of the unexposed film and if developing ink is present also aids in its removal. Moreover, in addition to expediting the removal of unexposed film from the surface one feature of the invention mitigates or substantially nullifies the ill effects of any unexposed film inadvertently left on the surface of the plate, as will be explained hereinafter.

According to the invention an aqueous mixture or solution is prepared containing a protein such as egg albumin, casein, animal glue or the like, a soluble chromate or dichromate such as ammonium dichromate, and a soluble phosphate, such as monoammonium ortho-phosphate, having a pH value higher than the isoelectric point of the protein, and the resulting mixture is applied in

an even coating to the surface of a suitable base such as a metal, coated paper, or equivalent printing plate base, to sensitize the said surface to actinic radiation. The sensitized plate so produced may be used in conventional manner from this point forward, but it possesses several advantages over similar plates conventionally sensitized with albumin and dichromate without addition of phosphate.

The sensitized plate may be exposed, under a mask, to a source of actinic rays and may then, if desired, be coated with developing ink. When a so-treated plate is washed with water the unexposed film and overlying developing ink are very easily removed. It is not necessary to immerse the plate beneath running water as in common practice, but it is sufficient merely to wipe the surface with a sponge wet with water.

The improvement in the facility with which the unexposed areas can be cleaned when phosphate is present is very marked even when metal plates are used. In the case of paper-base planographic plates, from which the unexposed sensitized film is ordinarily removed with considerable difficulty, the effect of phosphate in the film is even more remarkable. Especially noteworthy are the results obtained when one uses coated paper-base planographic printing plates which contain a water-soluble divalent metal salt such as zinc acetate in the coating layer, such as are disclosed in the applications of Stephen V. Worthen, Serial No. 747,138, filed May 9, 1947, and Serial No. 758,215, filed June 30, 1947, both now abandoned. When such plates are sensitized with the usual albumin-dichromate sensitizer containing no phosphate no amount of scrubbing with water will remove from the unexposed areas the yellow discoloration caused by the action of the dichromate. On the other hand, when phosphate is present in the sensitizing layer in sufficient quantity a single passage of a wet sponge over the unexposed surface suffices to expose the color of the original coated base and gentle swabbing cleans the unexposed areas completely. Part of the explanation for this result probably is the pore plugging action of insoluble phosphate formed by interaction of the phosphate with the divalent metal salt as disclosed in an application of Frederick H. Frost, Serial No. 791,447, filed December 12, 1947, now Patent No. 2,559,610, but almost certainly it is also partly due to the detergent action of the phosphate.

The ease with which unexposed areas are cleaned in the practice of the invention makes severe scrubbing unnecessary and accordingly the exposed and imaged areas likewise escape the effects of severe scrubbing. Consequently, it is found feasible to omit entirely the application of developing ink to the plate before washing. In the past it has indeed been possible to omit the developing step before washing, but the degree of scrubbing previously required to clean the unexposed areas was so severe that imaged areas likewise were liable to be weakened or damaged. Accordingly, in the past it has generally been considered unsafe to omit the use of developing ink prior to washing. Now, however, use of phosphate according to the invention makes it possible to eliminate entirely the troublesome and disagreeable application of developing ink prior to washing without at the same time endangering the quality of the image.

The defect commonly designated as "albumin scum" is well-known in the photolithographic art. This defect is caused by failure to remove all the albumin or other protein from the unexposed area of the plate. When the plate containing traces of albumin in the unexposed areas is run on a press the albumin gradually picks up ink and causes "tone" in the supposedly blank areas. This difficulty is common whether metal plates or paper-base plates are used. Use of phosphate according to the invention greatly decreases trouble from albumin scum, since removal of all the albumin is greatly facilitated by the action of the phosphate.

Another advantage derived from the incorporation of phosphate in the protein-dichromate sensitizing solution resides in the fact that hydrophilic gums or polysacharrides or similar hydrocolloids can be incorporated in the solution. Hitherto it has been the general belief that admixture of a gum such as gum arabic with a protein sensitizing solution was fatal to successful use of the solution in photolithography, common experience having indicated that such a sensitizing mixture of albumin and gum would not, after exposure, retain an image satisfactorily. Surprisingly it has now been found that a sensitizing coating comprising solubilized protein, soluble chromate or dichromate, soluble phosphate and water-soluble non-protein hydrocolloid in quantity up to equality by weight with the protein present can be used with very satisfactory results on plates designed for medium runs of up to 2,000 copies. Inclusion of the soluble non-protein hydrocolloid in the film is a considerable safeguard against development of albumin scum, for the non-protein hydrocolloid not only makes the unexposed film easier to wash away, but also in case traces of unexposed film are inadvertently left behind it makes such traces definitely more water-receptive and less ink-receptive and hence very definitely acts to keep the blank portions of the plate clean during the printing operation.

While, as has been stated, a sensitized coating yielding an image with life satisfactory for a medium run plate can be made by the use of a sensitizing solution containing in addition to the soluble phosphate and chromate or dichromate, equal parts by weight of protein and soluble non-protein hydrocolloid, it should be realized that inclusion of such a high proportion of soluble non-protein hydrocolloid definitely does act to cut down or decrease the potential image life of the plate. Consequently, it is generally desirable to use a smaller proportion of the non-protein hydrocolloid in the sensitized coating. It is found that quantities of soluble non-protein relatively less viscous hydrocolloid ranging from about 5% to about 25% of the weight of protein present are very effective in facilitating wash-off and preventing albumin scum as before described, and at the same time such quantities are much less detrimental to image life.

The preferred range of 5% to 25% of soluble non-protein hydrocolloid based on the protein content of the film applies to the less viscous hydrocolloids such as gum arabic and mesquite gum among the natural gums or polyvinyl alcohol and sodium carboxy methyl cellulose among the synthetic hydrocolloids. The more highly viscous hydrocolloids such as locust bean gum, guar gum, agar agar, karaya and the like must be used in smaller proportion, generally less than 3% and preferably about 1.5% based on the weight of the protein and probably for this reason are less effective than the less viscous hydrocolloids which may be used in larger proportions.

Proteins usable in the compositions of the invention include all those which are suitable for

use with chromates and dichromates in usual photolithography, such as albumin, (egg albumin, blood albumin, etc.) animal glue, casein, soy protein and other animal and vegetable proteins. In practice, egg albumin is the preferred protein as it is in ordinary photolithographic procedure.

The sensitizing chemical generally preferred for use under the invention is, as also in usual commercial photolithography, ammonium dichromate because of the greater speed with which it or compositions containing it react under light and the shorter exposure which is consequently required for formation of an image on the plate. Other soluble chromates, e. g. sodium and potassium chromates and dichromates and ammonium chromates are usable, however, provided longer exposure time can be afforded. Ratios of dichromate to albumin under the invention are in general the same as are customary in ordinary photolithography.

The optimum ratio of chromate or dichromate, calculated as ammonium dichromate, to protein, calculated as egg albumin, has been found to be about 1 to 3 by weight when the sensitizer is applied to a metal or other non-absorbent and non-reactive base. However, when a coated paper-base is used it may be found advantageous to use a sensitizing solution having a dichromate-albumin ratio of 2 to 3, and generally it is permissible to use a ratio of 1 to 1. Paper-base plates will tolerate a higher dichromate-albumin ratio than will metal plates, without developing trouble from excess crystallization of the salt. When phosphate is present in the sensitizing solution it is not necessary to use as high a dichromate-albumin ratio as is otherwise required on a paper-base plate, but apparently no disadvantage results from using a high ratio if desired. The excess dichromate used apparently is merely washed off in later treatment of the plate when phosphate is used, for in general there is no permanent discoloration of the paper-base plate by the dichromate as is seen when no phosphate is used.

The soluble phosphate included in the sensitizing solution according to the invention should when dissolved have a pH value above the isoelectric point of the particular protein used (3.8 for egg albumin and 4.5 for casein); otherwise the unexposed film will be difficult to remove from the plate. On the other hand, since films having a pH value of not over 7 are generally desired in the interest of shortening the required exposure time, the preferred phosphates to use are those which in cooperation with the chromium sensitizer used give a solution having a pH value of not over 7.0. For absolute certainty in this respect it is advantageous to use acidic phosphates which by themselves give solutions having pH values of not over 7.0. It is not, however, essential to use an acidic phosphate, for the chromium compound chosen for use in the solution may be one such as ammonium dichromate which exerts a buffering action to keep the pH value of the solution below 7.0. In such a case a phosphate as alkaline as trisodium orthophosphate may be used with good results, though naturally it is possible to use so much of a highly alkaline phosphate that the resulting solution may become too alkaline for satisfactory use. In the proper proportions an alkaline phosphate may be included in a solution of ammonium dichromate and albumin to yield a coating which when remoistened will be slightly acidic and very satisfactory for

the purpose of the invention. In general water-soluble inorganic phosphates and water-soluble organic phosphates are suitable for use.

While the particular base to which the sensitizing solution of the invention is to be applied is not a part of the invention, it may be mentioned in passing that the coated paper plates referred to above and containing soluble salts of divalent metals, especially zinc acetate, are exceptionally suitable for use with the phosphate-containing sensitizing solution of the present invention.

The invention is considered to reside in: (1) a coating composition for sensitizing photo-sensitive plates comprising an aqueous mixture of a protein, a soluble chromate or dichromate, and a soluble phosphate having in dilute solution a pH value higher than the isoelectric point of the protein, and if desired a non-protein hydrocolloid in amount not exceeding the weight of protein present, and (2) a photo-sensitive plate comprising a suitable base and a sensitized coating consisting of the dried residue of the composition described under (1).

The invention is illustrated by the following specific examples, all parts being by weight:

1. A sensitizing solution was made containing 30 parts of egg albumin, 10 parts of ammonium dichromate and 7 parts of mono-ammonium ortho-phosphate in 420 parts of water with enough ammonia added to give the solution a pH value of 8.

A thin film of this solution was applied by means of a plate whirler to a grained zinc lithographic plate and dried. The so-sensitized plate was exposed under a negative in conventional manner. The exposed plate was then wiped with a cotton pledget wet with water, which cleaned the unexposed areas very easily. The cleaned plate was then put on an offset press where it ran satisfactorily.

2. A sensitizing solution was made containing 30 parts of egg albumin, 5 parts of mesquite gum, 12 parts of ammonium dichromate, and 5 parts of mono-ammonium ortho-phosphate, in 500 parts of water with sufficient ammonia to give the solution a pH of about 8. This solution was spread by means of a whirler on a grained aluminum lithographic plate, and dried. The sensitized plate was exposed under a negative in conventional fashion. It was then coated with developing ink and then wiped clean with a wet cotton sponge which cleaned the unexposed areas readily. The plate was then run satisfactorily on an offset press.

3. A sensitizing solution containing 30 parts of egg albumin, 6 parts of mesquite gum, 18 parts of ammonium dichromate and 15 parts of di-ammonium ortho-phosphate in 660 parts of water with enough ammonia to give a pH value of 8.7 was sponged over a commercial paper-base planographic plate having a hydrophilic coating of the type disclosed in the Worthen applications referred to above comprising casein, inert filler, guar gum, and zinc acetate. The plate was then dried and exposed conventionally through a negative. The exposed plate was wiped over with a wet cotton sponge which cleaned the unexposed areas readily. It was then run satisfactorily on an offset press.

4. A sensitizing solution containing 30 parts of egg albumin, 5 parts of gum arabic, 19 parts of ammonium dichromate, and 12 parts of mono-ammonium ortho-phosphate in 640 parts of water with enough ammonia to give a pH of 9 was

applied by a sponge to the surface of a paper-base planographic plate having a surface coating of polyvinyl alcohol, and dried. The plate was then exposed conventionally under a negative. The exposed plate was wiped over with a cotton swab wet with water which cleaned the unexposed areas readily. The plate was then run satisfactorily on an offset press.

5. A sensitizing solution containing egg albumin 30 parts, low viscosity sodium carboxymethyl cellulose 4 parts, ammonium dichromate 18 parts, disodium ortho-phosphate 12 parts, in water 630 parts with enough ammonia to give the solution a pH value of 8 was applied to a paper-base planographic plate having a surface coating of sodium alginate insolubilized by subsequent treatment with zinc acetate as disclosed in said Worthen applications. The plate was then dried and exposed under a negative to an arc-light. The exposed plate was sponged with a cotton swab wet with water which readily cleaned the unexposed areas. The plate was then run satisfactorily on an offset press.

6. A sensitizing solution containing 30 parts of casein dissolved by ammonia, mesquite gum 7 parts, ammonium dichromate 15 parts, and di-ammonium ortho-phosphate 12 parts, in 630 parts of water with sufficient ammonia to give a pH value of 8.5 was applied by a sponge to a paper-base planographic plate having a surface coating of sodium alginate insolubilized by a subsequent treatment with zinc acetate as disclosed in said Worthen applications. This was dried and then exposed through a negative in conventional manner. The exposed plate was sponged with a wet cotton swab which cleaned the unexposed areas readily. The cleaned plate was run satisfactorily on an offset press.

7. A sensitizing solution containing low viscosity animal glue 30 parts, mesquite gum 6 parts, ammonium dichromate 16 parts, and mono-ammonium ortho-phosphate 10 parts, in 650 parts of water, with ammonia to give a pH value of 8.5 was applied by a swab to a paper-base planographic printing plate having a surface coating comprising zinc carboxymethyl cellulose and zinc acetate as disclosed in said Worthen applications. The plate was dried and exposed through a negative to an arc-light. The exposed plate was then sponged with a swab wet with water which readily cleaned the unexposed areas. The plate then ran satisfactorily on an offset press.

8. A sensitizing solution containing egg albumin 30 parts, low-viscosity sodum carboxy methyl cellulose 3 parts, ammonium dichromate 16 parts, and mono-ammonium ortho-phosphate 10 parts, in 540 parts of water with sufficient ammonia to give the solution a pH value of about 9 was applied by a swab to a paper-base planographic printing plate having a base-coat of casein and clay and a wash-coat of guar gum and zinc acetate as disclosed in said Worthen applications. The plate was dried and exposed under a negative in conventional manner. The exposed plate was sponged with water which cleaned the unexposed areas readily, and the plate then ran satisfactorily on an offset press.

9. A sensitizing solution containing egg albumin 30 parts, ammonium dichromate 16 parts, dextrin 7 parts, and mono-ammonium ortho-phosphate 10 parts in water 530 parts with ammonia to give pH value of 8.5 was applied by a sponge to a plate like that used in Example 8, and dried. The sensitized plate was exposed through a negative as usual. It was then sponged with water which cleaned the unexposed areas satisfactorily, and it was then run on an offset press with good results.

10. A sensitizing solution containing egg albumin 30 parts, ammonium dichromate 16 parts, and mono-sodium ortho-phosphate 11 parts, in water 540 parts, with ammonia to give pH value of 7.8 was applied to the same base as used in Example 8, and dried. The sensitized plate was exposed through a negative in the usual manner. The exposed plate was wiped with a sponge wet with water, which cleaned the unexposed areas easily. The plate was then run on an offset press satisfactorily.

In the foregoing examples, we have given the pH values of the coating solutions. It will be understood, however, that these are not the pH values of the resulting dried coatings because the pH values of the solutions are influenced by the presence of ammonia which generally is added to act as a preservative and which vaporizes when the coatings are dried. The pH value of the coating should, as stated, be within the range from the isoelectric point of the protein used in the coating, e. g. 3.8 in the case of egg albumin and 4.5 in the case of casein up to about pH 7. The pH value of the coating is determined by wetting the coating with water and determining the pH of the resulting solution and corresponds to the pH value of the dilute solution of the salt mixture used in the coating. Coatings above 9.0 in pH value are too alkaline to be used.

The quantity of phosphate in the coating composition, e. g. its ratio to the protein or to the chromate or dichromate ingredients of the composition may vary within a considerable range. As appears from the specific examples the ratio by weight of the phosphate to the protein varies from about 15% to about 50%. The quantity of phosphate to be used will depend, however, upon the particular phosphate used, the character of the protein, the quantity of non-protein hydrocolloid, if any, in the composition, the dilution of the composition, the character of the supporting surface, etc. and may be varied independently of such factors to vary the ease with which the unexposed portion of the film is removed from the supporting surface. The most useful range of phosphate concentrations, reckoned as mono-ammonium ortho-phosphate on the weight of the sensitizing solution is from 0.5% to 3.0%, with the lower concentrations more applicable to metal plates and the higher concentrations to paper-base plates.

Various other sensitizing solutions have been made up essentially like that of Example 10 except for the omission of ammonia and replacement of the 11 parts of mono-sodium ortho-phosphate by each of the following phosphates:

Example 11.—Sodium meta phosphate, 11 parts.

Example 12.—Sodium acid pyrophosphate, 11 parts.

Example 13.—Trisodium ortho-phosphate, 11 parts.

Example 14.—Pentaethyl potassium tripolyphosphate, 11 parts.

Example 15.—Ammonium hexametaphosphate, 11 parts.

Example 16.—Mono-isopropyl sodium ortho-phosphate, 11 parts.

Example 17.—Ethyl ammonium ortho-phosphate, 11 parts.

Example 18.—Monoethanolamine acid ortho-phosphate, 11 parts.

Example 19.—Dimethylamine acid ortho-phosphate, 11 parts.

Each of the foregoing solutions of Examples 11–19 was applied to the same kind of coated paper plate used in Example 8 and further treated in the same way. In every case the unexposed areas cleaned up readily with a wet swab and remained clean when the plate was run on a press. The imaged areas took ink readily on the press and gave a satisfactory number of good prints.

An effect of the phosphate content of the sensitizer is that it renders the exposed portion of the coating more water-shedding. This effect is not marked when the film-forming ingredient of the coating is substantially all protein because such coatings possess this quality to considerable extent but when the coating contains a considerable proportion of a non-protein hydrocolloid which has little or none of the water-shedding quality the effect of the phosphate in rendering the exposed coating more water-shedding is more noticeable.

We claim:

1. A photo-sensitive plate comprising a base having a planographic printing surface and a coating thereon consisting of the dried residue of an aqueous mixture consisting essentially of a light sensitive colloid comprising a protein, a water-soluble chromium compound of the group consisting of chromates and dichromates and a water-soluble phosphate a dilute aqueous solution of which has a pH value above the isoelectric point of the protein, the ratio of chromium compound to protein being within the range from 1 part of chromium compound to from 1 to 3 parts of protein and the ratio of phosphate to protein being within the range of from 15 to 50 parts of phosphate to 100 parts of protein.

2. A photo-sensitive plate as defined in claim 1 in which the phosphate is an acid salt of ortho-phosphoric acid of the group consisting of the mono- and di-alkali metal and ammonium ortho-phosphates.

3. A photo-sensitive plate as defined in claim 1 in which the phosphate is mono-ammonium ortho-phosphate.

4. A photo-sensitive plate as defined in claim 1 in which the phosphate is a salt of pyro phosphoric acid.

5. A photo-sensitive plate as defined in claim 1 in which the light sensitive colloid comprises a water-soluble non-protein hydrocolloid in quantity amounting to from about 1.5 to 100% by weight of the protein content of the composition.

6. A photo-sensitive plate as defined in claim 1 in which the protein is egg albumin, the chromium compound is ammonium dichromate, the phosphate is mono-ammonium ortho-phosphate in quantity amounting to from about 20% to about 50% by weight of the protein content of the composition and the composition comprises a water-soluble non-protein hydrocolloid in quantity amounting to from about 5% to 25% of the weight of the protein content of the composition.

7. A photosensitive plate comprising a paper base having a planographic printing surface, a first coating thereon consisting essentially of a pigment, a hydrophilic adhesive and a water-soluble divalent metal salt, and a second coating superposed upon said first coating, said second coating consisting essentially of a protein, a water-soluble chromium compound of the group consisting of chromates and dichromates and a water-soluble phosphate a dilute aqueous solution of which has a pH value above the isoelectric point of the protein, the phosphate amounting to from 15% to 50% of the protein and the chromium compound amounting to from one part thereof to from 1 to 3 parts of the protein.

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