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

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This invention relates to the art of photolithography and more particularly to a novel sensitizing composition for the production of photo-sensitive coatings.

The usual procedure for the preparation of plates for photolithography is as follows. A suitable base or support such as a grained metal plate or a coated paper surface is "sensitized" by application of a coating of an aqueous solution containing a film-forming agent such as egg albumin and a "sensitizing" chemical such as ammonium bichromate and the coating is dried to produce a photo-sensitive film. The sensitized plate is then 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 coating is said to "tan" the film and render it relatively water-insoluble in the exposed areas. In the unexposed areas under the opaque portions of the mask the film is not affected by the light and still 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 with 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 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 in a pattern like that on the plate to complete the printing operation. The plate is then repeatedly dampened, inked, and printed from until the desired number of copies have been made.

Egg albumin has been the film-forming material most commonly used in the past in photolithography. Other proteins are usable but they offer no advantages over egg albumin and possess some disadvantages in addition to those possessed by egg albumin. Some defects possessed by the egg albumin are (1) that the life of a sensitized coating is undesirably short, (2) that such coatings are sensitive to fluctuations in atmospheric humidity, (3) that slight traces of albumin left on unexposed areas of the plate cause "albumin scum," and (4) that it is generally considered practically necessary to use developing ink on albumin plates.

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To avoid at least part of the disadvantages of albumin various non-protein film-formers have been suggested to replace albumin in sensitized coatings. Of the non-protein film-formers so far suggested for such use the consensus of opinion seems to be that polyvinyl alcohol is by far the best. It is generally recognized, however, that polyvinyl alcohol after being exposed to light in the presence of chromate or dichromate is still deficient in resistance to water. To correct this deficiency of polyvinyl alcohol various water-repellent substances have been included in the sensitized polyvinyl alcohol solutions, e. g. rubber, sulfonated compounds, fatty oils, and the like. Unfortunately, however, the water-repellent substances which have a significant effect in increasing water-resistance of a polyvinyl alcohol image also tend to make unexposed portions of the coating difficult to remove, and any such material left on the unexposed areas of the plate may cause scumming which is even more harmful than albumin scum.

The present invention, without the addition of any difficultly removable water-repellent substance and without rendering the unexposed areas difficult to remove, increases the water-repellency of the exposed areas not only of polyvinyl alcohol but also of other useful non-protein film-formers which ordinarily are deficient in water-repellency. Moreover the invention, in cases where addition of auxiliary water-repellent substance is considered desirable, also facilitates removal of such added water-repellent substance or the film containing it from unexposed areas of the sensitized coating.

By ensuring a water-repellent image and facilitating the cleaning of the unexposed areas of a planographic plate the invention renders entirely unnecessary the application of developing-ink to the exposed plate prior to removal of the unexposed portions of the sensitized coating. The application of developing-ink and its subsequent removal along with unhardened colloid from unexposed areas is an objectionable procedure and its elimination is greatly to be desired. In the past, however, such use has been general in order (1) to ensure water-repellency of the image and (2) to prevent damage to or obliteration of the image by the scrubbing operation employed to clean the unexposed areas.

According to the invention an aqueous sensitizing solution is made comprising (1) a water-soluble hexavalent chromium compound such as ammonium dichromate or chromate (or other water-soluble dichromate or chromate such as those of sodium and potassium), (2) a hydrophilic non-protein colloid capable of being tanned by action of ammonium dichromate and actinic radiation, and (3) a water-soluble readily ionizable phosphate, with or without the addition of water-repellent substance to enhance water-repellency of the exposed areas of the film. This solution is applied in a thin, even layer to the surface of a suitable base such as a grained metal, coated paper, or equivalent planographic plate base and dried.

The sensitized plate prepared as described above may if desired be treated in conventional manner from this point forward, and if so, will be found to possess various advantages not found in plates which are similar in all respects except for the presence of phosphate radical. For example, the sensitized plate may be exposed, under a mask, to a source of actinic rays and may then be coated with developing ink. The inked plate may then be washed in running water as usual, whereupon it is found that the unexposed non-protein hydrophilic colloid film together with its overlying coating of developing-ink will wash away much more easily than will a similar film in the absence of phosphate radical. As has been pointed out previously, however, the use of developing-ink is not essential to the practice of the invention and usually it is preferred to operate without use of such ink. In cleaning the exposed plate it is not necessary to immerse the plate in running water as has previously been general practice, but instead it suffices merely to wipe the surface clean with a sponge wetted 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 some difficulty, the effect of phosphate in the film is even more pronounced. Especially noteworthy are the results obtained when one uses the coated paper-base phanographic printing plates which contain a hydrophilic colloid and a soluble metal salt in the base coating layer, e. g. such plates 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 colloid-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 sensitized layer in sufficient quantity a single passage of a wet sponge over the surface suffices to reveal the color of the original coated base at the unexposed areas. Gentle swabbing cleans the unexposed areas completely. Part of the explanation for this result doubtless is the pore plugging action of phosphate on the base coating as disclosed in the 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 needless, and accordingly the exposed and imaged areas likewise escape the effects of severe scrubbing. This is one reason which makes feasible the omission of the use of developing-ink. Another and more important reason making such omission feasible is that the practice of the invention yields images having marked water-repellent or water-shedding properties without any treatment with developing-ink or other greasy material. That is to say, exposure causes the sensitized coating of the invention not only to become relatively water-insoluble but also actually water-shedding to the degree that after the surface has been washed with water the image will immediately take ink satisfactorily when rolled with an inking-roller.

It is true that polyvinyl alcohol sensitized with ammonium dichromate alone and exposed to light yields an image having a slight degree of water-repellency, but not enough to make it generally considered safe to use without strengthening by developing-ink previous to washing. When ammonium phosphate or equivalent phosphate is included in the polyvinyl alcohol and dichromate solution, however, the resulting image is so definitely water-shedding that there can be no doubt in regard to the possibility of omitting use of developing-ink. Moreover use of phosphate in the sensitizing solution permits images of good water-repellency to be made even from hydrocolloids like gum arabic or mesquite gum which ordinarily show extremely little if any water-shedding properties when used with dichromate alone.

Just why the use of phosphate should so greatly enhance water-shedding in the image is not certain. One theory advanced is that because of its detergent action the phosphate washes out of the image all soluble particles of the colloid, which might otherwise remain and attract water, and leaves only the water-shedding portion of the colloid behind. Another theory is that some sort of a complex compound is formed of the colloid, chromate and phosphate, which compound is more water-shedding than the colloid-chromate product not containing phosphate.

Plates made with images produced as described by exposure of sensitized coatings containing a non-protein hydrocolloid, a soluble chromate or dichromate, and a soluble phosphate can be used satisfactorily on an offset press for medium runs of up to about one thousand copies. The life of such images is definitely short, however, presumably because of gradual attack of water thereon. The image life can be greatly increased by addition in known manner of auxiliary water-shedding material to the sensitizing solution. In such a case the phosphate greatly facilitates cleaning the film containing said auxiliary water-shedding material from the unexposed areas of the plate and is effective in decreasing or eliminating scumming troubles caused by incomplete removal of film from the unimaged portions of the plate.

The sensitized solutions described can be applied to any base which is suitable for use in photolithography. For example, grained zinc or grained aluminum plates may be used. The solutions are particularly well adapted for use also on various of the commercially available paper-base planographic plates. Especially suitable for use are coated paper plates having a hydrophilic surface containing a soluble salt of a divalent metal, especially zinc acetate, such as the plates described in the copending applications of Worthen, referred to above.

Any non-protein hydrophilic organic colloid which is tanned by action of light and chromate or dichromate can be used according to the invention. Those which are economically feasible for use, however, include only those which yield aqueous solutions which are both sufficiently fluid to spread easily and sufficiently concentrated to form a sufficiently thick coating or film by a single application of the coating solution. Such hydrocolloids which readily form reasonably concentrated solutions include natural gums like gum arabic, gum ghatti, mesquite gum, and the like and synthetic materials such as methyl cellulose, hydroxy-ethyl cellulose, sodium carboxymethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone, sodium acrylate and the like.

The sensitizing chemical preferred for use is ammonium dichromate or ammonium chromate, though other soluble chromates and dichromates such as those of sodium and potassium are usable but require a considerably longer time of exposure.

The phosphate ion required in the coating according to the invention may be provided for by the presence in the coating of any readily water-soluble and readily ionizable phosphate compound. Inorganic phosphates, organo-metallic phosphates, and organic phosphates are all usable provided, as has been stated, that they can exist in the coating in water-soluble, readily ionizable form. The preferred phosphates to use are those which in cooperation with the chromium sensitizer yield a solution having a pH value between 3.0 and 7.0. Solutions which are more acid than indicated by a pH value of 3.0 are not desired because of deleterious effects upon the base plate. Solutions which show pH values between 6.0 and 7.0 are considered most suitable. Solutions which are definitely alkaline are less suitable for use, because they tend either to shorten the life of the image or to make necessary the use of developing-ink before the image will hold ink. Solutions yielding coatings above 9.0 in pH value are not suitable for use.

The pH value of the coating of course is influenced by both the kind and quantity of phosphate used and by the kind and quantity of chromium sensitizer used. If the phosphate used is one like mono-ammonium, mono-sodium, or mono-potassium ortho-phosphate which by itself yields a solution having a pH value under 7, the resulting sensitized coating containing such phosphate is practically certain to have a pH value also less than 7. It is not, however, essential to use an acidic phosphate, for the chromium sensitizer chosen for use may be one such as ammonium dichromate which exerts a buffering action to keep the pH value of the solution at not above 7.0. In such a case a phosphate as alkaline as trisodium phosphate can 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. Alkalinity resulting from the presence of ammonia in the solution is generally innocuous, since the ammonia escapes rapidly from the coating after it is applied to the plate.

The weight ratio of dichromate or chromate to nonprotein hydrocolloid in the composition may vary over a fairly wide range depending upon the particular colloid used as well as the time permissible for exposure. Ordinarily the weight ratio will be between 1:4 and 2:1.

The quantity of soluble phosphate present may vary rather widely. Usually the optimum phosphate content will lie between about 10% and about 35% of the weight of colloid used. Not enough phosphate should be used to cause excessive crystallization of the salt on the surface, else this may cause the coating to come away in specks even from the exposed areas. The absolute maximum quantity usable will depend upon the particular hydrocolloid and especially the particular base plate used.



The most useful range of phosphate concentrations, reckoned as mono-ammonium phosphate, is from 0.5% to 4.0% of the total sensitizing solution, with the lower concentrations preferred for use on metal plates and the higher concentrations preferred for paper-base plates.

Some specific embodiments of the invention are shown in the following examples, all parts being by weight.

*Example 1*

A sensitizing solution containing 40 parts mesquite gum, 20 parts ammonium dichromate, and 10 parts mono-ammonium phosphate in 500 parts of water.

*Example 2*

A sensitizing solution containing 40 parts gum arabic, 20 parts ammonium dichromate and 10 parts mono-ammonium phosphate in 500 parts of water.

*Example 3*

A sensitizing solution containing 30 parts gum ghatti, 15 parts ammonium dichromate, and 15 parts diammonium phosphate in 800 parts of water.

*Example 4*

A sensitizing solution containing 15 parts polyvinyl pyrrolidone, 10 parts ammonium dichromate and 15 parts mono-ammonium phosphate in 800 parts of water.

*Example 5*

A sensitizing solution containing 20 parts low viscosity polyvinyl alcohol, 15 parts ammonium chromate, and 10 parts mono-ammonium phosphate in 600 parts of water.

*Example 6*

A sensitizing solution containing 20 parts low viscosity sodium carboxymethyl cellulose, 15 parts ammonium dichromate, and 15 parts di-sodium phosphate in 600 parts of water.

*Example 7*

A sensitizing solution containing 20 parts low viscosity methyl cellulose, 15 parts ammonium dichromate, and 15 parts mono-sodium phosphate in 800 parts of water.

*Example 8*

A sensitizing solution containing 20 parts hydroxyethyl cellulose, 15 parts ammonium dichromate, and 15 parts mono-ammonium phosphate in 800 parts of water.

The solutions of each of the preceding eight examples were applied by means of a cotton swab to a commercial paper-base planographic plate having a base coat of insolubilized casein and clay filler surface-treated with a solution of guar gum and zinc acetate as described in the Worthen applications referred to above. Solutions of Examples 1, 2, 5 and 6 were likewise applied to paper-base plates having thereon a coating of zinc alginate as described in said Worthen applications.

Each of the sensitized plates after being exposed through a negative was wiped with a damp pledget of cotton which readily removed the unexposed sensitized coating, and left an image which readily took ink from an inking-roll. Good prints could be made from all the plates but the image life in every case was shorter than when albumin was used as the film-forming ingredient, but from 500 to 2,000 good prints were obtained in every case.

To the solution of Example 1 was added ammoniated sulfonated castor oil in various quantities, namely 2, 4, 6, 8, and 10 parts by weight which amounted to 5, 10, 15, 20, and 25% on the quantity of hydrocolloid present. The mixtures so made were each applied to the beforementioned paper-base plate having a coating of casein and clay surface-treated with guar gum and zinc acetate. The so-sensitized plates were exposed and further treated like the previous ones. They all cleaned up readily under a wet swab. The image life of the plate sensitized with the solution containing 5% added sulfonated oil (based on the weight of colloid) was markedly superior to that of the similar plate in which the sulfonated oil was omitted. Increasing the sulfonated oil content to 10% on the colloid somewhat further increased the image life, and 15% oil improved it slightly more. No appreciable differences could be seen among the plates having 15%, 20%, and 25% of sulfonated oil. The various known water-repellent substances vary in effectiveness but generally are usable in quantities ranging from 2 or 3% up to about 50% based upon the weight of the hydrocolloid content of the sensitizer solution.

Further solutions were prepared as follows:

*Example 9*

To the sensitized mesquite gum of Example 1 was added 15%, based on the gum, of medicinal grade mineral oil emulsified in aqueous soap solution.

*Example 10*

To the composition of Example 1 was added 15%, on the gum, of tung oil emulsified in aqueous soap solution.

*Example 11*

To the composition of Example 1 was added 15%, on the gum, of castor oil emulsified in aqueous soap solution.

*Example 12*

To the composition of Example 1 was added 10%, on the gum, of paraffin wax emulsified with aqueous gum ghatti solution.

*Example 13*

To the composition of Example 1 was added 15% on the gum of lanolin emulsified in aqueous soap solution.

The sensitizing solutions containing the various water-repellency-imparting materials of Examples 9 to 13 were applied by use of a cotton swab to the same paper-base planographic printing plate used previously, namely a paper-base having thereon a coating of casein, clay filler, guar gum and zinc acetate. The plates were exposed, cleaned and printed from as before. All the plates except that of Example 12, containing paraffin wax, cleaned readily by merely wiping with a damp cotton pledget. The plate of Example 12 required considerable scrubbing with a wet sponge to clean the unexposed area, but it was finally cleaned without obliterating the image. Without phosphate in the mixture a similar plate could not be cleaned.



In all of the Examples 9 to 13 the image life was improved as compared to the corresponding blank not containing the auxiliary water-repellent agent.

To the sensitizing solutions of each of Examples 2 to 8 was added 15%, based on the hydrocolloid present, of tung oil emulsified in aqueous soap solution. In every case the plate cleaned up readily when wiped with a damp cotton swab, and in every case the image life was markedly improved as compared to that obtained in the absence of the oil. These solutions were used on the same paper-base plate previously used with the same improved results above noted.

*Example 14*

A sensitizing solution containing 40 parts mesquite gum, 15 parts ammonium dichromate, and 5 parts mono-ammonium phosphate in 500 parts of water.

*Example 15*

A sensitizing solution containing 40 parts gum arabic, 15 parts ammonium dichromate, and 5 parts mono-potassium phosphate in 500 parts of water.

*Example 16*

A sensitizing solution containing 15 parts polyvinyl pyrrolidone, 7 parts ammonium dichromate and 8 parts mono-ammonium phosphate in 800 parts of water.

*Example 17*

A sensitizing solution containing 20 parts low-viscosity polyvinyl alcohol, 8 parts ammonium dichromate and 6 parts sodium metaphosphate in 600 parts of water.

*Example 18*

A sensitizing solution containing 20 parts of low-viscosity sodium carboxymethyl cellulose, 8 parts ammonium dichromate, and 6 parts mono-ammonium phosphate in 600 parts of water.

The solutions of each of Examples 14, 16 and 18 were applied by means of a whirler to grained zinc planographic plates, while the solutions of Examples 15 and 17 were applied to grained aluminum planographic plates.

Each sensitized plate was exposed as usual through a negative and then wiped with a damp cotton swab which readily removed the unexposed sensitized layer and left an image which readily accepted lithographic ink. Each plate so prepared when used in an offset duplicator gave at least 1,000 good prints.

To each of the solutions of Examples 14 to 18 inclusive was added 10%, based on the hydrocolloid present, of tung oil emulsified in water by means of a little sodium stearyl sulfate and stearyl alcohol. The so-modified sensitizing solutions were applied as before to the same kind of metal plates used in Examples 14 to 18, and the sensitized plates were further treated exactly as in the case of those former examples. In every case when the tung oil modified sensitizer was compared with the similar sensitizer lacking the oil the image-life was found to be very definitely improved.

A further series of trials were made like that of Example 2 but in which various other phosphates were substituted for the mono-ammonium phos-

phate there used. That is, to a solution containing:

| | Parts |
|---|---|
| Gum arabic | 40 |
| Ammonium dichromate | 20 |
| Water | 500 |

was added in each case the particular phosphate mentioned in the following examples:

*Example 19.*—Sodium metaphosphate, 10 parts.

*Example 20.*—Sodium pyrophosphate, 10 parts.

*Example 21.*—Trisodium phosphate, 10 parts.

*Example 22.*—Ammonium hexametaphosphate, 10 parts.

*Example 23.*—Ethyl ammonium phosphate, 10 parts.

*Example 24.*—Pentaethyl potassium tripolyphosphate, 10 parts.

*Example 25.*—Mono-isopropyl sodium phosphate, 10 parts.

*Example 26.*—Monomethylamine acid phosphate, 10 parts.

*Example 27.*—Dimethylamine acid phosphate, 10 parts.

*Example 28.*—Monoethanolamine acid phosphate, 10 parts.

Each of the preceding sensitizing solutions was applied to the same guar-and-zinc acetate coated paper-base used in Examples 1 to 8 and the sensitized plates were further treated as in the Examples 1 to 8 series. In every case the unexposed areas cleaned up readily with a wet swab and the imaged areas took ink readily, giving satisfactory service when used as a plate on an offset duplicator.

We claim:

1. A photo-sensitive plate comprising a base having a planographic printing surface and a surface coating thereon consisting of the dried residue of an aqueous composition consisting essentially of water, a non-protein hydrophilic organic film-forming hydrocolloid of the group consisting of methyl cellulose, hydroxyethyl cellulose, sodium carboxymethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone, sodium acrylate, gum arabic, gum ghatti and mesquite gum which is capable of being tanned by actinic radiation in the presence of ammonium dichromate, a hexavalent chromium compound of the group consisting of water-soluble chromates and dichromates, a water-soluble ionizable phosphate and from 0% to 50% by weight based on the weight of the hydrocolloid of an organic, normally liquid, non-volatile water-repellent substance of the group consisting of natural and modified animal and vegetable oils and mineral oils, the pH value of the composition being above 3.0 and the pH value of the dried coating being not greater than 9, the weight ratio of chromium compound to hydrocolloid being within the range from 1:4 to 2:1 and the phosphate being within the range from 10% to 35% of the weight of the hydrocolloid.



2. A photo-sensitive plate as defined in claim 1 in which the water-repellent substance is within the range from 2% to 50% of the weight of the hydrocolloid.

3. A photo-sensitive plate as defined in claim 1 in which the phosphate constitutes from 0.5% to 4% by weight of the composition.

4. A photo-sensitive plate as defined in claim 1 in which the base is paper having a coating comprising a water-soluble, water-stable divalent metal salt.

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