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LIGHT-SENSITIVE COMPOSITIONS AND PLATES FOR PHOTOLITHOGRAPHY

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This invention relates to the art of photolithography and particularly to sensitized solutions or compositions for preparing light-sensitive plates and to the plates so prepared.

In the usual practice of photolithography a suitable base, such as a grained metal plate or a suitable coated paper of the kind well-known in the art, is coated with a thin even layer or film of a sensitized solution such as an aqueous solution of egg albumin sensitized with ammonium dichromate, and is then dried. The plate so treated is exposed through a mask or negative to the action of actinic radiation, as from an arc-light, which effectively "tans" or insolubilizes the film in the areas exposed to the light but leaves unchanged or still soluble the film on the unexposed areas. The exposed plate is next wiped over with greasy developing-ink which coats the entire surface; and then it is washed in water with rubbing which loosens the water-soluble areas of the film and removes them together with the ink overlying those areas, but leaves on the plate the exposed water-insoluble areas of the film together with the ink overlying them. After the preceding treatment the plate is ready to be used for planographic printing. The unexposed areas are kept wet with aqueous liquid which repels ink when the surface is rolled with an inking-roller coated with lithographic printing-ink. At the same time the inked areas repel water and are not wet by the aqueous liquid but are readily wet by the lithographic ink on the roller and are inked thereby. When the inked plate comes into contact with another surface it transfers thereto the ink 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.

In the past the sensitized coating material generally used has been one which dries as a solid film, e. g. albumin. After exposure of such a film through a negative all unexposed portions must be washed away. Any unexposed film inadvertently left on the surface causes scumming and consequent toning or discoloration in the unimaged portions of the prints made from the plate. Even when metal plates are used it is difficult to be certain that all unexposed film has been removed; paper-base planographic plates usually are still more difficult to free completely from unexposed film.

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In the present invention, on the other hand, the sensitized image-forming material in contradistinction to the solid film-formers previously used is one which before being exposed to action of light is not a solid film-former but instead is a liquid or semi-liquid substance. The portions of such sensitized substance which are exposed to actinic radiation are oxidized to a coherent solid film, but the unexposed portions remain liquid or semi-liquid and are removable with comparative ease. Moreover, the exposed areas of the film have a composition sufficiently similar to that of printing-ink that the image will pick up lithographic ink quickly without prior treatment with developing-ink.

In the past, use of developing-ink has been general in order (1) to ensure water-repellency of the image, and (2) to prevent damage to or obliteration of the image during the scrubbing operation to clean the unexposed areas. The application of developing-ink, however, and its subsequent removal along with unhardened film from unexposed areas together comprise a somewhat disagreeable procedure. Elimination of the necessity for use of developing-ink is much to be desired. This the present invention achieves.

By the present invention a sensitizing composition is provided in which the usual albumin or other solid film-forming material is replaced by a liquid or semi-liquid fatty or oily material which is capable of reducing bichromate under the influence of light. The preferred fatty or oily materials are highly unsaturated substances, e. g. tung oil, but material of a lower degree of unsaturation is usable. For the purpose of this disclosure any fatty or oily material is considered to be an unsaturated substance if it will reduce bichromate under the influence of light. They are generally naturally occurring glycerides of higher fatty acids, modifications and derivatives thereof and their synthetic equivalents. The sensitizing compositions of the invention likewise contain a light-sensitive chemical such as a soluble hexavalent chromium compound, i. e. chromate or bichromate and also a soluble ionizable phosphate such as an ammonium phosphate.

The presence of ammonium phosphate or equivalent phosphate capable of supplying phosphate ions seems to be essential. In the absence of phosphate the background does not clean up readily and a sharp image is not obtained quickly unless developing-ink is used. When phosphate is included in the sensitizing solution, however, the unexposed areas are easily cleaned, and the image will take ink readily without any treatment with developing-ink. Usable phos-

phates include water-soluble inorganic phosphates, organo-metallic phosphates, and organic phosphates such as the amine phosphates which can exist in the coating in water-soluble, readily ionizable form. The pH value of the sensitized coating is of course influenced by both the kind and quantity of phosphate used and by the kind and quantity of hexavalent chromium sensitizer used. Those phosphates are preferred which in cooperation with the chromium sensitizer used yield a solution having a pH value between 3.0 and 7.0 inclusive. Solutions more acid than indicated by a pH value of 3.0 are undesirable because of their marked effect on the base plate. On the other hand, solutions more alkaline than indicated by a pH value of 9.0 are unusable because of their deleterious effect upon the image. Mildly alkaline coatings having pH values between 7.0 and 9.0 are generally usable but are less desirable than those of not over 7.0 pH value. It is not, however, essential to use an acidic phosphate in the solution, for the chromium sensitizer chosen for use may be one like ammonium dichromate which exerts a buffering action to keep the pH value of the solution at 7.0 or below 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.

The sensitizing chemical preferred for use is a hexavalent chromium compound such as ammonium chromate or dichromate. Other soluble chromates and dichromates are usable but are somewhat slower in their action than are the ammonium salts.

The oily or greasy component of the sensitized coating may be any drying or semi-drying oil or a derivative thereof, particularly a water-soluble derivative such as a sulfonated oil. Naturally occurring oils may be used such as raw tung oil, or the oil may be modified as by heating such as heat-bodied tung oil. On the other hand the oil may be one which has been treated to increase its degree of unsaturation, e. g. dehydrated castor oil. Likewise are usable various compounds of the unsaturated fatty acids such as sorbitan oleate or polyoxyethylene derivatives of that or similar compounds.

The oily or greasy materials are, of course, applied in an aqueous medium along with the phosphate and dichromate. If the materials are not intrinsically soluble or dispersible in water they may be emulsified in water by means of known emulsifying agents.

The chief objects of the invention may be accomplished by use of a sensitizing solution comprising only dichromate, phosphate, and unsaturated oil dispersed in water. In some cases, however, it may be desirable to harden up the sensitized coating somewhat, for instance if the plate is to be stored or handled before use. If such is the desire a small proportion of easily soluble film-forming substance may be added to the sensitizing solution, e. g. dextrin, mesquite gum, or the like. It is found that such easily soluble gum does not hinder the removal of unexposed coating from the plate but on the contrary actually seems to facilitate such removal. At the same time, however, addition of such gum in small proportion to the sensitizing solution does not materially affect the life of the image in the exposed portions of the plate. As the proportion of such gum is increased the image-life

begins to decrease, but quantities of gum up to about twice the weight of oily material may be used without hurting the image-life seriously.

Permissible variation in the ratios of dichromate to oily material in the sensitizer appears to be considerably greater than can be tolerated in the ratio of dichromate to albumin in conventional albumin sensitizing solutions. While limiting ratios have been determined we have obtained good results with ratios of dichromate calculated as ammonium dichromate to oily material varying as widely as from 0.25:1 to 2:1 by weight.

The preferred concentration of phosphate, reckoned as mono-ammonium orthophosphate, ranges from 0.5% to 3.0% by weight of the sensitizing solution, with the lower concentrations being used on metal plates and the higher concentrations on paper-base plates.

The base plates which are suitable for use with the sensitizing solutions include the metal plates, e. g. zinc or aluminum, commonly used for lithographic printing and the various commercially available paper base plates used for planographic printing including parchment and coated papers. Especially suitable are the coated paper plates which contain a soluble multivalent metal compound capable of reacting with the soluble phosphate in the sensitizer solution to form a less soluble phosphate of the metal. Such plates are disclosed in the applications of Stephen V. Worthen Serial Nos. 747,138 and 758,215, filed May 9, 1947 and June 30, 1947, both now abandoned. In the case of a plate containing a lead salt such as lead acetate it is probable, since lead chromate is less soluble than lead phosphate, that lead chromate is formed by interaction of the lead salt with the chromate of the sensitizer solution and the results are less desirable than when the phosphate of the metal, e. g. zinc, is less soluble than the chromate thereof.

Typical oil emulsions suitable for use in practicing the invention are described below.

Example 1

Tung oil 100 parts was heated with 10 parts of cetyl alcohol (an agent to stabilize the emulsion) until the latter dissolved. This solution was then added to 215 parts of water containing 10 parts of a water-soluble polyoxyethylene derivative of linseed oil fatty acids (an emulsifying agent). The mixture was passed through a colloid mill and formed a stable emulsion which was readily dilutable with water.

Example 2

Dehydrated castor oil 100 parts was heated with 10 parts of stearyl alcohol until the latter dissolved. This solution was then added to 215 parts of water containing 5 parts of the polyoxyethylene derivative of sorbitan monolaurate and 5 parts of sodium mixed fatty alcohol sulfate (emulsifying agents). The mixture was then passed through a colloid mill and formed a stable emulsion which was readily dilutable with water.

Example 3

Linseed oil 100 parts and sorbitan monostearate 10 parts were mixed together and mixed with 215 parts of water containing 5 parts of a water-soluble polyoxyethylene derivative of sorbitan monostearate and 5 parts of sodium mixed fatty alcohol sulfate. The mixture was passed through a colloid mill and formed a stable emulsion which was readily dilutable with water.

For the particular oils used in the preceding

specific examples other unsaturated oils or semi-liquid organic materials capable of reducing hexavalent chromium and of thereby forming a solid film may be substituted. Soy-bean oil, rapeseed oil, perilla oil, oiticica oil and the like are all satisfactory for use. Any of these oils may be used with the emulsifying agents of any of these previous examples. The emulsions of these particular examples are all very stable and contain stabilizers. However, far less stable emulsions can be satisfactorily used. If the emulsion is to be used immediately after preparation it is merely necessary that the oil shall remain emulsified for a matter of minutes. Naturally, it is more convenient to have the emulsion stable enough so that stock emulsions can be prepared and stored.

The particular emulsifying agent used in emulsifying oils to be used in practicing the invention in itself forms no part of the invention. There is some advantage in using an emulsifying agent, like that shown in Example 1, which itself can be oxidized and rendered insoluble by the action of chromate and light. But emulsifying agents which are not affected by the conditions of plate exposure likewise are usable with complete satisfaction. When very efficient wetting agents are used to emulsify the oil large excesses thereof over the quantity needed to accomplish the emulsification should be avoided. If too large an excess is used undesirable penetration of the sensitizing solution into paper-base plates may result; furthermore, too high a proportion of a very efficient wetting agent may tend to shorten the life of the printing image formed. On the other hand an oil film deposited from an emulsion and containing an emulsifying agent undoubtedly is considerably easier to remove from the unexposed areas of a plate than would be an oil film merely spread on the surface or deposited from solution in a volatile solvent.

As has been before pointed out it is not necessary to use emulsified oil under the invention. Derivatives of oils which are soluble in water such as the polyethylene derivatives and sulfonated derivatives may be used with great satisfaction.

On the other hand, it is possible to use emulsifying oil varnishes as well as simple oils; that is an oil in which a resin such as copal, an oil-soluble phenolic resin, or an oil-soluble alkyd resin has been dissolved or cooked may be emulsified and used under the invention in place of a simple oil emulsion.

Some specific sensitizing solutions are shown in the following examples.

Example 4

A sensitizing solution containing 10 parts of ammoniated sulfonated oil, 10 parts of mono-ammonium phosphate, and 7.5 parts ammonium dichromate in 470 parts of water was applied to a coated paper lithographic plate having a base coat of insolubilized casein and clay and having been wash-coated with a solution of guar gum and zinc acetate as described in the applications of Stephen V. Worthen referred to above. The so-sensitized plate was exposed under a negative to light from an arc-lamp. The exposed plate was wiped with a cotton swab dampened with water which cleaned off the unexposed areas. The plate was then put on an offset duplicator where it gave satisfactory prints.

Example 5

Tung oil was heat-treated until its viscosity

was increased to value M on the Gardner-Holdt scale of oil viscosity standards. This bodied oil was emulsified like that in Example 2 preceding and then diluted with water until the oil concentration was 10%. Then 100 parts of the emulsion was mixed with 380 parts of water having dissolved therein 10 parts of mono-ammonium phosphate and 7.5 parts of ammonium dichromate. This solution was applied to the same kind of coated paper plate used in Example 4. The sensitized plate was then further treated exactly as in said Example 4. The image took ink quickly without any developing treatment and the unexposed areas remained satisfactorily clean.

Example 6

The emulsion of Example 1 was diluted with water until the oil concentration was 10%. A sensitizing solution was prepared by mixing 100 parts of this 10% emulsion in 570 parts of water in which were dissolved 17.5 parts of mono-ammonium phosphate, 15 parts of ammonium dichromate, and 8 parts of mesquite gum. This solution was used to sensitize a coated paper plate like that of Example 4 and the plate was further treated as in Example 4. The results were satisfactory in every way.

Example 7

Heat-bodied tung oil of M viscosity (Gardner-Holdt), 100 parts by weight, was heated with 10 parts of cetyl alcohol until the latter dissolved. The mixture was then added to a mixture of 5 parts of a commercial polyoxyethylene derivative of sorbitan monolaurate and 5 parts of a commercial emulsifier consisting of sodium mixed fatty alcohol sulfates in 200 parts of water. The mixture was then passed through a colloid mill and formed a stable emulsion which was diluted with water until it contained exactly 10% of tung oil.

Example 8

100 parts of the emulsion of Example 7 (containing 10 parts of tung oil)
10 parts of diammonium phosphate
7.5 parts of ammonium dichromate
400 parts of water

Example 9

Same as Example 8 except for the substitution of 10 parts of mono-potassium phosphate in place of di-ammonium phosphate.

Example 10

100 parts of the emulsion of Example 7
5 parts of gum arabic
10 parts of di-sodium phosphate
8 parts of ammonium dichromate
400 parts of water

Example 11

100 parts of the emulsion of Example 7
5 parts of mesquite gum
10 parts of ethyl ammonium phosphate
8 parts of ammonium dichromate
400 parts of water

Example 12

100 parts of the emulsion of Example 7
3 parts of mesquite gum
10 parts monomethylamine acid phosphate
8 parts ammonium chromate
400 parts of water

Each of the solutions of Examples 8–12 was applied to the same type of guar gum and zinc acetate treated coated plate used in Example 4. The sensitized plates were then dried, exposed to actinic radiation under a negative, and then swabbed with a damp cotton swab. The so-treated plates all ran satisfactorily on an offset duplicator.

In place of the phosphates mentioned in the preceding examples the following phosphates have also been used satisfactorily: sodium metaphosphate, sodium pyrophosphate, tri-sodium phosphate, ammonium hexametaphosphate, dipotassium phosphate, pentaethyl potassium tripolyphosphate, mono-isopropyl sodium phosphate, dimethyl amine acid phosphate, monoethanolamine acid phosphate.

Example 13

100 parts of the emulsion of Example 7
5 parts of mono-ammonium phosphate
3.5 parts of ammonium dichromate
4 parts of mesquite gum
400 parts of water

This solution was applied by means of a whirler to a grained aluminum plate and to a freshly cleaned grained zinc plate. The plates were dried, exposed through a negative to light, wiped with a damp sponge, and then placed in an offset duplicator where they ran satisfactorily in respect to definition, background clarity, and image-life.

The oily or fatty component of our sensitizer compositions are believed to be all embraced by the description or definition that they are normally structureless unsaturated fatty acid compounds which are capable in the presence of hexavalent chromium and actinic light of forming coherent films.

We claim:

1. A sensitizer composition for photosensitive planographic printing plates comprising an aqueous vehicle, a water-soluble hexavalent chromium compound of the group consisting of chromates and dichromates, a liquid to similiquid, unsaturated, organic, oily to fatty material capable of reacting with bichromate in the presence of actinic light to form a coherent solid film and a water-soluble phosphate, the weight ratio of said chromium compound to said material being within the range from 1 to 8 parts of the chromium compound to 4 parts of said material, and said composition containing from .5 to 3 percent by weight of said phosphate and having a pH value within the range from 3 to 9.

2. A sensitizer composition as defined in claim 1 in which the said material is an oil of the group consisting of drying and semi-drying oils.

3. A sensitizer composition as defined in claim 2 in which the said material is tung oil.

4. A sensitizer composition as defined in claim 2 in which the composition comprises an emulsifying agent for said material.

5. A sensitizer composition as defined in claim 1 in which the said material is an intrinsically water-dispersible derivative of an unsaturated fatty acid.

6. A sensitizer composition as defined in claim 5 in which the emulsifying agent is a water-soluble derivative of an unsaturated fatty acid.

7. A sensitizer composition as defined in claim 1 comprising a water-soluble, organic, hydrophilic, film-forming, non-protein hydrocolloid in quantity not exceeding twice the weight of said material.

8. A photosensitive plate comprising a base and a coating thereon consisting of the dried residue of the sensitizer composition defined in claim 1.

9. A photosensitive plate comprising a base containing a water-soluble, water-stable salt of a metal having a valence greater than 1 in at least the surface thereof and a photosensitive coating on said surface consisting of the dried residue of the composition defined in claim 1.

10. A planographic printing plate comprising a base and a partial coating thereon in the form of a configuration, said coating being the dried and insoluble residue of the composition defined in claim 1.

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