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3,136,639

DIAZO PRESENSITIZED LITHOGRAPHIC PLATE BASE COMPRISING A UREA-FORMALDEHYDE INTERMEDIATE LAYER AND PROCESS FOR MAKING

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The present invention relates to a lithographic plate, and more particularly, to a diazo presensitized lithographic plate which can be stored for an appreciable length of time prior to use.

This application is a continuation-in-part of an earlier copending application, Serial No. 693,815.

In the manufacture, sale and use of diazo presensitized lithographic plates, various factors are important. Among these are uniformity of product, quality of product, ease of control during manufacture, storage life prior to use, length of run on the press, and ease of control of the printing on the press. For example, it is well known that commonly used diazo compounds react with metals and that for this reason, where the lithographic plate is to comprise a metal support sheet, it is necessary to provide a barrier layer or sub-base between the diazo and the metal surface to prevent such reaction. Such barrier layer or sub-base must of course adhere to the support and provide a hydrophilic outer surface to which the light-exposed diazo compound will permanently adhere during printing and to which the unexposed diazo compound will releasably adhere.

One of the difficulties experienced with diazo presensitized plates having a metal support is that the sub-base may be discontinuous or the sub-base is so thin that reaction between the metal and diazo resin results. Such imperfections appear as flaws in the printed impressions from the plate. To avoid such conditions requires very careful control of the various stages in the manufacture of the presensitized plate and in the subsequent handling. Frequently a high percentage of spoilage results.

Another difficulty which has been experienced is that the water attractive character of the sub-base disappears after a time of use on the press and the plates begin to "scum." Thus the life of the plate is shortened or limited by a wearing off or deterioration of the hydrophilic sub-base. This may be due to the thinness of the sub-base or lack of toughness under operating conditions on the press. In an effort to minimize this effect and lengthen the useful life of the plate, the press operator must exercise careful control of operating conditions.

Two sub-base materials that have been proposed are polyacrylic acid and a siliceous substance such as sodium silicate. In this case, the material reacts with a metal support base to form a water-insoluble hydrophilic sub-base or barrier. Inasmuch as a chemical reaction with a metal base is needed to form the sub-base, it follows that the sub-base is necessarily quite thin, since the chemical reaction is confined to the interface between the metal base and the sub-base material. Especially in the case of the silicate, the sub-base is very thin and may, in fact, be only a few molecules thick. It has been our experience that this sub-base fails to prevent the metal from destroying a diazo compound or resin. Further, there is no way of building the sub-base or barrier to a suitable thickness which can adequately protect the diazo material from decomposition. Still further, if a siliceous sub-base becomes dry as by a loss of water during storage, the siliceous sub-base deteriorates and becomes ink receptive, making it unsuitable for use as a lithographic surface for lack of a contrasting oleophobic surface.

The present invention provides a lithographic plate

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base for receiving a diazo compound reactive to light to produce a diazo presensitized lithographic plate which obviates the foregoing objections. In particular, we have found that lithographic plates can be made with especial advantage by applying to a support member or base a novel hydrophilic, water-insoluble sub-base coat or layer formed from modified water-soluble urea-aldehyde resins. These materials have been discovered to be uniquely adapted for use on lithographic plates. Such materials are suitably hydrophilic for lithographic and related purposes and, in view of their water-solubility, are easily applied to a plate from a water medium. The present modified curable urea-aldehyde resins can be deposited on a backing member as a film or coat to provide after curing a water-insoluble layer which exhibits a hydrophilic character for lithographic applications. The sub-base or barrier of our lithographic plate is believed not to react chemically with a metal or other type of support member. In any event, a sub-base coat can be deposited having a sufficient thickness to protect an overlay of a diazo material by a single dip of the plate into a water solution of the urea-aldehyde resin, followed by a water rinse of the plate. Further, the present modified urea-aldehyde resins adhere well to a support member or base and are not stripped therefrom or otherwise damaged during the handling, shipping, and use of our lithographic plate. Moreover, the sub-base material of the present invention permits the diazo compound to form a film thereover which is sufficiently bonded thereto to permit handling and the like of the plate and whose photodecomposition products become tightly bonded to the sub-base material after exposure to light.

It is, therefore, a principal object of the present invention to provide an improved plate base receptive to a diazo compound reactive to light to provide a plate for lithographic printing and related uses and to provide a process for making it.

Another object is to provide an improved sub-base material for such a plate.

A further object is to provide a metallic lithographic plate base having an improved sub-base coat adapted to receive a light-sensitive diazo material thereover.

A still further object is to provide an aluminum lithographic plate base having an improved sub-base material comprising a modified urea-aldehyde resin adapted to receive thereover as a continuous film a light-sensitive water-soluble diazo material.

Other objects will become apparent as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention consists of the features hereinafter fully described and particularly pointed out in the claims, the following disclosure describing in detail the invention, such disclosure illustrating, however, but one or more of the various ways in which the invention may be practiced.

In accordance with the present invention, a plate base for a diazo presensitized plate for lithographic printing and related uses may be prepared by applying a coat or layer of a modified urea-aldehyde resin to a support member to provide a water-insoluble sub-base which has a hydrophilic character, to which can then be applied an overcoat or film of a light-sensitive diazo material.

For purposes of the invention, the modified urea-aldehyde resin may be a water-soluble polyfunctional amino-urea-aldehyde or a sulfonated urea-aldehyde, or a compatible mixture of the two may be used. The aldehyde preferred and usually employed is formaldehyde, although paraformaldehyde may be used.

Since the polyfunctional amino-urea-formaldehydes employed are water-soluble, they can be applied to a plate from a preferred aqueous solution. The preparation of a

polyfunctional urea-aldehyde resin is fully disclosed in United States Patent No. 2,554,475 and accordingly is not here disclosed in detail. In general, urea and an aqueous solution of formaldehyde are reacted at a temperature of about 70° C. to 80° C. for 15 to 30 minutes under alkaline conditions. A polyfunctional amine is then added, after which the pH is adjusted to between 1 and 4 and the reactants heated at a temperature of from 68° C. to reflux temperatures for 15 to 180 minutes so that there is no viscosity increase. The temperature is then reduced to a point within the range of room temperature to 55° C. to effect a viscosity increase.

The mol ratio of formaldehyde to urea does not appear to be critical in preparing a polyfunctional amino-urea-formaldehyde. Satisfactory results have been obtained with a mol ratio of from about 2.0 to about 3.0 mols of formaldehyde per mol of urea. For best results, the ratio of aldehyde to urea is preferably 2.3 to 2.8.

The quantity of polyfunctional amine employed does not appear to be critical, although a minimum amount must be employed to obtain solubility and other desirable properties. Satisfactory products may be obtained by reacting the amine at any stage of the reaction; it being preferred, however, to add the amine after the initial reaction of urea and aldehyde. It is usually the procedure in making these resins to use 2 to 80 percent polyfunctional amine based on the weight of urea, and for most utilities, it is preferable to use about 6 to 15 percent. As examples of polyfunctional amines which have been found to be satisfactory, there may be mentioned the polyamines; such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine; the condensation products of polyamines leading to amine polymers such as tetraethylenepentamine and epichlorohydrin or tetraethylenepentamine and formaldehyde; the guanidines, the biguanides, the guanylureas and the salts thereof; and the hydroxylamines such as monoethanolamine, diethanolamine, and the like. Any of the above amines may be first reacted with part of the total formaldehyde before adding to the reaction.

The sulfonated urea-aldehydes are also water-soluble and can therefore be applied to a plate from a preferred aqueous medium. The preparation of a water-soluble sulfonated urea-formaldehyde is fully disclosed in United States Patent No. 2,559,578 and therefore is not here discussed in detail. In general, urea, an aqueous solution of formaldehyde, and an alkali metal salt of sulfurous acid are reacted at reflux temperature for at least 30 minutes and at a pH varying between 8 and 9.4. The pH is then adjusted to a point within the range of 1 to 4, and the reaction mixture is heated again at reflux temperatures for approximately one hour. Thereafter, the mixture is cooled to a temperature between 25° C. and 85° C. while maintaining a pH of 1 to 4, thereby effecting an increase in viscosity.

Molar ratios of formaldehyde to urea do not appear to be critical. Satisfactory resins have been obtained with 1.5 to 3 mols of formaldehyde per mol of urea. It is preferred to employ urea-formaldehyde in the proportions of approximately 2.0 to 2.8 mols of formaldehyde per mol of urea. The amount of the alkali metal salt of sulfurous acid used does not appear to be critical. However, a minimum amount of about 5 percent based on the weight of the urea must be used to make the resulting resin water-dispersible and as much as 60 percent of the alkali metal salt by weight of the urea has been employed. Such alkali metal salts as sodium bisulfite and sodium metabisulfite may be used.

The terms "polyfunctional urea-formaldehyde resin," "sulfonated urea-formaldehyde resin," "modified urea-formaldehyde resin condensation product," and the like, as used here and in the claims include, except where otherwise more specifically defined, water-soluble condensates of urea and formaldehyde as disclosed in U.S. Patent No. 2,616,874, such as the water-soluble reaction

products formed by combining in a series of steps polyethylenepolyamines, dihaloalkanes, a urea, and formaldehyde as there defined; and also the co-condensation products of urea, formaldehyde, melamine, and an alkanolamine as disclosed in U.S. Patent No. 2,917,427, excepting those of this last-mentioned group which may be covered within the scope of the disclosure and claims of our copending application, Serial No. 120,188. Both of these last cited patents are also hereby incorporated by reference.

The type of backing or support member is not critical to the invention. Ordinarily a metallic support or plate is preferred because of its inherent strength. Metals such as aluminum, zinc, copper, tin, lead, chromium, magnesium, steel, and the like may be used. Aluminum has been found to give very satisfactory results and is preferred. In the case of metallic surfaces, oxides may be present, either through exposure to air or through special treatment. For example, in the case of aluminum, the surface may if desired be chemically or electrolytically anodized, although this is not necessary.

Other materials may also form the support member. For example, a paper sheet or plate suitably backed, or a paper sheet impregnated with a resin, such as a thermosetting resin like phenol formaldehyde can be employed. A heat-resistant resin is preferably used since it protects the paper during the heating steps which may be used in preparing a lithographic plate in accordance with the method herein disclosed. As used herein and in the claims, the term "plate" includes a plate, sheet, film, or foil, the foil being merely wrapped over a supporting surface.

The light-sensitive diazo compounds used may be those known in the art. A method of preparing a very satisfactory diazo compound is described in Patent No. 2,679,498 and in Patent No. 2,063,631. This compound is a condensation product of paraformaldehyde with p-diazo-diphenylamine sulfate. Diazo compounds are also described in U.S. Patent 2,667,415 which together with the previously mentioned patents and the diazos disclosed thereby are hereby incorporated by reference. Upon exposure to light, such as ultra-violet light, the light-sensitive diazo compounds expel nitrogen from the molecule and form a water-insoluble, hydrophobic and oleophilic material which then becomes the printing image. The unexposed portions of the compound are readily washed away by known developer solutions.

In preparing a plate of the present invention, a water solution of the modified urea-aldehyde resin is applied to a support or base in any convenient manner, such as by roller coating, blade coating, dipping, or spraying, and removal of any excess resin is effected as by rinsing. The concentration of the resin in the solution is not critical. As an example, the modified urea-aldehyde resin may range from about 0.3 percent to about 5 percent of the solution. After application of the solution, for example by a single dip and rinsing, the water is removed to deposit a sub-base coat or film of the resin and to insolubilize it on the backing member. Conveniently, this may be done by heating the assembly. Any temperature above the ambient temperature may be used, the upper temperature limit being determined by practical considerations, such as avoiding a temperature sufficiently high to anneal the metal of the plate.

During the heating step and removal of the water, there is further polymerization of the resin, and this aids the insolubilization and adherence of the resin to a backing member. However, the state or amount of polymeric growth is not in any sense critical to practicing the invention; except that the resin should adhere well and resist a water wash so as not to bare the backing plate. The modified urea-aldehyde resins prepared as described in Patent Nos. 2,554,475 and 2,559,578 are dissolved in water and applied as previously mentioned. Such resins are partially polymerized or cured at this time. The

heat is then conducted at such a temperature within the limits described and for such a time as to drive off substantially all of the water and further polymerize the resins such that a layer or coat of the resin is deposited having the desired adherence and resistance to a water wash. Such a coat has been surprisingly found to be hydrophilic and will accept a film of a diazo compound.

Whether the temperature employed is sufficiently high and/or the time of heating is sufficiently long can be easily determined by simply observing if the deposited coat of resin has the described desired characteristics. In practice, heating the assembly from about 140° C. to about 210° C. for approximately 3 to 12 minutes has been found to provide good results, although these ranges are not critical.

Instead of heating to deposit the resin coat as just described, it has been found possible to promote the additional polymeric growth by making the aqueous solution of the resin more acid. This can be accomplished by adding a salt of a strong inorganic acid and a weak inorganic base to the solution as it overlies the metal base. Salts that may be used include ammonium chloride, ammonium nitrate, and ammonium sulfate. Also organic acids such as oxalic acid, gluconic acid, and lactic acid are well suited for this purpose. Again, whether or not the amount of salt or acid added is sufficient to bring about the added polymeric growth can easily be determined by noting if the deposit resin has a satisfactory adherence to the support base and suitably resists a water wash. In general, the salt or acid is added by dipping in an aqueous solution containing from 1/2 to 5 percent by weight of said salt or acid. A period of about five minutes at an ambient temperature is sufficient to produce a satisfactory polymeric growth although these conditions are not critical. The water may be removed by evaporation at an ambient or slightly elevated temperature, whirling the plate, and the like.

Following the deposition of the resin coat, an aqueous solution of the diazo compound is applied, as by roller coating, dipping, spraying, and the like. A sufficient amount of the compound should be used to cover a desired area of the resin coat. The thickness of the diazo film is not critical, a residue of about 0.003 gram per square foot of the resin coat being an accepted practice. Aqueous solutions up to about one percent diazo compound have also been employed. The film is deposited by driving off the solvent. Since water is conveniently used as the solvent, the drying is ordinarily performed at an ambient temperature, although temperatures up to the decomposition temperature of the diazo compound can be used if desired.

If desired, the manufacturer of a lithographic plate of the present invention can stop short of the application of the diazo compound, so that a plate having only the sub-base material can be shipped to a consumer. The consumer can then apply the diazo compound at his own discretion.

In order to demonstrate the invention, the following examples are set forth for the purpose of illustration only. Any specific enumeration or detail mentioned should not be interpreted as a limitation of the invention unless specified as such in one or more of the appended claims and then only in such claim or claims.

Example I

A one percent aqueous solution of a sulfonated urea-formaldehyde is applied over a support. While the support is still wet, it is wiped with a squeegee and then dried at 120° F. The assembly is then heated at 150° C. for six minutes. The plate is then immersed in an aqueous solution containing about one percent of a diazo compound, consisting essentially of a condensation product of paraformaldehyde with p-diazo-diphenylamine sulfate, to deposit on the plate a continuous coat of this solution. The plate is then air dried to deposit a film

of the diazo compound thereover. The resulting sensitized plate is then packaged in a non-bleeding, plastic lined, paper backed foil and the margins thereof heat sealed together to permit storage of the plate.

Example II

An aluminum plate is grained by treatment with a ten percent aqueous solution of tri-sodium phosphate and then washed and desmuted. The plate is next dipped into a 0.8 percent aqueous solution of a polyfunctional urea-formaldehyde resin and then heated at 170° C. for six minutes. A diazo film is applied as in Example I.

Example III

A zinc plate is treated with a 1.5 percent aqueous solution of a sulfonated urea-formaldehyde resin formed by reacting formaldehyde with urea in a molar ratio of 2:1, respectively, and with sodium bisulfite present in an amount of five percent by weight of the urea. The resin is prepared in accordance with Patent No. 2,559,578 and therefore is water-dispersible. The plate is heated at 120° F. until dry and then further heated at 160° C. for eight minutes. The sulfonated urea-formaldehyde resin deposits as a coat over the plate and becomes strongly adhered thereto. The coat is sufficiently hydrophilic for lithographic purposes. The plate is then immersed in a one percent aqueous solution of a diazo compound and finished in the manner described in Example I.

Example IV

A procedure is carried out like the procedure of Example III except that the plate is not heated to effect further polymerization of the sulfonated urea-formaldehyde resin. Instead the resin treated plate is dipped into a solution containing two percent by weight of ammonium chloride, for about five minutes. This lowers the pH and is found to promote additional polymerization of the resin, probably as a catalyst. The resin is deposited as a hydrophilic coat which adheres well to the plate. The plate is dried at a temperature not higher than 120° F.

Example V

A copper plate is coated with a 1.2 percent aqueous solution of a polyfunctional urea-formaldehyde resin formed by reacting formaldehyde with urea in a molar ratio of 2.3:1 to which triethanolamine is added in an amount of about 10 percent based on the weight of the urea. The resin is prepared in accordance with Patent No. 2,554,475 and therefore is water-dispersible. The plate is heated at 120° F. until dry and then further heated at 200° C. for five minutes. The modified urea-formaldehyde resin deposits as a coat over the plate and becomes strongly bonded thereto. The coat is sufficiently hydrophilic for lithographic purposes. The plate is then immersed in a 0.7 percent aqueous solution of a diazo compound. The solution adhering to the plate is reduced to a thin film by whirling the plate as in conventional practice until dry. The plate thus prepared is ready for exposure to light.

Example VI

A procedure is carried out like the procedure of Example III except that the resin used is that prepared by Example 6 of Patent No. 2,559,578.

Example VII

A procedure is carried out like the procedure of Example V except that the resin used is that prepared by Example 1 of Patent No. 2,554,475.

Example VIII

A cleaned aluminum plate is treated in two percent chromic acid at 150° F. for about 4-5 minutes to form an oxide layer on the surface. It is then treated as in Example I.

In the foregoing examples, known equivalent materials such as those disclosed herein may be substituted for those stated in the example, the times and temperatures and other parameters being adjusted where and if needed as easily determined by trial and error.

Other forms embodying the features of the invention may be employed, change being made as regards the features herein disclosed, provided those stated by any of the following claims or the equivalent of such features be employed.

We therefore particularly point out and distinctly claim as our invention:

1. In a lithographic plate having a support member with a metal surface, an overlying layer on said metal surface of a diazo compound reactive to light to define printing and non-printing areas and a hydrophilic intermediate coat between said support member metal surface and diazo, the improvement wherein said intermediate coat is resin consisting essentially of a water-insoluble hydrophilic sulfonated urea-formaldehyde resin polymer.

2. In a lithographic plate having a support member with a metal surface, an overlying layer on said metal surface of a diazo compound reactive to light to define printing and non-printing areas and an intermediate coat between said support member and diazo, the improvement wherein said intermediate coat is a resin consisting essentially of a water-soluble modified urea-formaldehyde resin condensation product polymerized to a water-insoluble hydrophilic state selected from the group consisting of (a) a sulfonated urea-formaldehyde and (b) a condensation product of urea, formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanolamines.

3. A plate as claimed in claim 2 wherein said support member consists essentially of a metal selected from the group consisting of aluminum, zinc, tin, magnesium, lead, chromium, copper and iron.

4. In a lithographic plate having a support member with a metal surface, an overlying layer on said metal surface of a diazo compound reactive to light to define printing and non-printing areas and an intermediate coat between said support member and diazo, the improvement wherein said intermediate coat is a resin consisting essentially of a water-dispersible condensation product of urea, formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanol amines polymerized to a substantially non-water-dispersible hydrophilic state.

5. In a lithographic plate having a support member with a metal surface, an overlying layer on said metal surface of a diazo compound reactive to light to define printing and non-printing areas and an intermediate coat between said support member and diazo, the improvement wherein said intermediate coat is a resin consisting essentially of a water-soluble condensation product of urea, formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanolamines polymerized to a substantially water-insoluble hydrophilic state, said condensation product having a mol ratio of from about 2.0 to about 3.0 mols of formaldehyde per mol of urea, said amine being reacted therewith in an amount of from about 2% to about 80% based on the weight of the urea.

6. In a lithographic plate having a support member with a metal surface, an overlying layer on said metal surface of a diazo compound reactive to light to define

printing and non-printing areas and an intermediate coat between said support member and diazo, the improvement wherein said intermediate coat is a resin consisting essentially of a water-dispersible condensation product of urea, formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanolamines polymerized to a substantially non-water-dispersible hydrophilic state, said condensation product having a mol ratio of from about 2.3 to about 2.8 mols of formaldehyde per mol of urea, said amine being reacted therewith in an amount of from about 6% to about 15% based on the weight of the urea.

7. In a lithographic plate having a support member with a metal surface, an overlying layer on said metal surface of a diazo compound reactive to light to define printing and non-printing areas and an intermediate coat between said support member and diazo, the improvement characterized by providing as said coat a resin consisting essentially of a water-soluble urea-formaldehyde resin modified with an alkali metal salt of sulfurous acid polymerized to a water-insoluble hydrophilic state.

8. In a lithographic plate having a support member with a metal surface, an overlying layer on said metal surface of a diazo compound reactive to light to define printing and non-printing areas and an intermediate coat between said support member and diazo, the improvement wherein said intermediate coat is a resin consisting essentially of a water-dispersible sulfonated urea-formaldehyde resin polymerized to a substantially non-water-dispersible hydrophilic state, said resin being formed by reacting about 1.5 to 3 mols of formaldehyde for each mol of urea with an alkali metal salt of sulfurous acid present in an amount of at least about 5% by weight of the urea.

9. A plate as defined in claim 8 wherein said support member metal surface is of aluminum and the alkali metal salt of sulfurous acid is selected from the class consisting of sodium bisulfite and sodium metabisulfite.

10. A plate is claimed in claim 8 wherein said support member surface is of aluminum and the alkali metal salt of sulfurous acid is present in an amount of about 5% to 60% by weight of the urea.

11. In a process of preparing a lithographic plate by applying to a support member with a metal surface an intermediate coat and to said coat a diazo compound reactive to light to define printing and non-printing areas, the improvement wherein there is applied to said support member to form said intermediate coat an aqueous solution of a curable modified urea-formaldehyde resin selected from the group consisting of (a) a sulfonated urea-formaldehyde resin and (b) a condensation product of urea, formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanolamines, and converting such resin to a water-insoluble hydrophilic state thereby to apply a hydrophilic coat to said member.

12. In a process of preparing a lithographic plate by applying to a support member with a metal surface an intermediate coat and to said coat a diazo compound reactive to light to define printing and non-printing areas, the improvement wherein there is applied to said support member to form said intermediate coat an aqueous solution of a curable modified urea-formaldehyde resin selected from the group consisting of (a) a sulfonated urea-formaldehyde resin and (b) a condensation product of urea-formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide and alkanolamines, and heating to polymerize said resin to a water-insoluble

hydrophilic state and thereby insolubilize the resin as a hydrophilic water-insoluble coat over said support member.

13. In a process of preparing a lithographic plate by applying to a support member with a metal surface an intermediate coat and to said coat a diazo compound reactive to light to define printing and non-printing areas, the improvement wherein there is applied to said support member to form said intermediate coat an aqueous dispersion of a curable modified urea-formaldehyde resin selected from the group consisting of (a) a sulfonated urea-formaldehyde resin and (b) a condensation product of urea, formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanolamines, said resin being in an early stage of polymerization, and making such aqueous dispersion more acid further to polymerize the resin to a water-insoluble state and thereby insolubilize the resin as a hydrophilic water-insoluble coat over said support member.

14. A process as claimed in claim 13 wherein said step of making the aqueous solution more acid includes adding a salt of a strong inorganic acid and a weak inorganic base.

15. A process as claimed in claim 13 wherein said step of making the aqueous solution more acid includes adding an acid ingredient selected from the group consisting of ammonium chloride, ammonium nitrate, ammonium sulfate and oxalic acid.

16. In a process of preparing a lithographic plate by applying to a support member with a metal surface an intermediate coat and to said coat a diazo compound reactive to light to define printing and non-printing areas, the improvement wherein there is applied to said support member to form said intermediate coat an aqueous solution of a curable condensation product of urea, formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanolamines, and converting said condensation product to a water-insoluble hydrophilic state thereby to apply a hydrophilic coat to said member.

17. In a process of preparing a lithographic plate by applying to a support member with a metal surface an intermediate coat and to said coat a diazo compound reactive to light to define printing and non-printing areas, the improvement wherein there is applied to said support member to form said intermediate coat an aqueous dispersion of a curable condensation product of urea-formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanolamines, said condensation product being formed from a mol ratio of from about 2.0 to 5.0 mols of formaldehyde per mol of urea, said amine being reacted therewith in an amount from about 2% to about 80% based on the weight of the urea, and heating to drive off the water and polymerize said condensation product to a water-insoluble state, thereby to insolubilize said condensation product as a hydrophilic water-insoluble coat over said support member.

18. In a process of preparing a lithographic plate by

applying to a support member with a metal surface an intermediate coat and to said coat a diazo compound reactive to light to define printing and non-printing areas, the improvement wherein there is applied to said support member to form said intermediate coat an aqueous dispersion of a curable condensation product of urea, formaldehyde and an amine selected from the group consisting of alkylene polyamines, the condensation products of tetraethylene pentamine and epichlorohydrin, the condensation products of tetraethylene pentamine and formaldehyde, guanidine, biguanide, and alkanolamines, said condensation product being formed from a mol ratio of from about 2.3 to about 2.8 mols of formaldehyde per mol of urea, said amine being reacted therewith in an amount from about 6% to about 15% based on the weight of the urea, and heating to drive off the water and further polymerize said condensation product to a water-insoluble state, thereby to insolubilize such condensation product as a hydrophilic water-insoluble coat over said support member.

19. In a process of preparing a lithographic plate by applying to a support member with a metal surface an intermediate coat and to said coat a diazo compound reactive to light to define printing and non-printing areas, the improvement wherein there is applied to said support member to form said intermediate coat an aqueous solution of a curable sulfonated urea-formaldehyde resin, and converting said resin to a water-insoluble state thereby to apply a hydrophilic coat to said member.

20. In a process of preparing a lithographic plate by applying to a support member with a metal surface an intermediate coat and to said coat a diazo compound reactive to light to define printing and non-printing areas, the improvement wherein there is applied to said support member to form said intermediate coat an aqueous dispersion of a curable sulfonated urea-formaldehyde resin formed by reacting about 1.5 to 3 mols of formaldehyde for each mol of urea with an alkali metal salt of sulfurous acid present in an amount of at least about 5% by weight of the urea, and heating at a temperature sufficient to drive off the water and further polymerize said resin to a water-insoluble state, thereby to insolubilize the resin as a hydrophilic water-insoluble coat over the support member.

21. A process as claimed in claim 20 wherein said support member metal surface is aluminum and the alkali metal salt of sulfurous acid is present in an amount of about 5% to 60% by weight of the urea.

22. A process as claimed in claim 20 wherein said support member metal surface is aluminum and the alkali metal salt of sulfurous acid is selected from the group consisting of sodium bisulfite and sodium metabisulfite.

References Cited in the file of this patent

UNITED STATES PATENTS

2,230,982	Toland et al.	Feb. 4, 1941
2,354,662	Bryce	Aug. 1, 1944
2,554,475	Suen et al.	May 22, 1951
2,559,587	Suen	July 10, 1951
2,714,066	Jewett et al.	July 26, 1955
2,764,085	Shoemaker et al.	Sept. 25, 1956
2,772,972	Herrick et al.	Dec. 4, 1956
2,778,735	Brinnick et al.	Jan. 22, 1957
2,816,092	Kelly	Dec. 10, 1957
2,873,207	Weegar et al.	Feb. 10, 1959
2,918,387	Wooding	Dec. 22, 1959
3,017,827	McKnight et al.	Jan. 23, 1962