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3,323,451
PROCESS AND COMPOSITION FOR PRODUC ING PLANOGRAPHIC PHOTOELECTROSTATIC

PRINTING PLATES

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8 Claims. (Cl. 101-149.2)

This application is a continuation of our copending application, Ser. No. 435,080, filed Feb. 24, 1965, and now abandoned.

This invention relates to a treating solution for use with photoelectrostatic copy sheets to convert them to plano-

graphic printing plates.

Planographic printing involves the making of reproductions from a flat or planar surface having differentially 20 ink and water receptive areas. The ink receptive areas correspond to the image portions and the water receptive or hydrophilic portions correspond to the non-image areas. Printing from the planar surface or planographic plate is accomplished by first wetting the planographic 25 printing surface with an aqueous medium which is accepted only in the non-image areas, followed by the application of a grease-based printing ink which is accepted only in the imaged portions. The ink image may then be offset onto another receptive surface from whence it is transferred to a paper sheet producing a right reading printed copy and the cycle repeated. The offset step may be eliminated in favor of a direct transfer of the inked image to the paper sheet.

Planographic printing plates per se are well-known in 35 the art and comprise a wide variety of base materials including metals such as zinc or aluminum, and high wetstrength papers which have been treated or otherwise coated in order to provide a suitable surface that will accept grease or ink images when dry and which is water receptive in the non-image areas. A wide variety of imaging materials as well as techniques for creating the images

thereon are well-known.

The advent of photoelectrostatic copying processes has provided still another means of placing an ink receptive image on photoelectrostatic members. Typical photoelectrostatic members such as described in U.S. Reissue Patent 25,444 to Thomas J. Kucera and U.S. Patent 3,052,539 to Harold G. Greig comprise a photoconductive layer made up of finely divided photoconductive particles dispersed in an insulating resin binder solution applied to a suitably conductive substrate. Preferred photoconductive material is zinc oxide. In the practice of photoelectrostatic copying the photoelectrostatic members having a photoconductive insulating layer applied to a suitably conductive base are electrostatically charged in the dark. The charged photoconductive layer in then exposed to a light image. The light causes the photoconductive material, such as zinc oxide or selenium, to become electrically conducting and the charge is dissipated rapidly from the surface of the photoconductive insulating layer to the conductive base, or substrate, the rate of charge dissipation being proportional to the intensity of light to which any given area is exposed. After such exposure, the surface of the photoconductive insulating layer is contacted in the dark with electroscopic particles such as synthetic thermoplastic resin particles disclosed in the copending application, Ser. No. 357,743, and assigned to

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the same assignee. These particles adhere to these areas where the electrostatic charge is retained, or, in the case of negative working systems will adhere where the charge is depleted, thus forming a powder image that is ink receptive corresponding to the electrostatic image.

The imaged photoelectrostatic member at this point, in order to be rendered useful as a planographic printing plate, requires that the non-image or background portions of the image bearing surface be rendered hydro-10 philic since the zinc oxide-resin binder layer is not suffi-

ciently water receptive.

A wide variety of treatments have been suggested for converting the zinc oxide resin binder layer to a condition of hydrophilicity which are not completely satisfactory from the standpoint of having the photoelectrostatic members readily adapted to known techniques of lithographic printing. The use of strong acidic solu-tions, such as the halides and sulfates of aluminum and iron, while they might effectively render the non-image areas of the photoelectrostatic member hydrophilic, tend to corrode the metallic parts of the lithographic printing apparatus. In recent years there has been an increasing demand to provide apparatus capable of automatically etching a plate mounted on the duplicator as opposed to treating the plate as a separate step in making it ready for duplication. Highly corrosive etch solutions are particularly detrimental to the metallic parts of the automatic applicator and the duplicator generally.

The use of treating solutions which include mono-basic acid phosphates for processing zinc and aluminum metal planographic plates has been proposed in U.S. Patents 1,977,646 and 2,003,268, but which, because of the level of acidity, tend to temporarily blind the image portion; similarly, the conversion solutions disclosed in U.S. Patent 2,957,765, while capable of rendering the ZnO resin binder layers hydrophilic, tend to give an uncontrolled reaction with ZnO producing uneven conversion across the plate surface which may give rise to a streaked offset reproduction. These prior art treating solutions require great care and particularity in the manner of

their application.

There has been a need for a conversion solution that will convert photoelectrostatic copy sheets to planographic plates and can also function with the more conventional unsensitized direct image paper masters. The advantage of using a single etch solution for a variety of planographic reproducing materials will be readily appreciated, particularly where the solution is contained in the duplicator for use with automatic etching apparatus. The operator can process interchangeably conventional planographic plates and the photoelectrostatic type without removing or changing the solution in the automatic etch apparatus.

The instant invention provides a novel composition for converting the photoelectrostatic member to a planographic printing plate which provides a proper degree of hydrophilicity to the non-image areas without blinding the grease receptive image and which is compatible with

other planographic printing materials.

It is a general object of this invention to provide an improved composition and methods for converting photoelectrostatic members into planographic plates by a controlled reaction rate giving the optimum degree of hydrophilicity in the non-image areas without affecting the 65 image portions.

It is another object of the instant invention to provide an improved composition and methods for converting photoelectrostatic members to planographic printing

plates, comprising a solution of an acid phosphate, a humectant and a preservative, said solution being brought within a critical pH range to control the conversion reaction with the photoconductive layer.

Other objects and advantages will become apparent 5 from the following detailed description of the invention.

In carrying out the objects of the instant invention, an aqueous solution is prepared containing from 4% by weight to 22% by weight of a salt such as, for example, sodium or ammonium mono-basic phosphate; a humectant 10 in the range of from about 5% by weight to 20% by weight, such as, for example, glycerine; and a preservative ranging from 0.05% to 0.1% by weight such as formaldehyde; the rest distilled water and then adding a basic component to adjust the pH in the range of 4.5 to 15 6.0.

Suitable basic components such as the alkali metal hydroxides, ammonium hydroxide, triethanolamine, diethanolamine, and monoethanolamine can be added to shift the pH bringing it within the critical range without 20 interfering with the lithographic duplicating process.

In this pH range, it has been found that the reaction rate of the acid phosphate with the zinc oxide is sufficiently controlled so that only the desired amount of hydrophilic gel forms to render the background area hy- 25 drophilic without affecting the image portions.

At a pH less than 4.5, i.e., going toward greater acidity, the solution when applied to an imaged photoelectrostatic member would react with the zinc oxide to produce a hydrophilic gel-like material which would render the non- 30 image area water receptive. However, the extent of the reaction at the more acidic pH level is such that image portions on the planographic plate are covered with the gel and tend to be blinded, that is, the gel effectively overcoats the ink receptive image portions so that initial 35 II. ink acceptance is poor and the first copies reproduce with weak images.

At a pH level above 6, that is, approaching neutrality, the conversion treatment is extremely slow leaving portions of the planographic plate improperly treated and 40 therefore ink receptive. Further, at this pH range the solution affects the grease-based inks causing the ink to emulsify and the plate to tone in the background area producing an image of poor density.

An example of a suitable formula which may be followed in preparing the new composition, especially for use as a conversion solution, for direct application to photoelectrostatic members to convert them to planographic printing plates is shown in the following example in which all parts are indicated in percent by weight:

#### EXAMPLE I

Per	cent
Ammonium mono-basic phosphate NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	10
Glycerine (99%)	20
Formaldehyde (10% solution)	.5
Water (distilled)	69.5

The pH of the above identified solution was 3.8, which required that it be made more basic in order to bring it within the critical range of 4.5-6.0 acceptable for the con- 60 version of the photoelectrostatic members to a suitable planographic plate. To accomplish the change in the pH there was added 0.25% by weight of sodium hydroxide pellets which shifted the pH to about 5.0. The solution was then applied to a photoelectrostatic copy sheet which 65 was previously imaged by electrostatic means, the solution being applied with a cotton pad, spread thereover by gently rubbing the pad over the entire surface, converting the copy sheet to a planographic plate. Thereafter, the planographic plate was mounted on the cylinder of a conventional lithographic duplicator such as a Model 1250 offset duplicator manufactured by Addressograph-Multigraph Corporation which had been adjusted for the proper ink-water balance so that the first copy reproduced from the planographic plate was a usable print.

## 4 EXAMPLE II

The following example illustrates the preparation of a treating solution which is saturated with the acid phos-

Perc	ent				
Ammonium mono-basic phosphate NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	22				
Glycerine	10				
Formaldehyde (10% solution) 1					
Water (distilled)					

The pH of the solution as mixed read 3.8 on a pH meter. To the solution was added sufficient diethanolamine to shift the pH to a reading of about 5. The additional of 1.5% by weight of triethanolamine added to the batch produced a pH of about 5.0.

The thoroughly mixed conversion solution was then applied in the same manner as described in Example I covering a planographic plate in which the very first copy possessed the optimal condition of hydrophilicity and inkreceptivity so that the very first print from the offset duplicator was an acceptable, usable repoduction.

#### EXAMPLE III

The following formulation was prepared in the same manner as described in Example I:

Perce	ent
Sodium mono-basic phosphate (NaH <sub>2</sub> PO <sub>4</sub> )	10
Glycerine	10
Formaldehyde (10% solution)	
Water (distilled)	

To the mixed solution was added 0.25% of sodium hydroxide pellets. The solution gave results comparable to those obtained from the etch solutions of Examples I and

Other humectants may be used in the place of glycerine, suc has ethylene glycol, propylene glycol, diethylene glycol, sorbitol, urea or mixtures thereof.

A variety of preservatives may be employed such as formaldehyde, sodium chlorophenate and thymol, which represent the more common materials.

The precise reason for the optimum results obtained with the solutions of this invention having a critical pH range of 4.5 to 6.0 is not known. However, the surprising result wherein ammonium or sodium mono-basic phosphate can now be adapted for use with the zinc oxideresin binder type photoelectrostatic members as well as the unsensitized direct image type planographic materials was unsuspecting, particularly in view of the prior art teachings requiring highly acidic solutions. The conversion solution of the instant invention is non-toxic and noncorrosive. Indeed, the solutions of the instant invention are simple to formulate and equally simple in their use.

What is claimed is:

1. A composition for converting a photoelectrostatic copying sheet to a planographic plate comprising an aqueous solution consisting essentially of 10% by weight of ammonium mono-basic phosphate, 15% by weight of glycerine, a preservative and a basic component to produce a solution pH of about 5.0.

2. A composition for converting a photoelectrostatic copying sheet to a planographic plate comprising an aqueous solution consisting essentially of 10% by weight of ammonium mono-basic phosphate, 15% by weight of glycerine, a preservative and sufficient sodium hydroxide to produce a solution pH of about 5.0.

3. A composition for converting a photoelectrostatic copying sheet to a planographic printing plate consisting of an aqueous solution containing of from 10% to 22% by weight of a salt selected from the group consisting of sodium mono-basic phosphate and ammonium monobasic phosphate, from 5% to 20% by weight of glycerine and a preservative, the pH of said aqueous solution being adjusted to within the range of 4.5 to 6.0 by the addition 75 of a basic component.

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4. The composition as defined in claim 3 wherein the pH is about 5.0.

5. The method of converting a photoelectrostatic copy sheet having ink-receptive image areas and non-image areas to a planographic printing plate, said copy sheet including a layer comprising photoconductive zinc oxide particles dispersed in an insulating resin binder comprising the step of applying to the copy sheet an aqueous solution containing a salt selected from the group consisting of sodium mono-basic phosphate and ammonium mono-basic phosphate, the pH of said aqueous solution being adjusted within the range of 4.5 to 6.0 by the addition of a basic component whereby non-image areas of the copy sheet are rendered water receptive.

6. The method of as defined in claim 5 wherein said 1s aqueous solution includes a humectant and a preserva-

tive.

7. The method as defined in claim 5 wherein said salt is present in the solution in an amount of from 6% to 22% by weight.

8. The method of converting a photoelectrostatic copy sheet having ink-receptive image areas and non-image areas to a planographic printing plate, said copy sheet 6

including a layer comprising photoconductive zinc oxide particles dispersed in an insulating resin binder comprising the step of applying to the copy sheet an aqueous solution containing 10% by weight of a salt selected from the group consisting of sodium mono-basic phosphate and ammonium mono-basic phosphate, glycerine, a preservative and a basic component to produce a solution pH in the range of 4.5–6.0, whereby said non-image areas of the copy sheet are rendered water receptive.

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