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AQUEOUS COMPOSITION OF AN UNMODIFIED HYDROXYL-CONTAINING RESINOUS GLYCIDYL POLYETHER OF A DIHYDRIC PHENOL

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This invention relates to planographic printing-plate developers.

In one common form of planographic printing, a water-soluble light-sensitive coating on a grained metal plate is exposed to light through a suitable stencil or negative to insolubilize the exposed portion, and the unexposed portion of the coating is later washed away, leaving a hydrophobic image on a hydrophilic plate. Albumen sensitized with bichromate provides a typical water-soluble light-sensitive coating. After exposure, the plate is commonly lightly coated with developing-ink, which adheres over the entire coating. The plate is then wiped dry. Washing the plate with water then removes the soluble portions of the coating, together with the developing-ink adhering thereto, leaving the inked and therefore readily visible insolubilized exposed image portion in place ready for printing by the lithographic method.

In an alternative procedure, employing a more recently developed type of planographic printing-plate such as will be further identified hereinbelow, the plate is washed immediately after exposure to remove the soluble portions of the coating and leave the substantially invisible insolubilized image portion in condition for printing. Application of printing ink, as in a lithographic press, then renders the image visible. However, it is preferred, as in the earlier procedure described above, to develop the image to a visible state prior to placing the plate on the press, so that the operator can determine whether or not he has a good plate, and so that the plate may be correctly positioned on the press. The present invention supplies an improved developer composition for such applications.

While the novel developer of the present invention is entirely effective on dichromate-albumen type printing plates, it is particularly well adapted for use with pre-sensitized planographic printing plates, particularly such as are described in the co-pending application of Jewett and Case, Serial No. 199,566, filed December 6, 1950. Such plates employ extremely thin diazo resin light-sensitive coatings. The thinness of the coating requires that the unexposed areas be removed prior to application of printing ink or other developer. Application of prior art developing-inks to the resulting plate prior to placing on the press is unsatisfactory. Unless extreme precautions are taken in applying the ink to the image, some of the ink frequently adheres to image-free areas of the plate, particularly in half-tone areas. The ink offers no protection against wear when the press is in operation. Other prior art developers, protective asphalt solutions, etc., have also shown a tendency to adhere to areas of the plate other than the image areas, or have been affected by the oils of the ink employed on the press, or have not adequately protected the original image from mechanical abrasion and wear, or have been unsatisfactory in a number of these or other respects.

A primary object of the present invention is therefore to provide a developer for exposed pre-sensitized planographic printing plates which overcomes the difficulties experienced with prior art developers. A particular object is to provide a developer applicable to the developing of plates such as are described in the above-identified Jewett et al. application, especially after removal of the unexposed portions of the pre-sensitized coating. Another object is to provide a developer capable of producing a visible image of increased thickness and improved wear-resistance. Another object is to provide such a developer in permanently readily applicable form. A further object is to provide a developed printing-plate having greatly increased press life as well as improved inking and printing qualities. Other objects and advantages will be made apparent as the description proceeds.

Specific exemplary formulas of image-developers made in accordance with the invention and having the desired properties will now be supplied, for purposes of explanation but not of limitation. In these formulas, parts are given as parts by weight unless otherwise noted.

Example 1

Aqueous phase:	Parts
Water	90
25% gum arabic solution in water	18
Wetting agent (sodium lauryl sulfate; may be omitted if desired)	1.8
Non-aqueous phase:	
Ethylene dichloride	60
Cyclohexanone	40
Soft epoxy resin	30
Pigment (toluidine toner)	9

The resin employed was an epichlorohydrin-bisphenol (epoxy) resin stated to have a melting point of 40° C., epoxide equivalent of 300–375, hydroxy equivalent of 105, and was very viscous but still fluid at normal room temperatures.

The pigment, resin, and about eight parts of the cyclohexanone were combined on a paint mill, and the resulting mixture was then dispersed in the mixed remaining solvents in a churn. Combining the aqueous and non-aqueous phases in a mixer then produced a water-in-oil type emulsion of high viscosity, which did not separate even on prolonged standing. Applied to an exposed and washed lithographic plate, this developer provided a clearly visible image with no bridging of half-tone dots.

Example 2

Aqueous phase—as in Example 1.

Non-aqueous phase—as in Example 1 with the exception that a normally hard, brittle, rosin-like epoxy resin was substituted for the soft resin of Example 1. This hard resin was stated to have a melting point of 100° C., epoxide equivalent of 905–985, and hydroxy equivalent of 175.

Mixing the two solutions produced a water-in-oil type emulsion which did not separate. Used as a developer, the emulsion provided clear images with no bridging of half-tones. The developed image was extremely wear-resistant on the press, and in this respect was even better than that produced with the emulsion of Example 1, particularly at elevated temperatures.

Example 3

Aqueous phase—as in Example 1.

Non-aqueous phase:

	Parts
Ethylene dichloride	50
Cyclohexanone	50
Epoxy resin of Example 2	30
Toluidine toner	9

A non-separating water-in-oil type emulsion was produced by milling together the resin, pigment, and 10

parts of cyclohexanone, dissolving the mixture in the remaining solvents, and then mixing the liquid blend with the aqueous phase in a high-speed mixer.

Example 4

Aqueous phase—as in Example 1.

Non-aqueous phase—as in Example 3 with the exception that carbon black was substituted for the toluidine toner pigment.

In this example, mixing of the two phases produced an oil-in-water type emulsion which had some slight tendency to separate into two layers. Separation could be overcome and the emulsion re-formed by merely shaking the two layers in a bottle; or the rate of separation could be reduced by increasing the amount of gum arabic in the formula.

Example 5

	Parts
Aqueous phase:	
Water	112
25% gum arabic solution in water	23
Sodium lauryl sulfate	2.3
Non-aqueous phase:	
Ethylene dichloride	60
Epoxy resin of Example 2	30
Toluidine toner	9

The resulting emulsion was of the oil-in-water type. Lithographic images were satisfactorily developed with this emulsion, particularly at somewhat below normal room temperatures.

Example 6

Aqueous phase—as in Example 1.

Non-aqueous phase—as in Example 5 except that trichloroethane was substituted for ethylene dichloride.

As in Example 1, a water-in-oil emulsion was obtained. Some bridging of half-tone dots was noted when this emulsion was used in developing half-tone lithographic plates. Line drawings and the like were satisfactorily developed. After developing the plates, they were preferably allowed to stand for an hour or more, or briefly heated, in order to remove any stickiness caused by solvent retention in the resin coating.

Example 7

Aqueous phase—as in Example 1.

Non-aqueous phase:	
Ethylene dichloride	60
Epoxy resin as in Example 1	30
Toluidine toner	6

An oil-in-water type emulsion was obtained, which was equally as effective as the emulsion of Example 5 as a lithographic plate developer.

In the application of these developers to diazo sensitized printing-plates such as those described in the above-identified Jewett et al. application, the following procedure has been found effective.

The pre-sensitized plate is first exposed to light through a stencil or negative, an exposure of 2–4 minutes at 24 inches from a 35-ampere carbon arc being suitable. After exposure the plate is desensitized by wiping with water containing a small amount of gum arabic, to dissolve and remove the unexposed and unreacted soluble portion of the diazo sensitizer. At this point the remaining exposed image portion is substantially invisible. While the plate is still wet with the gum arabic solution, a quantity of the developer, e. g. as specified in Example 1 hereinabove, is poured on the plate and wiped over the image area with a soft pad or cotton wad until the image is uniformly coated. The same action effectively re-dissolves and removes any portion of the developer resin which may temporarily adhere to non-image areas of the plate such as the areas between half-tone dots. As soon as the image is completely coated, and before any further deposition of resin can occur, the excess developer is rinsed from the plate by flooding with water. The plate is then ready to be placed on the press. Alternatively, the developed plate may be coated with a protective layer of gum arabic solution, wiped dry, and stored for future reference. The color imparted by the developer makes it possible for the operator readily to determine the position and degree of perfection of the hydrophobic image areas.

In the printing operation, after the plate has been installed on a lithographic press, the gum arabic coating, if present, is first removed by sponging with water or with a weak fountain solution. The fountain rollers should be dropped first and, after a few revolutions of the press, the ink rollers may be dropped. The image should ink up quickly. No special inks or fountain solutions are required, and most materials commonly used for this purpose will be found to be satisfactory. A typical lithographic ink contains suitable colored pigments dispersed in a rapid-drying liquid vehicle having a drying-oil base. In order to obtain the maximum number of satisfactory impressions, the press should be carefully adjusted to the least pressure consistent with quality printing. The image may at intervals be re-developed and further protected from wear on the press by repeated applications of the developer.

The epoxy resins, as indicated by the foregoing examples, are well adapted for use in my novel lithographic plate developer emulsions. They are insoluble in water. They are soluble in suitable volatile organic solvents, from which they may be recovered in the form of strong tough films. They adhere firmly to the image portions of the plate to provide a surface which is desirably organophilic and ink-receptive without being soluble in, or otherwise objectionably affected by, the ink. The epoxy resin developed surface has excellent wear-resistance, which is particularly important with lithographic plates having extremely thin image layers such as the diazo-resin-coated plates of the aforementioned Jewett et al. invention.

The epoxy resins are produced by reacting together certain polyhydric phenolic bodies, of which bis-phenol (p,p'-dihydroxydiphenyl dimethyl methane) is a typical example, with polyfunctional alcohol-contributing reactants such as epichlorhydrin, the extent of reaction and hence the molecular weight of the product being determined by the ratio of the principal reactants and/or by the introduction of controlled small amounts of suitable monofunctional "short-stop" materials such as phenol or ethylene chlorhydrin. The resulting resin may be considered a polymeric polyhydric alcohol, and as such is capable of further reaction, e. g. with drying oil fatty acids, resin acids, acid anhydrides, aldehydes, etc.; and such reaction products in many instances are applicable as components of image-developers in accordance with this invention. These various epoxy resins, including derivatives as just described, are preferred by me as components of my novel developer compositions, although other equivalent resins and resinous materials are not thereby to be considered as excluded.

A further example will now be provided of a developer composition which has given excellent results when properly applied and treated, but is somewhat less desirable from the standpoint of rapidity of application than are the preceding compositions.

Example 8

Aqueous phase—as in Example 1.

Non-aqueous phase:	
Solution of melamine-formaldehyde-butanol resin	45
Xylol	45
Toluidine toner	9

Mixing the two solutions in a high-speed mixer produced a water-in-oil type emulsion, which was applied to an exposed and washed lithographic plate as a developer. The resin adhered well to the image, but remained too soft for prolonged effective press operation until cured

overnight at room temperature or for 10 minutes at 260° F. After curing, the plate was found to have excellent press life.

The resin solution consisted of 65 parts of resin dissolved in 35 parts of xylol. "Resimine No. 882" is a typical example of such a resin solution available commercially at the filing date of this application. In preparing such a resin, melamine is catalytically condensed with greater than an equal mol proportion of formaldehyde in the presence of butyl alcohol, which also largely enters into the reaction. Xylol is ordinarily present both to control the viscosity and as an aid in the removal of water.

The properties of the particular resins employed are thus seen to be highly important to the successful operation of the lithographic plate developers of my invention. However, the applicability and utility of these novel developer compositions does not depend solely on the properties of the resin employed. The solvent or solvent mixture, the pigment or other coloring agent, the water-soluble components, the proportions of these several materials, and other factors are all significant to the successful attainment of the objects of this invention, as will be further pointed out.

Ethylene dichloride is an effective water-immiscible volatile solvent for epoxy resins. Solutions of resin in this solvent are readily emulsified with an aqueous phase. The resin solution is a good solvent for additional resin such as may be accidentally deposited on non-image portions of the plate during the developing operation. Ethylene dichloride evaporates rapidly so that the developed plate is immediately ready for the press. As shown by Examples 5 and 7, ethylene dichloride may be used as the sole resin solvent. Trichloroethane is also an effective water-immiscible volatile solvent for epoxy resins, having somewhat lower volatility than ethylene dichloride.

While ethylene dichloride or the like, used alone, provides useful results, I have found that the addition of a further volatile solvent, e. g. cyclohexanone, provides still further improvement in the image-developing characteristics of the compositions of my invention. Cyclohexanone is soluble in water and, if used as the sole resin solvent, causes the deposition of a thin scum over the entire plate area. However, when cyclohexanone or other equivalent volatile and water-miscible solvent is added to ethylene dichloride, as in Examples 1–4 hereof, there is, surprisingly, even less of a tendency towards scum formation than occurs when ethylene dichloride is employed alone.

The concentration of resin in the solvent or solvent mixture may be widely varied. At excessive dilution, it will be apparent that prolonged treatment will be required in order to develop an adequately visible and wear-resistant coating, and hence I prefer to include at least about 30 parts of resin for each 100–150 parts of solvent. Too high a concentration, however, may cause "curdling" of the emulsion, and such viscous solutions are also more likely to form strings and thus cause "bridging" of half-tone dots and smearing of non-image areas. For example reducing the ethylene dichloride content of Example 1 to much less than about 20 parts has been found to cause curdling of the emulsion and bridging of the half-tones. I therefore prefer to use an amount of water-immiscible solvent at least about equal to the amount of resin.

The presence of both an aqueous and a non-aqueous or oily phase in the developer as applied to the exposed and washed plate in processes such as hereinabove described is found to be highly desirable in the proper development of the image. Application of a resin solution in the absence of the aqueous phase, for example, results in deposition of resin over substantially the entire plate area. Such a resin solution may effectively be applied to a bichromate-albumen type plate, where the unexposed portion of the sensitized coating is ordinarily not removed until after the application of the developer; and in this method of application the concentration of the resin may be widely varied. Even for such applications, however, the pre-formed emulsion is found to have a number of advantages.

Surprisingly, it has been observed that both the water-in-oil and the oil-in-water type emulsions are effective in developing lithographic plates, and particularly for plates prepared in accordance with the above-referred-to Jewett et al. application. In either case, the resin solution is selectively adsorbed at the image areas and is prevented from being adsorbed at the non-image areas of the plate; or, if some of the resin accidentally becomes deposited on such non-image areas, due for example, to excessive drying out of the material in localized areas, it is quickly re-dissolved and removed by other portions of the solution during the rubbing or swabbing operations incident to development.

It has also been observed that the oil-in-water type emulsions are more easily applied to the plate, since, as previously pointed out, the latter is first covered with an aqueous gum solution; and the oil-in-water emulsion is immediately and uniformly miscible therewith. The presence of a wetting agent is usually desirable, although not essential, in securing an oil-in-water type emulsion as well as in obtaining improved wetting action on the plate. In some instances the oil-in-water emulsions have separated into two layers on standing, a phenomenon which has not been observed with my water-in-oil emulsions. However, this separation may be retarded by increasing the proportion of water-soluble gum, or by other means; and in any event is not a serious disadvantage, since the two phases are readily re-combined and emulsified by brief stirring or shaking.

Examples have been provided of two specific pigments; many others are equally applicable. Soluble dyes, such as "DuPont Oil Red" may also be employed, although the developed image then ordinarily has less depth of color than is obtainable with pigments. The pigment or other coloring agent need not necessarily be combined with the resin components in the developer composition, although such combination is ordinarily preferred. When the pigment of Example 1 was omitted from the non-aqueous phase and introduced instead into the aqueous phase, the emulsion was of the oil-in-water type. On application as a lithographic plate developer, the pigment was taken up by the resin coating on the image areas, producing a colored image.

Gum arabic is widely employed in the lithographic printing art and hence is suggested here also. However other water-soluble gums are known which are fully or substantially equivalent to gum arabic for such operations, and substitution of such materials is considered as coming fully within the scope of this invention. Sodium carboxymethyl cellulose is one such water-soluble thickener. Likewise, the sodium lauryl sulfate of the foregoing examples may be effectively replaced by soap or various other wetting agents; and entirely satisfactory compositions have also been produced in which no wetting agents were used, or in which additional water-soluble gum replaced part or all of the wetting agent. In this connection, it has been observed that amine type wetting agents, e. g. triethanolamine oleate, have a tendency to cause the deposition of an adherent scum or residue over the entire plate; and these materials are therefore to be avoided.

This invention provides, in the lithographic printing art, a new and simplified method of obtaining visible printing-plate images, accurate inking and printing, and increased wear-resistance of the image, through application of a novel lithographic plate developer composition as herein above described and illustrated. The composition and application is particularly advantageous with lithographic plates of the type described in the Jewett et al. application Serial No. 199,566, wherein developing is carried out after the non-exposed portions of the pre-sensitized layer have been removed. The re-

sulting developed plates are superior to prior art plates, particularly as to wear-resistance.

What is claimed is as follows:

1. A lithographic printing-plate image developer comprising a colored two-phase liquid composition having an aqueous phase comprising water and a soluble thickener, and a non-aqueous liquid resinous phase comprising an unmodified hydroxyl-containing resinous glycidyl polyether of a dihydric phenol, and a water-immiscible volatile solvent.

2. A lithographic printing-plate image developer comprising a colored two-phase liquid composition having an internal aqueous phase comprising water and a soluble thickener, and an external non-aqueous liquid resinous phase comprising an unmodified hydroxyl-containing resinous glycidyl polyether of a dihydric phenol, and a water-immiscible volatile solvent.

3. A lithographic printing-plate image developer comprising a colored two-phase liquid composition having an external aqueous phase comprising water, a wetting agent and a soluble thickener, and an internal non-aqueous liquid resinous phase comprising an unmodified hydroxyl-containing resinous glycidyl polyether of a dihydric phenol, and a water-immiscible volatile solvent.

4. A lithographic printing-plate image developer comprising a colored two-phase liquid composition having an aqueous phase comprising water and a soluble thickener, and a non-aqueous liquid resinous phase comprising an unmodified hydroxyl-containing resinous glycidyl polyether of a dihydric phenol, a water-immiscible volatile solvent, and a water-miscible solvent.

5. A lithographic printing-plate image developer comprising a two-phase liquid composition having a liquid aqueous phase and a liquid non-aqueous phase, said non-aqueous phase comprising a pigment and a solution, in a mixture of a volatile water-immiscible solvent and a water-miscible solvent, of an unmodified hydroxyl-containing resinous glycidyl polyether of a dihydric phenol.

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