

1

3,455,688

LACQUER EMULSION FOR PRESENSITIZED LITHOGRAPHIC PLATES

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No Drawing. Filed Feb. 10, 1966, Ser. No. 526,350

Int. Cl. C09d 3/48; G03f 7/02

U.S. Cl. 96—33

13 Claims

This invention relates generally as indicated to a lacquer emulsion for lithographic printing plates and more particularly to an emulsion developer for surface lithographic plates which contains both oleophilic and hydrophilic constituents and which will simultaneously develop such plates after light exposure, desensitize the non-image areas and apply a film of an ink attractive lacquer on the surface of the image areas of such plates.

In recent years, the use of presensitized plates has become quite popular in the lithographic industry, the term "presensitized" meaning that the printing plate has been coated with a stable, light-sensitive material and is capable of being stored if necessary for long periods of time under ordinary conditions of temperature and humidity until required for use. In conjunction with the increased popularity of such plates, interest has also arisen in the development of simplified and effective ways of processing the plates after coating with the light-sensitive material and exposure to a suitable light source through a negative, transparency, stencil, etc. to produce the desired image thereon. Presently, the most commonly used method includes developing the light-exposed plate with a suitable solvent to remove the undesired areas of the light-sensitive material, rubbing the image areas with ink or a colored lacquer emulsion to render them plainly visible and to increase their chemical resistance and ink receptivity, and treating the plate with a lithographic desensitizing solution to render the non-image areas ink repellent. Such processing thus involves three separate and distinct operations which is especially objectionable from a commercial standpoint as it is undesirably time consuming and in certain instances involves the use of additional processing equipment.

It is accordingly an object of the present invention to provide an emulsion developing composition which will simultaneously perform the above-described three operations.

Another object of this invention is the provision of a lacquer emulsion which is suitable for the processing of surface type lithographic plates employing light-sensitive coatings of any of the various commercially available materials.

Yet another object of this invention is the provision of a lacquer emulsion which will simultaneously develop and desensitize the non-image areas of lithographic plates and deposit a colored resin film of abrasive and chemically resistant lacquer upon the image areas of such plate.

Another object of this invention is the provision of a lacquer emulsion which will not attack the image areas of the lithographic plate upon prolonged contact.

It is an additional object of this invention to provide a chemically stable lacquer emulsion which includes a high molecular weight phenoxy resin.

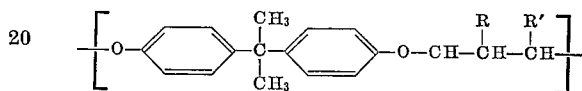
An additional object of this invention is the provision of a lacquer emulsion which will contribute to the production of lithographic plates with good press life and inking and printing qualities.

Other objects, features and advantages of this invention will become apparent to those skilled in the art after a reading of the following more detailed description.

2

These and other objects are achieved by means of the present invention in which an oil-in-water lacquer emulsion for the development of lithographic printing plates is provided in the form of a two-phase liquid composition in which the non-aqueous resinous phase includes a high molecular weight phenoxy resin of the type to be described hereinafter. As will be seen more clearly from the description and working examples which follow, such lacquer emulsion may be prepared in a relatively simple manner and is a very effective composition for processing lithographic plates with various light-sensitive coatings thereon.

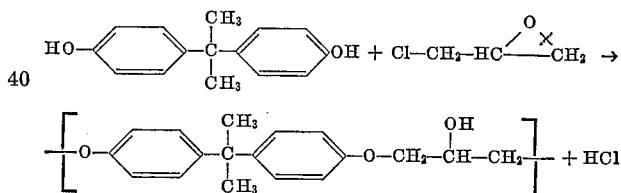
Specifically, the lacquer emulsion of this invention is a two-phase liquid composition having an aqueous phase including an aqueous desensitizing solution and a non-aqueous resinous phase comprising an essentially water-insoluble solvent and a high molecular weight phenoxy resin which contains as a recurring structure:



wherein R and R' are selected from the group consisting of hydrogen and hydroxide. The emulsion may also contain various other ingredients in both the aqueous and non-aqueous phases, as will be explained in more detail, such as a wetting agent, a pigment, or a thickening agent.

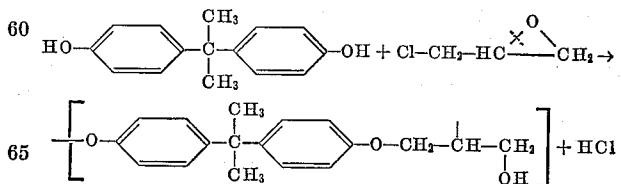
The terminology "phenoxy resin" as used herein refers to the above-described high molecular weight polyhydroxy ethers. As indicated by the above-described structure, the ether may contain primary or secondary alcohol groups depending upon the nature of the chemical reaction by which the compound is produced.

These compounds are generally formed by copolymerization of bisphenol A [2,2-bis(p-hydroxyphenyl)propane] and epichlorohydrin as illustrated below:



The phenoxy compound resulting from this reaction will have primary or secondary hydroxyl groups within the bracketed recurring structure depending upon which of the oxygen bridges of the terminal epoxide ring of the epichlorohydrin is broken during the reaction.

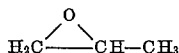
Thus as shown above, when the oxygen bridge on the righthand side of the ring is broken, as shown by the dotted line, a secondary hydroxyl group is produced within the recurring structure, which will generally be the reaction which occurs. If, however, the other oxygen bridge is broken (as shown in the reaction below), the phenoxy compound will have a terminal hydroxyl group within the recurring structure.



If an excess of epichlorohydrin is used during the copolymerization reaction, the polymer chain may have primary or secondary hydroxyl groups, depending upon which oxygen bridge is broken, since the polymer will have terminal epoxide rings prior to complete hydrolysis.

If an excess of Bisphenol A is used, however, the compound will have terminal phenolic hydroxyl groups.

The phenoxy resins which are used in this invention are to be distinguished from presently available epoxide resins which are based on similar raw materials, since the phenoxy resins contain no epoxy rings, i.e., there are no oxygen atoms attached to two different atoms of a chain as in 1,2 epoxy propane,



Moreover, the phenoxy resins have substantially higher molecular weights than the epoxy resins which are commercially known, being generally at least about ten to thirty times higher. Phenoxy resins usually have a molecular weight of at least about 20,000, generally 20,000 to 30,000 or even higher as for example 80,000 or even 200,000 if desired. In contrast, the highest molecular weight of most epoxy resins which are available is generally about 2,500 to 4,000. Additionally, phenoxy resins have an essentially linear molecular structure and do not require chemical curing to be suitable for use in lithographic processes.

The phenoxy resins used in this invention are produced according to the aforescribed reactions and are also commercially available from a number of sources, with specific examples of suitable resins being those sold by the Union Carbide Corporation, under the trade designation "Bakelite" PKDA, PAHJ, PKHC, and PKHH resins. Further illustrative examples of suitable such resins are those commercially available from the Shell Chemical Company under the trade designations "Eponol 55" and "Eponol 53-B-40." Reference may also be made to Modern Plastic's Encyclopedia for 1964, vol. 41/No. 1A, pages 209 and 210 for a more detailed discussion of such compounds.

To form the non-aqueous resinous phase of the emulsion, the phenoxy compound is dissolved in an essentially water-insoluble solvent to form a solution of resin in the solvent. The terminology "essentially water-insoluble solvent," as used herein, is intended to refer to those solvents which have a solubility of only approximately 2.4 grams per 100 ml. or less in water at room temperature. Illustrative examples include cyclohexanone, isophorone, and water immiscible aliphatic ketones, such as methylisobutyl ketone, ethylbutyl ketone, methylisobutyl ketone and diisobutyl ketone. Other examples include water-immiscible esters of aliphatic acids and aliphatic alcohols such as amyl acetate and methylamyl acetate. Blends of various solvents may also be used as, for example, any of the above-mentioned solvents or a blend of toluene and methylethyl ketone, toluene and Cellosolve acetate, or toluene, methylethyl ketone and Cellosolve acetate.

The non-aqueous resinous phase of the emulsion composition may also include a second resin which will modify the lithographic properties of the resin film which will be deposited from the emulsion on the image areas of a plate to decrease the solvent retention capabilities of such film and hence to promote the ability of the film to be air dried. This resin thus serves to make the film set to a hard tack-free film at room temperature, which in turn makes the film more resistant to scratching from improper handling and "blinding" (the inability to accept readily a full charge of ink) caused by desensitizing etches, water loving gums or from standing exposed to the air for a period of time before going to press. The preferred resins for this purpose are ureaformaldehyde or melamine formaldehyde resins which may be purchased commercially under the "Uformite" trade name from the Rohm & Haas Company.

The resinous phase of the emulsion may also include a wetting agent, or surfactant, which contributes to the stability of the emulsion. To be suitable, the wetting agent must not react chemically with the non-printing

areas of the plate to convert a hydrophilic surface into an oleophilic surface, and accordingly it is preferred to use non-ionic surface active agents. Suitable materials include various polyol compounds, particularly those marketed by the Wyandotte Chemical Corporation under the trade name "Pluronic" which is a hybrid compound of water-soluble polyoxyethylene chains added to both ends of water-insoluble polyoxypropylene. These materials are available in various molecular weights and percentages of hydrophilic polyoxyethylene content.

If desired, the resinous phase of the composition may also include a pigment which will form an easily visible color with the resin on the image areas of the plate to facilitate inspection of the finished plate and serve to indicate the presence of the lacquer after the plate has been in service on the press. The pigments should be easily dispersed and contribute to the stability of the dispersion and the oleophilic properties of the resin film. Suitable pigments may be readily selected by those skilled in the art; illustrative examples include the following commercially available pigments: Neo Spectra Mark III and Peerless Black 155 for the color black, Naphthol Red B for red, and Monastral Blue and Carbanthrene Blue for the color blue. The preferred pigment is Naphthol Red B because the resin film subsequently produced has less tendency to blind and the pigment is easily dispersible.

The concentration of phenoxy resin in the solvent may be varied to a considerable extent ranging from a very small quantity of resin up to the saturation point, but at the lower concentrations, extensive working of the lacquer on the plate will be required to deposit a layer of resin of adequate thickness. As a result, it is preferred to maintain the concentration in the range of from approximately 5% by weight of resin in the solvent up to the saturation point, which will normally be at approximately 10 weight percent of resin. When working with certain light-sensitive coatings, however, as will be explained, the concentration of the resin may be as low as approximately 1 to 2 weight percent.

With respect to the proportions of the modifying resin, wetting agent and pigment which may be used, these concentrations will also vary depending upon the practical working conditions being employed, and consequently, the desirable quantities of each ingredient will be determined for each operation. In general, the concentrations of each of these ingredients will not exceed approximately 10% by weight based on the solvent.

As indicated previously, the aqueous phase of the lacquer emulsion includes an aqueous desensitizing solution which is necessary for the formation of an oil-in-water emulsion and also for its action in the processing of lithographic plates as it dissolves the non-light hardened light-sensitive material if this is aqueous and acid soluble and leaves a protective film of a water loving colloid over the plate. Many such solutions are known and are suitable for use in this invention, but a preferred desensitizing solution is that commercially available from the Harris-Intertype Corporation having the following composition:

	Volumes
Gum arabic solution in water, 14° Bé.	40
CMC acid solution in water, 2%	17
Sorbitol solution in water, 70%	4.8
Triethylene glycol	3.4
Water	40
Lactic acid solution in water, 80%	3.4
Sterox AJ ¹	1.0
Methyl Cellosolve	4.6
Formaldehyde solution in water, 37%	0.1

¹ Sterox AJ is an 85% active aqueous dispersion of a non-ionic surface active material based upon a substituted phenol and ethylene oxide. It contains 85% surfactant, 14% inorganic salt, and 1% water, and it is a product of the Monsanto Chemical Company.

Other desensitizing solutions may, however, be used, such solutions generally comprising a water solution of a

5

hydrophilic colloid such as gum arabic and an acidic desensitizing agent such as phosphoric acid or the salt of such acid.

The aqueous phase of the emulsion composition may also, if desired, include a suitable thickening agent to give the emulsion a false body and thus increase the stability of the emulsion. Numerous suitable such agents are known in the art and are commercially available, an illustrative example being a pyrogenic silica compound commercially available under the "Cab-O-Sil" trade name. Also, if desired, for any given concentration of this particular silica compound, the amount of false body can be increased by adding a non-ionic or a long chain cationic amine wetting agent in a quantity up to approximately 10% by weight of the amount of silica material. Because of its fine particle size, this material tends to produce a slight scouring action on a plate surface which at times is beneficial.

A second organic solvent may also be used in the emulsion to slow down the evaporation rate of the organic solvent employed in the resinous phase and hence to modify the rate of deposition and drying of the resin film. The use of such a solvent makes it possible to work the emulsion over the plate for a longer period of time without its drying and forming a dry film on the non-printing areas. To achieve this result, the solvent may be water miscible, and thus included in the aqueous phase of the composition, although it may also be water immiscible and added as a part of the resinous phase, where in conjunction with the organic solvent therein, acts as a solvent for the resin. Suitable examples of such a solvent include Carbitol acetate, Cellosolve acetate, methyl Cellosolve, dioxane, any of the available Dowanol mixtures, and blends of such solvents.

In order to slow down the evaporation rate of the resinous phase solvent, the second solvent or solvent blend must have a higher boiling point than the solvent or blend of solvents of that phase. The selection of a suitable solvent will necessarily therefore depend upon the particular resinous phase solvent or blend employed. In general, to achieve sufficient modification of the rate of evaporation, the second solvent should have a boiling point of about 40 to 50° C. higher than that in the resin phase, but this may be varied depending upon the respective percentages of resin and solvent present.

If the second organic solvent is included in the non-aqueous resinous phase, it will normally be a maximum of approximately 20% by volume based on the essentially water insoluble solvent, although the quantity of such solvent may vary depending upon the solvent used, its boiling point relationship to the resin phase solvent, the quantity of resin and other ingredients, etc.

When such a solvent and thickening agent are included in the aqueous phase of the composition, a relatively small quantity of solvent will generally be used, preferably a maximum of approximately 15% by volume, based on the aqueous desensitizing solution. Similarly, the thickening agent will preferably be a maximum of approximately 5 percent by weight, with about 2 to 4 weight percent being preferred, although the quantities of each of these ingredients may be varied if desired.

The lacquer emulsion of this invention is suitable for use with lithographic plates using any of the available supports, i.e., metal, paper, etc. which have been coated with any of the various available light-sensitive materials and is especially suitable for use with any of the family of water soluble diazo resins and light-sensitive materials of the cinnamate photopolymer type, such as those disclosed in U.S. Patent 2,610,120 and British Patent 794,572. Another cinnamate type photopolymer for which the emulsion developer of this invention is particularly well suited is the phenoxy-cinnamate photopolymer disclosed in the co-pending application of Jack L. Sorkin, Ser. No. 384,533, now U.S. Patent No. 3,387,976, entitled "Photopolymer."

When the lacquer emulsion is to be used with a cin-

6

namate type photopolymer, the composition will include a solvent which will remove the non-light exposed polymer from the surface of the plate. This solvent must be selected so that it will not cause appreciable swelling and softening of the light-exposed polymer, for if this occurs, the emulsion will not operate satisfactorily as rubbing of the plate with the emulsion will smear the image areas. As mentioned previously, when the emulsion is to be used with such photopolymers, the resin content of the resinous phase will generally only be approximately 1 to 2 percent by weight, based on the solvent content, to accommodate the additional solvent. Illustrative examples of suitable formulations of the emulsions are the following:

Example I

15	Resinous phase:		
	Phenoxy resin	grams	100
	Cyclohexanone	mls	1000
	Wetting agent	grams	66
	Pigment	do	40
20	Aqueous phase:		
	Harris desensitizer solution (page 10)	mls	3370
	Thickening agent	grams	120
	Carbitol acetate	mls	450

Example II

25	Resinous phase:		
	Cyclohexanone	mls	1000
	Phenoxy resin	grams	100
	Ureaformaldehyde (60% solid solution,		
	Uformite F-240)	mls	102
30	Wetting agent	grams	66
	Pigment	do	95
	Aqueous phase:		
	Harris desensitizer	mls	3370
35	Thickening agent	grams	144
	Carbitol acetate	mls	450

Example III

40	Resinous phase:		
	Cyclohexanone	mls	1000
	Phenoxy resin	grams	100
	Uformite F-240	mls	102
	Wetting agent	grams	68
	Pigment	do	95
45	Aqueous phase:		
	Harris desensitizer solution	mls	4030
	Thickening agent	grams	144

Example IV

50	Resinous phase:		
	Cyclohexanone	mls	1000
	Phenoxy resin	grams	100
	Aqueous phase:		
	Harris desensitizer solution	mls	3370

Example V

This example shows a formulation of the emulsion modified to be particularly suitable for processing cinnamate type photopolymers.

60	Resinous phase:		
	Cyclohexanone	mls	1000
	Phenoxy resin	grams	100
	Wetting agent	do	76
	Pigment	do	100
65	Aqueous phase:		
	Harris desensitizer	mls	3860
	Thickening agent	grams	138
	Carbitol acetate	mls	500
	Cyclohexanone	mls	1840

The carbitol acetate and additional cyclohexanone may be included as a part of the resinous phase or alternatively may be added after formation of the emulsion.

To prepare the emulsion, the following procedure is generally used. The phenoxy resin is first dissolved into the essentially water-insoluble solvent, and the wetting

agent, if used, is then dissolved into the phenoxy solvent solution. If a pigment is to be used, it is then added to the above-described solution with stirring until the pigment is thoroughly wet. This product is then run through a colloid mill or other suitable mixing device to obtain a suitable dispersion. To determine when sufficient mixing has taken place, a reading of at least 3 on a fineness of grind gauge calibrated in 10 steps of .0000 to 0.001 is satisfactory. If the urea or melamine formaldehyde modifying resin is to be used, it will, of course, be dissolved in the resinous solution described above prior to mixing in the colloid mill.

If a thickening agent is to be included in the aqueous phase of the composition, it will be added to the desensitizing solution with stirring until a noticeable thickening is produced. This dispersion will then be blended with the resinous material with stirring to produce a coarse oil-in-water emulsion. Such emulsion will thereafter be run through a colloid mill to produce the fineness of dispersion of the oil phase which is desired. In general, the finer the dispersion, the creamier or more viscous the emulsion. A reading of at least 3 on a fineness of grind gauge, as explained above, is also considered satisfactory.

If a water-miscible solvent is to be included with the aqueous phase of the composition, it will be added to the desensitizing solution prior to addition of the thickening agent.

When preparing an emulsion for use with a cinnamate type photopolymer, the additional solvent may be added either to the resinous phase, as mentioned, or to the crude emulsion before going to the colloid mill or to the finer emulsion coming off the mill, but in either case it should be added with agitation.

The lacquer emulsion thus produced is applied simply by pouring a small pool of the emulsion liquid onto the surface of the exposed plate, after which the liquid is thoroughly worked over the plate surface with a wad of absorbent cotton, a sponge, etc. to remove the unexposed areas of the plate and produce an image.

This invention will be better understood by reference to the following specific but non-limiting examples.

Example VI

A 10" x 16" presensitized aluminum lithographic plate with a light-sensitive diazo coating thereon (Fairmount Chemical Co.'s Diazo Resin #4) was subjected to ultraviolet light through a negative pattern. The plate was thereafter rubbed up with an emulsion composition corresponding to Example I in which the wetting agent was "Pluronic F68," the pigment was "Peerless Black 155," the phenoxy resin was "Bakelite PKHH-8500," and the thickening agent was "Cab-O-Sil," for approximately 1 minute to remove the non-image areas from the surface of the plate. After working with the emulsion, the plate had a protective film of hydrophilic material over the non-image areas and a colored phenoxy film on the light-exposed image areas. After drying, the image of the plate could be seen in the areas where the diazo resin had been exposed. A good image on a clean background was obtained by use of the plate, and the plate was subsequently press tested for 10,000 impressions.

Example VII

The procedure of Example VI was followed except that the lacquer emulsion used was that exemplified by Example II, the phenoxy resin, pigment, and wetting and thickening agents being the same as in Example VI. After rubbing the emulsion for about 2 minutes, the non-light exposed areas of the light-sensitive material were removed from the surface of the 14" by 20" plate by the emulsion and the protective lacquer film was applied over the image areas thereof.

The thus developed plate was subsequently used on a printing press in standard lithographic processes with clear and distinct images being produced. Approximately 25,000 impressions were run therefrom.

Example VIII

The procedure of Examples VI and VII was followed but the developing composition was that of Example IV with the phenoxy resin again being Bakelite PKHH-8500. After development and drying, the image could be clearly seen in the areas where the light-sensitive coating had been exposed to the ultraviolet light. A good image on a clean background was obtained by use of the plate in standard lithographic processes.

Example IX

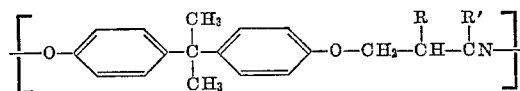
The general procedure of the preceding examples was followed, but in this example, the light-sensitive material was the phenoxy-cinnamate photopolymer described in the aforesaid Sorkin application, and the emulsion composition was that disclosed in Example X herein, the phenoxy resin, wetting agent and thickening agent being the same as in Example VI and the pigment being Naphthol Red B. The 14" by 20" plate was rubbed up with this emulsion for approximately 3 minutes, and after drying, the image was clearly visible in the light-exposed areas. A good, clear image on a clean background was subsequently obtained by use of the plate, and the plate was press tested for 50,000 impressions.

It will thus be appreciated that the objects of this invention have been achieved by the described lacquer emulsion which is capable of being used with various lithographic surfaces and light-sensitive materials, with the phenoxy resin being selectively attracted to the image areas of the plate as opposed to the non-image areas to avoid scumming or smearing and thus produce plates with good press life and inking and printing qualities. Also, the lacquer emulsion of this invention has sufficiently low solvent retention characteristics that a lacquer film may be provided over the image areas which will be tack free to avoid damage by fingerprints or other improper handling but sufficiently hard and durable to provide adequate protection for the image.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

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

1. A lacquer emulsion for lithographic printing plates comprising a two-phase liquid composition having an aqueous phase comprising an aqueous desensitizing solution and a non-aqueous resinous phase comprising an essentially water-insoluble solvent and a phenoxy resin of molecular weight greater than 20,000 containing as a recurring structure:



wherein R and R' are selected from the group consisting of hydrogen and hydroxide.

2. The lacquer emulsion of claim 1 in which said non-aqueous phase includes a second resin selected from the group consisting of ureaformaldehyde and melamine formaldehyde resins to decrease the solvent retention of the resin film deposited on the image.

3. The lacquer composition of claim 1 in which said non-aqueous phase includes a wetting agent.

4. The lacquer emulsion of claim 1 in which said non-aqueous phase includes a pigment to form an easily visible color upon the resin film deposited on the image.

5. The lacquer emulsion of claim 1 in which a second organic solvent is included to decrease the evaporation rate of said water insoluble solvent.

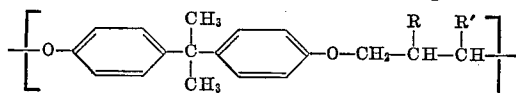
6. The lacquer emulsion of claim 1 in which said aqueous phase includes a thickening agent to increase the stability of the emulsion.

7. The lacquer emulsion of claim 1 in which said non-aqueous phase contains a maximum of approximately 10% by weight of said resin.

8. The lacquer emulsion of claim 1 in which said non-aqueous phase contains a maximum of about 10% by weight of said phenoxy resin, a maximum of approximately 10% by weight of a second resin selected from the group consisting of ureaformaldehyde and melamine formaldehyde resins, a maximum of approximately 10% by weight of a wetting agent, and a maximum of approximately 10% by weight of a pigment.

9. The lacquer emulsion of claim 1 in which said aqueous phase contains a maximum of approximately 15% by volume of an organic solvent and a maximum of approximately 5% by weight of a thickening agent.

10. A lacquer emulsion for lithographic printing plates comprising a two-phase liquid composition having an aqueous phase comprising an aqueous desensitizing solution, an organic solvent and a thickening agent, and a non-aqueous resinous phase comprising an essentially water-insoluble solvent, a maximum of approximately 10 weight percent of a phenoxy resin of molecular weight greater than 20,000 containing as a recurring structure:

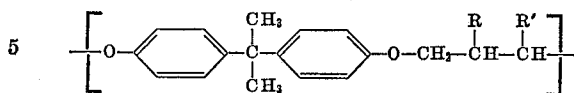


wherein R and R' are members selected from the group consisting of hydrogen and hydroxide, a maximum of approximately 10% by weight of a second resin selected from the group consisting of ureaformaldehyde and melamine formaldehyde resins, a maximum of approximately 10% by weight of a surface active non-ionic wetting agent, and a maximum of approximately 10% by weight of a pigment.

11. The lacquer emulsion of claim 10 wherein said non-aqueous phase contains approximately 1 to 2% by weight of said phenoxy resin.

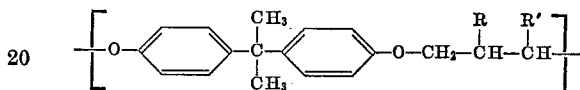
12. In a lithographic printing plate, the improvement comprising a film of abrasive and chemical resistant ink-

attractive lacquer upon the image areas thereof comprising a phenoxy resin of molecular weight greater than 20,000 containing as a recurring structure:



wherein R and R' are selected from the group consisting of hydrogen and hydroxide.

13. In a method of preparing lithographic printing plates, the step comprising developing a light-exposed surface of such plate with a lacquer emulsion comprising a two-phase liquid composition having an aqueous phase comprising an aqueous desensitizing solution and a non-aqueous resinous phase comprising an essentially water-insoluble solvent and a high molecular weight phenoxy resin containing as a recurring structure:



wherein R and R' are selected from the group consisting of hydrogen and hydroxide, to simultaneously remove undesired areas of such light exposed surface, provide a film of water loving colloid over such plate and deposit a film of abrasive and chemical resistant ink-attractive lacquer upon the image areas thereof.

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NORMAN G. TORCHIN, Primary Examiner

R. E. MARTIN, Assistant Examiner

U.S. Cl. X.R.

96—48, 49; 101—457, 462, 466; 260—29.2, 29.4

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,455,688 Dated July 15, 1969

Inventor(s) Dolor N. Adams, Jack L. Sorkin, and Daniel C. Thomas

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 18, for "Example X" read --Example V--;
that that portion at the end of the formula reading



should read



SIGNED AND
SEALED
DEC 23 1969

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents