



WATERBORNE PHOTORESISTS HAVING ASSOCIATE THICKENERS

The present invention is directed to photoresists, such as those used for forming printed circuit boards and more particularly to waterborne, liquid applied, contact imageable photoresists.

Photoimageable compositions useful as resists for forming printed circuits, printing plate, solder masks or the like have been used for some time now. The earliest photoresists were solvent-borne and solvent-developable. The development of aqueous-developable resists represented an advance in reducing solvent emissions in the immediate workplace and general environment. The continued emphasis in reducing organic solvent both from the workplace and from the general environment has spurred the search for waterborne photoresists which are formulated and applied as aqueous liquids.

U.S. patent No. 5,045,435, the teachings of which are incorporated herein by reference, describes a waterborne photoresist composition which is developable in alkaline aqueous solution. The composition comprises a multifunctional monomer, a photoinitiator and a latex of water-insoluble carboxylated acrylic copolymer. To stabilize the composition and to adjust the viscosity, this patent teaches neutralizing the latex polymer to at least 25% with a base, such as ammonia, another amine, or sodium hydroxide.

The high degree of neutralization required in the composition in U.S. patent 5,045,435 has several disadvantages. The neutralizer, e.g., amine, reacts with the acid functional polymer, producing water soluble salts.

Because all of the neutralizer is not removed during drying, the remaining salts become sites for potentially damaging chemical attack. It is therefore desirable to reduce the amount of neutralizers to improve chemical resistance. Amines or ammonia, when used as the neutralizer, have associated odors, amines having a characteristic "fishy" odor. Primary amine neutralizers and ammonia are highly reactive, resulting in viscosity drift in the lacquer prior to coating, the viscosity drifting as much as 3000 cps over one week.

In teaching and demonstrating the need for substantial neutralization in its compositions, U.S. patent No. 5,045,435 also teaches that obtaining the critical rheology cannot be obtained with the addition of thickening agents.

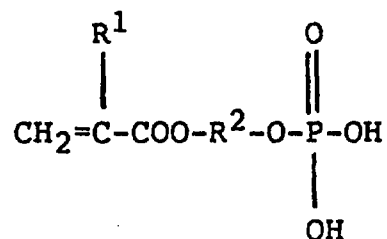
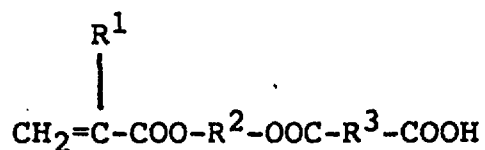
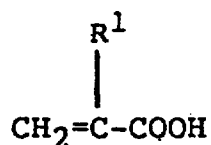
It is a general object of the present invention to provide a waterborne photoimageable composition requiring a substantially reduced amount of neutralization of the latex polymer.

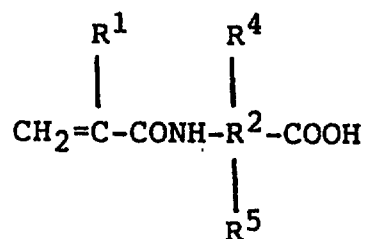
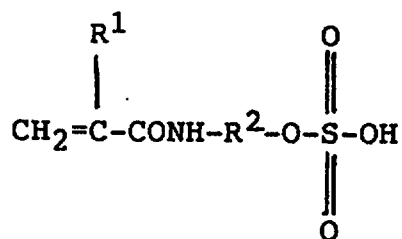
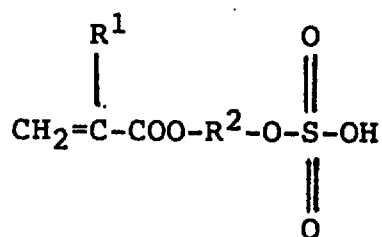
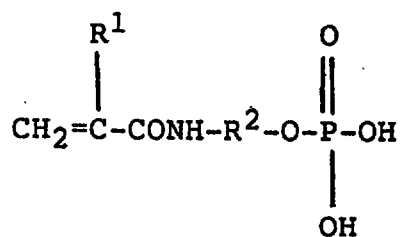
In accordance with the invention, a waterborne photoimageable composition comprises an aqueous composition containing A) between about 30 and about 80 wt% of a latex binder polymer having acid functionality, e.g., carboxylic acid functionality or sulfonic acid functionality, which provides an acid number of between about 50 and about 250, B) between about 20 and about 50 wt% of a fraction of alpha,beta-ethylenically unsaturated monomers, C) between about 0.1, preferably at least about 1, and about 25 wt% of a photoinitiator or photoinitiator chemical system which generates free radicals, and D) between about 1, preferably at least 2, and about 40 wt% of a polyether polyurethane associate thickener, the weight percentages being based on

total weight of components A-D. The acid content of the latex binder polymer is either not neutralized with base or is neutralized up to about 20% of its carboxylic functionality.

Latex binder polymers useful in the photoimageable composition of the present invention are typically prepared by emulsion polymerization of alpha, beta-unsaturated monomers, such as vinyl, acrylate or styrene monomers. Sufficient acid functional monomers are used to provide the acid number of between about 50 and about 250, preferably at least about 100. A typical emulsion polymerization procedure and some examples of suitable emulsions are found in U.S. Patent No. 3,929,743, the teachings of which are incorporated herein by reference. Suitable emulsions can also be obtained commercially, e.g., Neocryl[®] CL-340 (40% solids) available from ICI Resins U.S. and Acrysol[®] I-2074 (46% solids) available from Rohm and Haas.

Suitable acid functional monomers for use in forming the acid functional binder polymer have the formulae:





wherein R_1 represents a hydrogen atom or a methyl group, R_2 represents $(\text{CH}_2)_n$ wherein n is an integer of 1 to 6, R_3 represents an alkylene group having 1 to 6 carbon atoms or a phenylene group, and R_4 and R_5 are either R_1 or OH , provided R_4 and R_5 are not both OH .

Some specific examples of suitable acid functional monomers are acrylic acid, methacrylic acid, maleic acid, fumaric acid, citraconic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-hydroxyethyl acryloyl phosphate, 2-hydroxypropyl acryloyl phosphate, 2-

hydroxy-alpha-acryloyl phosphate, etc. One or more of such acid functional monomers may be used to form the binder polymer. The acid functional monomers may be copolymerized with non-acid functional monomers, such as esters of acrylic acids, for example, methyl acrylate, methyl methacrylate, hydroxy ethyl acrylate, butyl methacrylate, octyl acrylate, 2-ethoxy ethyl methacrylate, t-butyl acrylate, 1,5-pentanediol diacrylate, N,N-diethylaminoethyl acrylate, ethylene glycol diacrylate, 1,3- propanediol diacrylate, decamethylene glycol diacrylate, decamethylene glycol dimethacrylate, 1,4-cyclohexanediol diacrylate, 2,2-dimethylol propane diacrylate, glycerol diacrylate, tripropylene glycol diacrylate, glycerol triacrylate, 2,2-di(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol diacrylate, polyoxyethyl-2-2-di(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol dimethacrylate, polyoxypropyltrimethylol propane triacrylate, ethylene glycol dimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, 2,2,4- trimethyl-1,3-pentanediol dimethacrylate, pentaerythritol trimethacrylate, 1-phenyl ethylene-1,2-dimethacrylate, pentaerythritol tetramethacrylate, trimethylol propane trimethacrylate, 1,5-pentanediol dimethacrylate, and 1,4-benzenediol dimethacrylate; styrene and substituted styrene, such as 2-methyl styrene and vinyl toluene and vinyl esters, such as vinyl acrylate and vinyl methacrylate to provide the desired acid number.

So that the photoimageable composition is contact imageable, i.e., dries to a tack-free state, the glass transition temperature (T_g) of the latex binder polymer is preferably at least about 60°C as measured by Differential Scanning Calorimetry (DSC) @ 20°min. The polymers have a

weight average molecular weight (Mw) of between about 500 and about 200,000 as measured by gel permeation chromatography (GPS) using a polystyrene standard. To produce the image, this negative-acting photoimageable composition contains photopolymerizeable monomers, particularly alpha,beta-ethylenically unsaturated monomers, including a substantial portion of multi-functional monomers. Useful monomers include those, listed above, used to form the binder polymers. Particularly suitable monomers include multifunctional acrylic monomers, such as tetraethylene glycol diacrylate (TEGDA), trimethylol propane triacrylate (TMPTA); butanediol dimethacrylate (BDDMA) and pentaerythritol triacrylate (PETA). The monomer fraction may include both water-soluble and water-insoluble monomers; however, the monomer fraction should contain a sufficiently high proportion of water-insoluble (having solubilities in water at 20°C below about 0.3 g/100ml) monomers, e.g., above about 20 mole percent, so that the monomer fraction, as a whole, is insoluble in water.

To initiate polymerization of the monomers upon exposure to actinic radiation, the photoimageable composition contains an appropriate photoinitiator(s) or photoinitiator chemical system. Suitable photoinitiators include benzoin ethers, benzil ketals, acetophenones, benzophenones and related compounds with amines. Preferred initiators are thioxanthenes, e.g., 2-isopropyl thioxanthenes, particularly in conjunction with an amine.

In accordance with the invention, viscosity adjustment and stabilization of the aqueous photoimageable composition are achieved using a polyether polyurethane associate thickener. Polyether polyurethane thickeners are polymers having at least two hydrophobic segments which are

the residues of hydrophobic isocyanates, generally isocyanates having isocyanate functionality of 2 or higher, and at least one hydrophilic polyether segment joining the hydrophobic segments by urethane linkages. The block polymers which act as associate thickener may take a variety of forms including ABA, (AB)_n, star polymers and the like. The polyether segments are formed from poly(alkylene oxide) segments, formed from monomers such as propylene oxide and ethylene oxide. To be sufficiently hydrophilic, generally it is necessary that at least about 3 mole percent of the poly(alkylene oxide) segment(s) be ethylene oxide residues. The hydrophobic portion of the isocyanate residue is typically an alkyl, cycloalkyl or aromatic moiety. Polyether polyurethane associate thickeners and their function are described, for example by A.J.M. Knoef, and H. Slingerland, "Urethane-Based Polymeric Thickeners for Aqueous Coating Systems" JOCCA, Sept. 1992, pp 335-338; J.H. Bieleman et al. Polymers Paint Colour Journal 1986, V.176(4169) pp. 450-460; and A.J. Whitton and R.E. Van Doren Polymers Paint Colour Journal 1991, V.181(4286) pp. 374-377. Particularly suitable polyether polyurethane associate thickeners and their synthesis are described in U.S. Patent No. 4,079,028 to Emmons et al., the teachings of which are incorporated herein by reference. Suitable polyether polyurethane associate thickeners are also described in U.S. Patents Nos. 4,426,485 to Hoy et al. and 4,743,698 to Ruffner et al., the teaching of each of which are incorporated herein by reference. Examples of suitable commercially available associate thickeners are DSX1514 (Henkel) and QR708 (Rohm and Haas).

In addition to thickening the composition, the associate thickener acts as a surfactant, emulsifying the monomer fraction. The associate thickener also helps

stabilize the latex emulsion of binder polymer.

By using the polyether polyurethane associate thickener, less neutralization of the binder polymer latex is required. In some cases no neutralization is required. In other cases, it is desirable to neutralize the binder up to about 20% of the equivalent acid functionality of the binder polymer. Typically base will be added to neutralize at least about 2% of the acid functionality of the binder polymer. Neutralization may be done with ammonia; primary, secondary, or tertiary amines; or hydroxides. Preferred neutralizing bases are hydroxy functional tertiary amines. The addition of associate thickener in place of at least some of the neutralizer allows for a smoother more uniform coating. The improved coating quality minimizes potential circuit board defects caused by thin spots or pin holes in the coating. In addition, when applied by roller coating, the photoimageable composition with associate thickener produces a smoother coating at lower roller compression. Low roller compression results in extended life of the rubber rollers.

Reducing neutralizers improves chemical resistance of the applied and dried photoimageable composition layer. When ammonia or amine use is reduced, odor is reduced. Associate thickeners reduce viscosity drift of the aqueous photoimageable composition. Even under high shear, viscosity tends to remain stable.

In addition to components A-D listed above, minor amounts (generally less than about 10 wt% total based on the weight of A-D) of conventional additives may be used, including; antifoam agents, antioxidants, dyes, adhesion promoters, slip aids, surface tension modifiers, and additional surfactants. Surfactants, if used, are

preferably anionic or non-ionic. Up to about 5 wt.% of a high boiling solvent, such as propylene glycol monomethyl ether may be added as a coalescing agent.

A particularly desirable surfactant which combines excellent wetting characteristics without foaming is a non-ionic fluoroaliphatic oxyethylene adduct having the general formula:

$\text{CF}_3-(\text{CF}_2)_n-\text{Y}-\text{X}_m-\text{Z}$ where $n = 0$ to 20 , $\text{Y} = \text{SO}_2-\text{N}(\text{C}_1-\text{C}_{10}\text{alkyl})$, $\text{X} = \text{CH}_2-\text{CH}_2-\text{O}$ or $\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}$, $m = 0$ to 20 , and $\text{Z} = \text{CH}_2-\text{CH}_2-\text{OH}$ or $\text{CH}(\text{CH}_3)-\text{CH}_2-\text{OH}$.

An example of such a surfactant is sold under the trademark Fluorad FC170-C by 3M. Surfactants are typically used at levels of between about 0.5 and about 3.0 wt.% of photoimageable composition solids.

In a preferred method of preparing the waterborne photoimageable composition of the present invention, those components, such as initiators, antioxidants and dyes, most compatible with a hydrophobic phase are admixed with the monomer fraction to produce a monomer base and those components most compatible with an aqueous phase with the latex polymer, such as antifoam, neutralizer and associate thickener, are admixed to form a polymer mix. The hydrophobic phase and polymer mix are blended to form an hydrophobic phase-in-water emulsion. Subsequently, high boiling solvents, surfactants, including slip aids, surface tension modifiers, and adhesion promoters are added.

The final water-borne composition is generally between about 20 and about 40 wt. percent solids. In the waterborne composition, the binder comprises between about 10 and about 30 wt%, monomers from about 3 to 20 wt%,

initiator from about 0.3 to about 10 wt% and thickener from about 1.5 to about 20 wt%.

The composition may be coated by any of the coating systems known in the art for coating solvent-borne photoimageable compositions, such as roll coating, dip coating, spray coating or curtain coating.

The compositions of the present invention are applied in a conventional manner, either as liquid compositions directly to a metal clad blank laminate or to a polymeric support sheet to form a dry film. After coating, the composition is dried to remove water and also to remove volatiles, such as ammonia or amine, water, etc., thereby rendering the solution polymer insoluble in acidic or neutral aqueous medium. As the photoimageable composition dries, the system coalesces into a continuous film.

Drying is preferably carried out at somewhat elevated temperatures, both to hasten removal of the water, and to drive off the ammonia or volatile amine. Preferably, drying is carried out at a temperature of about 90°C.

In forming a dry film, a water-borne composition is applied to flexible support sheet, e.g., polyethylene terephthalate, and then dried to remove water and volatiles. Subsequently, a protective sheet, e.g., polyethylene, is applied to the photoimageable composition layer, and the dry film is rolled into reels. In drying the photoimageable composition layer, it is found desirable in some cases to leave a residual water content of between about 1 and about 2 wt. % (relative to solids of the photoimageable composition layer). This residual water

acts to allow the photoimageable composition layer to conform to surface defects of a substrate, e.g., a copper-clad board, when laminated thereto.

Processing is in a conventional manner. In a typical procedure, a photoimageable composition layer, either formed from a liquid composition or transferred as a layer from a dry film, is applied to a copper surface of a copper-clad board. The photoimageable composition layer is exposed to actinic radiation through appropriate artwork. Exposure to actinic radiation polymerizes the monomer in the light-exposed areas, resulting in a cross-linked structure that is resistant to developer. Next, the composition is developed in dilute alkaline aqueous solution, such as a 1% sodium carbonate solution. The alkali solution causes salt formation with the carboxylic groups of the binder polymers, rendering them soluble and removable. After development, an etchant may be used to remove copper from those areas where the resist was removed, thereby forming a printed circuit. The remaining resist is then removed using an appropriate stripper.

Not only can waterborne primary imaging photoresists be provided in accordance with the invention, but solder mask-forming compositions can be provided as well. By solder mask is meant herein a hard, permanent layer which meets at least the minimal requirements of the abrasion resistance tests as defined in IPC-SM-840B, Table 12, Summary of Criteria for Qualification/Conformance (Institute for Interconnecting Circuits). To become hard and permanent, it is generally necessary that the photoimageable composition be curable after exposure, development and processing of the board, e.g., by thermal and/or UV curing. One way to provide a post-cure is to provide binder polymer having free -OH groups in the

backbone that may be cured, for example, by cross-linking with aminoplast resins, such as melamine/formaldehyde resins and urea/formaldehyde resins. Alternatively, the photoimageable composition may contain a compatible epoxy resin and a curative for the epoxy resin. It is found that water-borne photoimageable compositions in accordance with the invention exhibit excellent shelf lives after application to copper substrates and can remain on a copper-clad board upwards of several days.

The invention will now be described in greater detail by way of specific examples.

Examples 1-9

Water-borne photoimageable compositions were formulated according to Table 1 below. Amounts are in grams. 2.3 grams of neutralizer represents about 15 % neutralization; 4.5 grams of neutralizer represents about 30% neutralization. Accordingly, Examples 3-6 are examples in accordance with the present invention; Examples 1-2 and 7-9 are comparative examples. Performance data is according to table 2 below; "n.a. is recorded when bad performance prohibited further processing conditions. "Monomer base" in Table 1 is per table 3; all materials being mixed together, filtered and subsequently added to the aqueous portion.

TABLE # 1

FORMULATION NAME	INGREDIENT TYPE	#1	#2	#3	#4	#5	#6	#7	#8	#9
Neocryl CL-340 (40% solids)	polymer	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
DMAMP-80 (Angus)	tertiary amine neutralizer	4.5	0.0	0.0	0.0	2.3	0.0	0.0	2.3	0.0
AMP-95 (Angus)	primary amine neutralizer	0.0	4.5	0.0	0.0	0.0	2.3	0.0	0.0	2.3
DSX-1514 (Henkel)	associative thickener	0.0	0.0	4.5	9.0	2.3	2.3	0.0	0.0	0.0
Deionized Water	primary solvent	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
BYK-033 (BYK/Chemie)	antifoam	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Monomer Base	see Table #3	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
Q4-3667 (Dow Corning)	slip aid	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Fluorad FC170-C (3M)	surface tension modifier	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Texanol (Eastman)	coalescing solvent	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5

Neocryl CL-340 is a styrene/acrylic polymer having an acid number of about 160.

Q4-3667 (Dow) is an 80:20 mixture of polyether modified dimethylsiloxanes and cyclodimethylsiloxanes.

TABLE # 2

FORMULATION <u>NAME</u>	<u>#1</u>	<u>#2</u>	<u>#3</u>	<u>#4</u>
DMAMP-80	4.5	0.0	0.0	0.0
AMP-95 (Angus)	0.0	4.5	0.0	0.0
DSX-1514 (Henkel)	0.0	0.0	4.5	9.0
PERFORMANCE RESULTS				
Viscosity (initial)	2300 cps	2800 cps	3500 cps	5000 cps
Viscosity (1 week holding)	1900 cps	800 cps	3500 cps	5000 cps
Odor	strong fishy	moderate ammonia	none	none
Emulsion Stability	fair	fair to good	good	very good
Substrate Staining	moderate stain	moderate stain	no stain	no stain
Alkaline Resistance	poor	poor	good	good
Coating Defects	10 voids/ft ²	5 voids/ft ²	0 voids/ft ²	0 voids/ft ²
Coating Uniformity	severe ribbing	moderate ribbing	slight ribbing	no ribbing
Developing Time	25 sec.	27 sec.	29 sec.	29 sec.
Photospeed (at 100 mj/cm ²)	Copper 6	Copper 7	Copper 8	Copper 8
Circuit Pattern Defects	5 defects/ft ²	5 defects/ft ²	1 defect/ft ²	0 defects/ft ²

DMAMP = 2-dimethylamino-2-methyl-1-propanol; AMP = 2-amino-2-methyl-1-propanol.

TABLE # 2 (continued)

FORMULATION					
<u>NAME</u>	<u>#5</u>	<u>#6</u>	<u>#7</u>	<u>#8</u>	<u>#9</u>
DMAMP-80 (Angus)	2.3	0.0	0.0	2.3	0.0
AMP-95 (Angus)	0.0	2.3	0.0	0.0	2.3
DSX-1514 (Henkel)	2.3	2.3	0.0	0.0	0.0
PERFORMANCE RESULTS					
Viscosity (initial)	2900 cps	3200 cps	0 cps	0 cps	0 cps
Viscosity (1 week holding)	2700 cps	2700 cps	0 cps	0 cps	0 cps
Odor	slight fishy	slight ammonia	none	slight fishy	none
Emulsion stability	fair to good	good	poor	poor	poor to fair
Substrate Staining	slight stain	slight stain	n.a.	n.a.	n.a.
Alkaline Resistance	fair to good	fair to good	n.a.	n.a.	n.a.
Coating Defects	2 voids/ft2	2 void/ft2	n.a.	n.a.	n.a.
Coating Uniformity	moderate ribbing	slight ribbing	n.a.	n.a.	n.a.
Developing Time	27 sec.	28 sec.	n.a.	n.a.	n.a.
Photospeed (at 100 mj/cm ²)	Copper 7	Copper 7	n.a.	n.a.	n.a.
Circuit Pattern Defects	3 defects/ft2	4 defects/ft2	n.a.	n.a.	n.a.

TABLE #3

<u>MONOMER BASE</u> <u>COMPONENTS</u>	<u>COMPONENT</u> <u>TYPE</u>	<u>GRAMS PER</u> <u>FORMULA</u>
Ethoxylated TMPTA (3 moles ethoxylation)	multi Functional acrylate	17.6
Modaflow	flow additive	0.05
Antioxidant 2246	antioxidant	0.03
Quantacure ITX (thioxanthone)	photosensitizer	0.59
Quantacure EPD (3° amine)	photoinitiator	1.49
Baso Blue 688	background dye	0.09
Triphenylphosphine	antioxidant	0.5
Benzotriazole	adhesion promoter	0.25

PROCESSING CONDITIONS

Coating - Burkle (single sided) Roller Coater, 22 threads per inch

Substrate - Copper Clad

Exposure - HMW ORC, model 301 B, diazo artwork

Development - 1% sodium carbonate monohydrate, 85° F, 2x breakpoint

Etching - 3 normal cupric chloride, 140° F, 1.3 x minimum etch

Stripping - 3% sodium hydroxide, 130° F

PERFORMANCE EXPLANATION

Viscosity - measured on a Brookfield viscometer initially and after one week at 70° F

Odor - the odor was observed after coating and before drying

Emulsion Stability - Stability was rated based on the overall uniformity of the lacquer mixture

Alkaline Resistance - the resistance was measured after alkaline etch at pH 9.2

Coating Defects - the number of coating voids (thin spots) were counted after roller coating

Coating Uniformity - the uniformity was observed immediately after coating

Developing Time - twice the amount of time required to remove the unexposed resist

Photospeed - using a Stouffer 21 step to measure the last remaining step (each step varies by $\sqrt{2}$)

(Note: a higher step would indicate a higher degree of polymerization)

Circuit Pattern Defects - the total number of

circuit shorts and opens were measured

(Note: the artwork pattern contained 4 mil lines and 4 mil spaces)



CLAIMS:

1. A photoimageable composition that can be borne in water comprising

A) between 30 and 80 wt% of a latex binder polymer having carboxylic acid functionality which provides an acid number of between 50 and 250;

B) between 20 and 50 wt% of a fraction of alpha,beta-ethylenically unsaturated monomers;

C) between 0.1 and 25 wt% of a photoinitiator or photoinitiator chemical system which generates free radicals; and

D) between 1 and 40 wt% of a polyether polyurethane associate thickener, said weight percentages being based on total weight of components A-D,

the carboxylic acid content of the latex binder polymer being either not neutralized with base or neutralized with base up to 20% of its carboxylic functionality.

2. A photoimageable composition according to claim 1 containing at least 2 wt.% of said associate thickner based on total weight of components A-D.

3. A photoimageable composition according to claim 1 or claim 2 having at least 1 wt.% of said photoinitiator chemical system.

4. A photoimageable composition according to claim 3 containing at least 2 wt.% of said photoinitiator or photoinitiator chemical system based upon total weight of components A-D.

5. A photoimageable composition according to any preceding claim dispersed in an aqueous medium.



6. A dry film comprising a polymeric support sheet and a layer of a photoimageable composition according to any one of claims 1 to 4 thereon.