

aids in physically adhering the applied photopolymerizable layer in subsequent processing steps. Adhesive aids include monomeric or polymeric silanes and nitrogen containing heterocyclic compounds such as disclosed in USP 3,645,722 and USP 3,622,234.

The present invention allows elimination of conventional adhesion promoters in photosensitive compositions.

SUMMARY OF THE INVENTION

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The present invention is directed to a process for forming a photoresist on a substrate comprising the following steps of:

- (a) laminating to said substrate a solid photosensitive film layer which is photopolymerizable and photocrosslinkable,
- 35 (b) imagewise exposing said layer to actinic radiation,
- (c) removing unexposed areas of said layer to form resist areas,
- (d) treating the areas of the substrate which are unprotected by said resist areas either by etching the substrate or by depositing a material onto said substrate areas, and
- (e) removing the resist areas from the substrate.

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the photosensitive layer comprising:

- (1) polymerizable or crosslinkable ethylenically unsaturated compound
- (2) radiation sensitive, free radical generating photoinitiator or photoinitiator system and characterizing that said photosensitive layer contains an additive to increase adhesion of said photosensitive layer to said substrate said additive being a condensation polymer formed from formaldehyde and a sulfonamide and either triazine or hydantoin. A preferred triazine is melamine. The photoresist also comprises optionally a binder.
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DETAILED DESCRIPTION OF THE INVENTION

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The photosensitive composition useful as a photoresist contains conventional components: a polymerizable ethylenically unsaturated monomer, photoinitiator or photoinitiator system which initiates polymerization of the photosensitive composition and binder.

The additive which imparts unique characteristics to the photosensitive composition is a condensation polymer of formaldehyde, toluene sulfonamide and either a triazine or hydantoin. Each of these polymers effectively function as an adhesion promoter. Mixtures of these polymers can be employed. Either a portion of prior art adhesion promoter can be replaced by the named condensation polymers. Exemplary prior art adhesion promoters are described in Hurley et al., U.S. Patent 3,622,334; Jones, U.S. Patent 3,645,772; and Taguchi et al. U.S. Patent 4,320,189.

the imaged element are typically removed from the surface of a printed circuit substrate by the developer liquid usually in a spray form for a duration of several minutes or less. Depending on the particular type of photoresist composition the developer liquid may be a simple organic solvent solution of an inorganic base, or, as in Alles U.S. 3,475,171, a combination of organic solvent and base to form a semi-aqueous developer liquid.

Suitable monomers which can be used as the sole monomer or in combination with others are those in conventional photoresist include the following: t-butyl acrylate, 1,5-pentanediol diacrylate, diethylaminoethyl acrylate, ethylene glycol diacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, hexamethylene glycol diacrylate, 1,3-propanediol diacrylate, decamethylene glycol diacrylate, dodecamethylene glycol dimethacrylate, 1,4-cyclohexanediol diacrylate, 2,2-dimethylolpropane diacrylate, 2,2,4,4-tetramethylolpropane diacrylate, tripropylene glycol diacrylate, glycerol triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, polyoxyethylated trimethylolpropane triacrylate and trimethacrylate and similar monomers as disclosed in U.S. Patent 3,380,831, 2,2-di(p-hydroxyphenyl)-propane diacrylate, 2,2,4,4-tetraacrylate, 2,2-di(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol diacrylate, 2,2,4,4-tetraacrylate, 2,2-di(p-hydroxyphenyl)-propane dimethacrylate, di-(3-methacryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(2-methacryloxyethyl) ether of bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of tetrachloro-bisphenol-A, di-(2-methacryloxyethyl) ether of tetrachloro-bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of tetrabromo-bisphenol-A, di-(2-methacryloxyethyl) ether of tetrabromo-bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of 1,4-butanediol, di-(3-methacryloxy-2-hydroxypropyl) ether of diphenyl ether, triethylene glycol dimethacrylate, polyoxypropyltrimethylol propane triacrylate (462), ethylene glycol dimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,3-trimethacrylate, 2,2,4-trimethyl-1,3-pentanediol dimethacrylate, pentaerythritol trimethacrylate, ethylene-1,2-dimethacrylate, pentaerythritol tetramethacrylate, trimethylol propane trimethacrylate, 1,4-butanediol dimethacrylate, diallyl fumarate, styrene, 1,4-benzenediol dimethacrylate, 1,4-diisopropylbenzene, and 1,3,5-triisopropenyl benzene.

In addition to the ethylenically unsaturated monomers mentioned above, the photohardenable compositions also contain one or more free radical-initiated, chain-propagating, addition-polymerizable, unsaturated compounds generally having a molecular weight of at least about 300. Preferred monomers of this type are an alkylene or a polyalkylene glycol diacrylate prepared from an alkylene glycol of 2 to 10 carbons or a polyalkylene ether glycol of 1 to 10 ether linkages, and those disclosed in U.S. Patent 2,927,022, e.g., those having a plurality of addition polymerizable ethylenic linkages particularly present as terminal linkages. Especially preferred are those wherein at least one and preferably two such linkages are conjugated with a double bonded carbon, including carbon double bonded to other carbon or to such heteroatoms as nitrogen, oxygen and sulfur. Outstanding are such materials wherein the unsaturated groups, especially the vinylidene groups, are conjugated with ester or amide structural groups.

acetate/acrylate, polyvinyl acetate/methacrylate and hydrolyzed polyvinyl acetate; ethylene/vinyl copolymers; polystyrene polymers and copolymers, e.g., with maleic anhydride and esters; 25 chloride copolymers, e.g., vinylidene chloride/acrylonitrile; vinylidene chloride/methacrylate and chloride/vinyl acetate copolymers; polyvinyl chloride and copolymers, e.g., polyvinyl chloride/saturated and unsaturated polyurethanes; synthetic rubbers, e.g., butadiene/acrylonitrile/butadiene/styrene, methacrylate/acrylonitrile/butadiene/styrene copolymers, 2-chloro-1,3 polymers, chlorinated rubber, and styrene/butadiene/styrene, styrene/isoprene/styrene 30 copolymers; high molecular weight polyethylene oxides of polyglycols having average molecular weight from about 4,000 to 1,000,000; epoxides, e.g., epoxides containing acrylate or methacrylate copolyesters, e.g., those prepared from the reaction product of a polymethylene glycol of the formula $(CH_2)_nOH$, where n is a whole number 2 to 10 inclusive, and (1) hexahydroterephthalic, sebacic, terephthalic acids, (2) terephthalic, isophthalic and sebacic acids, (3) terephthalic and sebacic 35 terephthalic and isophthalic acids, and (5) mixtures of copolyesters prepared from said glycol and (i) terephthalic, isophthalic and sebacic acids and (ii) terephthalic, isophthalic, sebacic and adipic acids or polyamides, e.g., N-methoxymethyl polyhexamethylene adipamide; cellulose esters, e.g., cellulose acetate, cellulose acetate succinate and cellulose acetate butyrate; cellulose ethers, e.g., methyl cellulose and benzyl cellulose; polycarbonates; polyvinyl acetal, e.g., polyvinyl butyral; 40 formal; polyformaldehydes. In place of or in addition to the polymeric binders listed above, thickeners with discrete, orderly orientation can be used such as disclosed in Kuchta U.S. Patent 3,458,311, e.g., silicas, clays, alumina, bentonites, kalonites, etc.

In the case where aqueous development of the photoresist is desirable the binder should contain sufficient acidic or other groups to render the composition processible in aqueous development. 45 Aqueous-processible binders include those disclosed in U.S. Patent 3,458,311 and in U.S. Patent 3,458,312. Useful amphoteric polymers include interpolymers derived from an aminoalkyl acrylate or methacrylate and an acidic film-forming comonomer and an alkyl or hydroxyalkyl acrylate such as those disclosed in U.S. Patent 4,293,635. For aqueous development the photosensitive layer will be removed in portions which are exposed to radiation but exposed portions will be substantially unaffected during development. 50 Such as wholly aqueous solutions containing 2% sodium carbonate by weight within the typical development duration of several minutes, e.g., two minutes.

Thermal polymerization inhibitors that can be used in the photosensitive compositions are: phenol, hydroquinone, and alkyl and aryl-substituted hydroquinones and quinones, tert-butyl phenol, pyrogallol, copper resinate, naphthylamines, beta-naphthol, cuprous chloride, 2,6-di-tert-butyl 55 phenothiazine, pyridine, nitrobenzene and dinitrobenzene, p-toluquinone and chloranil. Also useful as thermal polymerization inhibitors are the nitroso compositions disclosed in U.S. 4,168,982. No thermal polymerization inhibitor will be present to increase stability in storage of the photoresist compositions.

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Master 1 Composition	
Ingredient	
Binder 1	
Poly (methyl methacrylate/methacrylic acid) (90/10); mixture of 7 parts of the weight average M.W. of 25000 and 1 part of the polymer having a weight average M.W. of 5000	
Trimethylol propane triacrylate	
Benzophenone	
Michler's ketone	
Tricresyl phosphate	
Triethylene glycol diacetate	
Methylene chloride	
Methanol	

Each coating after drying was laminated to a copper clad circuit board substrate which was
with an abrasive brush, using a Riston® hot roll laminator. The laminated boards were imaged
through a $\frac{1}{2}$ Stouffer 41 stepwedge using a Riston® PC 24 exposure device and developed
30 aqueous developer containing 11% butyl Cellosolve® and 1% borax. The time of exposure was
provide a similar number, about 20, of developed image steps.

Samples of each developed board were tested using standard plating and etching techniques.

Plate and Etch Procedure:

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Each board was immersed for 5 minutes in a 8.5% aqueous solution of Metex® 9268 prepreg
at 130 ° F (54.4 ° C), rinsed for 30 seconds in flowing water, immersed for 1 minute at room temperature
10% aqueous sulfuric acid, immersed in flowing water for 1 minute, immersed in 18% aqueous
persulfate solution, rinsed in water again, immersed in sulfuric acid once again for 1 minute
40 immersed in acidic CuSO_4 plating solution and plated at 30 amps/sq. ft. (0.333 amps/sq. cm)
minutes to produce 0.001 in. (0.025 mm) plated copper.

The plated board was rinsed in water, is immersed for 1 minute in 20% aqueous flux
solution, and then immersed in a commercial tin/lead (60/40) fluoroborate solution (Hi-Thro®)
15 amps/sq. ft. (0.166 amps/sq. cm) for 15 minutes to deposit 0.0004 in. (0.01 mm) solder on
45 plated image.

The board was rinsed with water and then the photopolymerized resist was stripped from
board using 92% methylene chloride/8% methanol solvent solution.

The stripped board was sprayed at 30 psi with an aqueous ammoniacal copper chloride
7.8-8.2) (MacDermid Co. Ultra Etch® Fine Line) for 1 minute at 130 ° F (54.4 ° C) to produce a
50 copper circuit pattern.

Etching Procedure

Each imaged and developed board was sprayed at 30 psi with an etchant solution at 130 ° F
55 until all unprotected copper was removed. In the instance when an alkaline etchant was used
Ultra Etch® Fine Line was the etchant. In the instance when acid etchant was used, sulfuric
chloride and hydrochloric acid was used to produce an aqueous solution with a pH above 1
containing 24 ounces of copper/gallon (177 g/l) of etchant.

	A	B	C	D	E	F
25 Plate & etch	"ragged" "shorts"	NF	NF	NF	"ragged"	"ragged"
Alkaline Etch	"ragged"	NF	NF	NF	"ragged"	"ragged"
Acid Etch	"ragged" "breaks"	NF	NF	"ragged" "breaks"	"ragged" "breaks"	"ragged" "breaks"

30 Results indicate that the polymeric compounds added to the solvent coated film function at least as well as the conventional adhesion promoter for both the plate and etch procedure and the alkaline etch procedure. The hydantoin containing polymer also functioned satisfactorily for the acid etching procedure.

35 EXAMPLE 2

A solventless composition similar to coatings "B" and "D" of Example 1 were prepared having the following composition and were melt coated using the procedures described in Research Disclosure 24919 published January, 1985.

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MASTER 2 COMPOSITION	
Ingredient	Amount
Binder 1	56
Trimethylol propane triacrylate	36
Benzophenone	4
Michler's ketone	0.1
Tricresyl phosphate	2
Triethylene glycol diacetate	1
Crystal Violet	0.04
Red Dye CI 109	0.3

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EXAMPLE 3

A master solution was prepared as in Example 1 except the binder component was adjusted and the amount of adhesion promoter added as indicated in Table IV. In Table IV Formulation X is a composition that contains no adhesion promoter.

MASTER 3 COMPOSITION	
Ingredient	Amount
Trimethylol propane triacrylate	226
Benzophenone	25
Michler's ketone	0.63
Tricresyl phosphate	12.5
Triethylene glycol diacetate	6.3
Methylene chloride	1128
Methanol	38

TABLE IV

Coating Composition							
Ingredient	X	I	J	K	L	M	N
Master 3	229	229	229	229	229	229	229
Binder 1	55.2	54.7	53.2	52.2	51.2	50.2	49.2
HFS	0	.5	1.0	2.0	3.0	4.0	5.0

Each solution was coated, processed and evaluated as in Example 1. In addition, the photoresist to copper prior to exposure was measured by removing the polyethylene terephthalate tape and adhering 1 inch (2.54 cm) wide Scotch® brand masking tape 2262MSR to the resist surface. One end of the tape was attached to an Instron® Universal Testing Instrument model 1130 and peeled in the direction at 5 inches/min (12.7 cm/min) from the board substrate surface. The force needed to peel the resist from the copper surface was identified as the "Copper Adhesion" and represented as the

Six additional coatings were prepared and processed and evaluated as in Example 3 and 4. The adhesion promoter MFS was used in place of HFS.

TABLE VI

Coating Composition						
Ingredient	O	P	Q	R	S	T
Master 3	229	229	229	229	229	229
Binder 1	54.7	53.2	52.2	51.2	50.2	49.2
MFS	.5	1	2	3	4	5

The quantified results below in Table VII indicate that improvement of all functions begins with 3% of this adhesion promoter and rises rapidly to optimum performance by about 5%.

TABLE VII

Ingredient	X	O	P	Q	R	S	T
Plate and Etch	H,L,S	H&L	H&L	H*	H**	NF	NF
Alkaline Etch	3B + 8N	1B	6B	10B	4B	1N	NF
Copper Adhesion	13.4	13.4	16.2	16.2	21.5	25.8	26.8

* slight

** very slight

Results of the tests in Examples 3 and 4 indicate that addition of either HFS or MFS improve performance of the laminated solvent coated resist films either in the plate and etch mode or the etch mode or both.

EXAMPLE 5

Two solvent processable 0.002 inch thick photoresist films were prepared from the following solutions:

25	Victoria Blue Dye (C.I. 42595)	0.02	0.02
	HFS-UP**	4	-
	Santicizer®9 (mixed o and p toluene sulfonamide)	4.53	-
30	MHP***	-	8.53
	Propylene glycol methyl ether	11	11
	Methylene Chloride	175	175
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40	* Trimethylolpropane ethoxylated triacrylate (TMPEOTA) has the following ethoxylate distribution which constitutes a minimum of 92% of the distribution		
	None	6% Max	
	Monoethoxy	10-20%	
	Diethoxy-1	12-18%	
	Diethoxy-2	14-21%	
45	Triethoxy-1	21-29%	
	Triethoxy-2	6-10%	
	Tetraethoxy	12-20%	
50	** HFS-UP is an unpigmented condensation polymer of hydantoin, formaldehyde and mixed o and p toluene sulfonamide formulated with phthalic anhydride.		
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amps/sq. ft. for 34 minutes to produce 0.001 inch (0.0025 cm) plated copper.
25 solution, and then immersed in a commercial tin/lead (60/40) fluoroborate solution (Hi-Thro®) at 20 amps/sq. ft. (0.1667 amps/sq. cm.) for 12 minutes to deposit 0.0005 inch (0.01 mm) solder on plated image.

The board was rinsed with water and then the photopolymerized resist was stripped from board using methylene chloride solvent.

30 The stripped board was sprayed at 20 psi with an aqueous ammoniacal copper chloride solution (7.8-8.2) (MacDermid Co., Ultra Etch® Fine Line) at 130 °F (54.4 °C) to produce a solder plated circuit pattern.

For each of the plated and etched boards in which MHP was used in the resist formulation, staining occurred during the process which is a defect indicating the potential for underplating.
35 no defects were observed for the plated and etched boards which were prepared from the HFS-UP.

The plated board was rinsed in water, is immersed for 1 minute in 20% aqueous fluoroborate solution, and then immersed in a commercial tin/lead (60/40) fluoroborate solution (Hi-Thro®) at 15 amps/sq. ft. (0.166 amps/sq. cm) for 15 minutes to deposit 0.0004 in. (0.01 mm) solder on plated image.
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The board was rinsed with water and then the photopolymerized resist was stripped from board using 92% methylene chloride/8% methanol solvent solution.

The stripped board was sprayed at 30 psi with an aqueous ammoniacal copper chloride solution (7.8-8.2) (MacDermid Co. Ultra Etch® Fine Line) for 1 minute at 130 °F (54.4 °C) to produce a solder plated copper circuit pattern.
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EXAMPLE 6

Four solvent processable 0.002 in thick photoresist films were prepared and tested for use in rigorous plating and etching conditions.
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A Master coating solution was prepared for each coating having the following Composition:

formulated with 1% Brilliant Green Dye (C.I. 42040).

25 Coating Solution "Y" contains the ingredients of Master Solution 4 along with 51.01 g of which is the condensation polymer of hydantoin, formaldehyde and mixed o and p toluene s formulated with 1% Brilliant Green Dye (C.I. 42040) and 0.76% Victoria Blue Dye (C.I. 42595).

Coating Solution "Z" contains the ingredients of Master Solution 4 along with 51.01 g of which is the condensation polymer of hydantoin, formaldehyde and mixed o and p toluene s formulated with 1% Victoria Green Dye (C.I. 42000) and 0.8% Victoria Blue Dye (C.I. 42595).

30 These coating solutions were coated, laminated exposed and developed as in Example tested using the copper/tin-lead plating and etching procedure of Example 5 along with a copper/nickel/gold plating procedure. In this plating procedure the copper is plated as in Exa plated panel is rinsed in water for 1 minute and then nickel plated in an acidic nickel sulfam using a current density of 30 ampers/square feet for 15 minutes to produce nickel plating 0.0003
35 The nickel plated panel is then rinsed and immersed in a 10% aqueous sulfuric acid both fo rinsed again and then gold plied in a Orosene®999 gold plating bath at 83°F for 10 minutes density of 10 ampers/square foot. In evaluating the results of these tests a series of circuit board processed for each coting and each panel is given a numerical value from 0 to 5 depending on panel has no defects, e.g., "0", nonfunctional defects, e.g., 1, 2 and 3 (such as copper staining
40 produce acceptable circuit board or functional defects, e.g., 4 and 5, such as underplating and s disqualify the board for use. The average value for each series of panels for each type of plating Table VIII for each coating.

TABLE VIII

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Coating	Cu/Sn-Pb	Cu/Ni/Au
W(HFS-UP)	3.3	4.2
X(HFS-BG)	2.0	2.25
Y(HFS-BGVB)	1.3	0.8
Z(HFS-VGVB)	3	3.1

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While acceptable boards can be obtained from all of the coatings using Cu/Sn-Pb plating it i best results are obtained using condensation polymers formulated in the presence of Brilliant
55 and some improvement is obtained with polymers formulated in the presence of Victoria E Victoria Green. This same trend of improvement is also present for panels prepared under the m conditions of Cu/Ni/Au plating.

4. The process of claim 1 wherein the condensation polymer is formed from hydantoin, formaldehyde and toluene sulfonamide.
- 25 5. The process of claim 1 wherein the condensation polymer is present in a concentration in a range from 0.5 to 25% by weight of the photosensitive layer.
6. The process of claim 1 wherein the concentration is in a range from 1 to 10% by weight of the photosensitive layer.
- 30 7. The process of claim 1 wherein the concentration is in a range from 2 to 6% by weight of the photosensitive layer.
8. The process of claim 1 wherein binder is present in the photosensitive layer.
- 35 9. The process of claim 1 wherein binder is absent in the photosensitive layer.
10. The process of claim 1 wherein the condensation polymer is formulated in the presence of a dye comprising Brilliant Green (C.I. 42040), Victoria Green (C.I. 42000) and Victoria Blue.
- 40 11. The process of claim 10 wherein the dye is Brilliant Green (C.I. 42040).

Revendications

- 45 1. Procédé pour former une photoréserve sur un substrat comprenant les étapes de :
 - (a) feuilletage sur ce substrat d'une couche solide de film photosensible qui est photopolymérisable ou photoréticulable,
 - (b) exposition selon une image de cette couche à une radiation actinique,
 - 50 (c) élimination des zones non exposées de cette couche pour former des zones de réserve,
 - (d) traitement des zones du substrat qui ne sont pas protégées par ces zones de réserve par une attaque de ce substrat, soit par dépôt d'un matériau sur ces zones de substrat, et
 - (e) élimination des zones de réserve du substrat,
 la couche photosensible comprenant :
 - 55 (1) un composé insaturé éthyléniquement polymérisable ou réticulable, et
 - (2) un photoinitiateur ou un système photoinitiateur sensible à une radiation générant des radicaux libres,
 caractérisé en ce que cette couche photosensible contient un additif pour améliorer l'adhésion.

25 10. Le procédé suivant la revendication 1, dans lequel le polymère de condensation est en présence d'un colorant comprenant le Vert Brillant (C. I. 42040), le Vert Victoria (C. I. 42000) ou le Vert Victoria (C. I. 42595).

30 11. Le procédé suivant la revendication 1, dans lequel le colorant est le Vert Brillant (C. I. 42040).

Patentansprüche

1. Verfahren zur Bildung eines Photoresists auf einem Substrat, umfassend die Schritte:
- 35 (a) Laminieren einer festen lichtempfindlichen Filmschicht, die photopolymerisierbar oder vernetzbar ist, auf das Substrat,
- (b) abbildweises Belichten der Schicht mit aktinischer Strahlung,
- (c) Ablösen der unbelichteten Bereiche der Schicht, um Resistbereiche zu bilden,
- (d) Behandeln der Substratbereiche, die nicht durch die Resistbereiche geschützt sind, durch Ätzen des Substrats oder durch Abscheiden eines Materials auf die Substratbereiche,
- 40 (e) Ablösen der Resistbereiche vom Substrat,
- wobei die lichtempfindliche Schicht umfaßt:
- (1) eine polymerisierbare oder vernetzbare ethylenisch ungesättigte Verbindung, und
- (2) einen strahlungsempfindlichen, freie Radikale erzeugenden Photoinitiator oder ein Photosensibilisator-System,
- 45 dadurch gekennzeichnet, daß die lichtempfindliche Schicht ein Additiv enthält, um die Adhäsion der lichtempfindlichen Schicht zum Substrat zu steigern, wobei das Additiv ein Kondensationspolymer ist, das gebildet aus Formaldehyd und Toluolsulfonamid sowie entweder einem Triazin oder Hydantoin ist.
2. Verfahren nach Anspruch 1, wobei das Kondensationspolymer gebildet ist aus einem Triazin, Formaldehyd und Toluolsulfonamid.
- 50 3. Verfahren nach Anspruch 1, wobei das Triazin Melamin ist.
4. Verfahren nach Anspruch 1, wobei Kondensationspolymer gebildet ist aus Hydantoin, Formaldehyd und Toluolsulfonamid.
- 55 5. Verfahren nach Anspruch 1, wobei das Kondensationspolymer in einer Konzentration im Bereich von 0,5 bis 25 Gew.-% der lichtempfindlichen Schicht vorhanden ist.

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