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PHOTOSOLUBILIZATION PROCESS USING PHENOLS AS D_{max} MAINTAINERS

Jack Freshwater Strange, Highstown, N.J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

The invention of this application is concerned with a process of forming a silver halide image by selectively exposing a photosoluble silver halide layer and dissolving the exposed photosoluble silver halide in a silver halide solvent, said process being characterized by having present, during treatment in the solvent, a D_{max}-maintaining amount of a phenolic compound devoid of ionizable iodine, or oxidizing or reducing groups which are active at the working pH, preferably a mononuclear phenol having a hydrocarbon substitutent in the o-position selected from the group consisting of o-phenylphenol and o-allylphenol.

CROSS-REFERENCE TO RELATED APPLICATION

In assignee's copending application of Ralph Kingsley Blake (PDC–1034) entitled Improvement in Photosolubilization Image Formation, executed on even date with this application, there is described and claimed a similar process disclosing various other D_{max} maintainers. The phenolic D_{max} maintainers of this invention, in general, are equal to or superior to the preferred adjuvants of the Blake application.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a process for forming images from photosoluble (photosolubilizable) silver halide layers. The present invention constitutes an improvement in a silver halide photosolubilization process by the use of a phenolic compound adjuvant which helps to prevent dissolution of silver halide in unexposed areas while allowing dissolution to proceed in the exposed areas. Because of this characteristic, the adjuvant can be characterized as a maximum density maintainer, or D_{max} maintainer.

Description of the prior art

Photosolubilization image-forming process and photosoluble layers and elements useful in the basic process are described in U.S. Patents 3,155,507 and 3,155,514–9, Nov. 3, 1964, Blake application U.S. Ser. No. 629,426, filed Apr. 10, 1967, and Haugh U.S. Ser. No. 478,421, filed Aug. 9, 1965. In these patents and applications there are described simple and useful layers and processes for obtaining a positive silver halide image in a single processing step. Intensification of the image, e.g., by reduction to a black metallic silver image, constitutes an additional optional step.

SUMMARY OF THE INVENTION

This invention pertains to an improvement in a photosolubilization process of forming a direct positive silver halide image which process comprises

(a) exposing, imagewise, a photosoluble layer containing silver halide made relatively less soluble in a silver halide solvent by treatment with an organic compound containing sulfur and/or nitrogen, and capable of forming a silver salt of lower solubility in water than silver chloride, and

(b) dissolving the exposed silver halide in a silver halide solvent comprising an aqueous bath of an alkali metal or ammonium thiosulfate,

the improvement being characterized by the presence while said layer is in the bath at pH 4–11, preferably 7–10, of D_{max}-maintaining amounts of an aromatic hydroxy compound having at least one benzene ring containing a phenolic hydroxyl group, including unsubstituted phenol and naphthols and said compounds substituted with alkyl, e.g., methyl, ethyl, and isopropyl; vinyl, allyl; alkoxy, e.g., methoxy; carboxy; benzoyl, or aryl, e.g., phenyl, or a hydrolyzable precursor of the compound, e.g., formate or acetate, the phenolic compound being present in sufficient quantity and being present in the range of 0.1 to 20 g./liter of the aqueous bath, to retard solution of the unexposed silver halide.

The D_{max}-maintaining phenolic compound effects an improvement by retarding the dissolution of silver halide preferentially in the unexposed as compared to the exposed areas of the photosoluble element. The presence of the D_{max}-maintaining compound has the advantage that less precise control of processing conditions may be tolerated, e.g., concentration of silver halide solvent, temperature of the solution and period of time required for treatment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In practicing the process of the invention, a photosoluble silver halide layer as defined in Blake U.S. 3,155,519, preferably a layer of silver chloride emulsion insolubilized with 2-mercapto-4-phenylthiazole or a related mercaptan as disclosed in said patent is prepared. The element may advantageously have a photographic optical sensitizing dye associated with its silver halide crystals as disclosed in assignee's copending application of Blake, U.S. Ser. No. 390,460, filed Aug. 18, 1964 (U.S. Patent 3,384,485, May 21, 1968.) The photosoluble layer is exposed, imagewise, to actinic radiation and then treated in an aqueous bath comprising from 0.1 to 2 moles per liter of a thiosulfate, e.g., sodium thiosulfate, silver halide solvent and a phenolic D_{max} maintainer as defined above. A particularly preferred D_{max} maintainer is o-phenylphenol in a concentration of 0.1 to 1.0 g./liter, preferably from .4 to .6 g./liter. The time and temperature of treatment in the aqueous bath are obviously dependent variables but at a temperature of 70° F. the time should be about 1 to 5 minutes. This treatment removes silver halide from the exposed areas at a much faster rate than from the unexposed areas, leaving a positive silver halide image. The presence of an organic compound such as o-phenylphenol further lowers the rate of dissolution of the unexposed silver halide, relative to that of the exposed silver halide, contributing to better image formation, especially to higher densities in unexposed areas. A useful positive image can be produced, particularly for viewing by projection, by this single treatment, although a washing step is generally used. For most purposes, it is desirable to intensify the silver halide image, usually by treating with a photographic silver halide developer solution to reduce the image to one of black metallic silver. The silver halide image may be fogged prior to reduction by flashing to white light or, more conveniently, by use of a prefogged element such as described in assignee's copending applications, Blake U.S. Ser. No. 629,426 filed Apr. 10, 1967 and Haugh U.S. Ser. No. 478,421 filed Aug. 9, 1965. Other methods of intensifying the silver halide image, e.g., by toning, color developing, etc., are disclosed in U.S. 3,155,507.

Any of the various photosoluble silver halide elements described in the U.S. Patents and Blake and Haugh applications listed above can be used in the process of this invention. These, of course, may be modified as described in the patents and applications by variations in the silver halide, the binder (if present), the organic compounds for insolubilization of silver halide (whose utility can be established by the simple tests defined therein for determination of other useful compounds), the adjuvants generally employed in silver halide systems, the supports, and in the relative concentrations of the various components. Various auxiliary layers may be present, such as abrasion over-coatings, subbing layers, and antihalation undercoats or backing layers. The elements may include multilayer as well as monolayer structures. The various layers, including the support, may include inert ingredients, e.g., pigments, organic polymer latices, and matting agents. As disclosed in U.S. 3,155,507, the silver halide may be insolubilized by treatment with an appropriate organic compound either during emulsion manufacture or by treatment of the coated element with a solution of the organic compound.

The phenolic compound should be devoid of ionizable iodine because the iodide ion readily replaces the "organic compound" of step (a) to form silver iodide; it should be devoid of oxidizing groups because these tend to oxidize the silver salts of "organic compound" of step (a) so that exposed and unexposed areas cannot be easily distinguished in terms of their rates of solution in a silver halide solvent.

The dissolution developer (i.e., the solution of silver halide solvent) may contain adjuvants as given in Example III. The essential components for this invention, however, are water, silver halide solvent and a D_{max} maintainer. Numerous useful silver halide solvents are given in U.S. Patent 3,155,507 but in this application the use of preferred silver halide solvents containing the thiosulfate anion will be described.

The invention will be further illustrated by but is not intended to be limited to the following examples.

EXAMPLE I

A light-sensitive gelatino-silver chloride coagulum, made by precipitation and coagulation washing in the manner taught in Moede, U.S. Patent 2,772,165, was redispersed in an aqueous gelatin solution so as to achieve a gelatin to silver chloride weight ratio of 0.79. The resulting emulsion was digested at 170° F. for 20 minutes in the presence of 0.80 g. of 2-mercapto-4-phenylthiazole and 0.025 g. of the dye of Example I of Kendall 2,342,546 per mole of silver chloride. Normal emulsion adjuvants were added, including gelatin hardening agents and coating aids, and the emulsion was coated on a vinylidene chloride copolymer subbed polyester base prepared as described in Example IV of Alles, U.S. Patent 2,779,684 (and to which a gelatin sub-layer had been subsequently applied). The coating weight was 46 mg./dm.^{2} calculated as metallic silver.

A sample of the dried photosoluble film was exposed through a $\sqrt{2}$ stepwedge for 15 seconds a 24 inches distance from a high intensity, tungsten filament, incandescent lamp (General Electric Reflector Photoflood lamp, No. PH/RFL 2). The exposed film, serving as a control, was then processed for 3 minutes at 68° F. in a dissolution developer consisting of an aqueous solution containing 57.5 g./liter of sodium thiosulfate adjusted to a pH of 9.0 with 3 N H_2SO_4. A second sample of the identically exposed film was treated similarly except that, per liter of dissolution developer, there was added 10 ml. of a 1 N NaOH solution containing 5% by weight of o-phenylphenol; the solution pH again was adjusted to 9.0 Positive, AgCl images were obtained in both films but the D_{max} was greater in the film treated in the o-phenylphenol solution. Both films were given an overall exposure to white light from a suitable lamp after washing in water for 2 minutes and then the images were intensified by treatment for 1 minute in a photographic silver halide developer of the following composition, which had been diluted 1:1 with water before use:

Water	ml	750
p-Methylaminophenol sulfate	g	3
Na_2SO_3 (anhyd.)	g	45
Hydroquinone	g	12
$Na_2CO_3 \cdot 1H_2O$	g	79
KBr	g	1.9

Water to make 1 liter.
pH, 10.3.

The films were then washed in water for 3 minutes and dried in air. The intensified metallic silver image of the control film had a maximum transmission optical density of 2.94 while the film treated with D_{max} maintainer had a densty of over 4.0, i.e., a density greater than could be detected by the densitometer. The minimum densities were approximately the same (about 0.04) in both films. Also the contrasts were essentially identical in the two films.

EXAMPLE II

Example I was repeated except that both the control and the experimental dissolution developers (i.e., the aqueous solutions of silver halide solvent) contained additionally 4.5 g./liter of anhydrous Na_2SO_3. Both solutions were adjusted to pH 9.0 with 3 N H_2SO_4. The film processed in the solution containing o-phenylphenol again had a D_{max} above 4.0 but increased in apparent positive speed, i.e., optical densities began decreasing at steps corresponding to lower exposure, than the films in Example I. For the control film, the D_{max} was only 0.2 but an image was visible.

EXAMPLE III

The following silver halide solvent solution was prepared for use as a dissolution developer.

Water	ml	800
$Na_2S_2O_3$ (anhyd.)	g	153
Na_2SO_3 (anhyd.)	g	15
$Na_2B_4O_7 \cdot 10H_2O$	g	18
Glacial acetic acid	ml	12
$KAl(SO_4)_2 \cdot 12H_2O$	g	20

Water to 1 liter.
pH adjusted with 3 N NaOH to 6.0.

Prior to use, the above solution was diluted with an equal volume of water (as a control) or with an equal volume of aqueous solution containing an organic compound as a D_{max} maintainer as noted in the table above. A number of D_{max} maintainers were tested by using such solutions in processing exposed film samples as described in Example I. The samples were processed in solutions containing the D_{max} maintainers at pH of 6.0, some at a concentration of 0.05 and others at a concentration of 0.1% by weight, processing for 2 minutes at 68° F. The films were then washed, intensified, washed again and dried as in Example I. In the table below, the effectiveness of the D_{max} maintainer is indicated by the increase in D_{max} (optical transmission density) over the control (D_{max} 1.36).

TABLE I

Organic compounds

D_{max} maintainer:	D_{max}
Control	1.36
Phenol	3.0
o-Nitrophenol	3.4
p-Nitrophenol	3.1
3,4-dimethylphenol	4+
1-naphthol	4+
2-naphthol	3.8
3,5-dinitrosalicylic acid	3.0
Salicylic acid	2.8
m-Hydroxybenzoic acid	2.6
p-Hydroxybenzoic acid	2.5

TABLE I—Continued

D_{max} maintainer:	D_{max}
3-phenylsalicylic acid	2.8
5-phenylsalicylic acid	2.5
p-Phenylphenol	3.0
o-Phenylphenol	4+
Eugenol	3.8
1-naphthyl acetate	3.5
2-naphthyl acetate	3.3
Tetrahydrofurfuryl alcohol+p-phenylphenol	3.3
2-allylphenol	3.6

EXAMPLE IV

A photosoluble element was prepared by coating an aqueous gelatin dispersion of a spectrally sensitized silver chlorobromide (70 mole percent silver chloride and 30 mole percent silver bromide) which contained 0.67 gram of the insolubilizer, 2-mercapto-4-cyclohexylthiazole, per mole of silver halide, and the merocyanine dye of Example I of Kendall U.S.P. 2,342,546 on the film base described in Example I. The dried element was then exposed behind a $\sqrt{2}$ stepwedge for 5 seconds to the light source of Example I at a distance of about 20 inches. Exposed elements were immersed in a dissolution developer (compositions shown in Table II) for 30 seconds and 3 minutes, rinsed in water, reexposed, and bathed in a metol-hydroquinone intensifier (conventional photographic developer). As can be seen in Table II, the dissolution developers A and D serve as controls at pH values of 5 and 9, respectively.

TABLE II

Dissolution developer	pH of dissolution developer	G./liter $Na_2S_2O_3$	G./liter Na_2SO_3	D_{max} maintainer	G./liter D_{max} maintainer
A (control)	5	77	7.5	None	0
B	5	77	7.5	o-Phenylphenol	0.5
D (control)	9	32	7.5	None	0
E	9	32	7.5	o-Phenylphenol	.5
F	9	32	7.5	do	(1)

[1] Sat'd (~0.8).

The maximum transmission optical densities were then determined and are listed below.

	D_{max} after 30 seconds	D_{max} after 3 minutes
Dissolution developer:		
A (control)	2.1	0.3
B	2.8	2.5
D (control)		0.03
E		1.7

When the insolubilizer, 2-mercapto - 4-cyclohexylthiazole, was replaced with dodecanethiol or p-bromothiophenol, after 3 minutes of processing increases of D_{max} were also observed.

EXAMPLE V

A photosoluble element was prepared by coating an aqueous gelatin dispersion of a spectrally sensitized silver chloride which contained 1.18 grams of benzoxazolethiol per mole of silver chloride as insolubilizer and the merocyanine dye of Example I of Kendall U.S.P. 2,342,546 on the film base of Example I. The drided element was then exposed and processed as in Example IV.

	D_{max} after 30 seconds	D_{max} after 3 minutes
Dissolution developer:		
A (control)	1.0	0.29
B	2.3	2.1
D (control)	1.0	0.08
E	1.6	0.66

EXAMPLE VI

Example V was repeated except that 2.4 grams of 1-(1-napthyl)-2-thiourea per mole of silver chloride was substituted for the benzoxazolethiol.

	D_{max} after 30 seconds	D_{max} after 3 minutes
Dissolution developer:		
A (control)	0.4	0.05
B	1.39	1.3
D (control)	0.75	0.13
E	2.75	2.35

EXAMPLE VII

A photosoluble element, with 5-nitrobenzimidazole as insolubilizer, was prepared as described in Example VI of U.S. Patent 3,155,507. Film samples of the element were exposed and processed as in Example IV.

Dissolution developer:	D_{max} after 30 seconds
D (control)	3.1
L	4+

EXAMPLE VIII

A photographic element was prepared by coating an aqueous gelatin dispersion of silver bromochloride (30 mole percent silver bromide and 70 mole percent silver chloride) on a film base prepared as in Example IV of Alles U.S.P. 2,779,684. After drying, the film was soaked for 30 seconds in a solution of 0.15 g. of 2,5-dimercapto-1,3,4-thiadiazole in 500 ml. ethanol-water solution (17 parts ethanol-3 parts water) to produce a photosoluble element. Exposure and processing were as described in Example IV with exposure times as indicated.

	Exposure (seconds)	D_{max} after 40 seconds
Dissolution developer:		
A (control)	5	1.70
B	5	1.98
D (control)	2	2.16
E	2	3.60

EXAMPLE IX

In assignee's copending application of Haugh, Ser. No. 546,202, filed Apr. 29, 1966 a process was disclosed whereby a single exposure of a photosoluble element could be followed by the development of superimposed positive and negative images. With one or more color coupling development steps it is possible to obtain various types of unusual images, some of which may have considerably utility. Processing in the presence of the D_{max} maintainers of the present invention can provide improvements in the above Haugh process as demonstrated in the following working example:

Samples of the photosoluble film of Example I were exposed through a $\sqrt{2}$ step wedge as described in that example. A control sample was processed for 2 minutes in the following silver halide solvent solution:

H_2O	ml	800
$Na_2S_2O_3$ anhyd.	g	77
Na_2SO_3	g	7.5
$Na_2B_4O_7 \cdot 10H_2O$	g	9
Glacial acetic acid	ml	6
$KAl(SO_4)_2 \cdot 12H_2O$	g	10
CH_3COOK	g	5
H_2O to 1000 ml.		
pH		4.8

A second sample of the exposed film was processed for 2 minutes in the following silver halide solvent solution:

H_2O	ml	800
$Na_2S_2O_3$, anhyd.	g	58
Na_2SO_3	g	4.5
5% by wt. o-phenylphenol in 1 N NaOH	ml	10

H_2O to 1000 ml.

3 N H_2SO_4 added to reduce pH to 9.0.

After these treatments in the silver halide solvents, the two film samples were processed identically as follows (all processing steps being carried out at 68° F.):

	Minutes
Washed in water for	2
Color development in cyan color coupler solution	4
Washed in water for	5

Uniform (excess) exposure to lamp used for imagewise exposure—to expose all of the remaining silver halide.

	Minutes
Color development in yellow color coupler solution	5
Washed in water for	5
Bleach	2
Fix	2
Washed in water for	2

Dry in air.

The color coupling developer solutions contained p-aminodiethylaniline hydrochloride as the silver halide developing agent. The color coupler for the cyan developer solution was 2,4-dichloro-1-naphthol; for the yellow developer solution the color coupler was 2-methoxy-5-methacrylamido-2-benzoylacetanilide. In the conventional bleaching and fixing solutions the active agents were, respectively, $K_3Fe(CN)_6$ and $Na_2S_2O_3$.

In both samples a multicolor image resulted from the superimposing of a negative-positive cyan image and a positive yellow image. At the low exposure steps, the image was yellow. There was a gradual increase of cyan density with increasing exposure so that the image gradually changed from yellow-green to green as the positive yellow component of the image decreased in density. The cyan component of the image reached a peak density at intermediate exposure levels, changing from a negative to a positive image. At higher exposure levels there was a pure cyan positive image, while at the very highest exposure level all of the silver halide had been removed by dissolution development and there was no image present.

The sample processed with the D_{max} maintainer (o-phenylphenol) exhibited an effective speed increase of three steps in the positive, high exposure (pure cyan) region of the image. This sample also showed better color differentiation from step to step which is equivalent to more effective conveyance of information. The increased positive speed is probably attributable to the high pH of the silver halide solvent solution (the first processing solution). Processing at such a high pH (9.0) in the abesnce of the D_{max} maintainer would have resulted in very severe loss of image density.

EXAMPLE X

A silver chloride emulsion was prepared as described in Example I. Before coating, the emulsion was divided into a number of separate portions and various D_{max} maintainers were added, from siutable solvents, in the concentrations (expressed as grams of D_{max} maintainer per mole of AgCl) indicated in the table below. The portions were then coated as in Example I to give coating weights of 37 mg./dm.^{2}, calculated as metallic silver. Samples of the coated films were exposed and treated for 2 minutes in the silver halide solvent solution used for the control film sample of Example IX to form positive silver chloride images. These images were intensified by flashing to white light, developing, washing, and drying as described in Example I (using the same p-methylaminophenol sulfate/hydroquinone developer de scribed therein). From the results given below it is obvious that D_{max} maintainers are effective in the emulsions as well as in the processing solutions and the amounts used are in excess of that used for the photosolubilization effect.

TABLE 3

$D_{max.}$ maintainer in emulsion	Concentration	$D_{max.}$
None		3.36
Catechol	6	4.0+
2,4-dihydroxybenzophenone	1.6	3.83
Do	3.1	4.0+
2-naphthol	3.2	3.79
Do	6.1	3.99
p-Phenylphenol	2	4.0+
Do	4	4.0+

The present invention has the advantages of the basic process of photosolubilization, especially that of a very simple, single step process of obtaining a positive image. Advantages over the basic process include increased optical densities in unexposed or lightly exposed areas, both for silver halide images and for intensified images. Also, processing is simpler because the D_{max} maintainers make the effects of such variables as concentration of silver halide solvent, solution pH, processing times and temperatures less critical. The D_{max} maintainers often increase contrast and apparent speed although decreases in one or both of these variables sometimes occur. Thus, by proper selection of the D_{max} maintainer and its concentration, another method is available for controlling speed and contrast. Still other advantages will be apparent from the above description of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A photosolubilization process for forming a direct-positive silver halide image which comprises:

(a) exposing, imagewise, a photosoluble layer containing silver halide made relatively less soluble in a silver halide solvent by treatment with an organic compound containing sulfur and/or nitrogen and capable of forming a silver salt of lower solubility in water than silver chloride, and

(b) dissolving the exposed silver halide in a silver halide solvent comprising an aqueous bath of an alkali metal or ammonium thiosulfate,

said process being characterized by the presence while said layer is in said bath, at a predetermined pH, of D_{max}-maintaining amounts of an aromatic hydroxy compound containing at least one phenolic hydroxy group selected from the class consisting of unsubstituted phenol and naphthols and their alkyl; vinyl; allyl; alkoxy, carboxy, benzoyl, and aryl substituted derivatives, and their hydrolyzable precursors,

said aromatic hydroxyl compound being present in the range of 0.1 to 20 g./liter of the aqueous bath, to retard solution of the unexposed silver halide.

2. A process according to claim **1** wherein said aromatic hydroxyl compound is present in said bath initially in the specified quantities.

3. A process according to claim **2** wherein said aromatic hydroxyl compound is o-phenylphenol.

4. A process according to claim **2** wherein said aromatic hydroxyl compound is o-allylphenol.

5. A process according to claim **2** wherein the organic compound of step (a) is present in such an amount, in terms of the ratio of its weight to the surface area of the silver halide crystals, that when admixed in such ratio with an aqueous silver bromochloride, 30/70 mole percent, gelatin dispersion containing 0.29 mg. of Ag in one-half ml., and said silver bromochloride dispersion is treated with 10% by weight aqueous sodium thiosulfate, so that the resulting mixture contains 0.29 mg. of Ag and 100 mg. of sodium thiosulfate, at least three times the amount of silver bromochloride remains undissolved as compared with a similar dispersion successively treated with 5% by weight aqueous sodium hypochlorite and 10% by weight aqueous sodium thiosulfate, so that the resulting mixture contains 0.29 mg. of Ag, 25 mg. of sodium hypochlorite and 100 mg. of sodium thiosulfate, after vigorous agitation of both dispersions for 30 seconds at 25° C.

6. A process according to claim 2 wherein said aromatic hydroxyl compound is 1-naphthol.

7. A photosoluble layer containing light-sensitive silver halide made less soluble in a silver halide solvent by treatment with an organic compound containing sulfur and/or nitrogen and capable of forming a silver salt of lower solubility in water than silver chloride, said layer containing in addition a different auxiliary organic compound and which is a phenolic compound devoid of ionizable iodine, or oxidizing or reducing groups which are active at the working pH, in sufficient quantity to further retard solution of unexposed silver halide in said layer.

8. A layer according to claim **7** wherein said organic compound is present in such an amount, in terms of the ratio of its weight to the surface area of the silver halide crystals, that when admixed in such ratio with an aqueous silver bromochloride dispersion, 30/70 mole percent, gelatin emulsion containing 0.29 mg. of Ag in one-half ml., and said silver bromochloride dispersion is treated with 10% by weight aqueous sodium thiosulfate, so that the resulting mixture contains 0.29 mg. of Ag and 100 mg. of sodium thiosulfate, at least three times the amount of silver bromochloride remains undissolved as compared with a similar dispersion successively treated with 5% by weight aqueous sodium hypochlorite and 10% by weight aqueous sodium thiosulfate, so that the resulting mixture contains 0.29 mg. of Ag, 25 mg. of sodium hypochlorite and 100 mg. of sodium thiosulfate, after vigorous agitation of both dispersions for 30 seconds at 25° C.

9. A layer according to claim **7** wherein said auxiliary compound is an aromatic hydroxyl compound containing at least one phenolic hydroxyl group, said compound being selected from the class consisting of unsubstituted phenol and naphthols and their alkyl, vinyl, allyl, alkoxy, carboxy, benzoyl and aryl-substituted derivatives and their hydrolyzable precursors.

10. A layer according to claim **7** wherein said auxiliary compound is o-phenylphenol.

11. A layer according to claim **7** wherein said auxiliary compound is o-allylphenol.

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NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

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