Aug. 17, 1971 T. I. ABBOTT ET AL 3,600,177

LIQUID AMIDES AS SILVER HALIDE DEVELOPER SOLVENTS

Filed Sept. 22, 1967

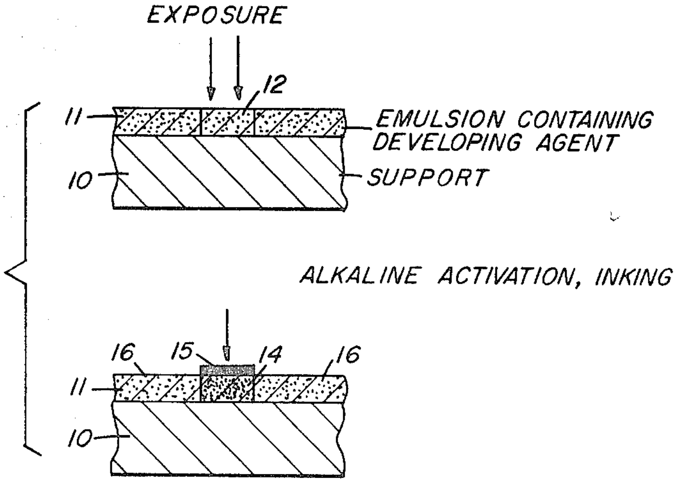

FIG. 1

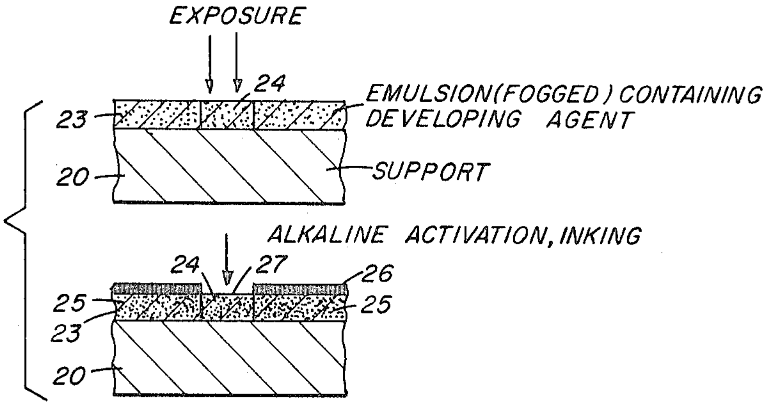

FIG. 2

THOMAS I. ABBOTT
ROBERT N. WOODWARD
INVENTORS

BY Henry E. Byers
ATTORNEY

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LIQUID AMIDES AS SILVER HALIDE DEVELOPER SOLVENTS

Thomas I. Abbott and Robert N. Woodward, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

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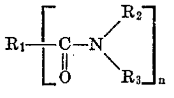
ABSTRACT OF THE DISCLOSURE

Developer solvents having the following general formula:



$$R_1\left[-\underset{\substack{\| \\ O}}{C}-N\begin{matrix}\diagup R_2\\ \diagdown R_3\end{matrix}\right]_n$$

wherein *n* is 1 or 2; R_1 represents an alkyl group of at least four carbon atoms when *n* is 1; R_1 represents an aryl group when *n* is 2; and R_2 and R_3 may be hydrogen, lower alkyl of from 1 to 4 carbon atoms, or may represent an aryl group or may be joined to form a heterocyclic nucleus, are used for incorporating developers in photographic emulsions either alone or in conjunction with high boiling oil solvents.

This invention relates to photographic emulsions and elements. In one embodiment, this invention relates to emulsions containing liquid amides as solvents for incorporated silver halide developing agents.

It is advantageous for some purposes to incorporate developing agents in silver halide emulsions. Water insoluble developing agents can be incorporated in certain oil solvents such as, for instance, tricresyl phosphate, dibutyl phosphate, etc. It appears that the solvent is in liquid particles in the dried emulsion. However, a large excess of the oil solvent is necessary to keep the development agent in a specific layer until released by an alkaline activator. In certain photographic emulsions, the use of the dispersed developing agents results in photographic elements exhibiting very low photographic speed. This is particularly evident in the use of direct positive elements. When these elements are used for making lithographic plates, for instance, complex structures are normally necessary involving at least two photographic emulsion layers and requiring complex processing techniques or unstable processing solutions for development. It has been desirable, therefore, to find a method of dispersing silver developing agents in photographic emulsions, particularly direct positive emulsions, which would not result in a decrease in speed but would have the advantages which are customarily associated with solvent incorporated developing agents.

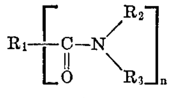
It also has been desirable to find a method of incorporating silver halide developing agents in photographic emulsions used in preparing lithographic plates. A particularly useful silver halide sensitized lithographic printing plate is described in U.S. Pat. 3,146,104, issued Aug. 25, 1964 to Yackel and Abbott. In one embodiment of this lithographic plate, the support contains a gelatin layer having therein an incorporated developing agent over which is coated a light sensitive silver emulsion followed by a top layer of a fogged emulsion. Following exposure and activation, the developing agent develops the light sensitive emulsion in the exposed areas while the developing agent in the unexposed areas migrates to the top fogged emulsion while development takes place to obtain a direct positive image.

It has been desirable to substitute the 3-layer system of the prior art product with a single layer which would be a direct positive but which would contain incorporated silver halide developing agents. Since the use of a direct positive emulsion containing an oil solvent resulted in a decrease in speed, this has not been practicable. Therefore, there has been a need for a method of incorporating the developer in the direct positive emulsion which would result in an emulsion having satisfactory speed as well as other desirable properties necessary in a lithographic printing plate; namely, acceptable ink-water differential between the developed areas and the undeveloped areas.

We have now found a method of incorporating developers in emulsions, particularly in direct positive emulsions for lithographic uses wherein liquid substituted amides are used instead of the oil solvents or in place of part of the oil solvents conventionally used.

One object of this invention is to provide substituted amides which can be used as liquid solvents for silver halide developing agents dispersed in silver halide emulsions. Another object is to provide a photographic element having at least one incorporated developing agent in the silver halide emulsion. A further object is to provide lithographic printing plates having thereon direct positive silver halide emulsions containing incorporated developing agents. A further object is to provide a lithographic element having better lithographic differential, better physical properties, better emulsion stability and higher photographic speed. A still further object is to provide a method of making silver halide emulsions having therein an incorporated developing agent. Additional objects will be evident from the following disclosure.

The above objects are obtained by incorporating in the silver halide emusion or in a colloid layer on the same support, liquid substituted amides as solvents for incorporated developers, provided the resulting amide is normally liquid, i.e., liquid at a temperature of about 25° C., of the general formula:



$$R_1\left[-\underset{\substack{\| \\ O}}{C}-N\begin{matrix}\diagup R_2\\ \diagdown R_3\end{matrix}\right]_n$$

wherein *n* is an integer of 1 or 2. When *n* is 1, R_1 represents an alkyl group of at least 4, and generally about 4 to 20 carbon atoms, such as, for example, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, tridecyl, lauryl, palmityl, stearyl, eicosyl; wherein each of R_2 and R_3 are hydrogen, lower alkyl from 1 to 4 carbon atoms, or represent an aryl group or are joined to form a heterocyclic nucleus. When *n* is 2, R_1 is aryl, such as, for example, phenyl or naphthyl which can contain substituents such as halogen, lower alkyl, amide, lower alkoxy, hydroxy and the like.

The amount of amide solvent to developer is advantageously within range of about 1:1 to about 1:15 by weight, preferably 1:4 to 1:7. If used in conjunction with an oil solvent such as liquid inert esters, it may be mixed in any proportion. However, a particularly advantageous solvent mixture comprises at least 25% by weight of the developer solvent of our invention. The oil solvents for developers substantially water insoluble, low molecular weight, organic oils having boiling points above about 175° C.

One embodiment of our invention relates to a lithographic printing plate comprising a direct positive emulsion having therein a liquid amide such as, for example, diethyllauramide in which is dispersed a silver halide developing agent such as, for example, 4-phenyl catechol. This plate is exposed, processed in an alkaline activator solution and printed on a lithographic printing press giving a positive lithographic print.

In another embodiment of our invention, the emulsion as described above also contains an oil solvent such as, for example, tricresyl phosphate. The lithographic plate is exposed as above and used on a lithographic printing press to give a positive lithographic print.

Silver halide emulsions which are used in the practice of our invention include the conventional silver halide emulsions such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide and silver chlorobromoiodide.

In the practice of this invention, the ink receptive areas of the printing plates on a background of hydrophilic material are obtained by alkaline activation of a silver salt, preferably silver halide, developing agent in the presence of a gelatin, silver salt emulsion layer. The result is to form a silver image and oxidized developing agent in the region of development. The element can then be inked in the developed areas with greasy printing ink and a positive print made therefrom in a lithographic press. The gelatin in the emulsion layer can undergo additional hardening at the same time as development.

The developing agents employed in the practice of this invention include any developing agents which are capable of oxidation in the presence of the hardened gelatin present in the photographic emulsion layer to produce an image receptive to greasy printing ink, i.e. upon development, they render the gelatin in the developed areas oleophilic. The polyhydroxy benzene developing agents substituted with halogen, monocyclic aryl groups of the benzene series and alkyl groups of at least 2 and preferably from 2 to 6 carbon atoms have this property. The 1,2-dihydroxy benzene developing agents substituted by halogen, monocyclic aryl of the benzene series and alkyl groups of at least 2 carbon atoms and preferably 2 to 6 carbon atoms are particularly useful in the process. Developing agents possessing the necessary properties thus include certain polyhydroxy benzene developing agents such as pyrogallol and substituted polyhydroxy benzene developing agents, particularly dihydroxy benzenes substituted with, for example, halogen, alkyl groups of at least 2 and preferably from 2 to 6 carbon atoms and a monocyclic aryl group of the benzene series, e.g. o-chlorohydroquinone, o-bromohydroquinone, t-butyl hydroquinone, 4-phenyl catechol, 4-t-butyl catechol, pyrogallol, 4-n-butylpyrogallol, nordihydroguiauretic acid, 4,5-dibromo catechol, 3,3,6-tribromo-4-phenyl catechol and 1-phenyl-3-(N-n-hexylcarboxamide) - 4 - [p-(β-hydroquinolylethyl)phenylazo]-5-pyrazolone. Esters of such developing agents, e.g. formates and acetates of pyrogallol hydrolyze in alkaline solutions and can be used in the process of the invention. Such esters are intended to be included in the specification and claims where reference is made to polyhydroxy benzene developing agents. In certain cases, it has been found to be advantageous to include with the polyhydroxy benzene developing agent such as pyrogallol, an auxiliary developing agent such as monomethyl-p-aminophenol or a 3-pyrazolidone which latter developing agents by themselves do not yield oleophilic images in the processes described, but which do appear to act synergistically with the polyhydroxy benzenes to yield oleophilic images. The developing agents are generally employed in the photographic elements at coverages of about 5 to about 200, preferably about 10 to about 50 mg./ft.^{2} of support and are incorporated in a layer which is no farther from the support than the photographic emulsion layer, i.e. they are incorporated into the photographic emulsion layer or a layer between the emulsion layer and the support, e.g. an adjacent or contiguous layer.

It will be appreciated that the photographic emulsion layer may advantageously be a gelatin layer having a hardness depending upon the purpose for which the emulsion is intended. For instance, if the emulsion is to be used in a colloid transfer system such as that described in U.S. Pat. 2,596,756, issued May 13, 1952 to Yutzy et al., the emulsion is substantially unhardened. However, if the intended emulsion is to be used for preparing a printing plate of the type disclosed in U.S. Pat. 3,146,104, the emulsion layer should be substantially hardened in order to prevent the process plate from adhering to printing blankets, papers, etc. For this purpose, the emulsion should

be as hard as a gelatin layer containing at least about 2 grams and preferably about 2 to 15 grams of dry formaldehyde per pound of gelatin, i.e. it should have a melting point in water greater than 150° F. and preferably greater than 200° F.

Various colloids can be used either with gelatin or substituted for gelatin as vehicles or binding agents in the photographic emulsion layers employed in the practice of this invention. However, gelatin or gelatin derivatives which are primarily gelatin, are used for at least a part, for example, at least 10%, by weight, of the binder in the photographic element. Other binding agents which can be used with the gelatin or colloidal material such as colloidal albumin, cellulose derivatives, synthetic resins, such as polyvinyl compounds, acrylamide polymers, or the like. Although gelatin can be the sole binding agent, it is often advantageous to employ combinations of binding agents, particularly mixtures of gelatin with aqueous dispersions of polymerized ethylenically unsaturated compounds. The binding agent is generally coated at a coverage in the range of about 50 to 2000, advantageously about 100 mg. to about 1000 mg. per square foot of support.

Direct positive emulsions which may be used include (1) solarizing silver halide emulsions and (2) internal latent image silver halide emulsions forming the latent image mostly inside the silver halide grains.

The solarizing direct positive silver halide emulsions are silver halide emulsions which have been effectively fogged either chemically or by radiation, to a point which corresponds approximately to the maximum density of the reversal curve as shown by Mees, The Theory of the Photographic Process, published by Macmillan Co., New York, N.Y., 1942, pages 261–297.

Typical methods for the preparation of solarizing emulsions are shown by Groves British Pat. 443,245, Feb. 25, 1936 who subjected an emulsion to roentgen rays "until the emulsion layer, when developed without additional exposure, is blackened up to the apex of its gradation curve"; Szaz British Pat. 462,730, Mar. 15, 1937, the use of either light or chemicals such as silver nitrate, organic sulfur compounds and dyes to convert ordinary silver halide emulsions to solarizing direct positive emulsions; Arens U.S. Pat. 2,005,837, June 25, 1935, the use of silver nitrate and other compounds in conjunction with heat to effect solarization of the silver halide, and Leermakers U.S. Pat. 2,184,013, the use of large concentrations of non-acid optical sensitizing dyes and reducing agents to effect solarization.

Kendall and Hill U.S. Pat. 2,541,472, Feb. 13, 1951, shows useful solarizing emulsions particularly susceptible to an exposure with long wavelength light to produce a Herschel effect described by Mees above, produced by adding nitro substituted electron acceptors and other compounds to the emulsion which is fogged either chemically or with white light. In using the emulsions, a sufficient reversal image exposure is employed using minus blue light of from about 500–700 millimicrons wavelengths, preferably 520–540 millimicrons, to substantially destroy the latent image in the silver halide grains in the region of the image exposure. In this procedures, of course, only non-hardening chemicals are selected for use in fogging the solarizing emulsions if an emulsion is used requiring a given hardness.

Conventional silver halide developing solutions can be used to develop a direct positive image in the solarizing emulsions.

The internal latent image direct positive silver halide emulsions used in the invention are those well known in the art which upon exposure form the latent image mostly inside the silver halide grains, the direct positive properties of the emulsions being attributable to the crystalline structure of the silver halide grains. That is, a number of authorities in the field of photography have shown that there are imperfections or flaws, in the crystal structure (on the surface or internally) of silver halide which is used in photography, at which flaws the latent image forms by trapping photoelectrons to give development centers. Development, therefore, commences at the sites of these flaws. Journal of Photographic Science. "Photographic Sensitivity," text of a lecture given on July 1, 1957 by J. W. Mitchell; vol. 6, No. 3 (1958).

Other photographic reversal emulsions may be used including those containing grains comprising a central core of a water insoluble silver salt containing centers which promote the deposition of photolytic silver and an outer shell or covering for such core of a fogged or spontaneously developable water insoluble silver salt. The fogged shell of such grains is developed to silver without exposure. Emulsions of this type are described in Berriman U.S. Pat. 3,367,778, issued Feb. 6, 1968.

Before the shell of water insoluble silver salt is added to the silver salt core, the core forming emulsion is first chemically or physically treated by methods previously described in the prior art to produce centers which promote the deposition of photolytic silver, i.e., latent image nucleating centers. Such centers can be obtained by various techniques as described by Antoine Hautot and Henri Saubenier in Science et Industries Photographiques, vol. XXVIII, January 1957, pages 57–65, are particularly useful. Such chemical sensitization includes three major classes, namely, gold or noble metal sensitization, sulfur sensitization, such as labile sulfur compound and reduction sensitization, i.e. treatment of the silver halide with a strong reducing agent which introduces small specks of metallic silver into the silver salt crystal or grain.

The core forming emulsions can be chemically sensitized by any method suitable for this purpose. For example, the core forming emulsions can be digested with naturally active gelatin or sulfur compounds can be added to those described in Shepard U.S. Pat. 1,574,944, issued Mar. 2, 1926, Shepard et al. U.S. Pat. 1,623,499, issued Apr. 5, 1927 and Shepard et al. U.S. Pat. 2,410,689, issued Nov. 5, 1946.

The core forming emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Pat. 2,399,083, issued Apr. 23, 1946 and Damschroder et al. U.S. Pat. 2,642,361, issued June 16, 1953. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, aurictrichloride and 2-aurosulfobenzothiazole methylchloride.

The core forming emulsions can also be chemically sensitized with reducing agents, such as stannous salts (Carroll U.S. Pat. 2,487,850, issued Nov. 15, 1949), polyamines such as diethylenetriamine (Lowe and Jones U.S. Pat. 2,618,598, issued Aug. 15, 1950), polyamines such as spermine (Lowe and Allen U.S. Pat. 2,521,925, issued Sept. 12, 1950) or bis-(beta-aminoethyl)sulfide and its water soluble salts (Lowe and Jones U.S. Pat. 2,521,926, issued Sept. 12, 1950).

The shell of the grains comprising the emulsions used in practicing this invention is prepared by precipitating over the core grains a light sensitive water insoluble silver salt that can be fogged and which fog is removable by bleaching. The shell is of sufficient thickness to prevent access of the developer used in processing the emulsions of the invention to the core. The silver salt shell is surface fogged to make it developable to metallic silver with conventional surface image developing compositions. The silver salt of the shell is sufficiently fogged to produce a density of at least about 0.5 when developed for 6 minutes at 68° F. in Developer A below when the emulsion is coated at a silver coverage of 100 mg. per square foot.

DEVELOPER A

	Grams
N-methyl-p-aminophenol sulfate	2.5
Ascorbic acid	10.0
Potassium metaborate	35.0
Potassium bromide	1.0

Water to 1 liter
pH of 9.6

Such fogging can be effected by chemically sensitizing to fog with the sensitizing agents described for chemically sensitizing the core forming emulsion, high intensity light and like fogging means well known to those skilled in the art. While the core need not be sensitized to fog, the shell is fogged, for example, reduction fogged with a reducing agent such as stannous chloride. Fogging by means of a reduction sensitizer, a noble metal salt such as gold salt plus a reduction sensitizer, high pH and low pAg silver halide precipitating conditions, and the like can be suitably utilized. The shell portion of the subject grains can also be coated prior to fogging.

Another direct positive silver halide emulsion which can be used is a fogged direct positive silver halide emulsion comprising silver halide grains which have a uniform diameter frequency distribution, i.e. silver halide grains which have substantially uniform diameter. In one embodiment of this type of emulsion, the direct positive photographic emulsion comprises fogged silver halide grains, at least 95% by weight of said grains having a diameter which is within about 40% of the mean grain diameter. Preferably, photographic emulsions of this type comprise reduction and gold fogged silver halide grains and a compound which accepts electrons. The use of low concentrations of reduction and gold fogging agents, in preparing such emulsions gives unique fogged silver halide grains which are characterized by a very high photographic speed in conventional photographic processing solutions.

The photographic layers described herein can be superimposed upon a wide variety of supports. Typical flexible supports include those generally employed in printing plates, as exemplified by metals such as aluminum, paper, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyene terephthalate and related films or resinous materials and other related materials. Supports include paper which may be partially acetylated or coated with an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2–10 carbon atoms, as exemplified by polyethylene, polypropylene, ethylenebutene copolymers and the like give good results.

The photographic elements or printing plates of this invention can include antihalation layers which are generally coated between the photographic emulsion layer and the support. Suitable layers of this type include gelatin layers containing organic and inorganic dyes or pigments such as Naphthol Red dye, pigments such as colloidal carbon or silver, zinc oxide, titanium dioxide, iron oxide and the like which can be dyed, if desired, with such dyes as the merocyanines and the like, or paper coated with an alpha-olefin polymer employed as the support. It is also convenient to incorporate a dye and/or a pigment into the resin coating on the photographic emulsion side surface of the support which serves as an antihalation layer. In addition, the dyes and/or pigments can be on the same layer with the polyhydroxybenzene developing agent when it is coated in a layer beneath the photographic emulsion layer.

In the accompanying drawing representative sensitive elements of the invention are shown in greatly enlarged cross-sectional view at various stages of the preparation of lithographic printing plates. In FIG. 1 a negative-positive process is illustrated and in FIG. 2 is shown a positive-positive process contemplated by our invention.

In FIG. 1, layer **10** of the element of stage one represents a support such as paper, film base, etc. Layer **11** is a hydrophilic organic colloid layer such as gelatin containing the developing agent and silver halide.

In the process of FIG. 1, after exposure to a subject as shown in area **12**, followed by alkaline activation and inking, the element appears substantially as shown in stage two. Area **14** which is composed of silver and the reaction product of the oxidized developing agent and the hydrophilic organic colloid present in the silver halide emulsion layer produced in the development reaction, carries the ink image **15**. The undeveloped area **16** of layer **11** remains hydrophilic and repellent of printing ink when moistened with water.

In FIG. 2 is shown a positive-positive system in stage one of which the element included a support **20** such as a paper or film support, layer **23** comprising a fogged silver halide emulsion layer containing a developing agent. Upon image exposure in region **24**, followed by alkaline activation and inking, the element appears substantially as shown in stage two, the silver halide developing agent of layer **23** having developed a positive silver halide image to silver in areas **25** of layer **23**. The ink images **26** are accepted in areas **25** which are composed of silver and the reaction product of the organic hydrophilic colloid present in the silver halide emulsion layer and the oxidized developing agent. The remaining areas **27** are hydrophilic and repel printing ink when the plate is moistened in the lithographic printing press.

Positive working lithographic plates can be made using conventional negative speed photographic silver halide emulsions containing an oxidizing developer solvent dispersion of this invention by the use of a processing cycle comprising the following steps:

(1) Exposure.

(2) Negative development in a developer, such as Kodak D-72 Developer, containing at least 10 grams of sodium sulfite per liter followed by a rinse. These developed areas are hydrophilic. The oxidizing development agents are quite insoluble in the pH range and, consequently, are not washed out during this negative development.

(3) The element is then flashed to light of sufficient intensity to fog the remaining silver halide.

(4) Final development to obtain the oxidized, ink-receptive, positive image takes place by immersing the element in a sulfite-free, alkaline solution, e.g. 5% sodium carbonate.

(5) The surface solution is then removed with a squeegee, press fountain solution applied and the prints run on the lithographic press.

Our invention will be further illustrated by the following examples of preferred embodiments thereof although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLE 1

A control element (Sample A) is made up as follows:

Layer I—Developer dispersion preparation

Solution (1):
Carbon black—400 g.
5% wetting agent solution of p-tert-octyl-phenoxy ethoxy ethyl sulfonate-sodium salt—6300 ml.

The wetting agent is added to the carbon black and stirred until a smooth slurry is formed.

Solution (2):
4-phenylcatechol—630 g.
Tricresyl phosphate solvent—6300 g.

The 4-phenylcatechol is added to the solvent and heated at 220° F. until dissolved.

Solution (3):
Dry photographic gelatin—4000 g.
Distilled water—60,000 ml.

The gelatin is dissolved and melted at 140° F. Solutions (1) and (3) are blended and stirred for 5 minutes. Solution (2) is added and stirred for 5 minutes. The mixture is colloid milled three times.

MELT PREPARATION

7.6 kgs. of dry photographic gelatin is dissolved in 56.5 kgs. of distilled water and melted at 150° F. This is cooled to 107° F. and 75.72 kgs. of the above dispersion is added; also 2000 ml. of 5% of the above wetting agent is added and the combination is coated on polyethylene coated paper base. The coating is applied at 7.16 ml. per square foot giving 31.5 mg. of 4-phenyl-catechol per square foot.

Layer II

Green sensitized silver chloride emulsion (1 mole)—3300 g.
15% saponin solution—200 cc.
2% formaldehyde—40 cc.
Water—2460 g.

The coating is applied at 40° on Layer I at 15.0 cc./sq. ft.

Layer III

Gelatin silver chloride emulsion (1 mole)—3300 g.
Water—2000 cc.
0.25/N NaOH—240 cc.
2% formaldehyde—46 cc.

Hold for 40 minutes at 40° C. to fog, then add:

2.0/N H_2SO_4—35 cc.
15% saponin solution—100 cc.
Water—729 cc.

The coating is applied at 40° C. on Layer II at 45 mg. of Ag/sq. ft.

Four similar elements are made, differing only in that in these elements, diethyllauramide is used, at various concentrations, in place of the tricresyl phosphate solvent. Thus,

	G.
Sample B utilized	1260
Sample C utilized	3150
Sample D utilized	4400
Sample E utilized	6300

Each of samples B, C, D and E is compared to sample A which requires 17 seconds exposure in a press camera to give an acceptable print. Processing and printing are in a conventional manner used in the art.

Sample E—the 1:10 developer to diethyllauramide solvent coating requires 12 seconds
Sample D—the 1:7 developer to diethyllauramide solvent coating requires 12 seconds
Sample C—the 1:5 developer to diethyllauramide solvent coating requires 13 seconds
Sample B—the 1:2 developer to diethyllauramide solvent coating requires 15 seconds

A material made with a tricresyl phosphate dispersion to a 1:2 developer to solvent ratio will not give an acceptable print with any exposure. Better lithographic latitude as well as increased speed shown above, is observed in coatings utilizing diethyllauramide.

EXAMPLE 2

Undercoats are prepared by coating dispersions containing the following, on a polyethylene coated paper support:

	Developer,[1] mg./ft.^{2}	Solvent,[2] mg./ft.^{2}	Gelatin, mg./ft.^{2}
Sample:			
A	30	300	580
B	30	300	580
C	30	150	580
D	30	60	580

[1] Developer—4-phenylcatechol.

[2] Solvent—Tri-o-cresyl phosphate in Sample A diethyllauramide in Samples B, C, and D.

The undercoats are overcoated with a fogged direct positive emulsion and coated at 72 mg. silver/ft.^{2} and 215 mg. gelatin/ft.^{2}. The resulting coatings are exposed by exposing to a 40 watt bulb at 27 inches through a parallel line test object covered with a step tablet, processed for 20 seconds at 85° F. in an 8% potassium phosphate solution containing 0.1 g. KBr/liter and stopped for 20 seconds in a phosphoric acid bath.

- Sample A—the 1:10 weight ratio tricresyl phosphate material requires 100 seconds exposure to produce an acceptable print
- Sample B—the 1:10 weight ratio developer to solvent material requires 60 seconds
- Sample C—the 1:5 weight ratio developer to solvent material requires 60 seconds
- Sample D—the 1:2 weight ratio developer to solvent material requires 100 seconds

A material made with tricresyl phosphate at 1:2 ratio will not produce any result.

EXAMPLE 3

An element utilizing an autopositive emulsion is prepared incorporating a developer dispersion made from a ratio of 4-phenyl catechol to solvent as follows:

- Sample A—One part by weight developer to 7 parts diethyllauramide. The developer is employed at a level of 35 g./mole of Ag.
- Sample B—The 4-phenylcatechol is employed at a level of 21.4 grams per mole of silver in a weight ratio of 1 part to 7 parts diethyllauramide.
- Sample C—The developer dispersion contains 1 part by weight of 4-phenylcatechol to 15 parts of tricresyl phosphate. The developer is employed at a level of 35 g./mole of Ag.
- Sample D—The 4-phenylcatechol is employed at a level of 21.4 grams per mole of silver in a weight ratio of 1 part developer to 15 parts tricresyl phosphate.

NOTE: Sample A—required 55 seconds to make an acceptable print; Sample B—required 65 seconds to make an acceptable print; Sample C—required 130 seconds to make an acceptable print; Sample D—required 180 seconds to make an acceptable print.

EXAMPLE 4

A positive working presensitized lithographic printing plate is prepared using a reversal emulsion of the type described in Berriman U.S. Pat. No. 3,367,778, issued Feb. 6, 1968 in combination with polyhydroxybenzene developing agents located in an adjacent layer beneath the photographic emulsion layer. To the emulsion are added the various oil solvent dispersions of 4-phenylcatechol as described below. The emulsion containing the incorporated developer agent dispersions is then coated, at 440 ft. per silver mole, over a paper support which contains a sublayer of TiO_2 pigmented polyethylene and a backing layer of clear polyethylene.

- Sample A—The emulsion contains a dispersion of 60 grams of 4-phenylcatechol in 300 grams tricresyl phosphate solvent.
- Sample B—The emulsion contains a dispersion of 60 grams of 4-phenylcatechol in 300 grams dibutyl phthalate solvent.
- Sample C—The emulsion contains a dispersion of 60 grams of 4-phenylcatechol in 300 grams diethyllauramide solvent.
- Sample D—The emulsion contains a dispersion of 60 grams of 4-phenylcatechol in a combination of 240 grams of tricresyl phosphate solvent and 60 grams of diethyllauramide solvent.
- Sample E—The emulsion contains a dispersion of 60 grams of 4-phenylcatechol in 180 grams of tricresyl phosphate solvent and 120 grams of diethyllauramide solvent.
- Sample F—The emulsion contains a dispersion of 60 grams of 4-phenylcatechol in 120 grams of tricresyl phosphate solvent and 180 grams of diethyllauramide solvent.

The direct positive photosensitive elements obtained are exposed by projection to a line original in a conventional process camera. After 20 seconds' activation at 75° F. in an 8% potassium phosphate solution, the plates are

"stopped" in a phosphoric acid bath. The plates are then printed on a lithographic press giving a positive lithographic print.

The following results are obtained from the testing of the elements represented by Samples A–F above.

	Solvent (per 60 grams developer)	Printing speed (seconds)
Sample:		
A	300 grams tricresyl phosphate	120
B	300 grams dibutylphthalate	250
C	300 grams diethyllauramide	35
D	240 grams tricresylphosphate plus 60 grams diethyllauramide.	75
E	180 grams tricresyl phosphate plus 120 grams diethyllauramide.	60
F	120 grams tricresyl phosphate plus 180 grams diethyllauramide.	50

EXAMPLE 5

A dispersion containing 4-phenylcatechol dissolved in tricresyl phosphate is added to a fogged direct positive gelation silver chloride emulsion which is coated on a polyethylene paper support at 72 mg. of silver, 215 mg. of gelatin, 45 mg. of 4-phenylcatechol and 340 mg. of tricresyl phosphate/ft.^{2} (11). A similar coating without the dispersion is prepared as the control.

Similar coatings are made with the 4-phenylcatechol dissolved in Solvent B and coated at 48 mg. of silver, 150 mg. of gelatin, 30 mg. of 4-phenylcatechol and 240 mg. of Solvent B/ft.^{2} (13) and (12) as the control without the dispersion. Exposure and processing as in Example 1 gives similar improvements for coating 13; the following table shows the improvement in speed. An arbitrary value of 100 is to control and the other speeds are given relative to the control.

Solvent B is N,N,N',N'-tetraethyl phthalamide.

Coating Number	Solvent	Relative speed
10	Control	100
11	Tricresyl phosphate	11.2
12	Control	100
13	Solvent B	63

EXAMPLE 6

Dispersions containing 4-phenylcatechol, Solvent B and gelatin are coated on polyethylene coated paper support at the following coverages:

Coating Number	4-phenyl-catechol, mg./ft.^{2}	Solvent B, mg./ft.^{2}	Gelatin, mg./ft.^{2}
14			300
15	30	240	300
16	30	120	300
17	30	60	300

Solvent B is N,N,N',N'-tetraethyl phthalamide.

These coatings are overcoated with fogged direct positive gelatino silver chloride emulsion at 48 mg. Ag and 152 mg. of gelatin/ft.^{2}. Exposure and processing as in Example 1 gives the following speed differences.

Coating Number	4- Phenyl-catechol to Solvent B ratio	Relative speed
14		100
15	1:8	80
16	1:4	58
17	1:2	25

Relative speed is as defined in Example 5.

EXAMPLE 7

Positive working lithographic plates are made using conventional negative speed photographic silver halide emulsions containing the oxidizing developer solvent dispersions of this invention by the use of a processing cycle comprising the following steps:

(1) Exposure.

(2) Negative development in a developer, such as Kodak D–72 Developer, containing at least 10 grams of sodium sulfite per liter followed by a rinse. These developed areas are hydrophilic. The oxidizing development agents are quite insoluble in the pH range and, consequently, are not washed out during this negative development.

(3) The element is then flashed to light of sufficient intensity to fog the remaining silver halide.

(4) Final development to obtain the oxidized, ink-receptive, positive image takes place by immersing the element in a sulfite-free, alkaline solution, e.g. 5% sodium carbonate.

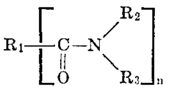
(5) The surface solution is then removed with a squeegee, press fountain solution applied and the prints run on the lithographic press.

By water insoluble developing agent is intended those which have a solubility of less than 5 gm. in one liter of water at 20° C. and preferably less than 1 gm. in one liter of water at 20° C.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A silver halide photographic emulsion containing a polyhydroxybenzene or substituted polyhydroxybenzene incorporated silver halide developing agent dissolved in a solvent comprising a normally liquid substituted amide of the general formula:



$$R_1-\left[\underset{\overset{\|}{O}}{C}-N\begin{matrix}R_2\\R_3\end{matrix}\right]_n$$

wherein *n* is an integer of 1 or 2, when *n* is 1, R_1 represents an alkyl group of at least four carbon atoms and when *n* is 2, R_1 is a divalent aryl group; wherein each R_2 and R_3 is hydrogen or lower alkyl from 1–4 carbon atoms.

2. A photographic emulsion of claim **1** in which said solvent contains 0–75% by weight of a substantially water insoluble, low molecular weight liquid ester having a boiling point above about 175° C. and having a high solvent action for said silver halide developing agent.

3. A silver halide emulsion of claim **1** in which said amide comprises a ratio of 1:1 to 1:15 developer to amide by weight.

4. A photographic element comprising a support having thereon said silver halide emulsion of claim **1**.

5. A photographic element of claim **4** in which said silver halide emulsion is a direct positive emulsion.

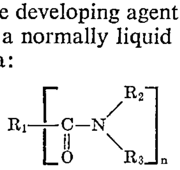
6. An emulsion of claim **1** in which said developing agent is a phenyl substituted polyhydroxybenzene.

7. An emulsion of claim **1** in which said developing agent is a 2–6 carbon atom containing alkyl substituted polyhydroxybenzene.

8. An emulsion of claim **1** in which said developing agent is a 4-phenylcatechol.

9. The emulsion of claim **1** in which said liquid solvent contains 25–100% by weight of said amide.

10. A photographic element comprising a support having thereon a silver halide photographic emulsion and intermediate to said emulsion a layer containing a polyhydroxybenzene or substituted polyhydroxybenzene incorporated silver halide developing agent dissolved in a liquid solvent comprising a normally liquid substituted amide of the general formula:



$$R_1-\left[\underset{\overset{\|}{O}}{C}-N\begin{matrix}R_2\\R_3\end{matrix}\right]_n$$

wherein *n* is an integer of 1 or 2, when *n* is 1, R_1 represents an alkyl group of at least four carbon atoms and when *n* is 2, R_1 is a divalent aryl group; wherein each R_2 and R_3 is hydrogen or lower alkyl from 1–4 carbon atoms.

11. A photographic element of claim **10** in which the said solvent contains 0–75% by weight of a substantially water insoluble, low molecular weight liquid ester having a boiling point above about 175° C. and having a high solvent action for the silver halide developing agent.

12. A silver halide element of claim **10** in which said amide comprises a ratio of 1:1 to 1:15 by weight developer to amide by weight.

13. A photographic element of claim **10** in which said solvent contains 25–100% by weight of the said amide.

14. A photographic element of claim **10** in which said silver halide emulsion is a direct positive emulsion.

15. An element of claim **10** in which said developing agent is a phenyl substituted polyhydroxybenzene silver halide developing agent.

16. An element of claim **10** in which said developing agent is a 2–6 carbon atom containing alkyl substituted polyhydroxybenzene silver halide developing agent.

17. An element of claim **10** in which said developing agent is a 4-phenylcatechol silver halide developing agent.

18. A photographic element of claim **10** in which the said layer is contiguous to a gelatin silver halide emulsion and contains a sufficient amount of a polyhydroxy benzene silver halide developing agent to develop the exposed silver halide in the said emulsion, said agent selected from the class consisting of halogen substituted, phenyl substituted and 2–6 carbon atoms containing alkyl substituted polyhydroxybenzene developing agents, the oxidation product of which renders gelatin oleophilic, said silver halide emulsion layer uniformly hardened with a hardener such that the emulsion has a hardness equivalent to that of a gelatin layer hardened with about 2 grams to about 15 grams of dry formaldehyde per pound of gelatin.

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J. TRAVIS BROWN, Primary Examiner

J. WINKELMAN, Assistant Examiner

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