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PHOTOGRAPHIC ELEMENTS, COMPOSITIONS AND PROCESSES

Herbert S. Elins and James P. Van Meter, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Continuation of abandoned application Ser. No. 787,616, Dec. 27, 1968. This application June 25, 1971, Ser. No. 157,056

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ABSTRACT OF THE DISCLOSURE

In photographic elements, compositions, especially emulsions, and processes an oleophilic complex of (a) a photographic addendum, especially a silver halide developing agent, with (b) an organic, Group V element oxide, which complex has the property of releasing the photographic addendum in the presence of an alkali provides reduced desensitization, improved latent image stability and improved photographic addendum release upon contact with alkali. Photographic elements, such as lithographic plates, containing an oleophilic complex of (a) a silver halide developing agent containing at least one hydroxyl group with (b) an organic phosphine oxide and/or an organic amine oxide are especially suitable. A wide range of photographic addenda can be employed, including, for instance, developing agents, filter dyes containing hydroxyl groups, couplers containing hydroxyl groups and the like. It is believed the moieties of the described complex are hydrogen bonded together.

This application is a continuation of application No. 787,616, filed Dec. 27, 1968 and now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photographic elements, compositions and processes. In one of its aspects this invention relates to photographic elements containing a photographic addendum, especially a silver halide developing agent in a complex providing reduced desensitization, improved latent image stability and improved photographic addendum release upon contact with an alkali. In another of its aspects it relates to photographic emulsions containing such a photographic addendum in a complex. A further aspect of the invention relates to a method of processing a photographic element containing a processing agent as described.

Description of the prior art

It is well known to employ photographic addenda, especially developing agents or so-called filter dyes in one or more layers of a photographic element. After exposure, the latent image in an element containing a developing agent can typically be developed by treating the elements with a suitable development activator such as an alkaline development activator solution which can, but need not, contain a developing agent. Following development the resulting image can be fixed or stabilized with conventional fixing or stabilizing compositions such as sodium thiosulfate or thiocyanate solutions. Typical elements containing incorporated processing agents, typically developing agents, are set out, for example, in U.S. Pat. 3,146,104 of Yackel and Abbott issued Aug. 25, 1964, relating to photographic elements employed in the graphic arts, especially lithographic printing plates; U.S. Pat. 2,596,756 of Yutzy and Yackel issued May 13, 1952 and U.S. Pat. 2,716,059 of Yutzy and Yackel issued Aug. 23, 1955,

relating to emulsions containing tanning silver halide developing agents, such as are applicable in colloid transfer processes; British Pat. 954,198 published Apr. 2, 1964, relating to photographic systems employing reducing agents but not silver halide systems; and U.S. Pat. 3,019,-108 of Dershowitz issued Jan. 20, 1962, relating to, for example, 2,5 - dihydroxyphenyl - triphenyl phosphonium halide and related phosphonium halides which can be incorporated in a photographic element useful in a diffusion transfer process. Also, photographic elements containing developing agents employed in rapid access processing or stabilization processing are set out, for example, in an article by H. D. Russell, E. C. Yackel and J. S. Bruce in Photographic Science and Technical Journal, August 1950, on pp. 59–62, entitled "Stabilization Processing of Film and Papers," as well as U.S. Pat. 2,448,857 of Bruce issued Sept. 7, 1958; U.S. Pat. 2,614,927 of Broughton et al. issued Oct. 21, 1952; U.S. Pat. 3,212,895 of Barbier et al. issued Oct. 19, 1955; and French Pat. 1,206,359. Photographic elements containing hydroquinone compounds in so-called dye-developer image transfer systems are described, for example, in U.S. Pat. 3,253,915 of Weyerts et al. issued May 31, 1966, and photographic elements containing hydroquinone compounds in image diffusion transfer processes are described, for example, in British Pat. 767,978 published Feb. 13, 1957. Further, photographic elements containing a filter dye are set out, for example, in U.S. Pat. 2,882,156 of Minsk issued Apr. 14, 1959.

In most cases it is necessary that the photographic addenda in the element, especially developing agents, not react prematurely with other components of the element, e.g., with photographic silver halide; that the element be stable in unexposed and/or undeveloped condition for extended periods under ambient keeping conditions; that the photographic addenda in the element not cause latent image instability or other undesired sensitometric properties; and, in some cases, that the photographic addenda be easily removed from the element. It is also essential that the photographic addenda in the presence of a suitable activator rapidly provide desired activity, e.g., in the case of a developing agent that the developing agent in the presence of an alkaline activator rapidly provide a suitable developed image. In many cases photographic elements containing, for example, developing agents and/or filter dyes have not provided this combination of properties. In some instances this has been due to undesired migration of a developing agent within and/or between one or more layers of the elements.

In other instances the so-called developer solvents, such as described in U.S. Patent 2,322,017 of Jelley and Vittum issued June 15, 1943, commonly employed in preparing coatings containing developing agents have not been entirely satisfactory. For instance, in preparing a lithographic printing plate, such as described in U.S. Patent 3,146,104 of Yackel and Abbott issued Aug. 25, 1964, a dispersion of tricresyl phosphate, which is a typical developer solvent, with 4-phenyl catechol, can provide undesired latent image instability.

In the case of materials for color photography, for example, it is common practice to employ a layer containing a yellow dye stuff, e.g., a so-called filter dye, or a layer containing yellow colloidal silver, e.g., a so-called CLS layer, to account for inherent sensitivity of silver halide to the blue region of the spectrum. It is desirable to provide a dye in such a layer which is non-wandering or non-migratory. Several methods have been proposed to provide this, such as dissolving the dye in a water immiscible oil and dispersing the resulting mixture in the emulsion to be used as the filter layer, or providing a group or groups, such as long chain alkyl groups, on the

dye molecule which provide non-wandering characteristics, or dispersing the dye in an emulsion employing basic mordants, as described, for example, in U.S. Patent 2,882,156 of Minsk issued Apr. 14, 1959. In some cases these have not been entirely satisfactory due to recrystallization of the dye upon addition to the colloid medium and/or, in the case of mordants, the mordant and/or mordanted dye being subject to wandering or diffusion within or between layers.

There has accordingly been a need for photographic elements, compositions and processes employing incorporated photographic addenda, especially developing agents and/or filter dyes, as complexes which have the described combination of properties. In particular there has been a need for complexes of developing agents with compounds which eliminate the need for use of a so-called developer solvent in, for example, a photographic emulsion, and which can provide suitable dispersions of the described developing agents for layers of photographic elements.

Accordingly, an object of the invention is to provide a photographic element which contains a photographic addendum especially a silver halide developing agent, as a complex and which provides the described combination of properties.

Another object of the invention is to provide an improved photographic emulsion containing a processing agent, especially containing a silver halide developing agent as a complex and which provides the described properties.

A further object of the invention is to provide an improved method of processing a photographic element containing a processing agent as a complex which provides release, especially rapid release, of the described processing agent in the presence of an activator, e.g., an alkaline activator solution.

SUMMARY OF THE INVENTION

According to the invention an oleophilic complex of (a) a photographic addendum, especially containing a hydroxyl and/or an amino group, especially a silver halide developing agent or filter dye, with (b) an organic Group V element oxide, which has the property of releasing, especially rapidly releasing, the described photographic addendum in the presence of alkali, provides reduced desensitization, improved latent image stability and improved photographic addendum release when used in elements, compositions or processes, especially in photographic elements and/or emulsions. An oleophilic complex of (a) a silver halide developing agent containing at least one hydroxy or amino group with (b) an organic Group V element oxide, especially an organic phosphine oxide and/or an organic amine oxide, which has the property of releasing the developing agent in the presence of alkali according to the invention not only provides reduced desensitization, improved latent image stability and improved developing agent release but also eliminates the need of a developer solvent commonly employed in elements containing a developing agent.

Also, an oleophilic complex of (a) a filter dye, especially one containing at least one group suitable for hydrogen bonding, e.g., at least one hydroxyl group, with (b) an organic Group V element oxide, especially an organic phosphine oxide, which has the described desired properties is also especially useful according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A wide range of organic Group V element oxides can be employed in the described oleophilic complexes according to the invention. These include any of the organic oxides of the Group V elements, i.e., the organic oxides of nitrogen, phosphorous, vanadium, arsenic, niobium, antimony, tantalum and/or bismuth which provide an oleophilic complex of (a) a photographic addendum, as described with (b) the described organic, Group V element oxide, which complex has the property of releasing, especially rapidly releasing the photographic addendum in the presence of alkali. These can be used alone or in combination.

These can include, for example, organic, Group V element oxides of the formula:

(I)



wherein R_1 and R_2 are individually selected from aryl, especially aryl containing up to 20 carbon atoms, e.g., 6 to 20 carbon atoms, such as phenyl, tolyl, xylyl and naphthyl; alkyl, such as alkyl containing 1 to 30 carbon atoms, including methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, and dodecyl; and



wherein R_4 and R_5 are the same or different alkyl, especially alkyl containing 1 to 5 carbon atoms, e.g., methyl, ethyl, propyl, butyl and pentyl, or aryl, as described; R_3 is hydrogen, alkyl or aryl, as described; and M is a Group V element, such as nitrogen, phosphorous, vanadium, arsenic, niobium, antimony, tantalum or bismuth, preferably nitrogen, phosphorous or arsenic. The alkyl and/or aryl groups can contain various substituents which do not adversely affect the described properties, especially the sensitometric properties of a photographic element when the Group V element oxide is employed in one or more layers of the element. Suitable substituent groups include amino, i.e., —NH_2(—NHR, or —NRR′ wherein R and R′ are alkyl containing 1 to 5 carbon atoms, as described, e.g., methylamino, ethylamino and dimethylamino; hydroxy, and the like.

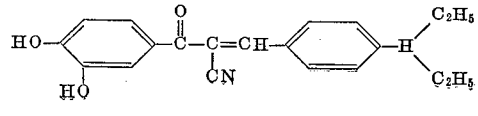
Examples of suitable Group V element oxides include organic phosphine oxides, e.g., triaryl phosphine oxides and trialkyl phosphine oxides, such as:

triphenyl phosphine oxide,
tributyl phosphine oxide,
trioctyl phosphine oxide, and
trihexyl phosphine oxide,

organic amine oxides, e.g., trialkyl amine oxides, such as: dimethyl dodecyl amine oxide, organic phosphoryl amides, such as described in U.S. Patent 2,756,252 of McKinnis issued July 24, 1956, e.g.: hexamethyl phosphoryl amide, and organic arsine oxides, e.g., triaryl arsine oxide, such as: triphenyl arsine oxide.

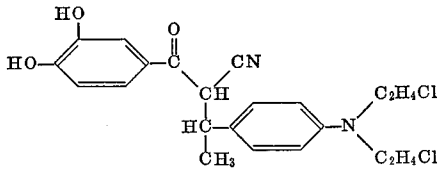
Also a wide range of photographic addenda can be employed according to the invention. Any photographic addendum can be employed which forms an oleophilic complex with the described Group V element oxide which complex has the property of releasing the photographic addendum in the presence of a suitable activator, especially alkali. Suitable photographic addenda include those which have groups suitable for hydrogen bonding with a Group V element oxide, as described, including developing agents as described, for example, on pages 282–295 of Mees, The Theory of the Photographic Process, 3rd Edition, 1966; couplers, described on pages 382–395 of the Mees reference, especially phenolic couplers; dyes, such as:

alpha-(p-diethylaminobenzylidene)-alpha-(3,4-dihydroxybenzoyl)-acetonitrile



and/or

2-(3,4-dihydroxybenzoyl)-3{4-[N,U-di(2-chloroethyl)]-amino-2-methylphenyl} acrylonitrile



and the like.

Any developing agent can be employed according to the invention which forms an oleophilic complex as described. These include, for example, polyhydroxybenzene developing agents such as hydroquinone developing agents, e.g., hydroquinone, alkyl substituted hydroquinones, such as t-butyl hydroquinone, methyl hydroquinone and 2,5-dimethyl hydroquinone; catechol and pyrogallol; chloro substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy hydroquinones such as methoxyhydroquinone or ethoxyhydroquinone; aminophenol developing agents, such as 2,4-diaminophenols, e.g., 2,4-diaminophenol or 2,4-diamino-6-methylphenol, methylaminophenols; ascorbic acid, ascorbic acid ketols such as those described in U.S. Pat. 3,337,342 of Green issued Aug. 22, 1967; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4,4-dimethyl - 1 - phenyl-3-pyrazolidone, including those described in British Pat. 930,572; and acyl derivatives of p-aminophenol such as described in British Pat. 1,045,303. These can be used alone or in combination.

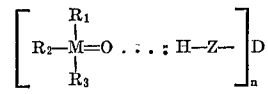
An oleophilic complex, as described, can be prepared using various methods, but is typically prepared employing the method described in an article by F. Ramirez and S. Dershowitz, Journal of Organic Chemistry, vol. 24, pages 704–705 (1959). For example, an oleophilic complex can be prepared by fusing a mixture of the organic, Group V element oxide with the photographic addendum, especially a polyhydroxybenzene developing agent. Suitable concentrations, temperature, pressure, and reaction conditions will vary depending upon the particular Group V element oxide and photographic addendum. A typical concentration range is about 0.5 to about 4 moles of organic Group V element oxide with each mole of photographic addenum. For instance, in the case of an organic phosphine oxide and a polyhydroxybenzene developing agent, a concentration ratio of about 2 moles of organic phosphine oxide to about 1 mole of polyhydroxybenzene developing agent is usually sufficient. A second method of preparing the described complexes consists of preparing an alcoholic solution of the described organic, Group V element oxide, especially an organic phosphine oxide, with the described photographic addendum, e.g., a polyhydroxybenzene developing agent or filter dye containing hydroxyl groups, in the desired molar ratio and then adding water to the alcoholic solution to separate the desired complex. Various alcohols can be employed, such as methanol, ethanol and butanol. In most cases the complexes described, especially the complexes of organic phosphine oxides with polyhydroxybenzene developing agents, are soluble in aromatic hydrocarbon solvents, e.g., benzene, toluene and cyclohexane, whereas the polyhydroxybenzenes alone are usually slightly soluble, if at all, in such solvents. The molar ratio of organic Group V element oxide to photographic addendum can vary employing this method, but usually the moles of Group V element oxide employed corresponds to the number of groups of the photographic addendum, such as hydroxyl or amino groups, suitable for hydrogen bonding. For example, in the case of an organic phosphine oxide and a hydroquinone or catechol developing agent, about 2 moles of organic phosphine oxide is typically employed for each mole of hydroquinone or catechol. Ratios outside these can also be employed.

Oleophilic is employed herein in its usual meaning, i.e., the complex described has an affinity for oils or fats. The complex is compatible with binders typically employed for photographic elements, e.g., gelatin and materials as described.

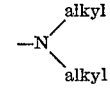
In preparing dispersions of the described complexes in a colloid, e.g., those typically employed in preparing layers of a photographic element, it is suitable to heat a mixture of the Group V element oxide, e.g., an organic phosphine oxide or organic amine oxide, with the described photographic addendum until fusion takes place. Typically the resulting fused composition is a water insoluble oil. The fused composition is then dispersed in the colloid employing suitable mixing means, e.g., a colloid mill.

If desired, the described complexes used in the practice of the invention can be prepared and/or used in combination with a developer solvent, such as those commonly employed in the photographic art for dispersions of developing agents or color couplers in emulsions for photographic elements. These include oleophilic so-called coupler solvents, as described, for example in U.S. Pat. 2,304,940 of Mannes et al. issued Dec. 15, 1942 and U.S. Pat. 2,322,027 of Jelley et al. issued June 15, 1943. Suitable developer solvents which can be employed in combination with the described complexes include, for example, tricresyl phosphate, dibutyl phthalate, N,N-diethyl lauramide, and N,N-tetraethyl phthalamide.

The exact structure of the described complexes employed in the practice of the invention is not fully understood. It is believed from analytical data that the complexes are hydrogen bonded and it is believed that they can be represented by the formula:

(II) 

wherein R_1, R_2 and R_3 are as described for Structure I; H—Z—D is a photographic addendum moiety, e.g., H—Z—D is a filter dye or developing agent, wherein H—Z is a group which is suitable for hydrogen bonding, especially —OH or —NH_2; n is a whole number, typically up to about 3, usually 1–2, and the dotted line is a hydrogen bond. An especially suitable complex of Formula II is one in which M is phosphorous, R_1, R_2 and R_3 are individually selected from phenyl, alkyl containing 1–20 carbon atoms or dialkylamino containing 1 to 5 carbon atoms, i.e.,



wherein alkyl is methyl, ethyl, propyl, butyl or pentyl; Z is oxygen or —NH—; D is phenyl; and n is 1–2.

Typical complexes useful in photographic elements, compositions and processes described, include, for example, complexes of:

(a) trioctyl phosphine oxide with 4-phenyl catechol,
(b) trioctyl phosphine oxide with hydroquinone,
(c) trioctyl phosphine oxide with 2,4-diamino phenol,
(d) trioctyl phosphine oxide with t-butyl hydroquinone,
(e) trioctyl phosphine oxide with trimethyl(1-phenyl-5-tetraazolylthio)hydroquinone,
(f) trioctyl phosphine oxide with 4-methylphenyl hydroquinone (also known as tolyl hydroquinone),
(g) tributyl phosphine oxide with 4-phenyl catechol,
(h) tributyl phosphine oxide with hydroquinone,
(i) trioctyl phosphine oxide with alpha-(p-diethylaminobenzylidene) - alpha - (3,4-dihydroxybenzoyl)-acetonitrile,
(j) trioctyl phosphine oxide with 2-(3,4-dihydroxybenzoyl) - 3 - {4-[N,N-di(2-chloroethyl)]amino-2-methylphenyl}acrylonitrile,
(k) dimethyl dodecyl amine oxide with 4-phenyl catechol,
(l) triphenylarsine oxide with 4-phenyl catechol,

(m) trihexylphosphine oxide with 4-phenyl catechol,
(n) trihexylphosphine oxide with hydroquinone, and
(o) trihexylphosphine oxide with 4-methylphenyl hydroquinone.

It is preferable that when employing complexes of an organic, Group V element oxide, especially an organic phosphine oxide or organic amine oxide, with a developing agent containing hydroxyl groups, as described, especially a polyhydroxybenzene developing agent that the percentage of free hydroxy groups in the complex be below about 20% for a complex employed in the practice of the invention, containing a ratio of one mole of Group V element oxide for each two moles of processing agent containing 2 hydroxyl groups.

Low percentage of free hydroxyl is one parameter useful in determining a suitable complex according to the invention. A test suitable for determining free hydroxyl groups in the described complexes is set out in an article by S. Mizushima et al., Spectrochemica Acta, vol. 7, page 107, (1955). For example, the percent free hydroxyl of the described complex using 4-phenyl catechol as a processing agent is determined by measuring the optical density at a wavelength of 3613 $cm.^{-1}$ of a solution of 4-phenyl catechol in CCl_4, i.e., 0.08% by weight of 4-phenyl catechol per part by volume CCl_4, complexed with varying concentrations of the Group V element oxide. The infrared absorption of the solution shows a sharp peak at 3613 $cm.^{-1}$ characteristic of free hydroxyl groups, i.e., hydroxy groups which are not hydrogen bonded or bonded in some other manner to another moiety in such a solution. The optical density at this wave length follows Beer's law with varying concentration. Higher concentrations of Group V element oxide in the complex, and accordingly, in the CCl_4 solution, provides reduction of optical density monotonically at this wave length. At the same time an absorption band at 3200–3400 $cm.^{-1}$ develops which is not as sharp as the peak at 3613 $cm.^{-1}$. This band at 3200–3400 $cm.^{-1}$ is characteristic of hydroxyl groups which are hydrogen bonded, and particularly hydroxyl groups of a polyhydroxybenzene developing agent hydrogen bonded to an organic Group V element oxide. The tests are carried out, employing a commercially available infrared spectrophotometer, at 35° C. Employing this test and 4-phenyl catechol as a processing agent, the complexes employed according to the invention, especially complexes of 4-phenyl catechol with an organic phosphine oxide, organic arsine oxide and/or organic amine oxide provide surprisingly lower percent free hydroxyl and, in turn, higher hydrogen bonded hydroxyl than combinations of compounds used for preparing dispersions of developing agents in emulsions employed before now, e.g., surprisingly lower free hydroxy than combinations of 4-phenyl catechol with tricresyl phosphate or dibutyl phthalate. This is demonstrated in following Example 2.

Hydrogen bonding, as described, is a well known term and phenomena. Hydrogen bonding is discussed in the book by Pimentel and McClellan entitled, The Hydrogen Bond, W. H. Freeman and Co., San Francisco, 1960, pages 1–9, 67–81, 142–166 and 193–201. Hydrogen bonding is also discussed in the book, The Nature of the Chemical Bond, by L. Pauling, Cornell University Press, 1960, Chapter 12, pages 449–503.

The described oleophilic complexes of the invention are suitable in a range of physical locations in photographic materials. They can be employed in one or more layers of a photographic element and/or in a processing composition if desired. For example, they can be employed in a layer such as a photographic silver salt emulsion layer, especially a silver halide emulsion layer and/or an overcoat layer and/or undercoat layer of a photographic element. They can also be employed in developer compositions such as solid developer compositions or developer solutions or concentrates, including aqueous solutions and/or mixtures or solutions containing non-aqueous solvents such as alcohols including, for example, methanol, ethanol, ethylene glycol and propanol. The described complexes can be employed in photographic elements and/or image receivers and/or processing compositions intended for use in diffusion transfer materials.

The described oleophilic complexes can be employed in elements and/or processing compositions in any suitable form for developing or otherwise processing an exposed photographic element. For example, they can be employed as mixtures, such as mixtures of the described oleophilic complexes of the invention with various processing agents. They can be employed as components of a solid particulate composition suitable for dissolving in or mixing with a solvent such as an aqueous solvent; as a viscous composition containing various thickening agents; as a packaged component kit for mixing of various processing agents or as a component of a fusible solid such as a solid containing an alkylene oxide polymer, which melts above about room temperature and the like. The described complexes can be employed in one or more layers of a photographic element.

One embodiment of the invention accordingly comprises in an element comprising a support having a layer containing a photographic addendum the improvement comprising an oleophilic complex of (a) the photographic addendum, as described, with (b) an organic Group V element oxide, wherein the complex has the property of releasing, especially rapidly releasing, the photographic addenda in the presence of alkali.

According to this embodiment, the invention includes in an element comprising a support having a layer containing a photographic addendum, as described, which is a silver halide developing agent containing at least one hydroxyl or amino group the improvement comprising an oleophilic complex of (a) a silver halide developing agent with (b) an organic Group V element oxide, the complex having the property of releasing the developing agent in the presence of alkali.

Typically the described element is a photographic element containing a photographic silver salt. Various photographic silver salts can be used in the practice of the invention. These include photographic silver halides such as silver iodide, silver bromide, silver chloride, as well as mixed halides such as silver bromoiodide, silver chloroiodide and the like. High contrast photographic silver halide emulsions are suitable, such as those containing at least 50 mole percent chloride.

The complexes described can be employed in a wide range of photographic emulsions in photographic systems and/or can be employed for processing an image in a wide range of photographic emulsions. Typically the emulsion is a photographic silver halide emulsion, but other emulsions are also suitable, such as emulsions which contain a photographic component other than photographic silver halide, e.g., titanium dioxide.

The photographic emulsions employed can be X-ray or other non-spectrally sensitized emulsions or they can contain spectral sensitizing dyes such as described in U.S. Pat. 2,526,632 of Brooker et al., issued Oct. 24, 1950 and U.S. Pat. 2,503,776 of Sprague issued Apr. 11, 1950. Spectral sensitizers which can be used include cyanines, merocyanines, styryls and hemicyanines.

Accordingly, another embodiment of the invention is in a photographic emulsion comprising a photographic addendum the improvement comprising an oleophilic complex of (a) a photographic addendum with (b) an organic, Group V element oxide, which complex has the property of releasing the photographic addendum in the presence of an alkali.

The use of the described complexes of the invention in a photographic direct positive emulsion has been found especially suitable.

Typically a photographic emulsion according to the invention comprises a photographic salt especially a pho-

tographic silver salt and an oleophilic complex of (a) a silver halide developing agent containing at least one hydroxyl or amino group with (b) an organic, Group V element oxide the complex having the property of releasing the developing agent in the presence of an alkali. Photographic developing agents which are especially useful are polyhydroxybenzene silver halide developing agents, as described. Group V element oxides, which have been found especially useful, are organic phosphine oxides and organic amine oxides, as described.

Coatings containing a complex used in the practice of the invention, especially photographic coatings, can be used on a wide variety of supports. Suitable supports include those generally employed for photographic elements, such as for example, cellulose acetate films, cellulose nitrate films, polyethylene terephthalate films or other polyester films, polycarbonate films and relating films or resinous materials; as well as papers, such as paper supports coated with resinous materials, e.g., coated with polyethylene, polypropylene and/or ethylene-butene copolymers; glass; metal and the like. The supports and/or layers coated on them can contain fluorescent brightening agents such as stilbenes, benzoazoles and benzoxazoles.

The photographic elements and/or emulsions according to the invention typically contain one or more layers comprising any of the known binding materials generally employed in the photographic art, such as gelatin, colloidal albumin, water soluble polymers, mono and polysaccharides, cellulose derivatives, various proteins, water soluble polyacrylamides, polyvinyl pyrrolidone and the like, as well as mixtures of such binding agents. The binding agents can also contain water insoluble polymers, such as polymerized ethylenically unsaturated compounds, e.g., polymers of acrylates and methacrylates, sulfoalkyl acrylates and methacrylates. The elements can also contain stripping layers and/or antistatic layers if desired.

The described complexes used according to the invention can be employed in combination with addenda, not part of the described complexes, known in the art to be useful in photographic elements and/or for processing photographic elements. For instance, the photographic emulsions in compositions of the invention can contain various photographic addenda particularly those known to be beneficial in photographic compositions. Suitable photographic addenda include hardeners such as those set out in British Pat. 974,317 issued Nov. 4, 1964; buffers which maintain the desired processing activity and/or pH level; coating aids; plasticizers; speed increasing addenda such as amines, quaternary ammonium salts, sulfonium salts and alkylene oxide polymers; and various stabilizing agents such as sodium sulfite.

The photographic silver salt emulsions of the invention can be chemically sensitized with compounds of the sulfur group, such as sulfur, selenium and tellurium sensitizers, noble metal salts, such as gold, or reduction sensitized with reducing agents or combinations of such materials.

A photographic element and/or composition according to the invention can also contain coating aids such as for example, polyvinyl inorganic salts of the type described in U.S. Patent 2,698,236 of Land issued Dec. 28, 1954; silica as described in U.S. Patent 2,698,237 of Land issued Dec. 28, 1964; and heterocyclic mercaptans such as mercaptoazoles, e.g., mercaptodiazoles, mercaptotriazoles and mercaptotetrazoles.

The described complexes employed according to the invention can also be used in photographic elements and/or processing compositions intended for use in monobath processing such as described in U.S. Patent 2,875,048 of Haist et al. issued Feb. 24, 1959 and British Patent 1,063,844 of Beavers et al. issued Mar. 30, 1967 and/or in so-called web type processing such as described in U.S. Patent 3,179,717 of Tregillus et al. issued Apr. 20, 1965.

The described oleophilic complexes can also be employed in photographic elements designed for processing in stabilization type processing. For example, they can be incorporated in one or more layers of a photographic element which is exposed, activated by contact with an alkaline activator and then contacted with a thiocyanate or thiosulfate stabilizer solution, such as ammonium thiocyanate. Such processes are described, for example, in U.S. Patent 3,326,864 of Nishio issued June 20, 1967; British Patent 1,004,302; French Patent 1,516,556; and in an article by H. D. Russell, E. C. Yackel and E. G. Grouse in the PSA Journal, August 1950, pages 59–62 entitled, "Stabilization Processing of Films and Papers."

The described complexes can be used according to the invention in one or more layers of a photographic element designed for recording color images and/or in processing compositions employed with such elements. For example, these compounds can be employed in one or more layers of a photographic element containing a photographic layer sensitive to the blue region of the spectrum, e.g., about 400 to 500 millimicrons, a photographic layer sensitive to the green region of the spectrum, e.g., about 500 to 600 millimicrons and a photographic layer sensitive to the red region of the spectrum, e.g., about 600 to 700 millimicrons. The layers sensitive to the blue, green and red regions of the spectrum can contain any suitable sensitizing dyes. Photographic elements designed for recording color images in which and/or for which the described complexes of the invention are useful are described, for example, in Mees, The Theory of the Photographic Process, 3rd Edition, (1966) pages 382–396.

Another embodiment of the invention is in a photographic process comprising developing a latent image in a photographic element employing a photographic addendum, as described, in the presence of an alkali the improvement comprising employing an oleophilic complex of (a) the photographic addendum, typically a photographic developing agent with (b) an organic Group V element oxide, said complex having the property of releasing the photographic addendum in the presence of alkali. In this process the photographic element typically contains the described oleophilic complex.

According to this embodiment a photographic process can comprise developing a latent image in a photographic element comprising a photographic silver salt and a silver halide developing agent in the presence of an alkali, employing an oleophilic complex of (a) the silver halide developing agent with (b) an organic Group V element oxide, the complex having the property of releasing the developing agent in the present of alkali. For example, according to this process, the oleophilic complex of (a) a polyhydroxybenzene developing agent, as described, with (b) an organic Group V element oxide which is:

triphenyl phosphine oxide,
tributyl phosphine oxide,
trioctyl phosphine oxide,
trihexyl phosphine oxide,
dimethyl dodecyl amine oxide, and/or
triphenyl arsine oxide,

can be contacted with a suitable alkali.

A wide range of activators, especially alkalies, can be employed for causing rapid release of the processing agent from the described oleophilic complexes. These include any alkali which provides a pH of about 8 to about 14, typically a pH of about 10 to about 14. Suitable alkaline materials include those commonly employed in the photographic art as development activators such as inorganic alkalies, e.g., alkali metal hydroxides including sodium hydroxide, potassium hydroxide and lithium hydroxide, alkali metal carbonates such as sodium carbonate, sodium bicarbonate and the like, as well as organic alkalies such as organic amines and amino alkanols, e.g., ethanol amine, iminodiethanolamine and/or morpholine. A suitable con-

centration of alkali can vary depending on the components of the system, the photographic emulsion employed, processing conditions, the desired image and the like. A concentration is usually employed which provides the desired pH. Materials which release alkali, such as release alkali upon heating, can also be employed.

The concentrations of the described complexes used in the practice of the invention can vary over wide ranges depending on the particular photographic and physical variables present in the system, for example, the location of the described complex in the photographic element, the developer composition, the desired image, etc. Suitable concentrations are also dependent on processing conditions, addenda present in the photographic element and/or processing compositions. Typically, when a complex of a developing agent with an organic, Group V element oxide is employed according to the invention in a photographic element, the developing agent is employed in a concentration which corresponds to about 0.1 to about 5 moles of developing agent per mole of silver present in the photographic element.

It is often advantageous to employ an antifoggant with and/or as a part of the described complexes used in the practice of the invention. Such antifoggants can be employed in compositions employed according to the practice of the invention and/or in photographic elements processed according to the invention. Suitable antifoggants include organic antifoggants such as benzotriazole, benzimidazole, 2 - mercaptobenzimidazole, nitroindazole and mercaptotetrazole antifoggants. Suitable antifoggants also include inorganic antifoggants such as potassium bromide, potassium iodide and/or sodium bromide. The concentration of antifoggant in either the processing composition or element employed according to the invention can vary depending on the desired image, other components present, subsequent processing steps and the like. A processing composition employed according to the invention typically contains less than about 2% by weight of the antifoggant and usually in the range of about 0.01 to about 2% by weight of the antifoggant.

Processing conditions employed according to the invention can vary depending on the desired image, the particular photographic element processed, the particular complex employed according to the invention and the like. Typically elements containing the described complex are processed under ambient conditions such as at about room temperature and pressure, e.g., about 19 to about 30° C. and atmospheric pressure. Conditions outside these can be employed if desired. Time of processing also can vary depending on the described factors. Normally a desired image can be provided in about a few seconds up to about several minutes or more.

The described complexes are especially useful in preparing and using lithographic printing plates, such as described in U.S. Pat. 3,146,104 of Yackel and Abbott issued Aug. 25, 1964. Typically a lithographic printing plate employing the complexes described is prepared by incorporating the described complexes in a photographic silver halide emulsion or in a layer contiguous to the emulsion. The resulting element is exposed and treated with an alkaline solution, which may contain a developing agent. In the resulting development reaction the processing agent moiety of the described complexes, especially a developing agent moiety, is oxidized in the presence of the hydrophilic organic colloid vehicle typically employed in the silver halide emulsion. This results in formation of an oleophilic image, i.e., an ink receptive image. Upon moistening the resulting lithographic printing plate, then inking the moistened plate and printing on a lithographic printing press, a desired lithographic reproduction which will be a negative of the original subject is obtained.

A so-called positive lithographic plate can be prepared in a similar manner containing a so-called fogged silver halide emulsion, typically as the upper most layer of the lithographic printing plate. This photographic element when exposed and activated with an alkaline solution causes the developing agent to react with the sensitive silver halide emulsion layer to form a negative image. Unused silver halide developing agents present in the unexposed areas of the lower silver halide emulsion layer migrate upward to the fogged, surface, silver halide emulsion layer and when oxidized in the presence of the hydrophilic colloid typically present in the layer form an oleophilic image in the surface which is positive with respect to the original subject.

A positive lithographic plate can also be obtained using a so-called direct-positive emulsion such as described in U.S. Pat. 2,541,472 of Kendall and Hill issued Feb. 13, 1951 or U.S. Pat. 2,497,875 of Fallesen issued Feb. 21, 1950.

In preparing a lithographic printing plate, as described, it is preferable to employ a silver halide developing agent as the photographic addendum moiety of the described oleophilic complexes. This developing agent is preferably one which is capable of oxidation in the presence of the hydrophilic organic colloid typically present in the silver halide emulsion layer to produce an image receptive to greasy printing ink. Such developing agents include, for example, certain polyhydroxybenzene developing agents and their esters such as pyrogallol and polyhydroxybenzene developing agents containing alkyl groups having at least 2 and preferably from 2 to 6 carbon atoms, e.g., ethyl, propyl, butyl, pentyl and hexyl groups, chloro polyhydroxybenzene developing agents, such as ortho-chloro hydroquinone, orthobromo hydroquinone; 4-phenyl catechol, 4-tertiary-butyl catechol and the like. Suitable developing agents of this type are described, for example, in U.S. Pat. 3,146,104 of Yackel and Abbott issued Aug. 25, 1964.

The described oleophilic complexes can be employed according to the invention in so-called colloid transfer processes as described, for example, in U.S. Pat. 2,716,059 of Yutzy et al. issued Aug. 23, 1955 and U.S. Pat. 2,596,756 of Yutzy et al. issued May 13, 1952. In such a process a photographic element containing an unhardened silver halide emulsion and also containing a complex as described, such as a tanning and non-tanning developing agent moiety, is exposed and subsequently developed employing an alkali. The resulting unhardened portions of the photographic emulsion can be transferred to a suitable matrix by transfer of the colloid.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

This illustrates the invention.

1.0 g. of 4-phenyl catechol is mixed with 4.0 g. of trioctylphosphine oxide. The mixture is gently heated to form a water insoluble oil which is the desired complex. This complex is dispersed in an aqueous solution of gelatin by means of a colloid mill. The dispersion is added to a fogged direct-positive gelatino silver chloroiodide emulsion and the mixture is coated on a paper support at 72 mg. of silver per square foot, 215 mg. of gelatin per square foot, 45 mg. of 4-phenyl catechol per square foot and 180 mg. of trioctylphosphine oxide per square foot. This photographic element is designated as Product A. An identical product is prepared as Product A. This is designated as Product B.

A control coating is prepared exactly like Product A with the exception that no 4 - phenyl catechol or trioctylphosphine oxide is employed. The resulting product is designated as Product C.

Product A and Product C are sensitometrically exposed

and the resulting latent image is immediately developed by immersion for 15 seconds in the following developer:

	G.
N-methyl-p-aminophenol, sulfate	3.0
Sodium sulfite, desiccated	45.0
Hydroquinone	12.0
Sodium carbonate monohydrate	80.0
Potassium bromide	2.0

Water to 1 liter.

An image is developed in both Product A and Product C. Products A and C have relative speeds respectively of 60 and 100. Product B is sensitometrically exposed and the resulting latent image is developed the same as Products A and C but one hour after exposure. The relative speed of Product B is 76. This demonstrates that the described complex provides desired latent image stability.

This also illustrates that a complex of a developing agent with an organic phosphine oxide can be employed according to the invention in a photographic emulsion without use of an auxiliary developer solvent.

EXAMPLE 2

This is a comparative example.

A photographic element is prepared exactly like Products A, B and C in Example 1 with the exception that 1.0 g. of 4-phenyl catechol is dispersed in 6.0 g. of tricresyl phosphate in place of trioctylphosphine oxide. The resulting emulsion coating contains 360 mg. of tricresyl phosphate per square foot. This is designated as Product D. An identical product to Product D is prepared. This is designated as Product E.

Product D is exposed and the resulting latent image immediately developed as set out in Example 1. The resulting product has a relative speed of 16. Product D is sensitometrically exposed the same as Product C but the resulting latent image is developed one hour after exposure. The relative speed of Product D is 47.

This demonstrates that Products A and B of the invention as described in Example 1 provide reduced desensitization and greater latent image stability than known Products D and E.

EXAMPLE 3

This illustrates the invention.

1.0 g. of 4-phenyl catechol is mixed with 1.23 g. of dimethyldodecyl amine oxide. The mixture is dissolved with heating in 8.0 g. of tricresyl phosphate. This is dispersed in an aqueous solution of gelatin by means of a colloid mill. The dispersion is added to a fogged direct-positive gelatino silver chloroiodide emulsion and the mixture is coated on a paper support at 72 mg. of silver per square foot, 215 mg. of gelatin per square foot and 45 mg. of 4-phenyl catechol per square foot.

The resulting photographic element is sensitometrically exposed and the resulting latent image is developed by immersion for 15 seconds in the developer described in Example 1. A good stable image is developed.

EXAMPLE 4

This illustrates the invention.

A photographic element is prepared the same as Product A of Example 1 with the exception that 3.2 g. of trihexylphosphine oxide is employed in place of trioctylphosphine oxide to prepare a mixture with 1.0 g. of 4-phenyl catechol. The product contains 144 mg. of trihexylphosphine oxide per square foot. This is designated as Product F. An identical product to Product F. is prepared. This is designated as Product G.

Control coatings are prepared exactly like Products F and G with the exception that 4-phenyl catechol and trihexylphosphine oxide are omitted. These are designated as Products H and I.

Both Product F and Product H are sensitometrically exposed and the resulting latent image immediately developed as described in Example 1.

Both Product G and Product I are sensitometrically exposed and the resulting latent image developed like Products F and H with the exception that the latent image is developed one hour after exposure.

An image is developed in each product. The relative speed of Products F, G, H and I are respectively 78, 100, 100, 118. This demonstrates that the described complex provides desired latent image stability.

EXAMPLE 5

This illustrates the invention.

A photographic element is prepare the same as in Example 3 with the exception that 1.8 g. of triphenylarsine oxide is employed in place of dimethyldodecyl amine oxide. The resulting element which contains 81 mg. per square foot of triphenylarsine oxide is sensitometrically exposed and the latent image developed as described in Example 3.

A good image is developed.

EXAMPLE 6

This illustrates preparation of a complex employed in the practice of the invention.

0.93 g. of 4-phenyl catechol and 1.39 g. of triphenylphosphine oxide are dissolved in 10 ml. of methanol. The solution is evaporated at room temperature leaving a yellow oil. This yellow oil is saturated with a few drops of water to provide a white precipitate which is recrystallized from a mixture of toluene and ligroin. This white solid melts at 108° C. and is identified by elemental and infrared spectral analysis as a complex of 4-phenol catechol with triphenylphosphine oxide in the molar ratio of 1:1.

EXAMPLE 7

This illustrates the invention.

1.0 g. of 4-phenyl catechol and 1.63 g. of tri-phenylphosphine oxide are dissolved in 4.0 g. of N-diethyl lauramide with heating. The resulting oil is dispersed in an aqueous solution of gelatin by means of a colloid mill. The dispersion is added to a fogged direct-positive gelatino silver chloroiodide emulsion and coated on a paper support at 72 mg. of silver per square foot, 215 mg. of gelatin per square foot and 45 mg. of 4-phenyl catechol per square foot.

This is sensitometrically exposed and the latent image developed as described in Example 1. A good stable developed image results.

EXAMPLE 8

This is a comparative example.

A product is prepared, as in Example 7 with the exception that the described phosphine oxide is omitted from the photographic element. The resulting positive image has significantly lower relative speed than the developed image of a photographic element of the invention as set out in Example 7.

EXAMPLE 9

This illustrates the invention.

1.0 g. of tolyl hydroquinone is mixed with 3.8 g. of trioctylphosphine oxide. The mixture is gently heated to form a water insoluble oil which is then dispersed in an aqueous solution of gelatin by means of a colloid mill. The dispersion is added to a gelatino silver chloroiodide emulsion and the mixture coated on a paper support at 72 mg. per square foot of silver, 215 mg. per square foot of gelatin, 45 mg. per square foot of tolyl hydroquinone and 170 mg. per square foot of trioctylphosphine oxide.

This is sensitometrically exposed and the resulting latent image developed as described in Example 1. A good stable image is developed.

EXAMPLE 10

This is a comparative example.

An identical product is prepared as in Example 9 except that the trioctylphosphine oxide is omitted and the tolyl hydroquinone is dispersed in gelatin from a methanol solution. The resulting product is exposed and processed as in

Example 9. The resulting image showed no reversal and demonstrated higher desensitization than the product of Example 9.

EXAMPLE 11

This illustrates the invention.

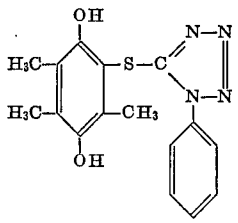
The product and procedure set out in Example 1 is repeated with the exception that 1.0 g. of t-butyl hydroquinone and 2.72 g. of tributyl phosphine oxide is used in place of 4-phenyl catechol and trioctylphosphine oxide. The resulting photographic element containing 115 mg. per square foot of tributyl phosphine oxide is exposed and processed as in Example 1.

The developed image showed minimized desensitization.

EXAMPLE 12

This illustrates the invention.

1.0 g. of 3,5,6-trimethyl-2-(1-phenyl-5-tetraazolylthio) hydroquinone:



is mixed with 3.0 g. of trioctylphosphine oxide. The resulting powder is heated to form a water insoluble oil. This is dispersed in 15 g. of an aqueous gelatin solution containing 10% by weight of gelatin. The dispersion is added to a gelatino silver chlorobromide emulsion and the mixture coated on a cellulose acetate film support at 160 mg. Ag per square foot, 300 mg. of gelatin per square foot, 24 mg. of the hydroquinone compound per square foot and 72 mg. of trioctylphosphine oxide per square foot. This is exposed sensitometrically and the resulting latent image is developed as set out in Example 1.

A good image is produced. This has significantly higher relative speed than an identical product without the hydroquinone compound and trioctylphosphine oxide.

EXAMPLE 13

Similar results are obtained as in Example 1 employing N-methyl-p-aminophenol sulfate also known as Elon, in place of 4-phenyl catechol.

EXAMPLE 14

This illustrates the invention employing a filter dye as a photographic addenda.

1 mole of trioctylphosphine oxide is mixed with 1 mole of a filter dye which is alpha-(p-diethylaminobenzylidene)-alpha-(3,4-dihydroxybenzoyl)-acetonitrile in acetone. This solution is added to an aqueous solution containing 10% by weight gelatin. The resulting mixture is stirred, coated on a glass plate and dried. This is designated as Plate A. A test is carried out to determine if the dye will wander in the resulting coating.

This test consists of measuring the percent loss of absorption density after placing the plate in running water at 19° C. for 5 minutes and then drying. Wandering of the dye in this test is expressed as percent bleed.

An identical plate, designated as Plate C is prepared the same as Plate A with the exception that no Group V element oxide is employed in preparation of the plate. This is tested in the same manner as Plate A of measuring the percent loss of absorption density after placing the plate in running water at 19° C. for 5 minutes and then drying. Wandering of the dye in this test is expressed as percent bleed.

An identical plate to Plate A is prepared with the exception that 3 moles of trioctylphosphine oxide is employed in place of 1 mole of trioctylphosphine oxide. This plate is designated as Plate B and tested the same as Plate A.

The results of these tests are set out in the following Table I:

TABLE I

	Maximum absorption density	Percent bleed
Plate A (invention)----	2.76	5
Plate B (invention)----	2.62	0
Plate C (control)------	2.47	13

This example demonstrates that complexes employed in the practice of the invention can provide the advantage of keeping a dye in a gelatin layer from wandering or being removed from the layer before desired.

EXAMPLE 15

This illustrates the invention employing a filter dye as the processing agent and a combination of organic, Group V element oxides.

3 moles of a mixture of equal parts by weight, trioctylphosphine oxide and triphenylphosphine oxide is mixed with 1 mole of alpha-(p-diethylaminobenzylidene)-alpha-(3,4-dihydroxybenzoyl)-acetonitrile in acetone. This solution is added to an aqueous solution containing 10% by weight gelatin. The resulting mixture is stirred, coated on a glass plate and dried. This is designated as Plate D. This plate is tested as described in Example 14 to determine whether the dye will wander or be removed from the layer. The results of the test indicate Plate D provides 4% bleed and maximum absorption of 3.08 compared to Plate C (control) in Example 14.

EXAMPLE 16

Similar results regarding percent bleed are obtained as in Example 14 employing 3 moles of triphenylphosphine oxide in place of 3 moles of trioctylphosphine oxide.

EXAMPLE 17

This illustrates preparation of a dispersion of a complex employed in the practice of the invention in gelatin for a layer of a photographic element.

The following components are mixed together:

(a) alpha-(p-diethylaminobenzylidene)-alpha-(3,4-dihydroxybenzoyl)-acetonitrile—11.6 g.
(b) trioctylphosphine oxide—20.0 g.
(c) ethyl acetate—30.0 ml.

This mixture is heated to about 70° C. and added to the following mixture:

(a) bone gelatin (aqueous solution containing 10% by weight bone gelatin)—272 g.
(b) surfactant (aqueous solution containing 13% by weight Alkanol B which is a sodium alkyl naphthalene sulfonate produced by E. I. du Pont Co., U.S.A.—30 ml.
(c) water to 424 g.

The molar ratio of the dye in the described composition to trioctyl phosphine oxide is 1 to 1.5. The resulting composition is mixed in a colloid mill to produce a dispersion.

The dispersion is mixed with additional gelatin and is coated on a cellulose acetate support at 20 mg. per square foot of described dye, 90.8 mg. per square foot of gelatin and 34.4 mg. per square foot of trioctyl phosphine oxide.

The element produced has maximum absorption density of 1.78.

EXAMPLE 18

This is a comparative example demonstrating advantages of the complex of a filter dye with a Group V element oxide employed in the practice of the invention over a filter layer of an element containing yellow colloidal silver.

An element is prepared the same as described in Example 17 with the exception that yellow colloidal silver is employed in place of the dye described in Example 17.

The resulting element contains 10 mg. per square foot of colloidal silver and 90.8 per square foot of gelatin.

The element produced has a maximum absorption density of 1.39. This is significantly lower than the element of Example 17. Also more undesired absorption of green light occurs with the element containing colloidal silver.

EXAMPLE 19

This illustrates preparation of a photographic element according to the invention.

A photographic element containing red sensitive, green sensitive and blue sensitive layers is prepared as described in U.S. Patent 3,046,129 of Graham and Sagal, issued July 24, 1962, with the exception that a layer consisting of a dispersion as described in Example 17 is employed in place of a filter layer containing colloidal silver.

The element has the following layers respectively:

blue sensitive layer
filter layer: complex of dye with Group V element oxide, i.e., a complex of (a) alpha-(p-diethylaminobenzylidene)-alpha-(3,4 - dihydroxybenzoyl)-acetonitrile with (b) trioctylphosphine oxide.
green sensitive layer
red sensitive layer
support

The filter layer contains 20 mg. per square foot alpha-(p-diethylaminobenzylidene) - alpha - (3,4-dihydroxybenzoyl)-acetonitrile, 34.5 g. per square foot of trioctylphosphine oxide and 90.8 g. per square foot of gelatin.

The element is sensitometrically exposed and processed in a color reversal process described by W. T. Hanson, Jr. and W. I. Kisner in an article in the "Journal of the Society of Motion Picture and Television Engineers," vol. 61, (1953), pages 667–701 with the process being carried out at 30° C.

A good color image is produced. The maximum and minimum density in the various layers are set out in Table II in Example 20.

EXAMPLE 20

This is a comparative example.

The procedure set out in Example 19 is repeated with the exception that a filter layer containing 10 mg. per square foot of yellow colloidal silver and 90.8 g. per square foot of gelatin is employed in place of the filter layer described in Example 19.

The resulting photographic element is sensitometrically exposed and processed the same as the photographic element as described in Example 19.

The results are set out in Table II:

TABLE II

	Maximum density			Minimum density		
Element	C	M	Y	C	M	Y
Example 19 (invention).....	3.30	3.26	3.31	.13	.30	.24
Example 20 (prior art).....	3.21	3.05	2.71	.13	.28	.19

NOTE.—C=Cyan layer; M=Magenta layer; Y=Yellow layer.

This illustrates that a complex as described in Example 19 provides an adequate blue light filter layer. No changes in relative speed are noted between the photographic elements of Examples 19 and 20. But, the photographic element of Example 19 has higher maximum density in each layer.

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.

We claim:

1. An element comprising a support having thereon at least one photographic silver salt and an oleophilic complex of (a) a photographic addendum containing a hydroxyl or amino group with (b) an organic Group V element oxide or an organic amine oxide said complex having the property of releasing said photographic addendum in the presence of alkali.

2. An element as in claim **1** in which said photographic silver salt is a light sensitive silver halide.

3. An element as in claim **1** wherein said photographic addendum is a silver halide developing agent.

4. An element as in claim **1** wherein said photographic addendum is a filter dye.

5. An element as in claim **1** wherein said oxide is an organic phosphine oxide.

6. An element as in claim **1** which is a lithographic printing plate.

7. An element as in claim **1** also containing an N,N-dialkyl lauramide or tricresyl phosphate.

8. An element as in claim **1** comprising a layer sensitive to the blue region of the spectrum, a layer sensitive to the green region of the spectrum and a layer sensitive to the red region of the spectrum.

9. An element as in claim **3** wherein said agent is a polyhydroxybenzene silver halide developing agent and said oxide is:
triphenyl phosphine oxide,
tributyl phosphine oxide,
trioctyl phosphine oxide,
trihexyl phosphine oxide,
dimethyl dodecyl amine oxide, or
triphenyl arsine oxide.

10. An element as in claim **1** in which said addendum is 4-phenyl catechol and said oxide is triphenyl phosphine oxide or trioctyl phosphine oxide.

11. An element as in claim **1** wherein said addendum is a silver halide developing agent containing at least one hydroxyl group, and said complex contains less than 20% free hydroxyl groups indicated at an infrared absorption frequency of 3613 $cm.^{-1}$ at the ratio of two moles of said organic Group V element oxide to one mole of said silver halide developing agent.

12. An element as in claim **1** wherein said support has thereon a layer sensitive to the blue region of the spectrum, a layer comprising an oleophilic complex of (a) a filter dye with (b) triphenyl phosphine oxide or triocetyl phosphine oxide; a layer sensitive to the green region of the spectrum; and a layer sensitive to the red region of the spectrum.

13. A photographic emulsion comprising a photographic silver salt and an oleophilic complex of a photographic addendum containing a hydroxyl or amino group, with an organic Group V element oxide or an organic amine oxide, said complex having the property of releasing said photographic addendum in the presence of alkali.

14. A photographic emulsion as in claim **13** in which said silver salt is a photographic silver halide.

15. A photographic emulsion as in claim **13** which is a direct positive emulsion.

16. A photographic emulsion as in claim **13** wherein said developing agent is a polyhydroxybenzene silver halide developing agent.

17. A photographic emulsion as in claim **13** wherein said oxide is an organic phosphine oxide.

18. A photographic emulsion as in claim **13** also containing an N,N-dialkyl lauramide or tricresyl phosphate.

19. A photographic emulsion as in claim **13** wherein said addendum comprises a polyhydroxybenzene silver halide developing agent and said oxide is:
triphenyl phosphine oxide,
tributyl phosphine oxide,
trioctyl phosphine oxide,
trihexyl phosphine oxide,
dimethyl dodecyl amine oxide, or
triphenyl arsine oxide.

20. A photographic emulsion as in claim **13** wherein said silver salt is a photographic silver halide and said

complex is of 4-phenyl catechol with triphenyl phosphine oxide or trioctyl phosphine oxide.

21. A photographic element of claim **4** wherein said silver salt is silver halide and said oxide is phosphine oxide.

22. A photographic element of claim **2** wherein said complex is trioctyl phosphine oxide with alpha-(p-diethylaminobenzylidene) - alpha - (3,4 - dihydroxybenzoyl)-acetonitrile.

23. In a photographic process comprising developing a latent image in an exposed photographic element employing a silver halide developing agent in the presence of an alkali, the improvement comprising employing an oleophilic complex of (a) said silver halide developing agent with (b) an organic Group V element oxide or an organic amine oxide, said complex having the property of releasing said silver halide developing agent in the presence of alkali.

24. A photographic process as in claim **23** wherein said photographic element contains said oleophilic complex.

25. A photographic process as in claim **23** wherein said photographic element comprises at least one photographic silver salt and said oleophilic complex.

26. A photographic process as in claim **23** wherein said

agent is a polyhydroxybenzene silver halide developing agent and said oxide is:

triphenyl phosphine oxide,
tributyl phosphine oxide,
trioctyl phosphine oxide,
trihexyl phosphine oxide,
dimethyl dodecyl amine oxide, or
triphenyl arsine oxide.

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WILLIAM D. MARTIN, Primary Examiner

B. D. PIANALTO, Assistant Examiner

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