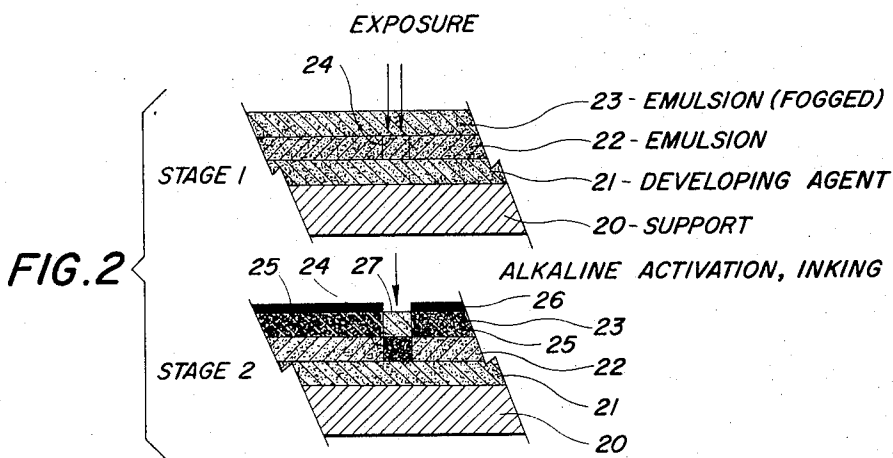
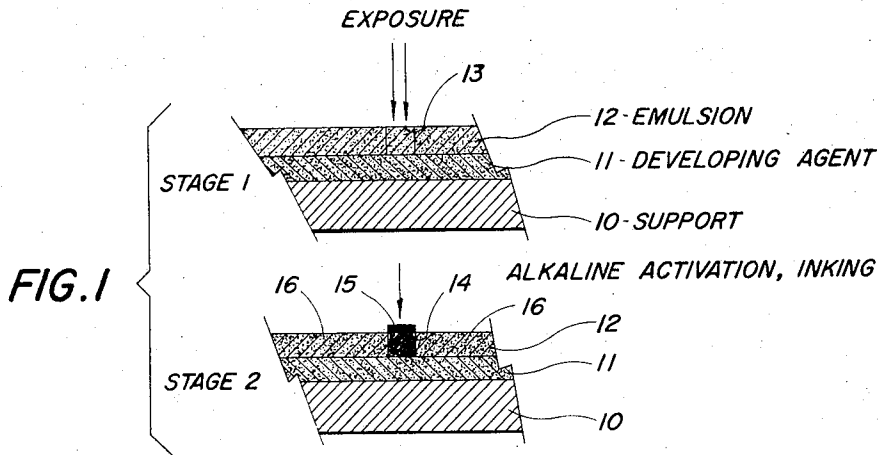


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3,369,902

LITHOGRAPHIC PLATES SENSITIZED WITH OXACARBOCYANINE
AND BENZIMIDAZOLE CARBOCYANINE DYES
Filed May 28, 1965



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LITHOGRAPHIC PLATES SENSITIZED WITH OXACARBOCYANINE AND BENZIMIDAZOLE CARBOCYANINE DYES

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ABSTRACT OF THE DISCLOSURE

Spectrally sensitized photographic elements, useful in processes adapted to the production of lithographic printing plates, having materially increased speed relative to the use of cyanine, styryl or merocyanine dyes therein are obtained by the use of oxacarbocyanine dyes or benzimidazole carbocyanine dyes.

This invention relates to spectrally sensitized novel high speed photographic elements useful in processes adapted to the production of lithographic printing plates.

Lithographic printing plates and the printing therefrom on a lithographic printing press involves the use of a plate, the printing surface of which is differentially ink-receptive when moistened with water. Usually the plate includes oleophilic characters or designs which are receptive of greasy printing ink and hydrophilic areas which repel ink when moistened with water. Thus, the printing of the plate does not depend upon the printing characters being either substantially above or below the hydrophilic nonprinting surface as opposed to other plates such as relief or intaglio printing plates.

A great many processes have been suggested for preparing lithographic printing plates. A well-known process involves forming an oleophilic design on a hydrophilic surface by photographic means, e.g., by differentially hardening a light-sensitive organic colloid layer on a lithographic surface with actinic rays and removing the unhardened areas to bare the hydrophilic non-printing areas. In other processes a preformed design may be transferred from one support to another to provide the requisite differentially ink-receptive element. Also, an oleophilic design may be formed photographically or by other means on a hydrophobic surface and the design used as a resist, to convert the uncovered hydrophobic areas to hydrophilic areas, for example, by hydrolysis as in the case of cellulose ester printing plates.

A simple photographic method for preparing lithographic printing plates is described in E. C. Yackel and T. I. Abbott U.S. Patent 3,146,104, issued Aug. 25, 1964, which involves formation of a developable silver halide image, as by means of exposure to a line or halftone subject, of a hydrophilic organic colloid-silver halide film such as a gelatino-silver halide sensitized plate, followed by silver halide development. No additional steps, such as etching or washing off the unhardened areas, are required for producing the plates. Moreover, the process in its various forms can be adapted to the production of positive plates from either positive or negative subjects.

U.S. Patent 3,146,104 thus includes the formation of a developable silver halide image by exposure to a subject of a silver halide emulsion layer and contiguous silver

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halide developing agent (developing agent present in the emulsion or a layer effectively adjacent thereto) which when oxidized in the development reaction in the presence of the hydrophilic organic colloid vehicle present in the silver halide emulsion layer, forms an oleophilic image (ink-receptive image), followed by treatment of the exposed emulsion with alkaline solution which may contain a developing agent if it is not present in the sensitive element, to initiate development of the exposed silver halide and the formation thereby of the oleophilic image areas receptive of printing ink. Upon inking the moistened plate and printing on a lithographic printing press, the desired lithographic reproduction, which will be negative to the original subject will be obtained. If, however, a positive-working plate is desired, the photographic element described above may contain, in addition, a fogged silver halide emulsion as the uppermost layer. This photographic element when exposed to a subject, and its contiguous silver halide developing agent is activated, the developing agent will react with the sensitive lower silver halide emulsion layer to form the negative image and the unused silver halide developing agent present in the unexposed areas of said sensitive lower silver halide emulsion layer will then migrate upward to the fogged surface silver halide emulsion layer and, when oxidized in the presence of the hydrophilic organic colloid present in this layer, will form an oleophilic image in the surface which is positive in respect to the original subject. A positive working plate also can be obtained by using a direct-positive emulsion such as those described in Kendall and Hill U.S. Patent 2,541,472 or Fallesen U.S. Patent 2,497,875. If desired, a positive working plate also can be obtained by processing the exposed plate first in a nontanning developer such as one containing hydroquinone and sulfite, exposing the undeveloped silver halide by flashing to white light and then processing in an alkaline solution containing the developing agent which when oxidized in the development reaction in the presence of the hydrophilic organic colloid vehicle present in the silver halide emulsion layer forms an ink-receptive image.

A number of other ways are described in U.S. Patent 3,146,104 for providing the silver halide image which is developed to form the oleophilic image. For example, a silver halide complex image resulting from the transfer of silver halide in a silver halide diffusion transfer process can be developed to form the oleophilic image. Likewise silver halide images arising from the rehalogenation of silver images can be developed with the developing agents described below to yield the oleophilic images. It was also found possible to prepare a suitable planographic printing plate of the type described above by transferring the unused developing agent, after initial development of a silver halide image, to a receiving sheet comprising a hydrophilic organic colloid, e.g., gelatin, and which may also contain, as oxidizing agents, manganese dioxide or fogged silver halide on a suitable support. When the unused developer agent is transferred to receiving sheets of the type described above, it is oxidized in the presence of the hydrophilic organic colloid present to form the imagewise oleophilic areas used in forming a planographic printing plate. A further modification of the above procedure is to transfer the unused developing agent to a receiving sheet composed of a hydrophilic organic colloid layer on a suitable support. This layer is then "swabbed" with a solution of a suitable oxidizing agent, e.g., ferric

chloride or ferric sulfate ethylene-diaminetetraacetic acid complex to oxidize the unused developer agent present in the receiver sheet apparently causing it to react with the hydrophilic organic colloid layer and form the imagewise oleophilic areas.

It has been desired to increase the sensitivity of photographic elements utilized in the preparation of lithographic printing plates. Such increases in sensitivity should be obtained without any concomitant changes which would disadvantageously affect other sensitometric characteristics, e.g., contrast, or the use of said materials.

I have found that when the oxacarbocyanine or benzimidazole carbocyanine dyes described hereinafter are included in photographic elements of the type described in U.S. Patent 3,146,104, for example, an unexpectedly large increase in speed, i.e., at least 25 percent greater, is obtained relative to the use of cyanine, styryl or merocyanine dyes therein. Furthermore, the increase in speed is obtained without deleteriously affecting other photographic characteristics therein.

An object of my invention is to provide a new and improved spectrally-sensitive photographic element useful in the preparation of the lithographic printing plates.

Another object of my invention is to provide a new spectrally-sensitive photographic element of improved sensitivity useful in the preparation of lithographic printing plates.

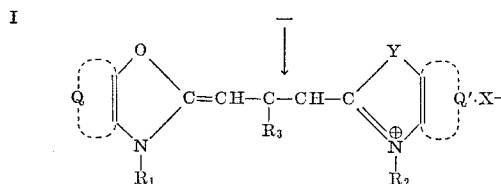
Another object of my invention is to obtain highly-sensitive materials of the type described hereinbefore without producing a concomitant decrease in photographic or lithographic quality.

A further object is to provide a new spectrally-sensitive photographic element useful in the preparation of lithographic printing plates, said photographic element containing a dye selected from the oxacarbocyanine and benzimidazole carbocyanine dyes described herein and having greater sensitivity than said element sensitized with a cyanine, styryl or merocyanine dye.

Other objects will become apparent from a consideration of the following description and examples.

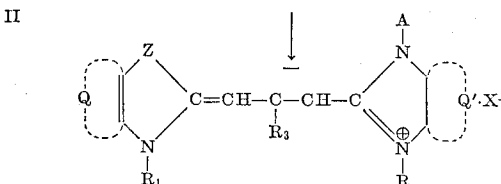
I have found that these and other objects of my invention can be obtained by including in photographic silver halide materials utilized in the preparation of lithographic printing plates, an oxacarbocyanine dye of the following general Formula I and/or a benzimidazole dye of Formula II.

The oxacarbocyanine compounds employed in the practice of the invention have the formula:



wherein Q and Q' each represents the non-metallic atoms necessary to complete a phenyl nucleus, R₁ and R₂ each represents an alkyl substituent, R₃ represents hydrogen, a lower alkyl group or an aryl group, X⁻ is an anion such as Cl⁻, Br⁻ or SO₃⁻ and toluene sulfonate, including inner salts, for example, and Y represents sulfur, oxygen, nitrogen or selenium.

The benzimidazole carbocyanine compounds employed in the practice of the invention have the formula:



wherein A represents an alkyl substituent, Z represents



or =NR₆, wherein R₄, R₅ and R₆ each represents a lower alkyl group and wherein Q, Q', R₁, R₂, R₃ and X⁻ have the meaning previously assigned to them.

The term alkyl as used herein, unless otherwise indicated, refers to an alkyl hydrocarbon group.

The phenyl nuclei represented by Q and Q' can be unsubstituted or substituted. Substituents that can be attached to the phenyl nuclei represented by Q and Q' include, for example, a halogen atom, such as a chlorine atom or a bromine atom, an alkoxy group such as methoxy, ethoxy, propoxy, isopropoxy or butoxy, an alkyl group such as methyl, ethyl, propyl, isopropyl or butyl, a hydroxy group, an amino group such as —NH₂, an alkylamino group such as methylamino, ethylamino, propylamino or butylamino, a dialkylamino group such as dimethylamino, diethylamino, dipropylamino, dibutylamino, methylethylamino, methylbutylamino, or ethylbutylamino, an aryl group such as phenyl, chlorophenyl, bromophenyl, methylphenyl, ethylphenyl, methoxyphenyl, ethoxyphenyl, α-naphthyl, β-naphthyl, 2-hydroxynaphthyl, 2-methoxynaphthyl, or 2-ethoxynaphthyl, a carbomethoxy group and a carbethoxy group. The substituents mentioned are intended to be illustrative and not limitative of the substituents that can be present on the phenyl nuclei Q and Q'. The phenyl nuclei Q and Q' when substituted can be substituted with the same or different substituents. Also, as shown hereinafter the phenyl nuclei Q and Q' can have more than 1 substituent.

R₁ and R₂ can each be the same alkyl substituent or different alkyl substituents. Alkyl, carboxyalkyl, sulfoalkyl and sulfoalkoxyalkyl, for example, are illustrative of the alkyl substituents R₁ and R₂ can be. When R₁ and R₂ represent an alkyl group, preferably each represents an alkyl group having 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl and butyl, although each can be a higher alkyl group such as pentyl and hexyl. Illustrative of the carboxyalkyl groups represented by each of the members R₁ and R₂ are carboxymethyl, β-carboxyethyl, γ-carboxypropyl and δ-carboxybutyl, for example. β-sulfopropyl, γ-sulfopropyl and δ-sulfobutyl are illustrative of the sulfoalkyl groups each of the members R₁ and R₂ can be.

β-Sulfomethoxyethyl, β-(β-sulfoethoxy)ethyl, γ-(β-sulfoethoxy)propyl, β-(γ-sulfopropoxy)ethyl and δ-(β-sulfoethoxy)butyl, for example, are illustrative of the sulfoalkoxyalkyl groups each of the members R₁ and R₂ can be.

When R₃ is a lower alkyl group it can be methyl, ethyl, propyl, isopropyl, butyl and isobutyl, for example. When R₃ is an aryl group it can be phenyl, chlorophenyl, bromophenyl, methylphenyl, ethylphenyl, methoxyphenyl, ethoxyphenyl, α-naphthyl, β-naphthyl, 2-hydroxynaphthyl, 2-methoxynaphthyl or 2-ethoxynaphthyl, for example.

Methyl, ethyl, propyl, isopropyl, butyl and isobutyl are illustrative of the lower alkyl groups each of the members R₄, R₅ and R₆ can be.

Illustrative of the alkyl substituents A can be lower alkyl groups such as methyl, ethyl, propyl, isopropyl and butyl, for example, carboxyalkyl groups such as carboxymethyl, β-carboxyethyl, γ-carboxypropyl and δ-carboxybutyl and dialkylaminoalkyl groups such as diethylaminoethyl and dimethylaminoethyl, for example.

Typical oxacarbocyanine dyes having the Formula I useful in my invention are set forth in the following tabulation. In these compounds R₃ is hydrogen and Y is O. Under the heading Q and Q' are illustrations of various substituents that can be attached to these nuclei. More than one substituent can be attached to each of the nuclei Q and Q'. Thus "dichloro" means that two chlorine atoms are attached thereto.

	Q	Q'	R ₁	R ₂
1.....	phenyl-	phenyl-	sulfobutyl	sulfobutyl
2.....	phenyl-	phenyl-	β -sulfomethoxy-ethyl	β -sulfomethoxy-ethyl
3.....	chloro-	chloro-	sulfobutyl	sulfobutyl
4.....	phenyl-	phenyl-	sulfopropyl	sulfopropyl
5.....	dichloro-	dichloro-	sulfopropyl	sulfopropyl
6.....	methoxy-	methoxy-	sulfopropyl	sulfopropyl
7.....	bromo-	bromo-	sulfopropyl	sulfopropyl
8.....	phenyl-	chloro-	sulfobutyl	sulfobutyl
9.....	phenyl-	methoxy-	sulfobutyl	sulfopropyl
10.....	chloro-	chloro-	ethyl	ethyl
11.....	chloro-	bromo-	sulfobutyl	sulfobutyl
12.....	hydroxy-	chloro-	sulfobutyl	sulfobutyl
13.....	phenyl-	phenyl-	ethyl	ethyl
14.....	bromo-	bromo-	methyl	methyl
15.....	ethoxy-	ethoxy-	ethyl	ethyl
16.....	unsubsti-	unsubsti-	methyl	methyl
	tuted	tuted		
17.....	bromo-	phenyl-	sulfobutyl	sulfobutyl
18.....	chloro-	chloro-	sulfobutyl	ethyl
19.....	dibromo-	dibromo-	β -carboxyethyl	ethyl
20.....	chloro-	phenyl-	sulfopropyl	ethyl

Typical benzimidazole carbocyanine dyes having the Formula II useful in my invention are tabulated herein-after.

	Q	Q'	R ₁	R ₂	Z	A
1.....	dichloro	dichloro	sulfobutyl	sulfobutyl	N—C ₂ H ₅	ethyl
2.....	dibromo	dibromo	sulfobutyl	ethyl	N—C ₂ H ₅	ethyl
3.....	unsubsti-	unsubsti-	sulfobutyl	sulfobutyl	N—C ₂ H ₅	ethyl
	tuted	tuted				
4.....	unsubsti-	dichloro	methyl	ethyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	carboxy-methyl
5.....	unsubsti-	dichloro	methyl	ethyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array}$	diethylamino-ethyl
	tuted					

While the oxacyanine compounds employed in the practice of the invention have been illustrated primarily with respect to those compounds having the Formula I wherein Y is oxygen it will be understood that compounds wherein Y is sulfur, nitrogen or selenium can be prepared and are useful in carrying out the invention. Similarly, while the invention is illustrated primarily with respect to compounds wherein R₃ is hydrogen it will be understood that compounds wherein R₃ is lower alkyl or aryl can be prepared and are useful in carrying out the invention. R₃ in the benzimidazole carbocyanine compounds of the foregoing tabulation is hydrogen.

In one embodiment of the invention a photographic emulsion containing an oxacarbocyanine dye is merely exposed to the subject in the presence of the developing agent, followed by treatment with an alkaline solution inking the resultant plate and printing. The developing agent can be incorporated in the photosensitive material or in the alkaline processing solution. If the photographic emulsion used is an ordinary developing-out emulsion, the plate obtained is a negative with regard to the subject. By use of direct positive emulsions, the plate obtained is a positive.

In another embodiment of the invention wherein a positive working plate is used, the same comprises a layer of a silver halide emulsion sensitized with an oxacarbocyanine or benzimidazole dye and contiguous developing agent of the type mentioned. Superimposed on this emulsion is a fogged silver halide emulsion layer. After exposure, activation of the exposed plate with alkaline solution results in the formation of a negative image in the exposed regions of the negative emulsion layer, the residual silver halide developing agent migrates to and then develops the fogged emulsion in the positive regions thereby producing a positive oleophilic design at the surface of the sensitive element which takes printing ink and can be printed on a lithographic printing press. Direct positive emulsions can also be used in this embodiment of the invention if a negative working plate is desired. Other specific embodiments of my invention are described hereinafter.

In the foregoing processes, the ink-receptive areas of the printing plates on a background of hydrophilic material are obtained by alkaline activation of a silver halide developing agent in the presence of a hydrophilic organic colloid silver halide emulsion layer. The result is to form a silver image and oxidized developing agent in the region of development. The organic colloid of the emulsion layer may undergo some additional hardening at the same time. However, the hardening of the hydrophilic organic colloid layer in the region of development is incidental to successful operation of the invention since some silver halide developing agents, such as catechol, hydroquinone and toluhydroquinone, which are known to be strong gelatin-tanning silver halide developing agents, are not useful in the sensitive elements presumably because the oxidation products formed in the presence of the hydrophilic organic colloid silver halide emulsion layer do not form oleophilic images, whereas other closely related silver halide developing agents such as chlorohydroquinone, are quite useful in the process of the invention. Also,

the invention is operative with various hydrophilic organic colloid silver halide emulsions which have been sensitized with an oxacarbocyanine or benzimidazole dye.

The silver halide developing agents used in my invention should be capable of oxidation in the presence of the hydrophilic organic colloid present in the silver halide emulsion layer to produce an image receptive to greasy printing ink. The polyhydroxybenzene developing agents substituted with halogen, a monocyclic aryl nucleus of the benzene series or an alkyl group of at least 2 and preferably from 2 to 6 carbon atoms have this property. The 1,2-hydroxybenzene developing agents substituted by halogen, a monocyclic aryl nucleus of the benzene series or an alkyl group of at least 2 carbon atoms and preferably 2 to 6 carbon atoms are particularly useful in the process. Silver halide developing agents possessing the necessary properties thus include certain polyhydroxybenzene developing agents and esters thereof, such as pyrogallol and substituted polyhydroxybenzene developing agents, particularly dihydroxybenzenes substituted with, for example, halogen (e.g. chlorine and bromine), an alkyl group of at least 2 and preferably from 2 to 6 carbon atoms and a monocyclic aryl nucleus of the benzene series, e.g., o-chlorohydroquinone, o-bromohydroquinone, 4-phenyl catechol, 4-t-butyl catechol, pyrogallol, 4-n-butylpyrogallol, nordihydroguaniaric acid, 4,5-dibromocatechol, 3,5,6-tribromo-4-phenylcatechol and 1-phenyl-3-(N-n-hexylcarboxamide)-4-[p(β -hydroquinolyethyl)-phenylazo]-5-pyrazolone. Esters of such developing agents, e.g., formates and acetates of pyrogallol hydrolyze in alkaline solutions can be used in the processes of the invention. In certain cases it has been found to be advantageous to include with the polyhydroxybenzene 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 in combination with the polyhydroxybenzenes to yield oleophilic images.

In the accompanying drawings 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 my invention.

In FIG. 1, layer 10 of the element of Stage 1 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 a quantity of black colloidal silver or carbon black, etc. for antihalation protection, layer 12 contains a gelatino-silver halide emulsion sensitized with an oxacarbocyanine or benzimidazole dye, for recording the line or halftone image.

In the process of FIG. 1, after exposure to a subject as shown in area 13, followed by alkaline activation and inking, the element appears substantially as shown in Stage 2, area 14 being composed of silver and the reaction product of the oxidized developing agent and the hydrophilic organic colloid present in the sensitized silver halide emulsion layer produced in the development reaction, carrying the ink image 15, the undeveloped area 16 of layer 12 remaining hydrophilic and repellent of printing ink when moistened with water.

In FIG. 2 is shown a positive-positive system in Stage 1 of which the element includes a support 20 such as a paper or film support, layer 21 an antihalation hydrophilic colloid layer containing developing agent and black colloidal silver, carbon black, etc., layer 22 a hydrophilic organic colloid orthosensitized silver halide emulsion layer, and layer 23 a fogged silver halide emulsion layer. Upon image exposure in region 24 followed by alkaline activation and inking, the element appears substantially as shown in Stage 2, the silver halide developing agent of layer 21 which has not been utilized in developing the negative silver image in areas 24 of layer 22 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 hydrophilic organic 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.

In the sensitive elements described the emulsion layers should be substantially hardened, particularly the outermost emulsion layer, e.g., layer 12 of FIG. 1 and layer 23 of FIG. 2, in order to prevent the alkaline activated and inked emulsions from adhering to printing blankets, printing paper, etc. For this purpose the emulsion should be as hard as a gelatin layer containing at least about 2 grams and preferably from about 2 to 15 grams of dry formaldehyde per lb. of gelatin.

In a preferred arrangement of my invention, the developing agent is incorporated in a separate layer under the orthochromatically-sensitized, silver halide emulsion layer since this arrangement gives improved sharpness, latitude and better quality ink images than when developing agent is incorporated directly in the emulsion layer.

The following examples illustrate representative photographic elements and processes of my invention.

EXAMPLE 1

Two spectrally-sensitized,¹ fine-grain silver chloride emulsions were treated in the following general manner:

I

Fine grain silver chloride emulsion containing 1 mole of Ag per 4350 cc. -----g-- 43.5

¹ The emulsions differed only in that one, Emulsion A, contained the merocyanine dye 3-ethyl-5-[(3-ethyl-2(3H)-benzoxazolylidene)isopropylidene]-rhodanine whereas the second emulsion, Emulsion B, contained an oxacarbocyanine dye of this invention, anhydro-9-ethyl 5,5'-diphenyl-3,3'-di(3-sulfo-butyl)oxacarbocyanine hydroxide monosodium salt.

Paraffin dispersion prepared as follows: 80 g. molten paraffin dispersed in 400 cc. 10% photographic gelatin solution containing 5 cc. of 10% Alkanol B solution -----g-- 10.0

III

4-phenyl catechol dispersion prepared as follows: 50 g. 4-phenyl catechol dissolved in 100 cc. dibutylphthalate at 60-70 cc. dispersed in 500 cc. 10% photographic gelatin and 50 cc. 7½% saponin solution and passed through the colloid mill five times -----g-- 10.0
15% saponin solution -----g-- 1.0
10% formaldehyde solution -----g-- 1.0
Water -----cc-- 20.0

The above emulsions were coated at the rate of 6.5 grams per square foot on a film base and dried.

The films were exposed to a line negative, then activated for 20 seconds in a 4 percent solution of sodium carbonate monohydrate. Thereafter, the plates were placed in a lithographic printing press, inked in the conventional manner and about 50 copies were printed. The ink-receptive regions of the plates corresponded to the exposed regions 14 of FIGURE 1 and the prints obtained therefrom were positives of the subject used for making the original line negative. During the process of making the above printing plates, the following sensitometric characteristic comparisons were noted for Emulsions A and B.

	Relative Speed	Contrast	Development Rate
Emulsion A -----	100	Control -----	Control -----
Emulsion B -----	280	Similar -----	Similar -----

In the above example, if desired, the developing solution may contain the silver halide developing agent rather than having the developing agent contiguous to the emulsion layer. In addition, in order to obtain an excellent degree of differentiation between the oleophilic and hydrophilic areas the printing surface may also contain a material such as ZnO, Al₂O₃, carboxy lower alkyl hydroxy ethyl cellulose or polyacrylamide. Acidifying the plate surface after its alkaline image development and stop bath steps may be done with a conventional lithographic desensitizing etch formula such as a 0.05% H₃PO₄ solution or the like.

EXAMPLE 2

Three radiation-sensitive elements having a structure substantially as shown in FIGURE 2, Stage 1, where prepared in the following general manner:

LAYER 21

Developer dispersion

Grams
4-phenyl catechol ----- 5
Dibutyl phthalate ----- 50

Dissolve the 4-phenyl catechol in dibutyl phthalate at room temperature 20-25° C. Disperse the solution in:

10% gelatin solution -----grams-- 290
7.5% saponin solution -----ml-- 25
Water -----ml-- 180

at 40° C., pass through well-cooled colloid mill three times and then coat it on a suitable paper support as follows:

Developer dispersion -----grams-- 400
3% gelatin solution containing 12.5 grams of neutral colloidal silver per 454 grams of solution -----grams-- 400
15% saponin solution -----ml-- 20
2% formaldehyde solution -----ml-- 2.5
Water -----ml-- 27.5

Coat at 40° C., at 11.7 grams per square foot.

LAYER 22

Silver chloroiodide emulsion containing 100 grams of gelatin per silver mole (mole weight 2.48 kg.)	grams	2480
Sensitizing dye in ethyl alcohol ¹	ml.	300
10% gelatin solution	ml.	840
7% Triton X-200 solution	ml.	90
10% formaldehyde solution	ml.	68
Water	ml.	222

This was coated at 5.35 ml. per square foot over layer 21.

LAYER 23

Layer 23 was coated from the following composition at 7.0 ml. per square foot of coating surface.

Silver chloride gelatin emulsion (3600 grams/mole)	g	360
Water	ml.	200
Sodium hydroxide (0.25 N aqueous solution)	ml.	24
2% aqueous formaldehyde solution	ml.	4.6

The above mixture of ingredients was chemically fogged by holding 40 minutes at 40° C. with stirring. If desired, light or other known methods may be used for fogging the emulsion.

The following ingredients were then added to the fogged emulsion above:

Sulfuric acid (2.0 N aqueous solution)	ml.	3.5
15% aqueous saponin solution		10.0
2% aqueous formaldehyde solution		2.0
Water		95.9

Samples of the three elements were exposed to a line positive, processed for 60 seconds in a 4 percent aqueous sodium carbonate monohydrate solution, treated in a 2 percent aqueous acetic acid stop bath for 1 minute, squeezed to remove excess liquid and run on a lithographic printing press using 0.1 percent phosphoric acid fountain solution. About 50 copies were obtained. The inked plate from which the copies were obtained appeared substantially as shown in FIGURE 2, Stage 2, of the drawings. In this procedure, the residual developing agent from the negative development step develops an image-wise distribution of non-image-wise exposed silver halide in the originally fogged layer 23.

During the process of making the above printing plates, the following sensitometric characteristic comparisons were noted for Emulsions C, D and E.

	Relative Speed	Contrast	Development Rate
Emulsion C	100	Control	Control
Emulsion D	398	Faster	Higher
Emulsion E	447	do	Do.

Thus, it is evident that the oxacarbocyanine dyes, when utilized alone or in combination, in photographic elements designed for the production of lithographic printing plates, provide elements of greater sensitivity than similar elements sensitized with commonly used merocyanine dyes. Furthermore, the increase in sensitivity of the elements of my invention is obtained without deleteriously affecting other sensitometric characteristics such as contrast or de-

¹ The three sensitive elements differed in that one emulsion, Emulsion C, contained 150 mg. of the merocyanine dye 3-ethyl-5 - [(3 - ethyl - 2(3H) - benzoxazolyldene)isopropylidene]rhodanine per silver mole; the second emulsion, Emulsion D, contained 600 mg. of the oxacarbocyanine dye, anhydro-5,5'-dichloro - 9 - ethyl-3,3'-di(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt per silver mole; and the third emulsion, Emulsion E, contained 100 mg. of anhydro-5,5',6,6'-tetrachloro-1,1' - diethyl - 3,3'-di(3-sulfobutyl)benzimidazolocarbo-cyanine hydroxide per silver mole in addition to the oxacarbocyanine dye contained in Emulsion D.

velopment rate and in some cases even improve these characteristics.

EXAMPLE 3

- 5 The dyes 2,3-diethyl-4-methyloxathiazolocarbocyanine iodide and 3,3',9-triethyl-5,5'-diphenyloxacarbocyanine iodide were tested in the manner described in Example 2. They were found to yield increased speeds of, respectively, 26 percent and 400 percent relative to a control element. Thus, while oxathiacarbocyanine dyes yield slight increases in speed, the use of the oxacarbocyanine dyes is to be preferred.

EXAMPLE 4

- 15 In order to further establish the superiority of the oxacarbocyanine and benzimidazole dyes of my invention over known sensitizing dyes of other types, the following experiments were performed:

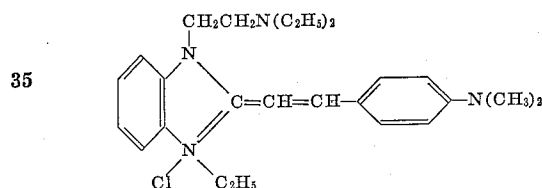
A number of elements similar to that described in Example 1 were prepared. The sensitized emulsions, containing 500 mg. of the dyes listed below per mole of silver halide, were coated over the layer containing a 4-phenyl catechol dispersion, at 145 mg. of silver per square foot.

25 Samples of these coatings were exposed on an Eastman Type IB Sensitometer and processed for 1 minute in Kodak D-72 Developer (1:1), fixed, washed and dried.

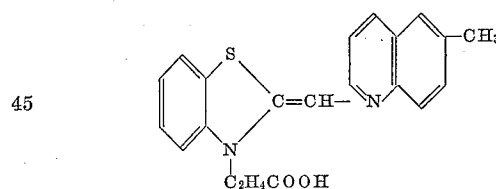
The results obtained are tabulated hereinafter.

- 30 The following dyes are typical known merocyanine, styryl and cyanine dyes which do not fulfill the objects of my invention.

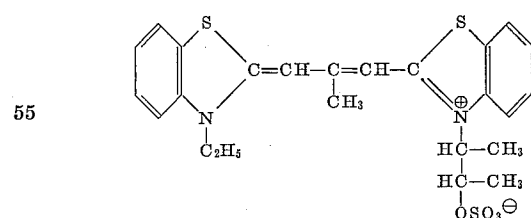
DYE I—STYRYL TYPE



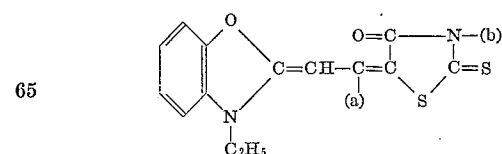
DYE II—THIACYANINE TYPE



DYE III—THIACARBOCYANINE TYPE



Merocyanine type



DYE IV

(a) H, (b) —CH2—COOH

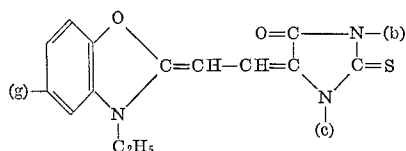
DYE V

(a) H, (b) —CH—CH2—COOH
COOH

11
DYE VI

(a) CH₃, (b) C₂H₅

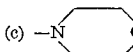
Merocyanine type



DYE VII

(b) C₂H₅, (c) —C₂H₄—N—(C₂H₅)₂, (g) H

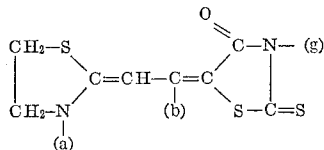
DYE VIII

(b) C₂H₅, (c) —N—, (g) H

DYE IX

(b) C₆H₅, (c) —CH₂—COOH, (g) C₆H₅

Merocyanine type



DYE X

(a) CH₂, (b) CH₃, (g) —CH₂COOH

DYE XI

(a) CH₃, (b) H, (g) —CH₂COOH

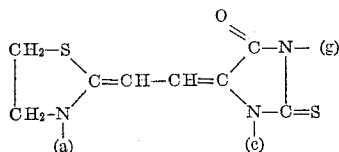
DYE XII

(a) CH₃, (b) C₆H₅, (g) —CH₂COOH


DYE XIII

(a) C₂H₄COOH, (b) CH₃, (g) —C₂H₄COOH

Merocyanine type




DYE XIV

(a) CH₃, (b) C₂H₅, (g) ——N(C₂H₅)₂

DYE XV

(a) CH₃, (b) C₂H₅, (g) —C₂H₄—N(C₂H₅)₂

DYE XVI

(a) CH₃, (b) C₂H₅, (g) —C₂H₄—N—

DYE XVII

(a) CH₃, (b) —C₆H₅, (g) —C₂H₄—N(C₂H₅)₂

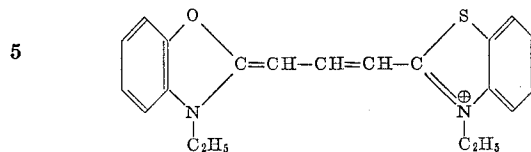
DYE XVIII

(a) C₄H₉SO₃K, (b) C₂H₅, (g) —C₆H₅

The following dyes are typical examples of oxacarbo-cyanine and benzimidazole dyes which fulfill the objects of my invention.

12
DYE XIX

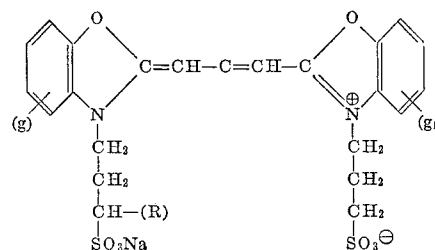
Oxathiocarbocyanine type



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Oxacarbocyanine type

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DYE XX

(g) Cl⁻, (g₁) Cl⁻, (R) H

DYE XXI

(g) CH₃O⁻, (g₁) CH₃O⁻, (R) H

DYE XXII

30

(g) C₆H₅⁻, (g₁) C₆H₅⁻, (R) CH₃

DYE XXIII

(g) C₆H₅⁻, (g₁) Cl⁻, (R) CH₃

DYE XXIV

35

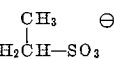
(g) C₆H₅⁻, (g₁) CH₃O⁻, (R) CH₃

DYE XXV

(g) C₆H₅⁻, (g₁) C₆H₅⁻, (R) CH₂CH₂CH₂CH₃

40

DYE XXVI

(g) C₆H₅⁻, (g₁) C₆H₅⁻, (R) CH₂—CH₂—

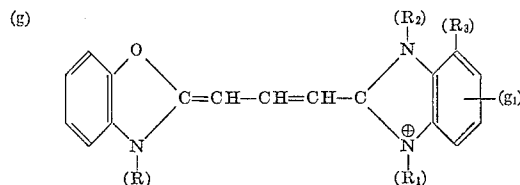
DYE XXVII

45

(g) C₆H₅⁻, (g₁) C₆H₅⁻, (R) —CH₂—CH₂COO⁻

Oxabenzimidazolocarbo-cyanine type

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DYE XXVIII

(g) H, (g₁) Cl₂, (R) CH₂CH₂CH₂SO₃Na,

60

(R₁) CH₂CH₂CH₂SO₃⁻, (R₂) C₂H₅, (R₃) C₂H₅

DYE XXIX

65

(g) H, (g₁) Cl₂, (R) CH₂CH₂CH₂CH₂SO₃Na,
(R₁) CH₂CH₂CH₂SO₃⁻, (R₂) C₂H₅, (R₃) C₂H₅

DYE XXX

70

(g) H, (g₁) Cl₂, (R) C₂H₅, (R₁) C₂H₅,
(R₂) CH₂CH₂COOH, (R₃) H

DYE XXXI

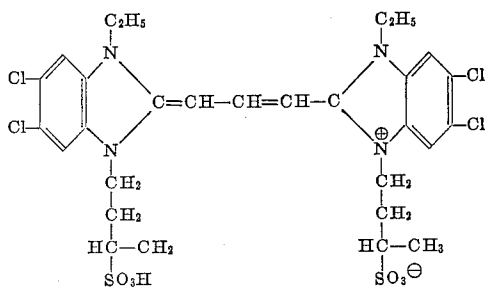
75

(g) H, (g₁) Cl₂, (R) C₂H₅, (R₁) C₂H₅,
(R₂) C₂H₄—N(C₂H₅)₂, (R₃) H

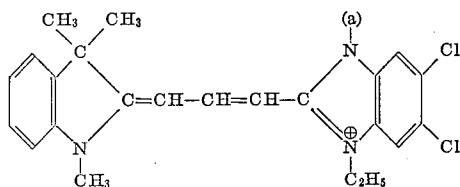
13

DYE XXXII

Benzimidazolocarbocyanine type



Benzimidazoloindocarbocyanine type



DYE XXXIII

(a) $-\text{CH}_2\text{COOH}$

DYE XXXIV

(a) $-\text{C}_2\text{H}_4-\text{N}(\text{C}_2\text{H}_5)_2$

Dye Number	Speed Increase Relative to Unsensitized Control (log E Units)	Remarks (Relative to Unsensitized Control)
I.....	0.80	
II.....	0.50	
III.....	0.15	Increased fog on incubation.
IV.....	0.63	Low contrast, increased fog on incubation.
V.....	0.22	Do.
VI.....	0.85	Do.
VII.....	0.75	Increased fog on incubation.
VIII.....	0.68	
IX.....	0.15	Do.
X.....	0.58	
XI.....	0.30	
XII.....	0.60	
XIII.....	0.45	
XIV.....	0.65	
XV.....	0.30	Do.
XVI.....	0.50	
XVII.....	0.65	
XVIII.....	0.43	
XIX.....	1.03	Less fog on incubation.
XX.....	1.32	
XXI.....	1.48	
XXII.....	1.30	
XXIII.....	1.55	
XXIV.....	1.46	
XXV.....	1.48	
XXVI.....	1.40	
XXVII.....	1.42	
XXVIII.....	1.22	Do.
XXIX.....	1.04	Do.
XXX.....	1.26	
XXXI.....	1.47	
XXXII.....	1.43	
XXXIII.....	1.46	
XXXIV.....	1.40	

The high-speed spectrally sensitized photographic emulsions of my invention may be utilized to advantage in various processes designed for the production of lithographic printing plates such as in the various transfer processes described in Examples 7-9 of U.S. Patent 3,146,104.

They may also be utilized in a positive-positive process in which an imagewise distribution of developable silver halide emulsion is processed to produce an oleophilic image at the surface of the emulsion layer as is described in the following example.

EXAMPLE 5

The large speed differential obtained by the use of an oxacarbocyanine sensitized emulsion of my invention

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relative to the same emulsion sensitized with a merocyanine dye may be utilized to form a positive-positive process plate. Thus, when the merocyanine Dye III of Example 4 is added to a fine-grain silver chloride emulsion and the emulsion is exposed and processed and a relative speed of 100 is assigned thereto, I have found that the same emulsion when sensitized with the oxacarbocyanine Dye XXIII of Example 4 yields a relative speed of 2510. Thus, the emulsion sensitized with Dye XXIII is 25 times faster than the same emulsion sensitized with Dye III. This large speed differential is then utilized in the following manner:

A paper support was coated with a gelatin-silver chloride photographic emulsion sensitized with Dye III of Example 4 to yield about 50 grams of gelatin, 20 grams of silver (as silver halide) and 4 grams of 4-phenyl catechol per 100 square foot. Over this slow-speed emulsion layer was coated a similar silver chloride emulsion but in which the major amount of the colloid vehicle was alkali-soluble acid-insoluble cellulose ether phthalate and the sensitizing dye was Dye XXIII of Example 4. This latter, considerably higher-speed emulsion, was coated to yield 28 grams of colloid vehicle and 30 grams of silver per 100 square foot.

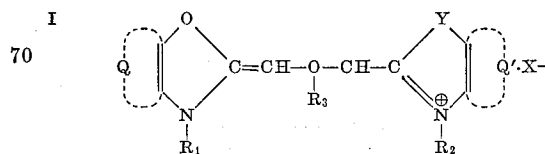
This photographic element was exposed to record a latent-image in only the high-speed outer emulsion layer after which development was carried out with a conventional Elon-hydroquinone developer until a visible negative silver image was obtained. Thereafter the lower emulsion was flashed to light through the negative image and development initiated with a 4 percent sodium carbonate monohydrate solution with the result that the 4-phenyl catechol caused tanning development of the silver halide emulsion in the positive region of the lower emulsion. Upon washing the element with water the overlying negative emulsion layer was washed off leaving the positive oleophilic image at the surface of the emulsion on the paper support, which image was inked and printed lithographically.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore, and as defined in the appended claims.

I claim:

1. In a light-sensitive photographic element capable of use as a lithographic printing plate, comprising a support having thereon a gelatin layer containing a sufficient amount of a polyhydroxybenzene silver halide developing agent to develop the exposed silver halide in the light-sensitive layer above it, the oxidation product of which renders gelatin oleophilic, and over said gelatin layer an unfogged gelatin-silver halide emulsion layer hardened with a hardener such that the gelatin 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, the improvement which comprises the spectral-sensitization of said emulsion layer by incorporating therein at least one dye selected from the class consisting of benzimidazole and oxacarbocyanine dye compounds and wherein the amount of spectral sensitizing dye present in said emulsion layer ranges from about 500 milligrams and upwards per mole of silver halide.

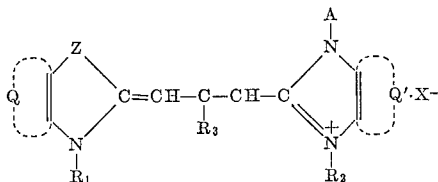
2. A photographic element according to claim 1 in which the oxacarbocyanine dye compounds have the formula:



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wherein Q and Q' each represents the non-metallic atoms necessary to complete a phenyl nucleus, R₁ and R₂ each represents an alkyl substituent, R₃ represents a member selected from the group consisting of hydrogen, lower alkyl and aryl, Y represents a member selected from the group consisting of S, O, N and Se and X⁻ is an anion, and the benzimidazole carbocyanine dye compounds have the formula:

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wherein Q, Q', R₁, R₂, R₃ and X⁻ have the meaning given hereinbefore, Z represents a member selected from the group consisting of



and =NR₆ wherein R₄, R₅ and R₆ each represents lower alkyl and A represents an alkyl substituent.

3. A photographic element according to claim 2 in which the silver halide developing agent is a member selected from the group consisting of a halogen substituted polyhydroxybenzene, a phenyl substituted polyhydroxybenzene and an alkyl substituted polyhydroxybenzene, said alkyl substituent containing 2 to 6 carbon atoms.

4. A photographic element according to claim 2 in which the dye is anhydro-1-carboxymethyl-5,6-dichloro-3-ethyl-1',3',3' - trimethylbenzimidazolindocarbocyanine hydroxide.

5. A photographic element according to claim 2 in which the dye is anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfobutyl)-benzimidazolocarbo-
cyanine hydroxide.

6. A photographic element according to claim 2 in which the dye is anhydro 5,5'-dichloro-9-ethyl-3,3'-di(3-sulfopropyl)oxacarbo-
cyanine hydroxide.

7. A photographic element according to claim 2 in which the dye is anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl) - 3 - (3-sulfopropyl) - oxacarbo-
cyanine hydroxide.

8. A photographic element according to claim 2 in which the dye is anhydro-9-ethyl-5,5'-dimethoxy-3,3'-di(3-sulfopropyl)oxacarbo-
cyanine hydroxide.

9. In a light-sensitive photographic element capable of use as a lithographic printing plate, comprising a support having thereon a gelatin layer containing a sufficient amount of a polyhydroxybenzene silver halide developing agent to develop the exposed silver halide in the light-sensitive layer above it, the oxidation product of which renders gelatin oleophilic, over said gelatin layer an unfogged gelatino silver halide emulsion layer and over said emulsion layer a fogged gelatino-silver halide emulsion layer hardened with a hardener such that the gelatin 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, the improvement which comprises the spectral-sensitization of the unfogged silver halide emulsion layer by incorporating therein at least one dye selected from the group consisting of benzimidazole and oxacarbo-
cyanine dye compounds and wherein the amount of spectral sensitizing dye present in said emulsion layer ranges from about 500 milligrams and upwards per mole of silver halide.

10. A photographic element according to claim 9 in which the oxacarbo-
cyanine and the benzimidazole carbocyanine dye compounds are as defined in claim 2.

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11. A photographic element according to claim 10 in which the silver halide developing agent is a member selected from the group consisting of a halogen substituted polyhydroxybenzene, a phenyl substituted polyhydroxybenzene and an alkyl substituted polyhydroxybenzene, said alkyl substituent containing 2 to 6 carbon atoms.

12. A photographic element according to claim 9 in which the dye is anhydro-1-carboxymethyl-5,6-dichloro-3-ethyl-1',3',3' - trimethylbenzimidazolindocarbocyanine hydroxide.

13. A photographic element according to claim 9 in which the dye is anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfobutyl) - benzimidazolocarbo-
cyanine hydroxide.

14. A photographic element according to claim 9 in which the dye is anhydro-5,5'-dichloro-9-ethyl-3,3'-di(3-sulfopropyl)oxacarbo-
cyanine hydroxide.

15. A photographic element according to claim 9 in which the dye is anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl) - 3 - (3-sulfopropyl) - oxacarbo-
cyanine hydroxide.

16. A photographic element according to claim 9 in which the dye is anhydro-9-ethyl-5,5'-dimethoxy-3,3'-di(3-sulfopropyl)oxacarbo-
cyanine hydroxide.

17. A lithographic printing process which comprises (a) exposing to a subject a photographic element comprising a support having thereon an unfogged gelatino-silver halide emulsion layer containing at least one spectral sensitizer selected from the oxacarbo-
cyanine dyes having the formula set forth in claim 2 and the benzimidazole carbocyanine dyes having the formula set forth in claim 2 and wherein the amount of spectral sensitizing dye present in said emulsion layer ranges from about 500 milligrams and upwards per mole of silver halide and hardened with a hardener such that the gelatin 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; (b) developing said exposed emulsion layer with an alkaline solution of a silver halide developing agent selected from the group consisting of a halogen substituted polyhydroxybenzene, a phenyl substituted polyhydroxybenzene and an alkyl substituted polyhydroxybenzene, said alkyl substituent containing 2 to 6 carbon atoms, the oxidation product of which renders gelatin oleophilic, to produce on said emulsion layer a printing surface in which the oxidation product of said developing agent is bound to the gelatin in the developed areas of the layer and has an oleophilic residue receptive of greasy printing ink, and (c) inking the developed areas with greasy printing ink and printing therefrom in a lithographic printing press.

18. A lithographic printing process which comprises (a) exposing to a subject a photographic element comprising a support having thereon a layer containing a sufficient amount of a polyhydroxybenzene silver halide developing agent to develop the exposed silver halide in the light-sensitive layer above it, said silver halide developing agent being a member selected from the group consisting of a halogen substituted polyhydroxybenzene, a phenyl substituted polyhydroxybenzene, and an alkyl substituted polyhydroxybenzene, said alkyl substituent containing 2 to 6 carbon atoms, the oxidation product of which renders gelatin oleophilic and over said layer an unfogged gelatino-silver halide emulsion layer containing at least one spectral sensitizer selected from the oxacarbo-
cyanine dyes having the formula set forth in claim 2 and the benzimidazole carbocyanine dyes having the formula set forth in claim 2 and wherein the amount of spectral sensitizing dye present in said emulsion layer ranges from about 500 milligrams and upwards per mole of silver halide and hardened with a hardener, such that the gelatin 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, and (b) developing said exposed emulsion layer with an alkaline solution to produce on said emulsion layer a

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printing surface in which the oxidation product of said developing agent is bound to the gelatin in the developed areas of the layer and has an oleophilic residue receptive of greasy printing ink.

19. A lithographic printing process which comprises (a) exposing to a subject a photographic element comprising a support having thereon a layer containing a sufficient amount of a polyhydroxybenzene silver halide developing agent to develop the exposed silver halide in the light-sensitive layer above it, said silver halide developing agent being a member selected from the group consisting of a halogen substituted polyhydroxybenzene, a phenyl substituted polyhydroxybenzene and an alkyl substituted polyhydroxybenzene, said alkyl substituent containing 2 to 6 carbon atoms, the oxidation product of which renders gelatin oleophilic and over said layer an unfogged gelatino-silver halide emulsion layer containing at least one spectral sensitizer selected from the oxcarbocyanine dyes having the formula set forth in claim 2 and the benzimidazole carbocyanine dyes having the formula set forth in claim 2 and wherein the amount of spectral sensitizing dye present in said emulsion layer ranges from about 500 milligrams and upwards per mole of silver halide, and over said emulsion layer a fogged gelatino-silver halide emul-

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sion layer hardened with a hardener, such that the gelatin 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, and (b) developing said exposed emulsion layer containing said developing agent with an alkaline solution to produce on said fogged emulsion layer a printing surface which is positive with respect to the original subject and in which the oxidation product of said developing agent is bound to the gelatin of the fogged emulsion layer in the areas corresponding to unexposed areas of the layer and has an oleophilic residue receptive of greasy printing ink.

References Cited

UNITED STATES PATENTS

2,921,067	1/1960	Larive et al.	96—106
3,146,104	8/1964	Yackel et al.	96—33
3,264,110	8/1966	Depoorta et al.	96—106

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