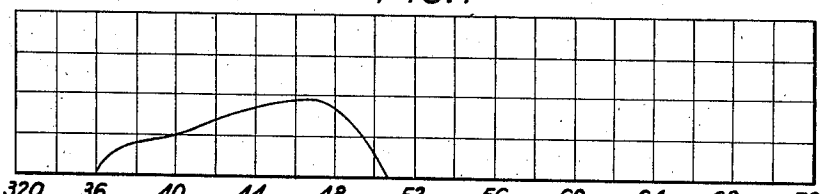
May 5, 1942. L. G. S. BROOKER 2,282,116

PHOTOGRAPHIC ELEMENT

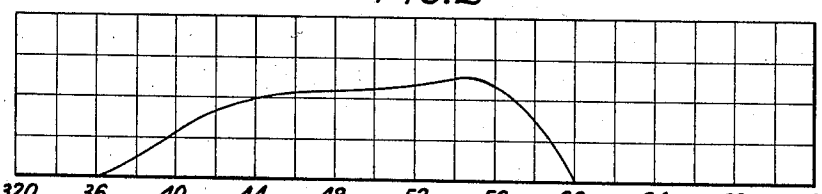
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FIG. 1



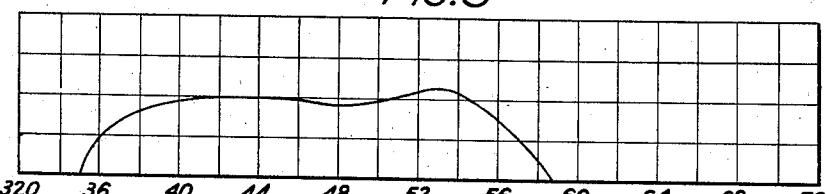

5-(2-ethyl-1(2)-benzothiazolylidene)-3-n-heptyl-rhodanine.

FIG. 2



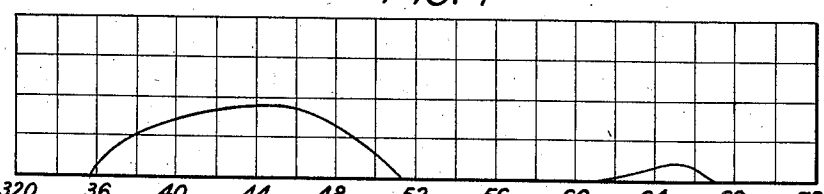

5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primaryheptyl-rhodanine.

FIG. 3




3-(n-primaryheptyl)-5-[(3-methyl-2(3)-thiozolinylidene)-ethylidene]-rhodanine.

FIG. 4




5-[4-(2-ethyl-1(2)-benzoxazolylidene)-butenylidene]-3-n-lauryl-rhodanine.

LESLIE G.S. BROOKER
INVENTOR

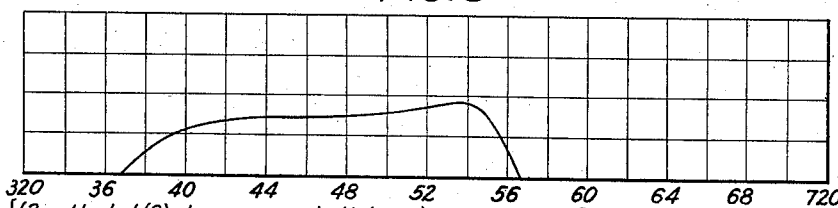
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May 5, 1942. L. G. S. BROOKER 2,282,116

PHOTOGRAPHIC ELEMENT

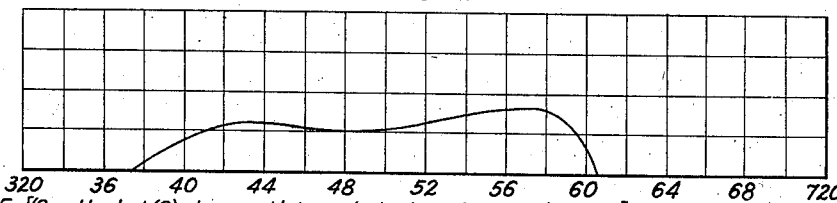
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FIG. 5



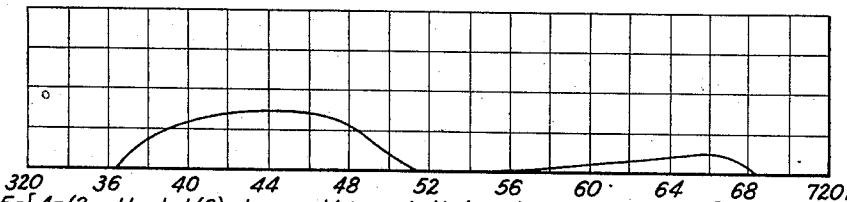

5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primaryheptyl-1-phenyl-2-thiohydantoin.

FIG. 6



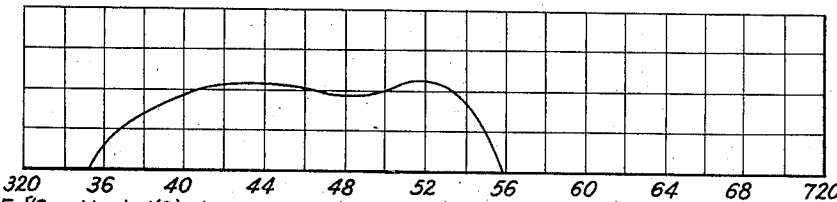

5-[(2-ethyl-1(2)-benzothiazolylidene)-ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin.

FIG. 7




5-[4-(2-ethyl-1(2)-benzothiazolylidene)-butenylidene]-3-n-heptyl-2-thio-2,4(3,5)-oxazoledione.

FIG. 8




5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-octyl-2-thio-2,4(3,5)-oxazoledione.

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Patented May 5, 1942

2,282,116

# UNITED STATES PATENT OFFICE

2,282,116

## PHOTOGRAPHIC ELEMENT

Leslie G. S. Brooker, Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

Application March 1, 1940, Serial No. 321,730
In Great Britain April 14, 1939

9 Claims. (Cl. 95—7)

This invention relates to photographic elements having one or more silver halide emulsion layers containing sensitizing dyes which are non-diffusing in character. More particularly, it relates to photographic elements having at least two silver halide emulsion layers superimposed, each of which contains a non-diffusing sensitizing dye of different spectral sensitivity.

In color photographic processes, it is common to employ photographic elements comprising two or more emulsions having different spectral sensitivities, coated on a single support. Thus, in monopack processes, the color photographic element may comprise a support coated upon which is an emulsion layer sensitized to the red, upon which is coated an emulsion layer sensitized to the green, upon which is coated an emulsion layer which is sensitive to the blue. The emulsion layers may be separated by intermediate layers of a colloidal substance like gelatin. Or, in monopack processes, the color photographic element may comprise a support coated on one side of which is an emulsion layer sensitized to the red, and upon the other side of which is coated an emulsion layer sensitized to the green, upon which is coated an emulsion layer which is sensitive to the blue. Or, in monopack processes, the color photographic element may comprise a support coated with an emulsion of the mixed-grain or mixed-emulsion type, i. e., in which two or more sets of grains of a photo-sensitive silver salt, such as silver halide, having different spectral sensitivities are mixed together in a colloid medium, such as gelatin. Such a mixed-grain emulsion is, of course, in effect a mixture of emulsions having different spectral sensitivities. Or in bipack processes, the color photographic element may comprise a support coated with an emulsion layer which is sensitive to the green upon which is coated an emulsion which is sensitive to the blue, while the red sensitive layer is coated on a different support.

In all such color photographic elements, the red-sensitive emulsion is rendered sensitive to the red by incorporation of sensitizing dyes in the emulsion; likewise the green-sensitive layer is rendered sensitive to the green by incorporation of sensitizing dyes in the emulsion; while ordinarily no sensitizing dyes are incorporated in the blue-sensitive emulsion, since the silver bromide emulsions ordinarily employed for such a purpose are sufficiently sensitive to blue light. However a sensitizing dye which sensitizes to the blue may be incorporated in the blue-sensitive emulsion layer and, in fact, when employing silver chloride emulsions as the blue-sensitive layer, sensitizing dyes are incorporated, in order to render the emulsion layer sensitive to about the same blue light to which a silver bromide emulsion is sensitive.

In practice, the sensitizing dyes present a considerable difficulty because there is a greater or lesser tendency for the dyes to diffuse from the emulsion in which they are incorporated, into the adjacent emulsion. Diffusion of the sensitizing dyes from the green-sensitive layer into the blue-sensitive layer has provided an especially troublesome situation.

I have now found that the aforesaid difficulties of diffusion can be overcome or at least greatly diminished by employing, as sensitizing dyes, dyes containing, as a substituent or addendum to the molecule of the sensitizing dye, a long-chain organic group. A few sensitizing dyes containing a long-chain organic group are available and while I have found that these available dyes do not diffuse to a great extent, I have also found that these available dyes are not strong sensitizers. Apparently, the presence of the long-chain organic group diminishes their sensitizing action. In the interest of obtaining dyes containing a long-chain organic group and which sensitize photographic emulsions strongly, I have found certain new merocyanine dyes.

It is an object of my invention, therefore, to provide a photographic element having one or more silver halide emulsion layers, at least one of which layers contains one or more sensitizing dyes which have a long-chain organic group as a substituent or addendum to their molecule. A further object is to provide a color photographic element comprising two or more silver halide emulsion layers having different spectral sensitivities, wherein at least one of the emulsion layers contains a sensitizing dye having a long-chain organic group, as a substituent or addendum to its molecule. A still further object is to provide a series of new sensitizing dyes which have a long-chain organic group as a substituent or addendum to their molecules. Another object is to provide a process for preparing such new dyes. Other objects will appear hereinafter.

I have found that photographic sensitizing dyes containing a long-chain organic group of at least seven non-metallic atoms as a substituent, can be employed in practicing my invention. The atoms forming the chain are advantageously from the group consisting of carbon atoms, oxygen atoms, sulfur atoms and nitrogen atoms. Where valence permits, non-metallic atoms such as hydrogen,

oxygen, sulfur, nitrogen, halogen or carbon atoms can be attached to the chain atoms. Most advantageously the atoms forming the chain are entirely carbon atoms and the atoms attached to the chain carbon atoms are hydrogen. Generally speaking, a sensitizing dye containing a hydrocarbon group comprising a chain of at least seven carbon atoms is especially advantageously employed in practicing my invention. Typical long-chain groups are as follows:

n-Primaryheptyl

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—$$

n-Primaryamyloxymethyl

$$CH_3—CH_2—CH_2—CH_2—CH_2—O—CH_2—$$

n-Primaryamylthiomethyl

$$CH_3—CH_2—CH_2—CH_2—CH_2—S—CH_2—$$

3-methyl-n-primaryheptyl

$$CH_3—CH_2—CH_2—CH_2—\underset{\displaystyle CH_3}{CH}—CH_2—CH_2—$$

n-Primarybutylcarbamylmethyl

$$CH_3—CH_2—CH_2—CH_2—\underset{\displaystyle H}{N}—\overset{\displaystyle O}{\overset{\|}{C}}—CH_2—$$

n-Primarypentadecyl

$$CH_3—(CH_2)_{13}—CH_2—$$

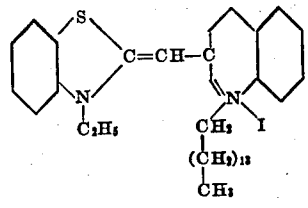
Stearyl

$$CH_3—(CH_2)_{16}—CH_2—$$

Lauryl

$$CH_3—(CH_2)_{10}—CH_2—$$

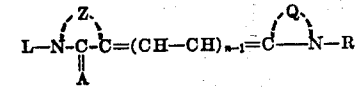
The position in the sensitizing dye where the long-chain organic group is attached has a considerable effect on the sensitizing action of the dye, I have found. Thus, when the long-chain group is attached to the polymethine chain of a polymethine sensitizing dye, the sensitizing power of the dye is ordinarily very considerably diminished. Likewise, when the long-chain group is attached to one of the auxochromic atoms of a sensitizing dye, as to one of the auxochromic nitrogen atoms of a cyanine dye, thus:



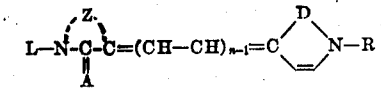
the sensitizing power is ordinarily very considerably diminished. While such sensitizing dyes of diminished sensitizing power are within the scope of my invention, I prefer to employ sensitizing dyes which have a long-chain organic group, and in which the sensitizing power is not greatly diminished.

Sensitizing dyes of the cyanine class, of the merocyanine class, of the hemioxonol class and of the hemicyanine class for example, contain a polymethine chain connecting two auxochromic atoms. In cyanine dyes, the two auxochromic atoms are both nitrogen atoms; in merocyanine dyes, the auxochromic atoms are oxygen (or sulfur) and nitrogen; in hemioxonol dyes, the auxochromic atoms are oxygen (or sulfur) and nitrogen; and in hemicyanine dyes, the auxochromic atoms are both nitrogen atoms. I have found that sensitizing dyes of the aforesaid classes containing, as a substituent, a long-chain organic group on a portion of their molecules other than the polymethine chain or the auxochromic atoms, have not only a greatly diminished tendency to diffuse, relative to many sensitizing dyes which do not contain a long-chain organic group substituent, but are very strong sensitizers, relative to sensitizing dyes having a long-chain organic groups, as a substituent on the polymethine chain or on the auxochromic atoms.

I have found new dyes of the merocyanine class which contain a long-chain organic group, as a substituent on other than the polymethine chain and on other than the auxochromic atoms, which show but a relatively small diminution of sensitizing power owing to the long-chain organic group. Such dyes can be represented by the following general formulas:

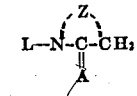


and



wherein A represents oxygen or sulfur, D represents a divalent organic group, such as a vinylene or a phenylene group for example, L represents a long-chain organic group substituent, $n$ represents a positive integer of from one to three, Q represents the non-metallic atoms necessary to complete an organic heterocyclic nucleus, such as a thiazole nucleus (e. g. 4-methylthiazole, 4-phenylthiazole, benzothiazole, 4-chlorobenzothiazole, $\alpha$-naphthothiazole, $\beta$-naphthothiazole), an oxazole nucleus (e. g. 4-methyloxazole, 4-phenyloxazole, benzoxazole, $\alpha$-naphthoxazole and $\beta$-naphthoxazole), a selenazole nucleus (e. g. 4-methylselenazole, 4-phenylselenazole and benzoselenazole), a thiazoline nucleus, a quinoline nucleus (e. g. 5-methylquinoline and benzoquinoline) or a pyridine nucleus for example, and Z represents the non-metallic atoms necessary to complete a five-membered heterocyclic organic nucleus, such as, a 2-thio-2,4(3,5)-thiazoledione (rhodanine) nucleus, a 2-thio-2,4(3,5)-oxazoledione nucleus, a 2-thio-2,4(3,5)-imidazoledione (2-thiohydantoin) nucleus, a 2,4-dithio-2,4(3,5)-thiazoledione, or a 2,4-dithio-2,4(3,5)-imidazoledione nucleus, for example.

I have found that the above formulated merocyanine dyes can be prepared by condensing a cyclammonium quaternary salt containing a $\beta$-arylaminovinyl group (advantageously an acylated $\beta$-arylaminovinyl group) in the alpha or gamma position, i. e. one of the so-called reactive positions, with a compound of the following formula:

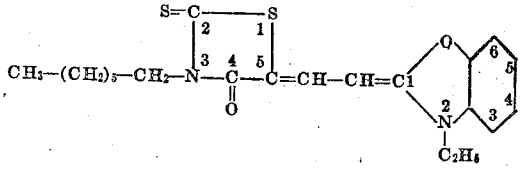


wherein A represents oxygen or sulphur, L represents a long-chain organic group containing a chain of at least seven members each of which is composed of non-metallic atoms and Z represents the non-metallic atoms necessary to complete a five-membered heterocyclic organic nucleus, such as a 2-thio-2,4(3,5)-oxazoledione nucleus, a 2-thio-2,4(3,5)-thiazoledione nucleus, a 2-thio-2,4(3,5)-imidazoledione nucleus or a

5-thiopyrazolone nucleus for example. As quaternary salts, the alkyl halides, are advantageously employed. The condensations are advantageously effected in the presence of a basic condensing agent. Sodium and potassium acetates are suitable basic condensing agents, and when these agents are employed, condensations are advantageously carried out in the presence of acetic anhydride. Strong organic bases (i. e. organic bases having a dissociation constant substantially greater than that of pyridine), particularly tertiary organic bases, like triethylamine, tributylamine or N-methylpiperidine, are advantageously employed as condensing agents. When these strong organic bases are employed, the condensations are advantageously carried out in the presence of alcohol solvents, such as alcohols of the formula $C_nH_{2n+1}OH$ wherein $n$ represents a positive integer of from one to four. Heat accelerates the formation of my new dyes.

The following examples are offered by way of illustration of the preparation of the above formulated new merocyanine dyes. These examples are not intended to limit my invention.

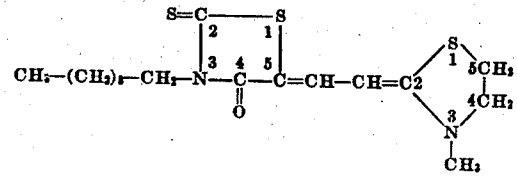
EXAMPLE 1.—*5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primaryheptyl-rhodanine*



2.3 g. (1 mol.) of 3-n-primaryheptyl-rhodanine, 4.34 g. (1 mol.) of 1-(β-acetanilido-vinyl)-benzoxazole ethiodide and 1.0 g. (1 mol.) of triethylamine were placed in 15 cc. of absolute ethyl alcohol. The resulting mixture was heated on a steam bath, under reflux, for about 15 minutes while stirring. The reaction mixture assumed an orange coloration. The reaction mixture was chilled to about 0° C. and the dye which separated was filtered. The dye was twice recrystallized from methyl alcohol and obtained as reddish crystals having a blue reflux and melting at 130° to 131° C. The dye is a powerful sensitizer of gelatino-silver-bromide emulsions for the green, its effect extending to 600 mu with a maximum at 540 mu.

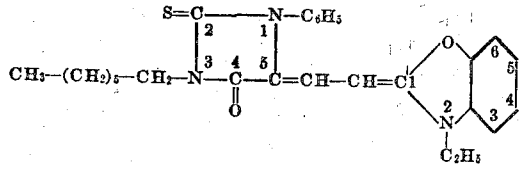
In a similar manner to that illustrated in the foregoing example, 3-n-primaryoctyl-rhodanine, 3-n-primarydecyl-rhodanine, and 3-n-primarylauryl-rhodanine can be condensed with 1-(β-acetanilido-vinyl)-benzoxazole ethiodide to yield 5-[(2-ethyl-2(2)-benzoxazolylidene)-ethylidene]-3-n-primaryoctyl-rhodanine in the form of scarlet crystals having a melting point of 124–125° C. and sensitizing a gelatino-silver-bromide emulsion out to about 605 mu with a maximum at about 555 mu, 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primarydecyl-rhodanine in the form of reddish crystals with blue reflex having a melting point of 111–112° C. and sensitizing a gelatino-silver-bromide emulsion out to about 600 mu with a maximum at about 555 mu and 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primarylauryl-rhodanine in the form of red crystalline needles with blue reflex having a melting point of 109–110° C. and sensitizing a gelatino-silver-bromide emulsion out to about 580 mu with a maximum sensitivity at about 560 mu respectively.

EXAMPLE 2.—*3-(n-primaryheptyl)-5-[(3-methyl-2(3)-thiazolinylidene)ethylidene]-rhodanine*



6.8 g. (1 mol.) of 2-anilidovinylthiazoline methiodide, 4.6 g. (1 mol.) of 3-n-primaryheptyl-rhodanine and 2.2 g. (1.1 mol.) of triethylamine were placed in 75 cc. of absolute ethyl alcohol. The mixture was heated on a steam bath, under reflux, for about 30 minutes. The mixture was then chilled to 0° C. and the dye which separated was filtered off, washed with methyl alcohol and dried. After two recrystallizations from methyl alcohol, the dye was obtained as amber-colored crystals melting at 120° to 123° C. The dye is a powerful sensitizer of gelatino-silver-bromide emulsions for the green, its effect extending to 580 mu with a maximum at 530 mu.

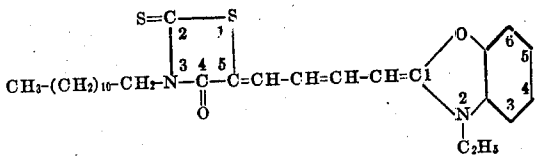
EXAMPLE 3.—*5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primaryheptyl-1-phenyl-2-thiohydantoin*



2.6 g. (1 mol.) of 3-n-primaryheptyl-1-phenyl-2-thiohydantoin, 3.9 g. (1 mol.) of 1-(β-acetanilidovinyl)-benzoxazole ethiodide and 5 cc. of triethylamine were placed in 50 cc. of absolute ethyl alcohol. The mixture was warmed greatly on a steam bath, under reflux, for 5 minutes. The mixture was then allowed to stand at 20° to 25° C. for about 16 hours and was finally chilled to about 0° C. The dye which separated was filtered off. After four recrystallizations from methyl alcohol, it was obtained as brownish needles having a blue reflex and melting at 178° to 179° C. The dye is a strong sensitizer for gelatino-silver-bromide emulsions, its effect extending to 560 mu with a maximum at 530 mu.

In place of 3-n-primaryheptyl-1-phenyl-2-thiohydantoin, there may be substituted in the above example, 3-n-heptyl-2-thiohydantoin to give the dye 5-[2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primaryheptyl-2-thiohydantoin in the form of orange crystals having a melting point of 207–209° C. with decomposition, and sensitizing a gelatino-silver-bromide emulsion out to about 560 mu with a maximum sensitivity at about 525 mu; 3-n-primarynonyl-1-phenyl-2-thiohydantoin to give the dye 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primarynonyl-1-phenyl-2-thiohydantoin in the form of orange crystalline needles having a melting point of 179–181° C. and sensitizing a gelatino-silver-bromide emulsion out to about 570 mu with a maximum sensitivity at about 530 mu; and 3-n-primarydecyl-1-phenyl-2-thiohydantoin to give the dye 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primarydecyl-1-phenyl-2-thiohydantoin in the form of yellow crystals having a melting point of 170–172° C. and sensitizing a gelatino-silver-bromide emulsion out to about 565 mu with a maximum sensitivity at about 530 mu.

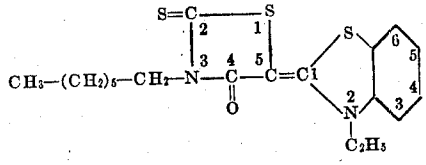
EXAMPLE 4.—*5-[4-(2-ethyl-1(2)-benzoxazolylidene) butenylidene]-3-n-lauryl-rhodanine*



2.3 g. (1 mol.) of 1-(4-acetanilido-$\Delta^{1,3}$-butadienyl)-benzoxazole ethiodide, 1.5 g. (1 mol.) of 3-n-laurylrhodanine and 0.5 g. (1 mol.) of triethylamine were placed in 15 cc. of absolute ethyl alcohol. The mixture was heated on a steam bath, under reflux, for 10 minutes. The mixture took on a deep purple color. The mixture was chilled to 0° C. The dye which separated was filtered off. The residue on the filter was extracted with 100 cc. of boiling methyl alcohol. The undissolved residue was then twice recrystallized from methyl alcohol and the dye was obtained as a mat of greenish crystals melting at 91° to 93° C. The dye sensitized a gelatino-silver-bromide emulsion from about 620 mu to about 670 mu with a maximum at 650 mu.

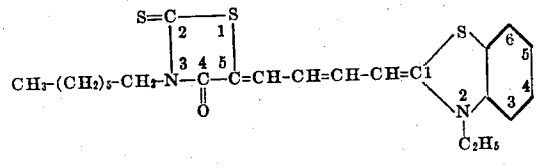
Instead of 3-n-laurylrhodanine, there may be employed in the above example, 3-n-heptylrhodanine to give the dye 5-[4-(2-ethyl-1(2)-benzoxazolylidene) butenylidene] - 3 - n - heptylrhodanine in the form of minute blue crystals having a melting point of 127–129° C. with decomposition, and sensitizing a gelatino-silver-bromide emulsion from about 540 mu to 690 mu with a maximum sensitivity at about 660 mu.

EXAMPLE 5.—*5 - (2 - ethyl - 1(2) - benzothiazolylidene) -3-n-heptylrhodanine*



1.15 g. (1 mol.) of 3-n-heptylrhodanine and 2.0 g. (1 mol.) of 1-phenylmercaptobenzothiazole ethiodide were heated to reflux in 10 ccs. of absolute ethyl alcohol and 0.53 g. (1.05 mol.) of triethylamine added with shaking. The mixture was then refluxed for about 15 minutes, followed by chilling for several hours at about 0° C. The crude crystals which formed were filtered off, washed with methyl alcohol, and purified by recrystallization twice from methyl alcohol. The dye thus obtained had a melting point of 174–175° C. and sensitized a gelatino-silver-chloride emulsion to about 505 mu with maximum sensitivity at about 470 mu.

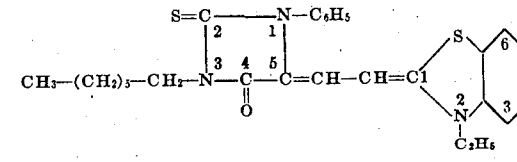
EXAMPLE 6.—*5-[4-(2-ethyl-1(2)-benzothiazolylidene) butenylidene]-3-n-heptyl-rhodanine*



2.4 g. (1 mol.) of 1-(-acetanilido-$\Delta^{1,3}$-butadienyl)-benzothiazole ethiodide, 1.1 g. (1 mol.) of 3-n-heptylrhodanine, and 0.5 g. (1 mol.) of triethylamine were heated to reflux for 10 minutes in 20 ccs. of absolute ethyl alcohol. The mixture was then chilled and the crude dye crystals which formed were filtered off, washed well with methyl alcohol and subjected to two recrystallizations from a mixture of pyridine and methyl alcohol. The purified dye obtained as minute blue crystals had a melting point of 161–163° C. with decomposition, and sensitized a gelatino-silver-bromide emulsion from about 655 mu to about 710 mu with maximum sensitivity at about 690 mu.

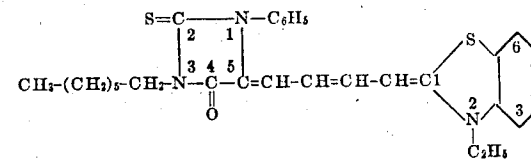
In place of 3-n-heptylrhodanine, there may be substituted 3-n-octylrhodanine in which case there is obtained the dye 5-[4-(2-ethyl-1(2)-benzothiazolylidene) butenylidene] - 3 - n - octylrhodanine in the form of a mat of minute blue crystals having a melting point of 161–163° C. with decomposition, and sensitizing a gelatino-silver-bromide emulsion from about 620 mu to 715 mu with maximum sensitivity at about 690 mu.

EXAMPLE 7.—*5-[(2-ethyl-1(2)-benzothiazolylidene)-ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin*



2.9 g. (1 mol.) of 3-n-heptyl-1-phenyl-2-thiohydantoin, 4.5 g. (1 mol.) of 1-(β-acetanilidovinyl)-benzothiazole ethiodide, 5 ccs. of triethylamine, and 50 ccs. of absolute ethyl alcohol were heated under reflux for 15 minutes. The reaction mixture was then chilled, and the crystals which formed were filtered off, and recrystallized three times from methyl alcohol. The purified dye thus obtained in the form of red crystals with blue reflex had a melting point of 116–118° C. and sensitized a gelatino-silver-bromide emulsion to about 610 mu with maximum sensitivity at about 580 mu.

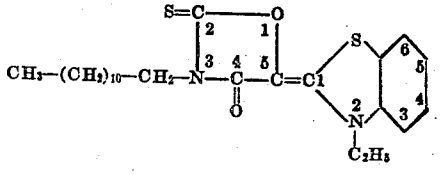
EXAMPLE 8.—*5-[4-(2-ethyl-1(2)-benzothiazolylidene) butenylidene]-3-n-heptyl - 1 - phenyl - 2-thiohydantoin*



A mixture of 2.9 g. (1 mol.) of 3-n-heptyl-1-phenyl-2-thiohydantoin, 4.8 g. (1 mol.) of 1-(4-acetanilido-$\Delta^{1,3}$-butadienyl)-benzothiazole ethiodide, 1.0 g. (1 mol.) of triethylamine, and 30 ccs. of absolute ethyl alcohol was allowed to stand at room temperature for a period of about 17 hours. At the end of this time the reaction mixture had developed a blue color and some crystals had separated out of solution. The mixture was then chilled and the crystals filtered off, washed with methyl alcohol, and recrystallized from methyl alcohol, then from absolute ethyl alcohol, and finally from 95% ethyl alcohol. The purified dye obtained in the form of a dark green felt had a melting point of 189–

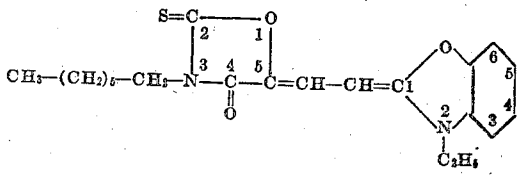
190° C. and sensitized a gelatino-silver-bromide emulsion from about 540 mu to about 715 mu with maximum sensitivity at about 690 mu.

EXAMPLE 9.—*5-(2-ethyl-1(2)-benzothiazolylidene)-3-n-lauryl-2-thio-2,4(3,5)-oxazoledione*



1.43 g. (1 mol.) of 3-n-lauryl-2-thio-2,4(3,5)-oxazoledione and 2.00 g. (1 mol.) of 1-phenyl-mercaptobenzothiazole ethiodide were heated in 10 ccs. of absolute ethyl alcohol to the refluxing temperature, and 0.53 g. (1.05 mol.) of triethylamine added with shaking. The reaction mixture was then refluxed for a period of about 15 minutes, followed by chilling for several hours at 0° C. The crude crystals which formed were filtered off, washed with methyl alcohol, and recrystallized twice from methyl alcohol. The purified dye obtained in the form of a pale yellow solid had a melting point of 73–74° C. and sensitized a gelatino-silver-chloride emulsion up to 445 mu with maximum sensitivity at about 435 mu.

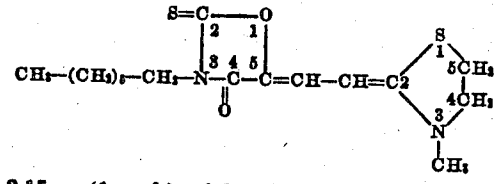
EXAMPLE 10.—*5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-heptyl-2-thio-2,4(3,5)-oxazoledione*



A mixture of 2.15 g. (1 mol.) of 3-n-heptyl-2-thio-2,4(3,5)-oxazoledione, 4.35 g. (1 mol.) of 1-(β-acetanilido-vinyl)-benzoxazole ethiodide, 1.01 g. (1 mol.) of triethylamine, and 50 ccs. of absolute ethyl alcohol was heated under reflux on a steam bath for a period of 15 minutes. At the end of this time, the reaction mixture was chilled and the crystals which formed were filtered off, washed with alcohol, and recrystallized two times from absolute ethyl alcohol. The purified dye obtained as fluffy yellow needles had a melting point of 197–198° C. and sensitized a gelatino-silver-bromide emulsion up to 555 mu with maximum sensitivity at about 525 mu.

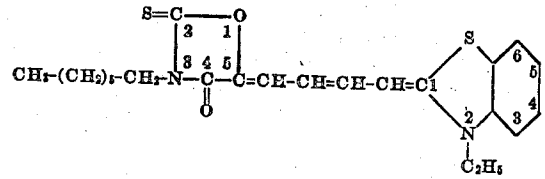
In place of 3-n-heptyl-2-thio-2,4(3,5)-oxazoledione, there may be substituted in the above example 3-n-lauryl-2-thio-2,4(3,5)-oxazoledione to give the dye 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-lauryl-2-thio-2,4(3,5)-oxazoledione in the form of yellow crystals having a melting point of 177–178° C. and sensitizing a gelatino-silver-bromide emulsion to about 540 mu with maximum sensitivity at about 520 mu, or 3-n-octyl-2-thio-2,4(3,5)-oxazoledione to give the dye 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-octyl-2-thio-2,4(3,5)-oxazoledione in the form of yellow crystals having a melting point of 190–191° C. and sensitizing a gelatino-silver-bromide emulsion up to about 560 mu with maximum sensitivity at about 520 mu.

EXAMPLE 11.—*5-[(3-methyl-2(3)-thiazolinylidene)-ethylidene]-3-n-heptyl-2-thio-2,4(3,5)-oxazoledione*



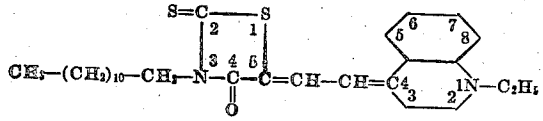
2.15 g. (1 mol.) of 3-n-heptyl-2-thio-2,4(3,5)-oxazoledione, 3.50 g. (1 mol.) of 2-β-anilidovinyl thiazoline methiodide, 1.01 g. (1 mol.) of triethylamine, and 25 ccs. of absolute ethyl alcohol were heated to reflux for a period of 20 minutes. The reaction mixture was then chilled, and the dye crystals which formed were filtered off, washed with methyl alcohol, and recrystallized three times from methyl alcohol. The purified dye obtained in the form of yellow flakes had a melting point of 147–149° C. and sensitized a gelatino-silver-chloride emulsion to 520 mu with maximum sensitivity at about 500 mu.

EXAMPLE 12.—*5-[4-(2-ethyl-1(2)-benzothiazolylidene)butenylidene]-3-n-heptyl-2-thio-2,4-(3,5)-oxazoledione*



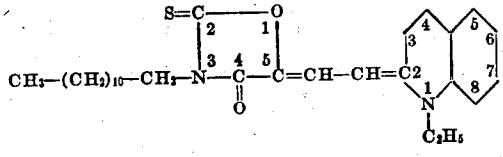
2.4 g. (1 mol.) of 1-(4-acetanilido-Δ1,3-butadienyl) benzothiazole ethiodide, 1.05 g. (1 mol.) 3-n-heptyl-2-thio-2,4(3,5)-oxazoledione, 0.5 g. (1 mol.) of triethylamine, and 15 ccs. of absolute ethyl alcohol were heated together under reflux for a period of about 10 minutes. The reaction mixture was then chilled, and the crystals which formed were collected on a filter and washed with methyl alcohol. The solid was then extracted with hot methyl alcohol, the extract chilled, and the crystals which formed were recrystallized once more from methyl alcohol. The dye obtained in the form of blue crystals had a melting point of 141–143° C. and sensitized a gelatino-silver-bromide emulsion from about 550 mu to about 695 mu with maximum sensitivity at about 665 mu.

EXAMPLE 13.—*5-[(1-ethyl-4(1)-quinolylidene)-ethylidene]-3-n-lauryl-rhodanine*



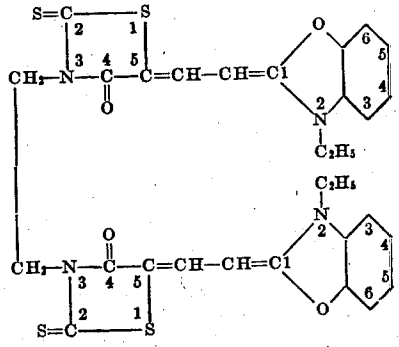
A mixture of 0.75 g. (1 mol.) of 3-n-lauryl-rhodanine, 1.11 g. (1 mol.) of 4-(ω-acetanilido-vinyl) quinoline ethiodide, 0.25 g. (1 mol.) of triethylamine, and 30 ccs. of absolute ethyl alcohol was heated under reflux for a period of about 20 minutes. Dye separated from the hot reaction mixture. After chilling, the crystals were filtered off, washed with cold methyl alcohol, boiled with 75 ccs. of methyl alcohol, and the insoluble residue purified by two recrystallizations from a pyridine-methyl alcohol mixture. The dye obtained in the form of blue crystals had a melting point of 157–158° C. and sensitized a gelatino-silver-bromide emulsion.

EXAMPLE 14. — *5 - [(1-ethyl-2(1)-quinolylidene)-ethylidene)] - 3 - n - lauryl - 2 - thio - 2,4 - (3,5)-oxazoledione*



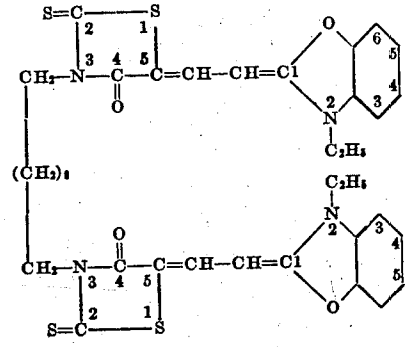
A mixture of 0.70 g. (1 mol.) of 3-n-lauryl-2-thio-2,4(3,5)-oxazoledione, 1.11 g. (1 mol.) of 2-(ω-acetanilido-vinyl) quinoline ethiodide, 0.25 g. (1 mol.) of triethylamine, and 15 ccs. of absolute ethyl alcohol was heated under reflux for a period of about 20 minutes. The reaction mixture was then chilled, and the crystals which formed were collected on a filter, washed repeatedly with hot methyl alcohol, and recrystallized from a pyridine-methyl alcohol mixture. The dye obtained in the form of a reddish felt had a melting point of 176–177° C. and sensitized a gelatino-silver-bromide emulsion.

EXAMPLE 15.—*Ethylene-bis [5 - [(2-ethyl-1(2)-benzoxazolylidene) - ethylidene] - rhodanine-(3)]*



A mixture of 1.46 g. (1 mol.) of ethylene-bis (3,3'-rhodanine), 4.34 g. (2 mol.) of 1-(β-acetanilido-vinyl) benzoxazole ethiodide, 1.01 g. (2 mol.) of triethylamine, and 200 ccs. of absolute ethyl alcohol was heated under reflux for a period of about 20 minutes. The reaction mixture was then chilled, and the dye crystals which formed were filtered off, washed with methyl alcohol, and purified by recrystallizations from a pyridine-methyl alcohol mixture. The dye obtained in the form of a scarlet powder had a melting point greater than 300° C. and sensitized a gelatino-silver-bromide emulsion to about 610 mu with maximum sensitivity at about 565 mu.

EXAMPLE 16.—*Decamethylene-bis [5 - [(2-ethyl-1(2)-benzoxazolylidene) - ethylidene] - rhodanine(3)]*



0.47 g. (1 mol.) of decamethylene-bis(3,3'-rhodanine), 1.09 g. (2 mol.) of 1-(β-acetanilido-vinyl) benzoxazole ethiodide, 0.40 cc. (2 mol.) of triethylamine, and 20 ccs. of absolute ethyl alcohol were heated under reflux for a period of about 20 minutes. The reaction mixture was then chilled, and the crystals which formed were filtered off, washed with methyl alcohol, and purified by two recrystallizations from a solvent mixture of pyridine and methyl alcohol. The dye obtained in the form of a reddish-brown powder had a melting point of 164–166° C. and sensitized a gelatino-silver-bromide emulsion out to about 570 mu with maximum sensitivity at about 550 mu.

EXAMPLE 17.—*3-n-heptylrhodanine*

7.6 g. (1 mol.) of carbon disulfide was added dropwise with stirring to a mixture of 10.5 g. (1 mol.) of n-heptylamine and 6.0 g. of 85% potassium hydroxide in 150 ccs. of water. The reaction proceeded with the evolution of heat. After a period of about 30 minutes, there was added with stirring 9.5 g. (1 mol.) of chloracetic acid neutralized with sodium carbonate in 100 ccs. of water, and the stirring continued for about one hour. The reaction mixture was then allowed to stand for 24 hours at room temperature, when it was acidified with sulphuric acid to litmus paper, chilled to 0° C. for a period, and the yellow fatty mass which formed was filtered off, dissolved in benzene, and dried by distillation of the solvent. The product obtained in this manner was used for dye condensations without further purification.

In a manner generally similar to that above described, but using the corresponding octylamine, decylamine, and laurylamine compounds, 3-n-octylrhodanine, 3-n-decylrhodanine and 3-n-laurylrhodanine may be prepared.

EXAMPLE 18.—*3-n-heptyl-2-thio-2,4(3,5)-oxazoledione*

A mixture of 12.1 g. (1 mol.+100% excess) of n-heptylamine, 10.5 g. (1 mol.) of acetamido-carbothiolonglycollic acid, 2.8 g. of 85% potassium hydroxide, and 150 ccs. of water was stirred at room temperature for a period of about 5½ hours. The reaction mixture was then acidified by dropwise addition of sulphuric acid, followed by heating with stirring on a steam bath for about one hour. A solid waxy mass which separated on chilling was washed with water by decantation, and dried in a vacuum desiccator, and after recrystallization from methyl alcohol and then from ligroin yielded the desired product as white soapy flakes having a melting point of 55–56° C.

In a manner generally similar to the above described process, but using the corresponding octylamine and laurylamine compounds, 3-n-octyl-2-thio-2,4(3,5)-oxazoledione and 3-n-lauryl-2-thio-2,4(3,5)-oxazoledione may be prepared.

EXAMPLE 19.—*3-n-heptyl-2-thiohydantoin*

5.0 g. (1 mol.) of glycine was dissolved in a solution of 4.3 g. of 85% potassium hydroxide in 7 ccs. of water, and 10.5 g. (1 mol.) of n-heptyl isothiocyanate dissolved in 40 ccs. of absolute ethyl alcohol added. The mixture was then heated under reflux for about 90 minutes, the alcohol solvent evaporated for the most part, and the residue treated with 5 ccs. of water and then with 10 ccs. of concentrated hydrochloric acid. A yellow precipitate was formed at once.

After cooling the reaction mixture, the solid was filtered off, washed with water, suspended in 60 ccs. of 12% hydrochloric acid, and the suspension heated at 95° C. for about two hours. The suspension was then chilled, and the solid filtered off, washed with water, and recrystallized from ligroin. The product obtained as pale yellow plates had a melting point of 90–92° C.

EXAMPLE 20.—*3 - n-nonyl - 1 - phenyl-2-thiohydantoin*

A mixture of 6.1 g. (1 mol.) of nonyl isothiocyanate and 5.9 g. (1 mol.) of N-phenylglycine ethyl ether was heated in an oil bath at 185–190° C. for a period of about four hours. The reaction mixture was then distilled under reduced pressure and the fraction boiling at 218–220° C. at 1 mm. pressure was recrystallized twice from petroleum ether. The purified product had a melting point of 35–38° C.

If the nonyl isothiocyanate is replaced in the above example by n-heptyl isothiocyanate or n-decyl isothiocyanate, there is obtained the corresponding 3-n-heptyl-1-phenyl-2-thiohydantoin and 3-n-decyl-1-phenyl-2-thiohydantoin, respectively.

EXAMPLE 21.—*Ethylene-bis(3,3'-rhodanine)*

15.2 g. (2 mol.) of carbon disulfide was added with stirring over a 15 minute period to a mixture of 6.0 g. (1 mol.) of ethylene-diamine and 11.2 g. (2 mol.) of 85% potassium hydroxide in 200 ccs. of water, and stirring continued for 3 hours. At the end of this time, a solution of 18 g. (2 mol.) of chloracetic acid neutralized with 10.6 g. (1 mol.) of sodium carbonate in 100 ccs. of water was added to the reaction mixture. After standing at room temperature with occasional shaking for about 18 hours, the mixture was acidified to litmus paper with dilute sulphuric acid. The yellow, tarry product thus obtained solidified upon washing with water and ether, after which it was filtered off, washed well with water, then with methyl alcohol, and recrystallized twice from acetic acid. The purified product obtained as straw-colored crystals had a melting point of 195–196° C.

If the ethylene diamine is replaced in the above example by decamethylene diamine, there is obtained the compound decamethylene-bis(3,3'-rhodanine) as a yellow powder having a melting point 85–90° C.

EXAMPLE 22.—*n-heptylisothiocyanate*

25.4 g. (1 mol.) of carbon disulfide was added dropwise with stirring to a mixture of 29.8 g. (1 mol.) of n-heptylamine and 41 ccs. of 26% ammonia solution. The reaction took place with an evolution of heat, during which time the ammonium n-heptyl dithiocarbonate separate from solution in the form of a gel. After 20 minutes, the reaction mixture was diluted with water until the precipitate dissolved, when 92.2 g. (1 mol.) of lead nitrate dissolved in 200 ccs. of water was added. A light brown precipitate, turning black, of lead sulfide formed immediately. The mixture was then steam distilled into a receiver containing 10 cc. of dilute sulphuric acid and the distillate extracted several times with ether. After drying over calcium chloride, the solvent was removed from the distillate by evaporation, and the residue fractioned under reduced pressure. The product was isolated in the fraction having a boiling range of 112–113° C. at 13 mm. pressure.

In place of n-heptylamine in the above example, there may be substituted an equivalent quantity of n-nonylamine, in which case the compound n-nonylisothiocyanate is obtained in the fraction having a boiling range of 127–129° C. under 10 mm. of pressure.

EXAMPLE 23.—*n-decylisothiocyanate*

A mixture of 5.0 g. (1 mol.) of sym-di-n-decylthiocarbamide and 5.0 g. of phosphorous pentoxide was heated gently over a free flame for about 5 minutes. The temperature was then raised sufficiently to distill the n-decylisothiocyanate formed at normal pressure. The fraction boiling in a range 175–250° C. was used for the preparation of 3-n-decyl-1-phenyl-2-thiohydantoin without further purification.

My invention is directed to any photographic element having one or more silver halide emulsion layers, but more particularly to any color photographic element comprising two or more photographic silver halide emulsions which have different spectral sensitivities, and still more particularly to the ordinary gelatino-silver-bromide emulsions ordinarily employed in the preparation of color photographic elements. According to my invention, I incorporate in the emulsion to be sensitized for the red, one or more of the non-diffusing dyes which sensitize for the red, in the emulsion to be sensitized for the green, one or more of the non-diffusing dyes which sensitize for the green, etc. The dyes are advantageously incorporated in the washed, finished emulsions prior to coating the emulsions on a support. Ordinarily, from 3 to 30 mg. of the sensitizing dye per liter of ordinary gelatino-silver-bromide emulsion (about 40 grams of silver halide per liter of emulsion) suffices to give the optimum sensitization attainable with these non-diffusing sensitizers, although larger or smaller quantities can be employed. It is, of course, well known that the sensitization produced by a sensitizing dye does not increase proportionately to the concentration of the dye in the emulsion, but passes through a maximum as the concentration is increased. It is further well known that the sensitization produced by a particular sensitizing dye varies somewhat with the type of emulsion in which the dye is incorporated. The optimum concentration (i. e. the concentration at which optimum sensitization is attained) for a sensitizing dye on a particular emulsion can be readily determined in a manner well known to those skilled in the art, by measuring the sensitivity of a series of emulsions containing different concentrations of the sensitizing dye.

The dyes are advantageously incorporated in the emulsions in the form of solutions in appropriate solvents. Methanol has proven satisfactory as a solvent for these non-diffusing dyes. Ethyl alcohol or acetone can also be used. The dyes should be thoroughly incorporated in the emulsion by stirring the emulsion during incorporation of the solution of the dye.

The following procedure is considered quite satisfactory: A quantity of the dye is dissolved in methyl alcohol and a volume of this solution (which may be diluted somewhat with water) containing from 10 to 30 mg. of dye is slowly added with stirring to 1000 ccs. of a flowable gelatino-silver-halide emulsion, and stirring continued until the dye is thoroughly incorporated.

The so-prepared emulsions can then be utilized in the preparation of color photographic ele-

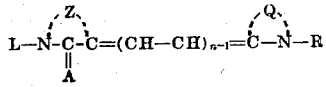
ments in a manner well known to those skilled in the art. Typical color photographic processes and typical color photographic elements comprising two or more emulsions having different spectral sensitivities are described in United States Patent 2,113,329, dated April 5, 1938, in British Patents 500,611 and 500,826, each accepted February 10, 1939, in United States Patent 1,985,344, dated December 25, 1934, in United States Patent 1,956,122, dated April 24, 1934, and in United States Patent 1,517,049, dated November 25, 1924, for example.

The accompanying drawings are by way of further illustrating my invention. Each figure is a diagrammatic reproduction of a spectogram showing the sensitivity of an ordinary gelatino-silver-bromide or gelatino-silver-chloride emulsion containing one of my new merocyanine sensitizing dyes. In Fig. 1, the curve depicts the sensitivity of an ordinary gelatino-silver-chloride emulsion containing 5-(2-ethyl-1(2)-benzothiazolylidene)-3-n-heptyl-rhodanine. In Fig. 2, the curve depicts the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primaryheptylrhodanine. In Fig. 3, the curve depicts the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 3-(n-primaryheptyl)-5-[(3-methyl-2(3)-thiazolinylidene)-ethylidene]-rhodanine. In Fig. 4, the curve depicts the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 5-[4-(2-ethyl-1(2)-benzoxazolylidene) butenylidene]-3-n-lauryl-rhodanine. In Fig. 5, the curve depicts the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-primaryheptyl-1-phenyl-2-thiohydantoin. In Fig. 6, the curve depicts the sensitivity of an ordinary gelatino-silver-bromide emulsion 5-[(2-ethyl-1(2)-benzothiazolylidene)-ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin. In Fig. 7, the curve depicts the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 5-[4-(2-ethyl-1(2)-benzothiazolylidene) butenylidene]-3-n-heptyl-2-thio-2,4(3,5)-oxazoledione. In Fig. 8, the curve depicts the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 5-[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-octyl-2-thio-2,4(3,5)-oxazoledione.

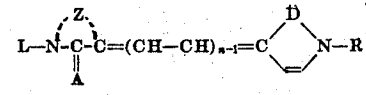
Still further illustrations of my new non-diffusing sensitizing dyes, their application and spectral sensitivities in ordinary gelatino-silver-halide emulsions could be given, but the foregoing will suffice to teach those skilled in the art the manner of practicing my invention. It is to be understood that my invention is not limited to the foregoing examples or to the specific details given therein. Numerous other embodiments are possible and I contemplate as included within my invention all such modifications and equivalents as fall within the scope of the appended claims.

What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A photographic element comprising a photographic silver halide emulsion which is sensitized with a sensitizing dye characterized by one of the following two formulas:

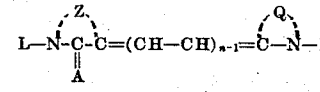


and



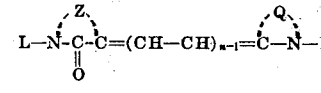
wherein A represents an atom selected from the group consisting of oxygen and sulphur atoms, D represents a radical selected from the group consisting of vinylene and phenylene groups, $n$ represents a positive integer of from one to three, L represents a long-chain organic group comprising a chain of at least seven non-metallic members, Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, R represents an alkyl group, and Z represents the non-metallic atoms necessary to complete a 2-thio-2,4(3,5)-thiazoledione nucleus, a 2-thio-2,4(3,5)-imidazoledione nucleus, and a 2-thio-2,4(3,5)-oxazoledione nucleus.

2. A photographic element comprising a photographic silver halide emulsion sensitized with a sensitizing dye characterized by the following formula:



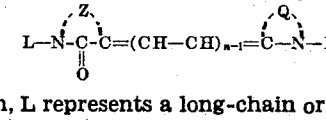
wherein A represents an atom selected from the group consisting of oxygen and sulphur atoms, L represents a long-chain organic group comprising a chain of at least seven non-metallic members, Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, R represents an alkyl group, and Z represents the non-metallic atoms necessary to complete a 2-thio-2,4(3,5)-thiazoledione nucleus, a 2-thio-2,4(3,5)-imidazoledione nucleus, and a 2-thio-2,4(3,5)-oxazoledione nucleus.

3. A photographic element comprising a photographic silver halide emulsion sensitized with a sensitizing dye characterized by the following formula:



wherein, L represents a long-chain organic group comprising a chain of at least seven non-metallic members, Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, R represents an alkyl group, and Z represents the non-metallic atoms necessary to complete a 2-thio-2,4(3,5)-thiazoledione nucleus.

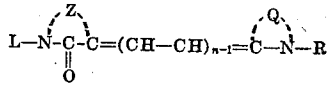
4. A photographic element comprising a photographic silver halide emulsion sensitized with a sensitizing dye characterized by the following formula:



wherein, L represents a long-chain organic group comprising a chain of at least seven non-metallic members, Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, R represents an alkyl group, and Z represents the

non-metallic atoms necessary to complete a 2-thio-2,4(3,5)-imidazoleidione nucleus.

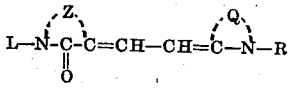
5. A photographic element comprising a photographic silver halide emulsion sensitized with a sensitizing dye characterized by the following formula:



wherein, L represents a long-chain organic group comprising a chain of at least seven non-metallic members, Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, R represents an alkyl group, and Z represents the non-metallic atoms necessary to complete a 2-thio-2,4(3,5)-oxazoledione nucleus.

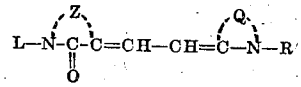
6. A photographic element comprising a photographic silver halide emulsion which is sensitized with a sensitizing merocyanine dye containing a long-chain organic group comprising a chain of at least seven non-metallic members, said long-chain organic group being attached to the dye at a position other than the polymethine chain and the auxochromic atoms.

7. A photographic element comprising a photographic silver halide emulsion which is sensitized with a sensitizing dye characterized by the following formula:



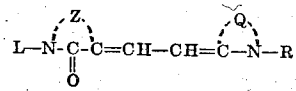
wherein L represents a long-chain hydrocarbon group comprising a chain of at least seven carbon atoms, Q represents the non-metallic atoms necessary to complete a benzoxazole nucleus, R represents an alkyl group selected from the group consisting of methyl and ethyl groups, and Z represents the non-metallic atoms necessary to complete a 2-thio-2,4(3,5)-thiazoledione nucleus.

8. A photographic element comprising a photographic silver halide emulsion which is sensitized with a sensitizing dye characterized by the following formula:



wherein L represents a long-chain hydrocarbon group comprising a chain of at least seven carbon atoms, Q represents the non-metallic atoms necessary to complete a benzoxazole nucleus, R represents an alkyl group selected from the group consisting of methyl and ethyl groups, and Z represents the non-metallic atoms necessary to complete a 2-thio-2,4(3,5)-oxazoledione nucleus.

9. A photographic element comprising a photographic silver halide emulsion which is sensitized with a sensitizing dye characterized by the following general formula:



wherein L represents a long-chain hydrocarbon group comprising a chain of at least seven carbon atoms, Q represents the non-metallic atoms necessary to complete a benzoxazole nucleus, R represents an alkyl group selected from the group consisting of methyl and ethyl groups, and Z represents the non-metallic atoms necessary to complete a 2-thio-2,4(3,5)-imidazoledione nucleus.

LESLIE G. S. BROOKER.