Photographic element and process incorporating a high dye-yield image coupler providing improved granularity.

The invention provides a photographic element comprising a support bearing a light sensitive photographic silver halide emulsion layer wherein the layer has associated therewith a coupler capable of combining with oxidized developer to form a first dye, the coupler also containing a coupling-off group which is released during development to form a precursor of a second dye, the precursor having an electrically neutral dye chromophore bonded to a linking group selected from the group consisting of -OC(O)-, -OC(S)-, -SC(O)-, -SC(S)-, and -OC(=NSO2R)- where R is substituted or unsubstituted alkyl or aryl; wherein the amount of said coupler associated with the layer and the amount of silver in the layer is such that the molar ratio of the dye formable from the coupler to the silver contained in the layer is less than 1.0 and the silver and coupler levels are each below 1 g/m²; and further wherein the second dye has a calculated logarithm of its neutral partition coefficient (ClogP) in the range of 3.5 to 5.5.

The invention also provides a method of forming an image in a photographic element of the invention.
Field of the Invention

This invention relates to a photographic element that employs a high dye yield coupler having a particular type of linking group, chromophore, and calculated log of its neutral partition coefficient which provides an element which exhibits improved granularity.

Background of the Invention

Improved film granularity is one of the most important objectives in the design of new photographic materials. Improvements in this property enable a greater degree of enlargement. Advances in emulsion design can also improve the speed/fog ratio generating more efficient emulsions. This can enable reduction of the silver levels in an imaging layer of a photographic element. A lower silver loading enables the imaging layer to be made thinner and so the optical sharpness response of that layer and of the layers coated below it in a film structure can be improved. Lower silver loading means that there is a potentially lower usage of processing chemicals needed to develop, bleach and fix out the silver. Lower silver loading also reduces the environmental concerns associated with disposal and/or recovery of silver values from processing solutions. Further, the reduction in silver can also have a beneficial effect on manufacturing costs. Finally, lower silver is a benefit since it renders the element less sensitive to ambient radiation.

The problem encountered when reducing the level of silver laydown (and so the number of imaging centers in a layer) is that there is a rise in the granularity of the image formed. In some cases this increase in granularity may be acceptable provided that sensitometry is maintained, but, if not, then the reduction in silver cannot be accomplished without unacceptable rise in the granularity of the resulting image.

Useful high dye yield (HDY) couplers have been disclosed by Mooberry and Singer in U.S. Patent 4,840,884. Such couplers react with oxidized color developer to form one dye and in doing so release a precursor of a second dye. In accordance with the patent, the new couplers described therein enable lower concentrations of silver halide in the photographic element without lowering image quality. It has been found, however, that the effect that the silver laydown reduction has on the granularity of a resulting image is generally not acceptable in light of the ever increasing demands for speed, larger image blow-up, and smaller film size, particularly where conventional high laydowns of dye-forming coupler and silver are employed.

It is a problem to be solved to provide a photographic element that matches the desired sensitometry but that contains reduced material laydowns compared to conventional photographic elements and that also maintains acceptable levels of granularity.

Summary of Invention

The invention provides a photographic element comprising a support bearing a light sensitive photographic silver halide emulsion layer wherein the layer has associated therewith a coupler capable of combining with oxidized developer to form a first dye, the coupler also containing a coupling-off group which is released during development to form a precursor of a second dye, the precursor having an electrically neutral dye chromophore bonded to a linking group selected from -OC(O)-, -OC(S)-, -SC(O)-, -SC(S)-, and -OC(=NS02R)- where R is substituted or unsubstituted alkyl or aryl; wherein the amount of said coupler associated with the layer and the amount of silver in the layer is such that the molar ratio of the dye formable from the coupler to the silver contained in the layer is less than 1.0 and the silver and coupler levels are each below 1 g/m²; and further wherein the second dye has a calculated logarithm of its neutral partition coefficient (ClogP) in the range of 3.5 to 5.5.

The invention also provides a method of forming an image in a photographic element of the invention.

The invention advantageously provides a photographic element that matches the desired sensitometry using reduced laydowns and without degradation of granularity.

Brief Description of the Drawings

Figure 1 is a graph showing the density obtained at standard log exposure levels for a photographic element of the invention and for comparatives as described in Example 1.

Figure 2 is a graph showing the RMS granularity obtained at standard log exposure levels for the same photographic element of the invention and for the same comparatives as shown in Figure 1.

Figure 3 is a graph showing the density obtained at standard log exposure levels for a photographic element of the invention and for comparatives as described in Examples 2-4.
Figure 4 is a graph showing the RMS granularity obtained at standard log exposure levels for the same photographic element of the invention and for the same comparatives as shown in Figure 3.

Detailed Description of the Invention

The invention provides a photographic element comprising a support bearing a light sensitive photographic silver halide emulsion layer wherein the layer has associated therewith a coupler capable of combining with oxidized developer to form a first dye, the coupler also containing a coupling-off group which is released during development to form a precursor of a second dye, the precursor having an electrically neutral dye chromophore bonded to a linking group selected from the group consisting of -OC-(O)-, -OC(S)-, -SC(O)-, -SC(S)-, and -OC(=NSOR)- where R is substituted or unsubstituted alkyl or aryl;

wherein the amount of said coupler associated with the layer and the amount of silver in the layer is such that the molar ratio of the dye formable from the coupler to the silver contained in the layer is less than 1.0; and

further wherein the second dye has a calculated logarithm of its neutral partition coefficient (Clogp) in the range of 3.5 to 5.5.

The dye forming coupler of the invention has the general formula:

\[ \text{COUP}-(T)_{m+L}-\text{DYE} \]

where COUP is the parent group of the coupler capable of reacting at the coupling position with oxidized color developer to form a first dye, T is one or more optional timing groups with m = 0 to 2, L is a particular linking group, and DYE is a second dye.

COUP is the parent portion of a coupler that is capable of coupling with oxidized developer to form a dye. As described more fully hereafter, the dye may be of any desired color or may be colorless and if desired, it may be of the so-called universal type which washes out of the element during processing.

Image dye-forming couplers may be included in the element such as couplers that form cyan dyes upon reaction with oxidized color developing agents which are described in such representative patents and publications as: U.S. Pat. Nos. 2,311,082, 2,333,106, 2,877,293, 2,895,826, 3,002,836, 3,034,892, 3,041,236, 4,333,999, 4,883,746 and "Farbkuppler-eine LiteraturÜbersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961). Preferably such couplers are phenols and naphthols that form cyan dyes on reaction with oxidized color developing agent.

Couplers that form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Pat. Nos. 2,298,443, 2,407,210, 2,677,162, 2,722,923, 2,905,826, and "Farbkuppler-eine LiteraturÜbersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Preferably such couplers are phenols and naphthols that form magenta dyes upon reaction with oxidized color developing agent.

Couplers that form black dyes upon reaction with oxidized color developing agent are described in such representative patents as U.S. Patent Nos. 2,367,531, 2,772,162, 2,895,826, 3,002,836, 3,034,892, 3,041,236, 4,333,999, 4,883,746 and "Farbkuppler-eine LiteraturÜbersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Preferably such couplers are phenols and naphthols that form magenta dyes upon reaction with oxidized color developing agent.

In addition to the foregoing, so-called "universal" or "washout" couplers may be employed. These couplers do not contribute to image dye-formation. Thus, for example, a naphthol having an unsubstituted carbamoyl or one substituted with a low molecular weight substituent at the 2- or 3- position may be employed. Couplers of this type are described, for example, in U.S. Patent Nos. 5,026,628, 5,151,343, and 5,234,800.

T is a timing group which, as indicated by the value range for m of from 0 to 2, may be absent or may represent one or two such timing groups. Such groups are well-known in the art such as (1) groups utilizing the cleavage reaction of a hemiacetal (U.S. 4,146,396, Japanese Applications 60-249148; 60-249149); (2)
groups utilizing an electron transfer reaction along a conjugated system (U.S. 4,409,323; 4,421,845; Japanese Applications 57-188035; 58-86728; 58-209736; 58-209738); (3) groups utilizing the cleavage of imino ketals (U.S. 4,546,073); (4) groups that function as a coupler or reducing agent after the coupler reaction (U.S. 4,438,193; U.S. 4,618,571); and (5) groups using an intramolecular nucleophilic substitution reaction (U.S. 4,248,962). The timing group to which the L-DYE group of the invention is optionally attached is any one which will permit release of the L-DYE group. Foregoing group (5) is not suitable as the group to release L-DYE but could serve as the first of a sequence of two timing groups. Other timing groups are generally suitable for releasing -L-DYE. Timing groups as described under (2) and the listed patents are most suitable. Generally these consist of a bond from COUP or another timing group to an oxygen atom which is bonded to a substituted or unsubstituted aromatic hydrocarbyl or heterocyclic ring at a location in conjugation with a methyl group on the ring which may optionally be substituted with one or two alkyl groups, where the methyl group is bonded to L-DYE or a second timing group. A typical such group based on an aromatic hydrocarbyl group has the formula:

\[
\begin{array}{c}
\text{O} \\
\text{R} \\
\text{C} \text{(R}_{11}^{11}) \text{(R}_{12}^{12})
\end{array}
\]

wherein Z is selected from the group consisting of nitro, cyano, alkylsulfonyl; sulfamoyl (-SO_{2}NR_{2}); and sulfonamido (-NRSO_{2}R) groups; R is hydrogen or a substituent such as alkyl; R_{1} R_{11} and R_{12} are independently hydrogen or substituents that do not adversely affect the coupling and release reactions or the properties of the dyes formed thereby.

One example of such a group containing an aromatic heterocycle is:

\[
\begin{array}{c}
\text{R}^{9} \\
\text{N} \\
\text{R}^{10} \\
\text{R}^{11} \\
\text{R}^{12} \\
\text{R}
\end{array}
\]

where R_{9} through R_{12} are independently hydrogen or substituents that do not adversely affect the coupling and release reactions or the properties of the dyes formed thereby.

L is a group which serves to connect COUP (or T, if present) to the second dye. L has a formula so as to permit -L-DYE or -(T)m-L-DYE to be cleaved from the coupler upon the coupler’s oxidative coupling with color developer during development processing. COUP combines with the oxidized developer to form the first dye and the fragment -L-DYE or -(T)m-L-DYE is then freed from COUP. Suitable groups for L are -OC-(O)-, -OC(S)-, -SC(O)-, -SC(S)-, or -OC(=N=SO_{2}R)-, where R is substituted or unsubstituted alkyl or aryl.

Such groups permit the cleavage of the fragment from COUP and are cleaved from DYE. U.S. Patent 4,840,884 generally describes photographic elements employing high dye yield couplers having electrically neutral chromophores, and the contents thereof are incorporated herein by reference. Further, particularly suitable couplers containing a methine dye chromophore are described in an application of Mooberry et al entitled "Photographic Element Containing A High Dye-Yield Coupler With A Methine Dye Chromophore" which is cofiled herewith.

While not wishing to be bound by theory, it is believed that the coupler of the invention is adapted to allow some diffusion of the -L-DYE and/or -(T)m-L-DYE fragment while the linking group is attached to the second dye but, once the linking group is cleaved from the second dye, diffusion of DYE is no longer possible. This result is achieved through the provision that the second dye has a calculated neutral partition coefficient (ClogP) in the range of 3.5 to 5.5. Thus, when the linking group is cleaved from the second dye, the dye no longer contains the charged highly polar portion represented by the linking group. It follows that the second dye is no longer free to diffuse after the linking group has separated and this
provides good stability of the image dye from the standpoint of long term image stability.

The neutral partition coefficient is the ratio of the distribution at equilibrium of a compound between octanol and water. The calculated values are derived using Medchem software, version 3.54, Medical Chemistry Project, Pomona College, Claremont, California. For a recent discussion of this method see Albert J. Leo, in "Comprehensive Medicinal Chemistry", edited by C. Hansch, P.G. Sammes, and J.B. Taylor, Pergamon Press, New York, Volume 4, 1990).

If the ClogP of the second dye is greater than 5.5, the beneficial effects of the invention are not realized. Under such circumstances, the second dye will be too hydrophobic, even in the presence of the L or the L and T groups, and will not diffuse effectively during the period when such groups are still attached to the fragment. Without diffusion, improvement in the granularity is not realized and the problem in the art is not solved.

If the ClogP is less than 3.5, the second dye cannot be expected to remain in the photographic element during processing. It will be too soluble in the aqueous gelatin phase of the photographic element and will be significantly washed out into the processing solution during processing. It is suitable to provide a ClogP of 4.5 if it is desired to help minimize the extent of dye washed out of the element. However, this value will be dependent on the thickness and contents of the photographic layer.

The coupler of the invention releases a second dye having an electrically neutral chromophore. By this is meant that the chromophore at its characteristic hue bears no formal electrical charge. The second dye of the invention suitably contains a substituted nitrogen group which is bonded to the linking group. Such dyes may be any of the types disclosed, for example, in the aforementioned U.S. 4,840,884 and may be synthesized as described therein.

The DYE as described includes any releasable, electrically neutral dye that enables dye hue stabilization without mordanting the dye formed. The release mechanism can be initiated by oxidized reducing agent.

In U.S. Patent 4,840,884, the term DYE is defined so that the adjacent -NR1- group is not a part of DYE while the definition herein does include the -NR1-. In either case, the composition of the dye formed by release is the same.

The R1 substituent on -NR1- can be any substituent that does not adversely affect the coupler. When the -NR1- is part of an auxochrome, R1 can be, for example, hydrogen or alkyl, such as alkyl containing 1 to 42 carbon atoms, including methyl, ethyl, propyl, n-butyl, t-butyl or eicosyl, or aryl, such as phenyl. When the nitrogen atom attached to L is part of a chromophore, R1 becomes an integral part of the chromophore. Preferred R1 groups are alkyl, such as alkyl containing 1 to 18 carbon atoms when R1 is part of the dye auxochrome. R1 when part of the chromophore is, for example, unsubstituted or substituted aryl, such as phenyl.

The selection of the type and size of the substituents of DYE can be made in order to provide a partition coefficient of DYE which permits the desired degree of diffusion.

Particularly useful classes of DYE moieties are:

I. Azo dye moieties including the -NR1- group represented by the structure:

wherein R25 is hydrogen or a substituent, such as alkyl and R26 and R27 independently represent hydrogen or one or more substituents such as alkyl.

II. Azamethine dye moieties including the -NR1- group represented by the structure:
wherein R^28 is hydrogen or one or more substituents, such as alkyl; R^29 is hydrogen or a substituent, such as alkyl; and EWG is an electron withdrawing group.

III. Methine dye moieties including the -NR^1- group represented by the structure:

wherein R^30 and R^31 are independently hydrogen or a substituent, such as alkyl; R'^30a is hydrogen or one or more substituents such as alkyl; and EWG is an electron withdrawing group having a positive Hammett's sigma(para) value.

The term DYE also includes dye precursors wherein the described substituted nitrogen atom is an integral part of the chromophore, also described herein as leuco dye moieties. Such dye precursors include, for example:

wherein R'^32 is a group that is cleaved during processing to leave NH, or N=N, and R'^33 is aryl, such as substituted phenyl.

wherein R'^34 is a group that is cleaved during processing to leave NH, or N=C, and EWG is an electron withdrawing group as defined above.

Examples of cyan, magenta, yellow and leuco dyes are as follows:

A. Cyan
wherein $R^{35}$ is a substituent that does not adversely affect the dye, such as alkyl; $R^{36}$ is a substituent, such as an electron releasing group having a Hammett's $\sigma_{para}$ value less than 0; and $R^{37}$ is one or more substituents, such as a strong electron withdrawing group having a Hammett's $\sigma_{para}$ value of at least 0.23.

B. Magenta

wherein $R^{38}$ is a substituent that does not adversely affect the dye, such as alkyl; $R^{39}$ is a substituent, such as an electron releasing group as defined above; and $R^{40}$ is a substituent, such as a strong electron withdrawing group as defined above.

C. Yellow

wherein $R^{41}$ is alkyl; $R^{42}$ is alkoxy, alkyl, or H; and $R^{43}$ is alkyl or H; and
wherein $R^{44}$ is alkyl; $R^{45}$ is alkoxy, alkyl, or $H$; $R^{46}$ is alkyl or aryl; and $X$ is $-O-$ or $-NR^*$ where $R^*$ is $H$, alkyl, or aryl.

D. Leuco

wherein $R^{47}$ and $R^{48}$ are individually hydrogen or alkyl; $R^{49}$ is an electron releasing group as defined above; and $R^{51}$ is a strong electron withdrawing group as defined above.

wherein $R^{52}$ and $R^{54}$ are individually hydrogen or a substituent; $R^{53}$ is $-NHR^3$ or $-NHSO_2R^3$ wherein $R^3$ is a substituent; and $R^{55}$ and $R^{56}$ are individually hydrogen or a substituent.
The following are examples of suitable high dye yield couplers of the invention:

INV 1

\[
\begin{array}{c}
\text{CONH(CH}_2\text{)}_4\text{CH}_3 \\
\text{N=O} \\
\text{O CO} \\
\text{NHCO} \\
\text{CH}_3 \text{O} \\
\text{(CH}_2\text{)}_3\text{CO}_2\text{H} \\
\text{O CO} \\
\text{NHCO} \\
\text{Cl} \\
\text{N=O} \\
\text{NH}_2 \text{SO}_2\text{(CH}_2\text{)}_{15}\text{CH}_3
\end{array}
\]
INV 4

INV 5
INV 12

INV 13
INV 16

INV 17
In addition to the foregoing, it may generally desired that the photographic element of the invention contain reduced laydowns of silver and have a low molar ratio of dye theoretically formable from the coupler of the invention to silver present in the layer. More specifically, the element contains less than 90% of the silver typically employed in an element employing conventional couplers and having the same sensitometry. It is not possible to specify the absolute levels of silver that may be employed since the amounts will vary depending on the coupler reactivities and many other components of the element. However, the applicable level of silver required for a conventional coupler to achieve a given aim sensitometry can be reduced significantly, i.e. by 10% to 35% and approaching 50% when the inventive couplers are used. The silver and coupler levels are each below 1 g/m².

The present invention provides low silver laydowns in conjunction with low molar ratios of dye theoretically formable from the high dye yield couplers of the invention to silver. This enables not only conservation of the silver and dye required to attain the desired sensitometry, but also provides mass efficiency in the coupler necessary to produce the necessary color image density and contrast.

It is possible to provide a coupler in accordance with the invention so that the first dye is ballasted to be completely immobile or so that it has limited mobility in the developer or other processing solution. It is also within the contemplation of the invention to include in association with the silver halide emulsion of the invention one or more additional couplers that are conventional image couplers or that are PUG releasing couplers, as described more fully herein.

The dyes formed by the coupler of the invention may be within any desired color range. Yellow, cyan and magenta are the ranges most commonly used in color negative today. The first and second dyes of the invention are the same color if they have maximum absorbance in the same range, i.e. 400-500nm, 500-600nm, or 600-700nm. Where the two dyes are the same color they will typically have absorption maxima within 25nm of each other. Photographic elements which may use the invention include image capture color negative, color print, and reversal to name a few.

In a particularly suitable form of the invention, the silver halide layer of the invention represents at least one layer, preferably the fast or high sensitivity layer, of a multilayered color record. Such a layer is normally above the slower layers of the color record and contains a larger silver halide grain size for speed purposes. Use of the invention with respect to that layer provides significant improvement in granularity while permitting thinning of the layer allowing less degradation of the light image formed in underlying layers. The invention has particular suitability with tabular grains to enable superior grain reduction. It may also be desirable to employ the coupler of the invention in a slow imaging layer where finer grain emulsions are typically employed.

The desired results are enabled in part through providing low laydown of the imaging coupler and formable image dye relative to the laydown of silver in the layer. Thus the molar ratio of formable dye (theoretical amount of first and second dye) to silver halide is less than 1.0. More suitably, the ratio is less than 0.8 and often less than 0.55 provides good results.
The method of the invention provides for the imagewise exposure of a photographic element of the invention followed by contacting the element with a color developing chemical to form a color image. Color forming chemicals are described more fully hereinafter.

The invention disclosed herein can be used in combination with one or more of the inventions disclosed in applications cofiled herewith under attorney Docket Nos. 66957, 67332, 67358, and 69927.

As used herein, the term substituent, unless otherwise specifically stated, has a broad definition. The substituent may be, for example, halogen, such as chlorine, bromine or fluoride; nitro; hydroxyl; cyano; and -CO₂H and its salts; and groups which may be further substituted, such as alkyl, including straight or branched chain alkyl, such as methyl, trifluoromethyl, ethyl, t-butyl, 3-(2,4-di-t-amylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butenyl; alkyloxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, sec-butoxy, hexoxy, 2-ethylhexyloxy, tetraacryloxy 2-(2,4-di-t-pentylphenoxy)ethoxy, and 2-dodecylacryloxyethoxy; aryl such as phenyl, 4-t-butylphenyl, 2,6-trimethylphenyl, naphthyl; arylamido, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthylamido, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-t-pentylphenoxy)acetamido, alpha-(2,4-di-t-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)butyramido, alpha-(4-hydroxy-3-f-butylphenoxy)butyramido, alpha-(2,4-di-t-pentylphenoxy)hexanamido, alpha-(3-pentadecylphenoxy)hexanamido, alpha-(2-oxo-pyrrolidin-1-yl), 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzoyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-t-butyloxyphenoxycarbonylamino, phenylcarbonylamino, 2,5-di-(t-pentylphenoxy)-carbonylamino, p-dodecylphenoxy carbonylamino, p-tolylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-diocetyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-p-tolylureido, N-(m-hexadecylphenyl)ureido, N,N-(2,5-di-t-pentylphenyl)-N'-ethyleureido, and t-butylcarbamido; sulfonylamido, such as methylsulfonylamido, benzencesulfonylamido, p-tolylsulfonylamido, p-dodecylbenzensulfonylamido, N-methyltetradecylsulfonylamido, N,N-dipropylsulfonylamino, and hexadecylsulfonylamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N,N-dipentylsulfamoyl, N,N-diethylsulfamoyl, N,N-dimethylsulfamoyl, N-[3-(dodecylphenoxy)propyl]-sulfamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N,N-dodecylsulfamoyl; carbamido, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylylcarbamoyl, N-[2,4-(2-di-t-pentylphenyl)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-diocetylcarbamoyl; acyl, such as acetyl, (2,4-di-t-amylphenoxy)acetyl, phenoxyacarbonyl, p-dodecylphenoxy carbonylamino, butyoxycarbonyl, ethoxycarbonyl, benzoyloxy carbonyl, 3-pentadecyloxy carbonyl, and dodecylcarboxyloxy carbonyl; sulfonyl, such as methoxysulfonyl, octylosulfonyl, tetradecylcarboxyloxy sulfonyl, 2-ethylhexyloxysulfonyl, phenoxy carbonyl, and 2,4-di-t-pentylphenoxysulfonyl, methylsulfonyl, octylosulfonyl, 2-ethylhexyloxysulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and p-tolylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyloxy, such as methylsulfinyl, octylsulfinyl, 2-ethylhexysulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and p-tolylsulfinyl; thiio, such as ethylthio, ethylthio, benzylthio, tetradecylthio, 2-(2,4-di-t-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-toctylphenoxythio, and p-tolylthio; acylxy, such as acetylxy, benzoyloxy, octadecanoyloxy, p-dodecylamidobenzoxyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbonyloxy; amine, such as phenylamino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1-(N-phenylimido)ethyl, N-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylophosphite; a heterocyclic group, a heterocyclic oxo group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the above groups.

The particular substituents used may be selected to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, etc. Generally, the above groups and substituents thereof may typically include those having 1 to 42 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected. Moreover, as indicated, the substituents may themselves be suitably substituted with any of the above groups.

The materials of the invention can be used in any of the ways and in any of the combinations known in the art. Typically, the invention materials are combined with a silver halide emulsion and the mixture is coated as a layer on a support to form part of a photographic element. Alternatively, they can be incorporated at a location adjacent to the silver halide emulsion layer where, during development, they will be in reactive association with development products such as oxidized color developing agent. Thus, as used herein, the term “associated” signifies that the compound is in the silver halide emulsion layer or in an
adjacent location where, during processing, it is capable of reacting with silver halide development products.

Subject to the ClogP requirements of the second dye of the invention, it may be desirable to include a high molecular weight hydrophobe or "ballast" group in the component molecule to control the migration of various components. Representative ballast groups include substituted or unsubstituted alkyl or aryl groups containing 8 to 42 carbon atoms. Representative substituents on such groups include alkyl, aryl, alkoxy, aryloxy, alkythio, hydroxy, halogen, alkoxy carbonyl, aryloxy carbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkyloxyl, aminofuryl, sulfonamido, and sulfamoyl groups wherein the substituents typically contain 1 to 42 carbon atoms. Such substituents can also be further substituted.

The photographic elements can be single color elements or multicolor elements. Multicolor elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like.

If desired, the photographic element can be used in conjunction with an applied magnetic layer as described in Research Disclosure, November 1992, Item 34390 published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, ENGLAND; and in U.S. Patents 5,252,441; 5,254,449; and 5,254,446; the contents of which are incorporated herein by reference.

Color negative films employing such layers can be employed, in combination with cameras that can record and cause to be stored on such a layer, various useful information related to the use and history of the film. Specific examples include exposure information on a per scene and per roll basis. These films can then be processed in automated processing apparatus that can retrieve film characteristic information as well as film exposure and use information, and optionally modify the processing to ensure optimal performance and optionally record the details of processing of the magnetic layer. The films can then be printed using automated printers that can retrieve both film and process history information and optionally alter, based on the information, exposure characteristics chosen from printing time, printing light intensity, printing light color balance, printing light color temperature, printing magnification or printing lens adjustment, exposure, or printing time, and the color filters so as to enable production of well-balanced display prints from various color originating materials. These layers can be located on the same side of the support as light sensitive layers or arranged so that the support is between the magnetic layer and the light sensitive layers. This information is useful in altering film processing and printing conditions so as to aid in producing a pleasing image.

It is specifically contemplated to employ supports bearing magnetic layers as described.

In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, December 1989, Item 308119, available as described above, which will be identified hereafter by the term "Research Disclosure." The contents of the Research Disclosure, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the Research Disclosure. The materials of the invention may also be used in conjunction with the materials described in Koukai Gihou No. 94-6023, Hatsumei Kyoukai, March 1994, available from the Japanese Patent Office, which is incorporated herein by reference.

The silver halide emulsions employed in the elements of this invention can be either negative-working or positive-working. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through IV. Color materials and development modifiers are described in Sections VII and XXI. Vehicles are described in Section IX, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described, for example, in Sections V, VI, VIII, X, XI, XII, and XVI. Manufacturing methods are described in Sections XIV and XV, other layers and supports in Sections XIII and XVII, processing methods and agents in Sections XIX and XX, and exposure alternatives in Section XVIII.
Coupling-off groups are well known in the art. Such groups can determine the chemical equivalency of a coupler, i.e., whether it is a 2-equivalent or a 4-equivalent coupler, or modify the reactivity of the coupler. Such groups can advantageously affect the layer in which the coupler is coated, or other layers in the photographic recording material, by performing, after release from the coupler, functions such as dye formation, dye hue adjustment, development acceleration or inhibition, bleach acceleration or inhibition, electron transfer facilitation, color correction and the like.

The presence of hydrogen at the coupling site provides a 4-equivalent coupler, and the presence of another coupling-off group usually provides a 2-equivalent coupler. Representative classes of such coupling-off groups include, for example, chloro, alkoxy, aryloxy, hetero-oxy, sulfoniloxy, acyloxy, acyl, heterocyclyl, sulfonamido, mercaptotetrazole, benzo thiazole, mercaptopropionic acid, phosphoniloxy, arylthio, and arylazo. These coupling-off groups are described in the art, for example, in U.S. Pat. Nos. 2,455,169, 3,227,551, 3,432,521, 3,476,563, 3,617,291, 3,880,661, 4,052,212 and 4,134,766; and in U.K. Patents and published application Nos. 1,466,728, 1,531,927, 1,533,039, 2,006,755A and 2,017,704A, the disclosures of which are incorporated herein by reference.

It may be useful to use a combination of couplers any of which may contain known ballasts or coupling-off groups such as those described in U.S. Patent 4,301,235; U.S. Patent 4,853,319 and U.S. Patent 4,351,897. The coupler may contain solubilizing groups such as described in U.S. Patent 4,482,629. The coupler may also be used in association with "wrong" colored couplers (e.g. to adjust levels of interlayer correction) and, in color negative applications, with masking couplers such as those described in EP 213,490; Japanese Published Application 58-172,647; U.S. Patent Nos. 2,983,608; 4,070,191; and 4,273,861; German Applications DE 2,706,117 and DE 2,643,965; U.K. Patent 1,530,272; and Japanese Application A-113935. The masking couplers may be shifted or blocked, if desired.

For example, in a color negative element, the materials of the invention may replace or supplement the materials of an element comprising a support bearing the following layers from top to bottom:

1. One or more overcoat layers containing ultraviolet absorber(s);
2. A two-coat yellow pack with a fast yellow layer containing "Coupler 1": Benzoic acid, 4-chloro-3-((2-(4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolidinyl)-3-(4-methoxyphenyl)-1,3-dioxopropyl)amino)-dodecyl ester and a slow yellow layer containing the same compound together with "Coupler 2": Propionic acid, 2-[[5-[[4-[[2,4-bis(1,1-dimethylpropyl)phenoxy]acetyl]amino]-5-[[2,2,3,3,4,4,4-heptatfluoro-1-oxobutyl]amino]-4-hydroxyphenoxy]-2,3-dihydroxy-6-[[propylamino]carbonyl[phenyl][thio]-1,3,4-thiadiazol-2-yl][thio]—, methyl ester and "Coupler 3": 1-((dodecylxoy)carbonyl ethyl(3-chloro-4-((3(2-chloro-4-((1-tridecanoylethoxy) carbonyl)anilino)-3-oxo-2-(45(46)(phenoxycarbonyl)-1H-benzotriazol-1-yl)propionylo)amino)benzoic;
3. An interlayer containing fine metallic silver;
4. A three-coat magenta pack with a fast magenta layer containing "Coupler 4": Benzamide, 3-((2,2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl), "Coupler 5": Benzamide, 3-((2,2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl), "Coupler 6": Carbanilic acid, (6-((3-(dodecylxoy)propyl) amino)carbonyl)-5-hydroxy-1-naphthalenyl), 2-methylpropyl ester, "Coupler 7": Acetic acid, ((2-((3-(dodecylxoy)propyl)amino)carbonyl)-4-hydroxy-8-((2-methylpropoxy)carbonyl)amino)-1-naphthalenyl)oxy ethyl)(thio)-, and "Coupler 8" Benzamide, 3-((2,2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-4-((4-methoxyphenyl)azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl); a mid-magenta layer and a slow magenta layer each containing "Coupler 9": a ternary copolymer containing by weight in the ratio 1:1:2 2-Propanoic acid butyl ester, styrene, and N-[1-(2,4,6-trichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl]-2-methyl-2-propenamide; and "Coupler 10": Tetradecanamide, N-(4-chloro-3-((4-((2,2-dimethyl-1-oxo propyl) amino)phenyl)azo)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl); in addition to Couplers 8 and 3;
5. An interlayer;
6. A triple-coat cyan pack with a fast cyan layer containing Couplers 6 and 7; a mid-cyan containing Coupler 6 and "Coupler 11": 2,7-Naphthalenedisulfonic acid, 5-(acetylamino)-3-[[4-[[3-(2,4-bis(1,1-dimethylpropyl)phenoxy) propyl]amino]carbonyl]-4-hydroxy-1-naphthalenyl oxy]ethoxy)phenyl)azo)-4-hydroxy-, disodium salt; and a slow cyan layer containing Couplers 2 and 6;
7. An undercoat layer containing Coupler 8; and
8. An antihalation layer.

In a color paper format, the materials of the invention may replace or supplement the materials of an element comprising a support bearing the following layers from top to bottom:

(1) one or more overcoats;
(2) a cyan layer containing "Coupler 1": Butanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-[3,5-dichloro-2-hydroxy-4-methylphenyl]-, "Coupler 2": Acetamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(3,5-dichloro-2-hydroxy-4-), and UV Stabilizers: Phenol, 2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylthyl)-; Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylthyl)-6-(1-methylpropyl)-; and Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)-
and a poly(t-butylacrylamide) dye stabilizer;
(3) an interlayer;
(4) a magenta layer containing "Coupler 3": Octanamide, 2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-N-[2-(7-chloro-6-methyl-1H-pyrazol[1,5-b][1,2,4]triazol-2-yl)]- together with 1,1'-Spirobi(1H-indene), 2,2',3,3',3',3'-tetrahydro-3,3,3',3'-tetramethyl-5,5',6,6'-tetrapropoxy-;
(5) an interlayer; and
(6) a yellow layer containing "Coupler 4": 1-imidazolidineacetamide, N-[5-[2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl]amino]-2-chlorophenyl)-alpha.-(2,2-dimethyl-1-oxopropyl)-4-ethoxy-2,5-dioxo-3-(phenylmethyl)-.

In a reversal format, the materials of the invention may replace or supplement the materials of an element comprising a support bearing the following layers from top to bottom:
(1) one or more overcoat layers;
(2) a nonsensitized silver halide containing layer;
(3) a triple-coat yellow layer pack with a fast yellow layer containing "Coupler 1": Benzoic acid, 4-[1-(((2-chloro-5-((dodecylsulfonyl)amino)phenyl)amino)carbonyl)-3,3-dimethyl-2-oxobutoxy]-, 1-methylthyl ester; a mid yellow layer containing Coupler 1 and "Coupler 2": Benzoic acid, 4-chloro-3-[2-[4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolidinyl]-4,4-di-methyl-1,3-dioxopentyl]amino]-, dodecylester; and a slow yellow layer also containing Coupler 2;
(4) an interlayer;
(5) a layer of fine-grained silver;
(6) an interlayer;
(7) a triple-coated magenta layer containing "Coupler 3": 2-Propenoic acid, butyl ester, polymer with N-[1-(2,5-dichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl]-2-methyl-2-propenamide; "Coupler 4": Benzamide, 3-[2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl]amino]-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl); and "Coupler 5": Benzamide, 3-[[2,4-bis(1,1-dimethylpropyl)phenoxy]acetyl]amino]-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl); and containing the stabilizer 1,1'-Spirobi(1H-indene), 2,2',3,3',3',3'-tetrahydro-3,3,3',3'-tetramethyl-5,5',6,6'-tetrapropoxy-; and in the slow magenta layer Couplers 4 and 5 with the same stabilizer;
(8) one or more interlayers possibly including fine-grained nonsensitized silver halide;
(9) a triple-coated cyan layer containing "Coupler 6": Tetradecanamide, 2-(2-cyanophenoxy)-N-(4-[2,2,3,3,4,4,4-heptafluoro-1-oxobutyl]amino)-3-hydroxyphenoxy)-; a mid cyan containing "Coupler 7": Butanamide, N-(4-[[(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl]amino]-2-hydroxyphenyl]-2,2,3,3,4,4,4-heptafluoro- and "Coupler 8": Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-[2,2,3,3,4,4,4-heptafluoro-1-oxobutyl]amino)-3-hydroxyphenyl)-; and a slow cyan layer containing Couplers 6, 7, and 8;
(10) one or more interlayers possibly including fine-grained nonsensitized silver halide; and
(11) an antihalation layer.

The inventive materials may be used in association with materials that accelerate or otherwise modify the processing steps e.g. of bleaching or fixing to improve the quality of the image. Bleach accelerator releasing couplers such as those described in EP 193,389; EP 301,477; U.S. 4,163,669; and U.S. 4,859,578, may be useful. Also contemplated is use of the compositions in association with nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; U.K. Patent 2,131,188); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

The invention materials may also be used in combination with filter dye layers comprising colloidal silver sol or yellow, cyan, and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. 4,306,237; EP 96,570; U.S. 4,420,556; and U.S. 4,543,323.) Also, the compositions may be blocked or coated in protected form as described, for example, in Japanese Application 61/256,249 or U.S. 5,019,492.

The invention materials may further be used in combination with image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIR'S). DIR's useful in conjunction with the compositions of the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022;
Such compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photog-
(1969), incorporated herein by reference. Generally, the developer inhibitor-releasing (DIR) couplers include
a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the
time-delayed type (DIAR couplers) which also include a timing moiety or chemical switch which produces a
delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles,
triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles, benzotriazoles, tetrazoles, benzimidazoles,
indazoles, isindazoles, mercaptotetrazoles, selenotetrazoles, mercaptobenzotriazoles, selenoben-
zoeketrazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles,
benzimidazoles, mercaptooxazoles, mercaptothiadiazoles, mercaptothiazoles, mercaptox-
adiazoles, mercaptotriazoles, mercaptothiazoles, tellurotetrazoles or benzisodiazoles. In a preferred
embodiment, the inhibitor moiety or group is selected from the following formulas:

\[
\begin{align*}
&\text{S} \\
&\text{N} \\
&\text{N} \\
&\text{R}_I
\end{align*}
\]

\[
\begin{align*}
&\text{S} \\
&\text{O} \\
&\text{N} \\
&\text{N} \\
&\text{R}_I \\
&\text{R}_I
\end{align*}
\]

\[
\begin{align*}
&\text{S} \\
&\text{N} \\
&\text{N} \\
&\text{R}_I
\end{align*}
\]

wherein \( R_I \) is selected from the group consisting of straight and branched alkyls of from 1 to about 8 carbon
atoms, benzyl, phenyl, and alkoxy groups and such groups containing none, one or more than one such
substituent; \( R_R \) is selected from \( R_I \) and -SR; \( R_m \) is a straight or branched alkyl group of from 1 to about 5
carbon atoms and \( m \) is from 1 to 3; and \( R_{IV} \) is selected from the group consisting of hydrogen, halogens
and alkoxy, phenyl and carbonamido groups, -COOR and -NHCOOR wherein \( R_V \) is selected from
substituted and unsubstituted alkyl and aryl groups.

Although it is typical that the coupler moiety included in the developer inhibitor-releasing coupler forms
an image dye corresponding to the layer in which it is located, it may also form a different color as one
associated with a different film layer. It may also be useful that the coupler moiety included in the developer
inhibitor-releasing coupler forms colorless products and/or products that wash out of the photographic
material during processing (so-called "universal" couplers).

As mentioned, the developer inhibitor-releasing coupler may include a timing group, which groups have
been described earlier with respect to the high dye-yield coupler of the invention. Suitable developer
inhibitor-releasing couplers for use in the present invention include, but are not limited to, the following:
It is also contemplated that the concepts of the present invention may be employed to obtain reflection color prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, England, incorporated herein by reference. Materials of the invention may be coated on pH adjusted support as described in U.S. 4,917,994; on a support with reduced oxygen permeability (EP 553,339); with epoxy solvents (EP 164,961); with nickel complex stabilizers (U.S. 4,346,165; U.S. 4,540,653 and U.S. 4,906,559 for example); with ballasted chelating agents such as those in U.S. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium; and with stain reducing compounds such as described in U.S. 5,068,171. Other compounds useful in combination with the invention are disclosed in Japanese Published Applications described in Derwent Abstracts having accession numbers as follows: 90-072,629; 90-072,630; 90-072,631; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,337; 90-079,338; 90-079,390; 90-079,691; 90-080,487; 90-080,488; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,360; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-103,409; 83-62,586; 83-09,959.

Especially useful in this invention are tabular grain silver halide emulsions. Specifically contemplated tabular grain emulsions are those in which greater than 50 percent of the total-projected area of the emulsion grains are accounted for by tabular grains having a thickness of less than 0.3 microns (0.5 microns for blue sensitive emulsion) and an average tabularity (T) of greater than 25 (preferably greater than 100), where the term "tabularity" is employed in its art recognized usage as

\[ T = \frac{ECD}{t^2} \]

where

- \( ECD \) is the average equivalent circular diameter of the tabular grains in micrometers and
- \( t \) is the average thickness in micrometers of the tabular grains.

The average useful ECD of photographic emulsions can range up to about 10 micrometers, although in practice emulsion ECD's seldom exceed about 4 micrometers. Since both photographic speed and granularity increase with increasing ECD's, it is generally preferred to employ the smallest tabular grain ECD's compatible with achieving aim speed requirements.
Emulsion tabularity increases markedly with reductions in tabular grain thickness. It is generally preferred that aim tabular grain projected areas be satisfied by thin (t < 0.2 micrometer) tabular grains. To achieve the lowest levels of granularity it is preferred that aim tabular grain areas be satisfied with ultrathin (t < 0.06 micrometer) tabular grains. Tabular grain thicknesses typically range down to about 0.02 micrometer. However, still lower tabular grain thicknesses are contemplated. For example, Daubendiek et al U.S. Patent 4,672,027 reports a 3 mole percent iodide tabular grain silver bromoiode emulsion having a grain thickness of 0.017 micrometer. Ultrathin tabular grain high chloride emulsions are disclosed by Maskasky U.S. 5,217,658.

As noted above tabular grains of less than the specified thickness account for at least 50 percent of the total grain projected area of the emulsion. To maximize the advantages of high tabularity it is generally preferred that tabular grains satisfying the stated thickness criterion account for the highest conveniently attainable percentage of the total grain projected area of the emulsion. For example, in preferred emulsions, tabular grains satisfying the stated thickness criteria above account for at least 70 percent of the total grain projected area. In the highest performance tabular grain emulsions, tabular grains satisfying the thickness criteria above account for at least 90 percent of total projected area.

Suitable tabular grain emulsions can be selected from among a variety of conventional teachings, such as those of the following: Research Disclosure, Item 22534, January 1983, published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire PO10 7DD, England; U.S. Patent Nos. 4,439,520; 4,414,310; 4,433,048; 4,643,966; 4,647,528; 4,665,012; 4,672,027; 4,678,745; 4,693,964; 4,713,320; 4,722,888; 4,755,456; 4,775,617; 4,797,354; 4,801,522; 4,806,461; 4,835,095; 4,853,322; 4,914,014; 4,962,015; 4,985,350; 5,061,069 and 5,061,616.

Silver chloride tabular grains useful in this invention include those having \{100\} major faces. These grains are both morphologically stable and capable of being readily sensitized with a variety of sensitizing dyes. Silver chloride emulsions characterized by at least 50 percent of the grain population projected area being accounted for by tabular grains (1) bounded by \{100\} major faces having adjacent edge ratios of less than 10 and (2) each having an aspect ratio of at least 2, as described by House et al in allowed U.S. Application Serial No. 112,489 and by Maskasky in U.S. Patent No. 5,264,337 and allowed U.S. Serial No. 035,349 the disclosures of which are incorporated herein by reference, are suitable for the invention.

The emulsions can be surface-sensitive emulsions, i.e., emulsions that form latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type, which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image and can then be processed to form a visible dye image. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to development exposed silver halide, but not form dye, and followed by uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Preferred color developing agents are p-phenylenediamines such as:

- 4-amino-N,N-diethylaniline hydrochloride,
- 4-amino-3-methyl-N,N-diethylaniline hydrochloride,
- 4-amino-3-methyl-N-ethyl-N-(\(\beta\)-(methanesulfonamido) ethyl)aniline sesquisulfate hydrate,
- 4-amino-3-methyl-N-ethyl-N-(\(\beta\)-hydroxyethyl)aniline sulfate,
- 4-amino-3-\(\beta\)-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and
- 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

Development is usually followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.
It is understood throughout this specification and claims that any reference to a substituent by the identification of a group containing a substitutable hydrogen (e.g. alkyl, amine, aryl, alkoxy, heterocyclic, etc.), unless otherwise specifically stated, shall encompass not only the substituent's unsubstituted form, but also its form further substituted with any photographically useful substituents. Usually the further substituent will have less than 30 carbon atoms and typically less than 20 carbon atoms.

The couplers of the invention can be prepared by methods known in the organic synthesis art including those methods described in U.S. Patent 4,840,884.

**Synthesis Example**

The overall scheme for the synthesis is illustrated below in Scheme I. The intermediate 1 in the linking group synthesis was prepared from glutaric anhydride (22.8 g, 0.2 mole), anisyl alcohol (27.6 g, 0.2 mole), and diisopropyl-ethylamine (24.4 mL, 0.2 mole). These reagents were stirred in 80 mL of tetrahydrofuran (THF) at 40 °C for 30 min. Intermediate 1 was not isolated. The mixture was then cooled to 0 °C, and 26.2 mL (0.2 mole) isobutylchloroformate in 60 mL THF was added over 1-2 min. This mixture was stirred at 0 °C for 60 min to give 2. This mixture was added slowly over 3-4 min to a solution of 3-amino-4-hydroxy benzyl alcohol (13.9 g, 0.22 mole) in 160 mL pyridine cooled to 0 °C. The reaction mixture was stirred for an additional 10 min and then poured into a separatory funnel containing 500 mL of ethyl acetate. 400 mL of brine, 1000 mL of 2N HCl, and 100 g of ice. The aqueous layer was separated and extracted with 200 mL of ethyl acetate. The combined ethyl acetate layers were washed with 200 mL of brine, washed with 400 mL of 0.5N NaHCO₃, washed with 100 mL of brine, and dried over Na₂SO₄. This ethyl acetate solution was filtered, and then concentrated to a yellowish oil in vacuo at less than 30 °C. The resulting oil was stirred with about 400 mL of anhydrous ether overnight at room temperature. White crystals began forming in about 15 min. The ether mixture was then cooled, and the white solid was collected, washed with cold ether, and air dried to yield 51.7 g of crude 3. This crude was reslurried in about 400 mL of dry ether and reisolated to yield 50 g of 3.

Coupler 4 (59.2 g, 0.1 mole) was dissolved in 250 mL of dry dimethylformamide (DMF) and warmed to about 30 °C with a water bath to effect dissolution. This solution was kept under nitrogen. The phenolic intermediate 3 (37.35 g, 0.1 mole) was then added to the reaction mixture and the solution was cooled to about 20 °C with a cold water bath. A solution of tetramethylguanidine (TMG; 12.52 mL in 45 mL DMF) was added dropwise over about 15 min. Diazabicyclo[5.4.0]undec-7-ene (DBU; 4.0 g, 0.026 mole) was added dropwise and the reaction mixture was slowly allowed to come to room temperature and was stirred for 30 min. The mixture was diluted with 50mL of 0.5 N Na₂CO₃ and 1 liter of water to precipitate the solid dye. This solid was recrystallized from methanol to yield 15.4 g of 7. Intermediate 1 (15.4 g, 0.042 mole) and lutidine (5.35 g, 0.05 mole) were dissolved in 200 mL of methylene chloride and cooled in an ice water bath. Phosgene (26.3 mL of 0.05 mole, 1.93M in toluene) was added dropwise, the reaction was slowly allowed to come to room temperature, and the reaction was stirred overnight. The mixture was washed with about 300 mL of cold 5% HCl, dried over MgSO₄, filtered, and stripped to an oil. This oil was slurred with ETOH/heptane to give an orange solid. This solid was collected and air dried to yield 7 g of 8.

Coupler 5 (10.4 g, 0.011 mole), dye intermediate 8 (5.6 g, 0.013 mole), and dimethylaminopyridine (DMAP; 1.3 g, 0.01 mole) were stirred in 40 mL of methylene chloride at room temperature. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU; 4.0 g, 0.026 mole) was added dropwise over 15 min, and the reaction was stirred at room temperature for 4 hr. This solution was washed with cold 0.2N HCl until the wash turned acidic. The solution was then dried over MgSO₄ and stripped to an orange oil. This oil was dissolved in 100 mL of methylene chloride and chromatographed on a 400g of silica gel using heptane/ethyl acetate mixtures as eluent. Heptane to ethyl acetate was varied from 2:1 to 1:1 in the elution. The product fractions were combined and stripped to yield 8.0 g of 9 as a foam.
Coupler 9 was dissolved in 50 mL of methylene chloride at room temperature. Trifluoroacetic acid (10.0 mL) was added dropwise over 5 min, and the reaction mixture was stirred another 10-15 min. The reaction solution was washed twice with 500 mL of cold water, once with IN NaHCO₃ to wash out trifluoroacetic acid, and once with cold 5% HCl. The reaction solution was then dried over MgSO₄ and stripped to an orange oil. This oil was dissolved in 100 mL of methylene chloride and chromatographed on a 400 g of silica gel. Fast moving yellow impurities were removed by eluting with 1:1 ethyl acetate/heptane. The product was eluted with 0.5% acetic acid in 1:1 ethyl acetate/heptane. The product fractions were combined and stripped and taken up into ethyl acetate. This solution was washed with 5% NaHCO₃, with 5% HCl, dried over MgSO₄, and stripped to yield 6.3 g of coupler INV 1.

**SCHEME I**

```
CH₂OH
OCH₃

+ O

O
```

30
1) **Ethylidimethylamine**

2) **Isobutylchloroformate**

1. $R=H$

2. $R=\text{CO}_2\text{i-butyl}$

2 +

\[
\text{OH} \quad \text{NH}_2
\]

\[
\text{CH}_2\text{OH}
\]

\[
\rightarrow
\]

\[
\text{OCH}_3
\]

\[
\text{OCH}_3
\]

3

\[
\text{OH}
\]

\[
\text{CH}_2\text{OH}
\]

\[
+ 3
\]

\[
\text{Cl}
\]

\[
\text{NH}
\]

\[
\text{NH}_2\text{SO}_2\text{(CH}_2\text{)}_{15}\text{CH}_3
\]

4
1) triethylamine / ethylchloroformate

2) pentyamine

7
phosgene + 7 lutidine → NETCOCl

\[
\text{OMe} \quad \text{N}=\text{N} \quad \text{CONH}\left(\text{CH}_2\right)_4\text{CH}_3
\]

DMAP/DBU

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O} & \quad \text{N} \\
\text{CH}_2\text{COONET} & \quad \text{Me}
\end{align*}
\]

\[
\text{N}=\text{N} \quad \text{CONH}\left(\text{CH}_2\right)_4\text{CH}_3
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O} & \quad \text{N} \\
\text{CH}_2\text{COONET} & \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O} & \quad \text{N} \\
\text{CH}_2\text{COONET} & \quad \text{Me}
\end{align*}
\]

\[
\text{N}=\text{N} \quad \text{CONH}\left(\text{CH}_2\right)_4\text{CH}_3
\]
Photographic Examples

The invention is illustrated by the following.

Example 1

A monochrome yellow dye-forming silver halide emulsion layer was prepared in the following format on an acetate film base having a remjet coating.

Format:

Blue light sensitive layer

Layer 1 - Emulsion layer containing:
- Silver halide (AgBr, 1.83 μm, 15 mole% I) 1.29 or 0.65 g/m² Ag
- Conventional image coupler C-1 at 0.36mM/m² or HDY coupler at 0.18mM/m²
- Gelatin 2.69 g/m², and spreading agents, 1.0 wt % of melt weight.

Overcoat

Layer 2 - Emulsion layer containing:
- Gelatin 1.29 g/m², 1,1'-{methylenebis-sulfonyl}bis-ethene hardener 1.75% of total gelatin, and spreading agents, 1.0 wt % of melt weight.

The high dye-yield imaging coupler was provided as a dispersion in d-n-butyl phthalate in a weight ratio of 2 : 1. The conventional imaging coupler C-1 was provided as a dispersion without a permanent coupler solvent.

Coatings were exposed to blue light through a graduated density step wedge and processed using the Kodak Flexicolor™ C-41 development protocol and the coatings were tested to determine blue sensitometry and granularity in the conventional manner. The tested coatings were prepared to provide equivalent sensitometry. The similarity of the curves serves to confirm that the three samples have nearly equivalent sensitometry. Figure 1 shows the Density vs log Exposure curves A1, A2, and A3 for samples 1, 2, and 3 respectively. The tested coatings were prepared to provide equivalent sensitometry. Figure 2 shows granularity curves B1, B2, and B3 for samples 1, 2, and 3 respectively a comparison of which shows the differences in granularity as a function of exposure level between coatings containing conventional coupler Comp-1, comparative high dye-yield coupler CHDY-1, and inventive high dye-yield coupler INV 1. Compared to a coating containing conventional coupler Comp-1 at 0.36mM/m² and silver at 1.29 g/m² (0.012 mM/m²) (Curve B1), the comparative high dye-yield coupler CHDY-1, having a ClogP of released dye of 8.5, at half the Comp-1 level and the silver emulsion at half the level of silver (Curve B2) gave an undesirable increase in granularity in the lower exposure scale.

When the high dye-yield coupler used was INV 1, having a ClogP of released dye = 4.82, (Curve B3) there was a significant lowering of granularity versus the conventional coupler without any significant increase in the lower scale granularity as experienced with the comparative high dye-yield coupler in the lower scale.

Coupler Generic Structure:

\[
\text{SNAPLE COUPLER} \quad \text{X}
\]

\[
\text{NO.}
\]
Example 2 (Comparative)

A color photographic recording material (Photographic Sample 1) for color negative development was prepared by applying the following layers in the given sequence to a transparent support of cellulose triacetate. The quantities of silver halide are given in g of silver per m². The quantities of other materials are given in g per m².

Layer 1 {Antihalation Layer} black colloidal silver sol containing 0.15 g of silver, with 2.44 g gelatin.

Layer 2 {First (least) Red-Sensitive Layer} Red sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55 microns, average thickness 0.08 microns] at 0.45 g, red sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.0 microns, average thickness 0.09 microns] at 0.43 g, cyan dye-forming image coupler C-1 at 0.54 g, cyan dye-forming masking coupler CM-1 at 0.027 g, BAR compound B-1 at 0.038 g, with gelatin at 1.83 g.

Layer 3 {Second (more) Red-Sensitive Layer} Red sensitive silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.3 microns, average grain thickness 0.12 microns] at 0.70 g, cyan dye-forming image coupler C-1 at 0.23 g, cyan dye-forming masking coupler CM-1 at 0.022 g, DIR compound D-1 at 0.011 g, with gelatin at 1.66 g.

Layer 4 {Third (most) Red-Sensitive Layer} Red sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 2.6 microns, average grain thickness 0.13 microns] at 1.08 g, cyan dye-forming image coupler C-1 at 0.13 g, cyan dye-forming masking coupler CM-1 at 0.032 g, DIR compound D-1 at 0.024 g, DIR compound D-2 at 0.050 g, with gelatin at 1.36 g.

Layer 5 {Interlayer} Yellow dye material YD-1 at 0.11 g and 1.33 g of gelatin.
Layer 6 {First (least) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55 microns, average grain thickness 0.08 microns] at 0.55 g, green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.0 microns, average grain thickness 0.09 microns] at 0.31 g, magenta dye-forming image coupler M-1 at 0.26 g, magenta dye-forming masking coupler MM-1 at 0.024 g with gelatin at 1.78 g.

Layer 7 {Second (more) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.25 microns, average grain thickness 0.12 microns] at 0.97 g, magenta dye-forming image coupler M-1 at 0.076 g, magenta dye-forming masking coupler MM-1 at 0.065 g, DIR compound D-1 at 0.024 g with gelatin at 1.48 g.

Layer 8 {Third (most) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 2.16 microns, average grain thickness 0.12 microns] at 0.97 g, magenta dye-forming image coupler M-1 at 0.061 g, magenta dye-forming masking coupler MM-1 at 0.065 g, DIR compound D-3 at 0.01 g, DIR compound D-4 at 0.011 g, with gelatin at 1.33 g.

Layer 9 {Interlayer} Yellow dye material YD-2 at 0.11 g with 1.33 g gelatin.

Layer 10 {First (less) Blue-Sensitive Layer} Blue sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55, average grain thickness 0.09 microns] at 0.28 g, blue sensitized silver iodobromide emulsion [6.0 mol % iodide, average grain diameter 1.0 microns, average grain thickness 0.26 microns] at 0.57 g, blue sensitized silver iodobromide emulsion [4.1 mol % iodide, average grain diameter 0.8, average grain thickness 0.09 micrometers] at 0.19 g, yellow dye-forming image coupler Y-2 at 0.7 g, yellow dye-forming image coupler Y-1 at 0.28 g, cyan dye-forming image coupler C-1 at 0.03 g, DIR compound D-5 at 0.065 g, BAR compound B-1 at 0.003 g with gelatin at 2.22 g.

Layer 11 {Second (More) Blue-Sensitive Layer} Blue sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 3.0 microns, average grain thickness 0.14 microns] at 0.23 g, blue sensitized silver iodobromide emulsion [6.0 mol % iodide, average grain diameter 1.1 microns] at 0.57 g, yellow dye-forming image coupler Y-2 at 0.20 g, yellow dye-forming image coupler Y-1 at 0.08 g, cyan dye-forming image coupler C-1 at 0.03 g, DIR compound D-5 at 0.05 g, BAR compound B-1 at 0.005 g with gelatin at 0.99 g.

Layer 12 {Protective Layer} 0.111 g of dye UV-1, 0.111 g of dye UV-2, unsensitized silver bromide Lippmann emulsion at 0.22 g, with gelatin at 2.03 g.

This film was hardened at coating with 2% by weight to total gelatin of hardener H-1. Surfactants, coating aids, scavengers, soluble absorber dyes and stabilizers were added to the various layers of this sample as is commonly practiced in the art.

The formulas for the component materials are given at the end of the examples.

Example 3 (Comparative)

This multilayer photographic element was prepared like Example 2 except:

Layer 10

The yellow image couplers Y-1 and Y-2 were replaced with CHDY-2 at 0.63 g, DIR compound D-5 was coated at 0.097 g, the silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55, average grain thickness 0.09 microns] at 0.14 g, blue sensitized silver iodobromide emulsion [6.0 mol % iodide, average grain diameter 1.0, average grain thickness 0.26 microns] at 0.28 g, blue sensitized silver iodobromide emulsion [4.1 mol % iodide, average grain diameter 0.8, average grain thickness 0.09 microns] at 0.097 g.

Layer 11

The yellow image couplers Y-1 and Y-2 were replaced with CHDY-2 at 0.18 g, blue sensitized silver iodobromide emulsion [9 mol % iodide, average grain diameter 1.1 microns] at 0.29 g.
Example 4 (Invention)

This sample was prepared like Example 3 except:

Layer 10

The yellow image coupler CHDY-2 was replaced with INV 22 at 0.74 g.

Layer 11

The yellow image coupler CHDY-2 was replaced with INV 22 at 0.21 g.

Figure 3 shows the responses of the blue light sensitive layers to a blue light exposure. The responses of the control coating containing a conventional coupler (Example 2), the comparison high dye-yield coating (Example 3) and the Inventive coating (Example 4) are well matched for contrast.

According to Figure 4, when the silver laydowns of Example 2 are reduced, in Layer 10 by 50% and in Layer 11 by 36% (Example 3) there is a large increase in granularity, although the use of the high dye-yield image coupler CHDY-2 gives retention of sensitometric performance.

Use of the inventive coupler INV 22 yields a substantial reduction in granularity throughout the imaging scale. This makes it possible to realize the benefits of lower silver laydowns in blue light sensitive layers, without the large granularity increase.

The formulas for the component materials are as follows:

CHDY-2

![Chemical structure of CHDY-2]
C-1:

\[ \text{n-C}_4\text{H}_9\text{CONH} - \text{OH} - \text{NHCONH} - \text{PhCN} \]

\[ \text{n-C}_4\text{H}_9\text{CONH} - \text{Ph} - \text{C}_5\text{H}_{11-\text{t}} \]

CM-1

\[ \text{OH} - \text{CONH(CH}_2)_4\text{O} - \text{Ph} - \text{C}_5\text{H}_{11-\text{t}} \]

\[ \text{Ph} - \text{N=N} - \text{OH} - \text{NHCOCH}_3 \]

\[ \text{CH}_3\text{SO}_3 - \text{H} - \text{SO}_3\text{H} \]

B-1

\[ \text{OH} - \text{CONH(CH}_2)_4\text{O} - \text{Ph} - \text{C}_5\text{H}_{11-\text{t}} \]

\[ \text{SCH}_2\text{CH}_2\text{CO}_2\text{H} \]
D-1:

\[
\begin{align*}
&\text{OH} \\
&\text{CONH} \quad \text{OC}_{14}H_{29} \\
&\text{O} \\
&\text{NO}_2 \\
&\text{CH}_2S \quad \text{N} = \text{N} \\
&\text{N} \quad \text{N} \\
&\text{C}_2H_5 \\
\end{align*}
\]

D-2

\[
\begin{align*}
&\text{OH} \\
&\text{CONH} \quad \text{OC}_{14}H_{29} \\
&\text{S} \\
&\text{N} = \text{N} \\
&\text{N} \quad \text{C}_2H_5 \\
\end{align*}
\]
Y-2:

M-1:

M-2:
M-3:

\[
\begin{align*}
&\text{CH}_3 \\
&\text{Cl} \\
&\text{H}
\end{align*}
\]

\[
\begin{align*}
&\text{(CH}_2\text{)}_3 \\
&\text{N} \text{HCOCHC}_{10}\text{H}_{21} - n
\end{align*}
\]

\[
\begin{align*}
&\text{O} \\
&\text{HO} \\
&\text{SO}_2
\end{align*}
\]

YD-1:

\[
\begin{align*}
&\text{t-C}_4\text{H}_9 \\
&\text{N} \text{H} \\
&\text{Cl}
\end{align*}
\]

\[
\begin{align*}
&\text{N(C}_2\text{H}_5\text{)}\text{C}_2\text{H}_4\text{OH} \\
&\text{NHSO}_2\text{C}_{16}\text{H}_{33} - n
\end{align*}
\]

YD-2:

\[
\begin{align*}
&\text{O} \\
&\text{CN} \\
&\text{NHSO}_2\text{C}_4\text{H}_9 - n
\end{align*}
\]
The preceding examples are set forth to illustrate specific embodiments of this invention and are not intended to limit the scope of the materials or combinations of this invention. Additional embodiments and advantages within the scope of the claimed invention will be apparent to one skilled in the art. All previously cited patents, publications, and cofiled and copending patent applications are incorporated herein by reference in their entirety.

Claims

1. A photographic element comprising a support bearing a light sensitive photographic silver halide emulsion layer wherein said layer has associated therewith a coupler capable of combining with oxidized developer to form a first dye, said coupler also containing at the coupling position a coupling-off group which is released during development to form a precursor of a second dye, said precursor having an electrically neutral dye chromophore bonded to a linking group selected from -OC(O)-, -OC-(S)-, -SC(O)-, -SC(S)-, and -OC(=NSO₂R)- where R is substituted or unsubstituted alkyl or aryl;

wherein said second dye is an image dye;

wherein said linking group is cleavable during processing;

wherein the amount of said coupler associated with said layer and the amount of silver in said layer is such that the molar ratio of the dye formable from said coupler to the silver contained in said layer is less than 1.0 and the silver and coupler levels are each below 1 g/m²; and

further wherein the second dye has a calculated logarithm of its neutral partition coefficient (ClogP) in the range of 3.5 to 5.5.

2. The element of claim 1 wherein said first dye is ballasted to render it immobile.

3. The element of claim 1 wherein said first dye exhibits a ClogP of at least 5.5.
4. The element of claim 1, 2 or 3 wherein said first and second dyes are the same color.

5. The element of claim 4 wherein both the first and second dyes are magenta dyes.

6. The element of claim 4 wherein both the first and second dyes are cyan dyes.

7. The element of claim 4 wherein both the first and second dyes are yellow dyes.

8. The element of claim 4 wherein the wavelengths of maximum absorption ($\lambda_m$) of the first and second dyes are less than 25 nm apart.

9. The element of claims 1 to 8 wherein the ClogP of the second dye is in the range of 4.0 to 5.5.

10. The element of claims 1 or 3-9 wherein said coupler is capable of combining with oxidized developer to form a first dye which is capable of being washed out upon processing.
FIG. 3
LOG EXPOSURE

RMS GRANULARITY

Ex. 3 (COMP.)
Ex. 4 (INVENTION)
Ex. 2 (COMP.)

FIG. 4
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)</th>
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<tr>
<td>D, A</td>
<td>US - A - 5 234 800 (BEGLEY) * Claims *</td>
<td>1, 2</td>
<td>G 03 C 7/305</td>
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<td>US - A - 4 840 884 (MOOBERRY) * Claims *</td>
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**TECHNICAL FIELDS SEARCHED (Int. Cl.6)**

G 03 C

The present search report has been drawn up for all claims.

**Place of search**

VIENNA

**Date of completion of the search**

18-09-1995

**Examiner**

SCHÄFER

**CATEGORY OF CITED DOCUMENTS**

- X: particularly relevant if taken alone
- Y: particularly relevant if combined with another document of the same category
- A: technological background
- T: theory or principle underlying the invention
- E: earlier patent document, but published on, or after the filing date
- D: document cited in the application
- L: document cited for other reasons
- P: intermediate document
- &: member of the same patent family, corresponding document