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(54) **Light-sensitive silver halide photographic material**

Photographisches Silberhalogenidmaterial

Matériau photographique à halogénure d'argent

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(56) References cited:

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EP-A- 0 374 751 **DE-A- 2 505 309**

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Description

FIELD OF THE INVENTION

5 The present invention relates to a light-sensitive silver halide photographic material containing an UV absorbent.

BACKGROUND OF THE INVENTION

The influence of ultraviolet rays on photographic materials is widely known.

10 Examples of such influence include an undesirable sensitization attributable to static light generated in coating and drying processes or in transit of a photographic material, and deterioration in color reproducibility due to difference in ultraviolet intensities of various light sources in photographing.

When a photographic product which forms images with dyes other than metallic silver is used in outdoor ornamental display, dye images are so susceptible to ultraviolet rays that a large color fading is caused during display by the sunlight containing much ultraviolet rays, losing the aesthetic value.

15 Further, when a polyethylene coated support is used in such a photographic material, deterioration of polyethylene occurs due to ultraviolet rays, causing cracking in the support.

Moreover, various other organic additives contained in a photographic product are frequently photolyzed, yielding colored matters. Therefore, stain is often observed, particularly in nonimage areas. For example, it is known that an undeveloped area (white area) of a color photographic paper tends to yellow under irradiation of light; this is called light stain and desired to be solved.

In order to reduce the adverse influence of ultraviolet rays, it is widely known and practiced to introduce an UV absorbent to a silver halide emulsion layer or a nonlight-sensitive photographic layer of a photographic product. For this purpose, there are proposed a large number of UV absorbents, and general characteristics required of them are 25 (1) having no absorption in a visible light area, (2) having no influence on a photographic product, (3) being highly soluble in a high boiling organic solvent and (4) being highly light-fast in themselves because they are used to prevent the adverse influence of light irradiation over a long period.

Such proposals of using an UV absorbent in a light-sensitive material are seen in, for example, Japanese Patent Examined Publication No. 26139/1974, Japanese Patent O.P.I. Publication Nos. 222853/1985, 178954/1987 and 178961/1987.

Though light-fastness of images can be improved with the addition of such UV absorbents, there has been observed the fact that use of an UV absorbent having a large light-fastness enhancing capability is liable to deteriorate whiteness, and contrary, use of an UV absorbent less in deterioration of whiteness tends to lower the light-fastness enhancing capability. Accordingly, a satisfactory enhancement of both the whiteness and light-fastness is not attained by conventional techniques.

35 Further, when an UV absorbent is added in a light-sensitive material in a large amount, an oily component comes up to the surface of the light-sensitive material in a long storage. This phenomenon is called sweating and desired to be removed.

Other typical compounds used as an UV absorbent are described in U.S. Patent Nos. 2,685,512, 2,719,086, 2,739,888, 2,739,971, 2,747,996, 2,784,087, 2,811,461, 3,112,338, 3,168,492, 3,206,431, 3,253,921, 3,692,525, 3,754,919, Japanese Patent Examined Publication Nos. 4786/1967, 25337/1975, 12587/1980, 36984/1980, International Publication No. 01473/1981 and European Provisional Publication No. 57,160.

As a measure to disperse these UV absorbents, several methods have been proposed.

One method is what is called Fisher type dispersing method in which finely pulverized particles are dispersed.

45 Another method is to add a polymer latex and water little by little to a water-miscible organic solvent dissolving an UV absorbent until the UV absorbent becomes insoluble, so that the UV absorbent is incorporated into particles of the polymer latex. Japanese Patent O.P.I. Publication Nos. 59942/1976 and 59943/1974 describe in detail such water-miscible organic solvents and polymer lattices capable of being filled with an UV absorbent.

A third method comprises the steps of dissolving an UV absorbent in a water-insoluble high boiling organic solvent or polymer and then dispersing it finely in a hydrophilic colloid to obtain an oil-in-water type dispersion. This dispersing method is described in U.S. Patent Nos. 2,322,027, 2,801,170, 2,801,171, 2,870,012 and 2,991,177. The application of this method to an UV absorbent is disclosed in U.S. Patent No. 2,739,888.

Among these methods, the third method is most widely used for reasons that it is suitable for a large-scaled production because it does not thicken a coating solution in preparation thereof as well as it allows an UV absorbent to exhibit a good adsorbency.

55 However, this method has a disadvantage that dispersed particles tend to become coarse ones or to crystallize owing to a low stability of the dispersion, which may cause a big trouble in a production process.

Use of an UV absorbent is effective to improve the light-fastness (and resistance against static marks), but any of

conventional methods could hardly prevent the color fading of a dye image exposed to various light sources. Using an UV absorbent in a large amount can improve the light-fastness in various light sources to some extent, but it is not substantial. Moreover, use of an excessive UV absorbent causes a suspensoid to deposit and thereby ultraviolet absorbency decreases rapidly, deteriorating the light-fastness or causing a trouble in the coating process.

On the other hand, there is proposed a technique to prevent the deposition by combining two or more types of UV absorbents as described in Japanese Patent Examined Publication Nos. 5496/1973, 30493/1973, 41572/1973 and Japanese Patent O.P.I. Publication Nos. 85425/1978, 215378/1984.

This method is effective in lessening the liability to deposition but not satisfactory, and is less effective to prevent dispersed particles becoming coarse ones as time elapses. The light-fastness in various light sources is not improved so much, either.

In a photograph for direct appreciation, whiteness of a background has a large influence on an image. An enhanced whiteness sharpens contrast, improves color purity and increases aesthetic value; therefore, many methods to enhance the whiteness have been contrived. Use of a fluorescent brightener is known as an effective means to enhance the whiteness of a light-sensitive material. In one method of using a fluorescent brightener, the photographic processing is carried out with a color developer containing a fluorescent brightener as described in Japanese Patent Examined Publication Nos. 35240/1971, 20975/1974 and 25336/1975. This method, however, is insufficient in fluorescent brightening effect and in stability of the developer. Therefore, it cannot meet the recent demand for rapid and diversified processing.

Another method of using a fluorescent brightener comprises to contain a fluorescent brightener in a light-sensitive material. Such a method can be seen in, for example, Japanese Patent Examined Publication Nos. 21189/1971, 27692/1973, 10696/1974, 28225/1976, and 32254/1977. This method is more effective than the above method in which a fluorescent brightener is contained in a developer, and provides a larger fluorescent intensity; thereby the whiteness in an unexposed area is much more enhanced. In a conventional method to incorporate a fluorescent brightener into a light-sensitive material, the fluorescent brightener is contained in one of photographic structural layers including a support covering layer, emulsion layer and non-emulsion layer, singly or in combination with a compound in addition to the fluorescent brightener to strengthen the brightening effect. This method is effective in enhancing the whiteness of an unexposed area, but it has a serious drawback of generating a static trouble such as static marks when a photographic structural layer is coated on a support at a high speed, when a light-sensitive material is conveyed in a color printer for printing, or when a tape stuck on the surface of a light-sensitive material is peeled off.

Despite of many problems left unsolved including those described above, use of an UV absorbent is effective in improving the light-fastness and practiced widely; many useful methods are proposed for further improvement.

One serious problem in the use of an UV absorbent is that in most cases an UV absorbent absorbs excitation light for a fluorescent brightener and makes the fluorescence function to enhance the whiteness inactive. Therefore, it has been difficult to enhance the whiteness concurrently with the light-fastness of a color image or the static resistance.

As a measure to solve this problem, utilization of a fluorescent brightener's dispersibility was proposed in Japanese Patent O.P.I. Publication No. 71050/1984. This method was effective to some extent but still insufficient, and a much improved measure has been demanded.

In general, silver halide photographic light-sensitive materials are continuously processed in an automatic developing machine installed in each processing laboratory. And as a service to customers, processing laboratories are demanded to process photographic materials and return them to customers on the very day that the photographic materials are brought in for processing, and even a returning within several hours is demanded in recent years; therefore, the necessity for rapid processing has come to be much stronger. Moreover, a shorter processing time improves the production efficiency and reduces the processing cost. This is another reason why rapid processing and high-speed printing are required.

To realize a much improved rapid processing, researches are conducted from two angles of light-sensitive material and processing solution. In color developing, there are tried the adoption of a higher temperature, a higher pH and a higher concentration developing agent, as well as the addition of a developing accelerator. Examples of such developing accelerators include 1-phenyl-3-pyrazolidone described in U.S. Patent No. 811,185, N-methyl-p-aminophenol disclosed in U.S. Patent No. 2,417,514 and N,N,N',N'-tetramethyl-p-phenylenediamine described in Japanese Patent O. P.I. Publication No. 15554/1975. Any of these methods, however, cannot provide a sufficient rapidness and entails a performance deterioration such as increased fogging.

Meanwhile, it is known that the shape, size and composition of silver halide grains in a silver halide emulsion used in a light-sensitive material have a large influence on developing speed. Among them, the halogen composition has the largest influence, and use of a high-chloride-containing silver halide gives a particularly higher developing speed.

In such a rapid processing, however, components in processing solutions such as developer are liable to be left in a light-sensitive material, causing deterioration in light-fastness and yellowing attributable to exposure to light. Particularly, the yellowing becomes much larger as the processing becomes rapider. Further, a static light fog is apt to be generated in a high-speed printer. UV absorbents enhance the light-fastness of color images and reduce the yellowing;

but conventional UV absorbents are still insufficient in these functions and cannot prevent enough light stains particularly in rapid processing. Accordingly, an addition in a large amount is needed, which causes deterioration in whiteness and sweating resistance.

Under the circumstances, there has been desired a method which enhances the light-fastness and controls yellow stains caused by light even when a light-sensitive material is subjected to rapid processing.

The present inventors tried various approaches to solve the problems and have found that a light-sensitive material excellent in both whiteness and light-fastness and having an improved resistance to sweating is obtained with specific UV absorbents.

One object of the present invention is to provide a light-sensitive material improved in both whiteness and light-fastness.

Another object of the present invention is to provide a light-sensitive material free from sweating and excellent in both whiteness and light-fastness over a long period of storing.

A third object of the present invention is to provide a photographic element excellent in light-fastness of dye images and whiteness of a white area.

A fourth object of the present invention is to provide a silver halide photographic light-sensitive material having an excellent resistance to static marks and a high whiteness.

A fifth object of the present invention is to provide a dispersion capable of imparting a stable and high ultraviolet absorbing effect.

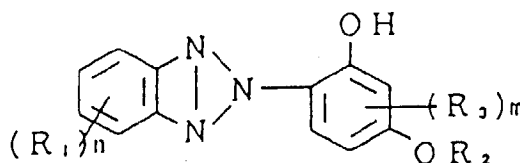
A sixth object of the present invention is to provide a dispersion capable of imparting an enhanced light-fastness stable enough against various light sources when used in a photographic product.

A seventh object of the present invention is to provide a silver halide photographic light-sensitive material free from light-fastness deterioration and light stain even when subjected to rapid processing.

An eighth object of the present invention is to provide a silver halide photographic light-sensitive material having an improved resistance against static light fogging in rapid processing or in printing in a high-speed printer.

The light-sensitive material of the invention comprises at least one light-sensitive layer, wherein at least one light-sensitive layer and/or at least one nonlight-sensitive layer contains the compound represented by Formula I.

Formula I:



wherein R_1 represents a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryloxy group; R_2 represents a substituted or unsubstituted alkyl group having a total number of carbon atoms of eight or more, or a substituted or unsubstituted aryl group; R_3 represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryloxy group; n represents an integer of zero to 4, and m represents an integer of zero to 3, provided that in case

a) R_1 being a substituted alkoxy or aryloxy group or

b) R_2 being a substituted alkyl, or aryl group

the substituent cannot be a quaternary ammonium moiety.

In the compound represented by Formula I, R_1 is a halogen atom (e.g., fluorine atom, chlorine atom, bromine atom), an alkyl group (e.g., methyl, ethyl), an aryl group (e.g., phenyl), an alkoxy group (e.g., methoxy) or an aryloxy group (e.g., phenoxy).

R_2 is a substituted or unsubstituted alkyl group (e.g., 2-ethyl-hexyl, sec-dodecyl, iso-tridecyl, cis-9-octadecenyl, octyloxycarbonyl-ethyl) or an aryl group (e.g., phenyl).

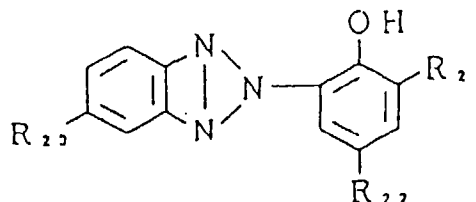
R_3 is an alkyl group (e.g., t-amyl, methyl), an aryl group (e.g., phenyl), an alkoxy group (e.g., methoxy, 2-ethyl-hexyloxy) or an aryloxy group (e.g., phenoxy).

The compound represented by Formula I may be added in either a light-sensitive layer or a nonlight-sensitive layer, but preferably it is added at least in a nonlight-sensitive layer, and more preferably it is added at least in a nonlight-sensitive layer farther from a support than the farthest light-sensitive layer from the support. An addition amount is not

particularly limited, but preferably 0.05 to 15 g/m², and more preferably 0.1 to 5 g/m².

In the invention, it is preferred that a dispersion suspending oily droplets containing another UV absorbent than those represented by the Formula I be used, in order to provide a stable and high ultraviolet absorption function and thereby to impart a function of enhancing light-fastness to various light sources. Such plural UV absorbents are preferably contained as a mixture of at least one of the compound represented by the foregoing Formula I and at least one of the compound represented by the following Formula II.

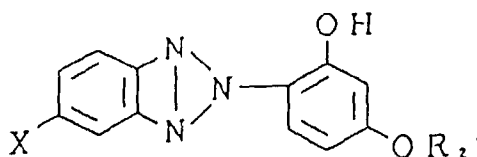
Formula II:



wherein R₂₁, R₂₂ and R₂₃ each represent a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryloxy group, a substituted or unsubstituted alkenyl group, a nitro group or a hydroxyl group.

Among the compounds represented by Formula I, those represented by the following Formula I-A are preferred.

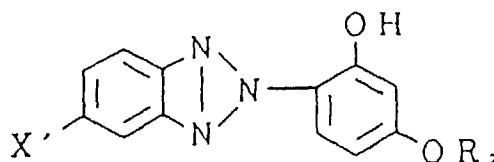
Formula I-A:



wherein X represents a hydrogen atom or a halogen atom, and R₂' is the same as those defined for R₂ in Formula I.

Among the compounds represented by Formula I-A, those represented by Formula I-B are more preferable.

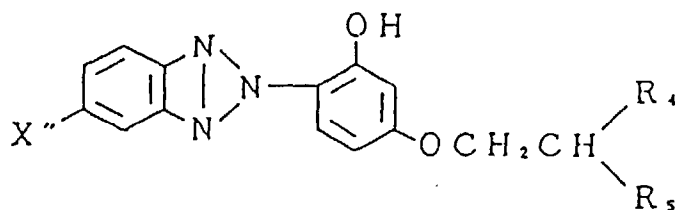
Formula I-B:



wherein R₂" represents a branched alkyl group having a number of carbon atoms of eight or more (e.g., iso-tridecyl), and X' represents a hydrogen atom or a chlorine atom.

The most preferable compounds are those represented by the following Formula I-C.

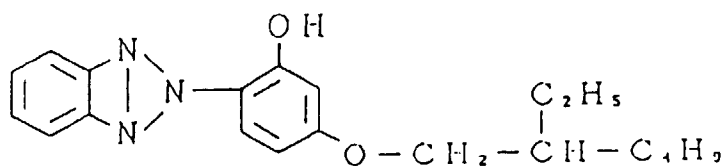
Formula I-C:



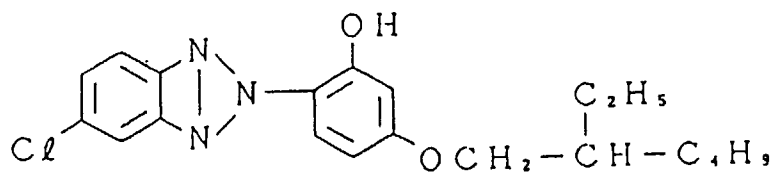
wherein X'' represents a hydrogen atom or a chlorine atom, preferably a chlorine atom, R₄ and R₅ each represent an alkyl group the total number of carbon atoms of R₄ and R₅ being six or more (e.g., ethyl and butyl respectively).

Typical examples of the compound represented by Formula I are illustrated below.

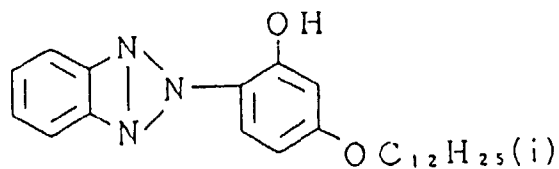
I-1



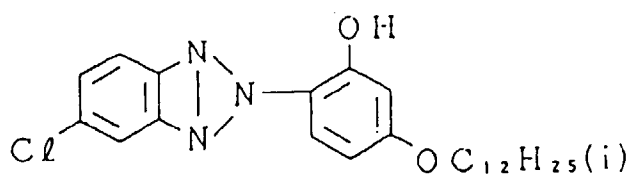
I-2



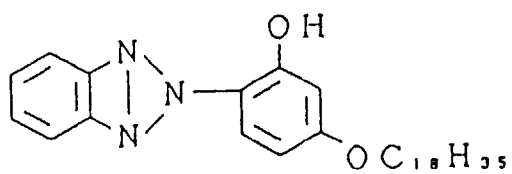
I-3



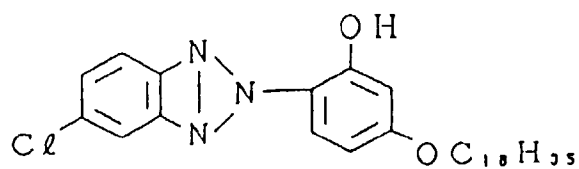
I-4



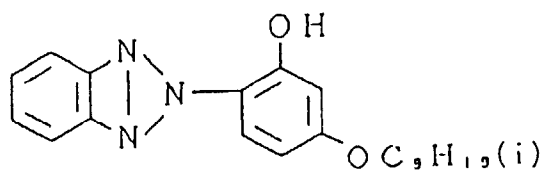
I-5



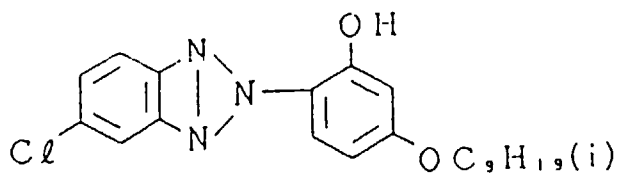
I-6



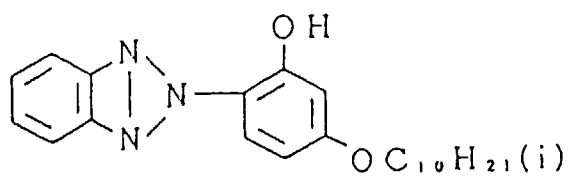
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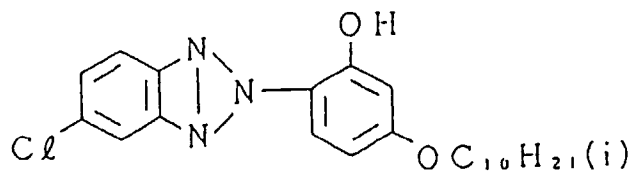
I-8



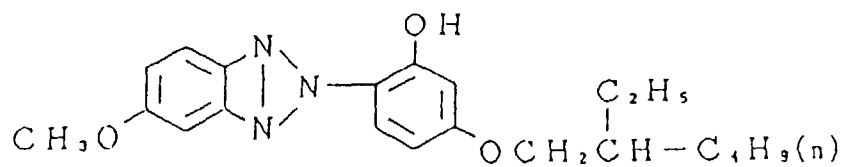
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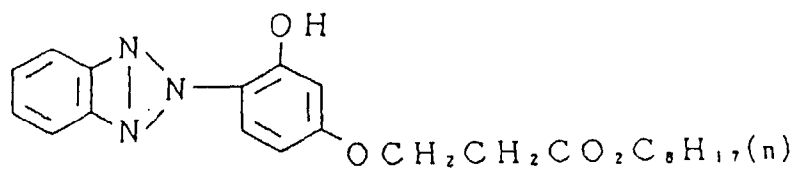
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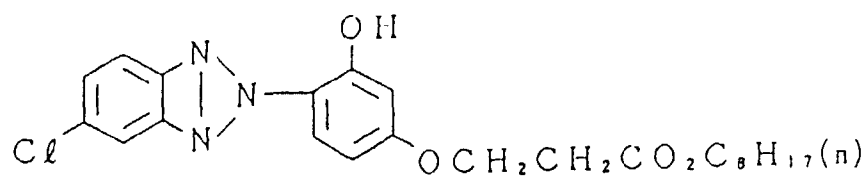
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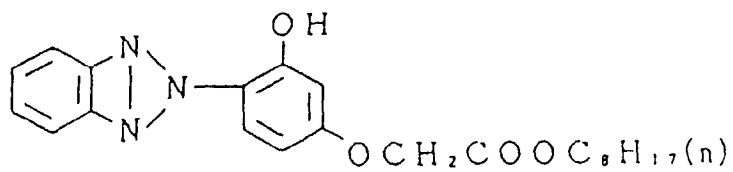
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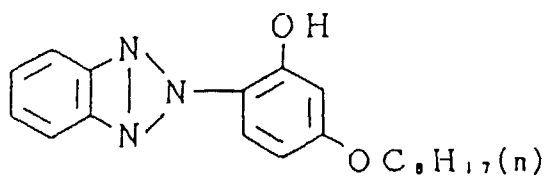
I-13



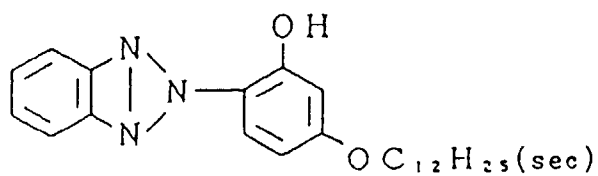
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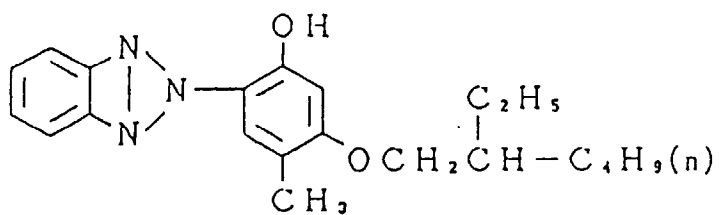
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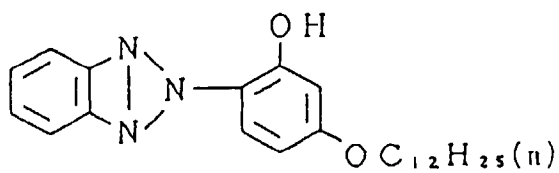
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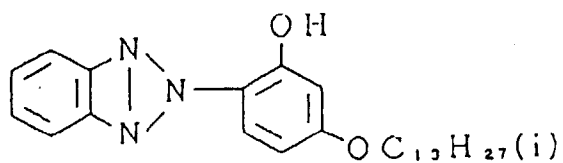
I-17



I-18

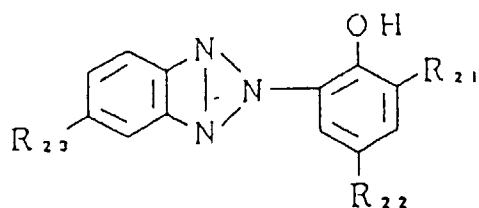


I-19



Next, the compound represented by the foregoing Formula II will be described.

Formula II:



wherein R_{21} , R_{22} and R_{23} each represent a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryloxy group, a substituted or unsubstituted alkenyl group, a nitro group or a hydroxyl group.

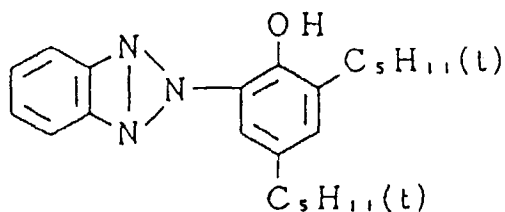
Among the groups represented by R_{21} or R_{22} , the preferred ones are a hydrogen atom, an alkyl group, an alkoxy group and an aryl group. The particularly preferred ones are a hydrogen atom, an alkyl group and an alkoxy group.

Among the groups represented by R_{23} , the particularly preferred ones are a hydrogen atom, a halogen atom, an alkyl group and an alkoxy group.

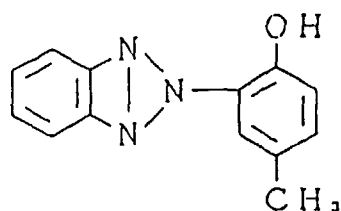
Among R_{21} to R_{23} , at least one is preferably an alkyl group, and more preferably at least two are alkyl groups.

Typical examples of the compound represented by Formula II will be shown below.

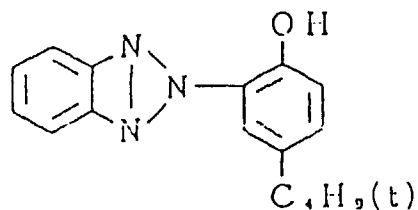
II - 1



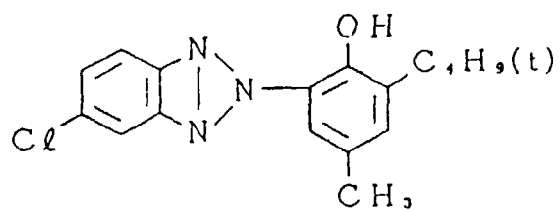
II - 2



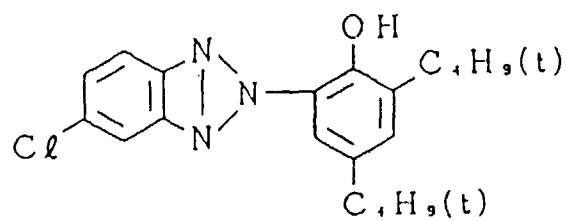
II - 3



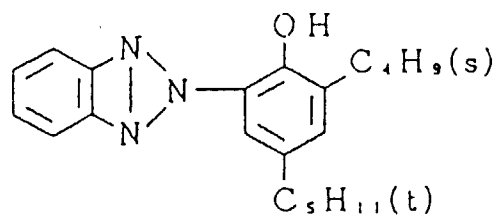
II - 4



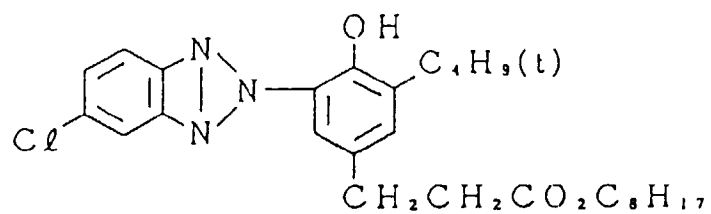
II - 5



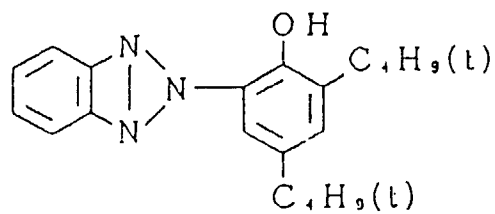
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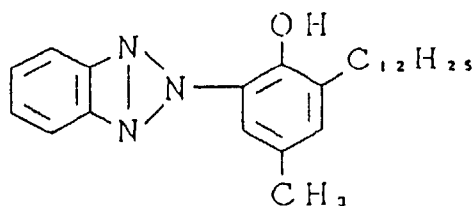
II - 7



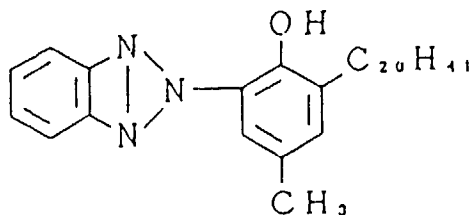
II - 8



II - 9



II - 10

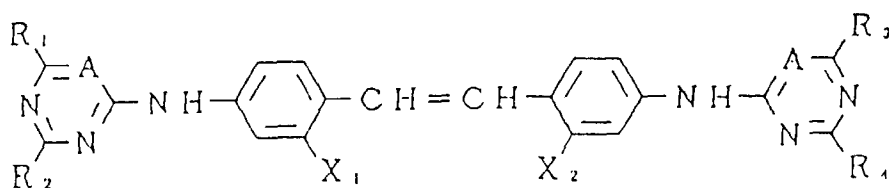


A dispersion containing the compounds represented by Formulas I and II (hereinafter referred to as a dispersion of the invention) can be favorably used in a silver halide photographic light-sensitive material. When the dispersion of the invention is used in a light-sensitive material, it may be added in either a light-sensitive layer or a nonlight-sensitive layer, but preferably it is added in a nonlight-sensitive layer farther from a support than the farthest light-sensitive layer from the support. Addition amounts of the compounds of Formula I and the compound of Formula II in a light sensitive material are not particularly limited, but preferably 0.05 to 15 g/m², and more preferably 0.1 to 5 g/m², respectively.

An addition ratio of the compound of Formula I to the compound of Formula II is preferably 1:99 to 99:1, and more preferably 20:80 to 80:20.

In order to obtain a better light-fastness of dye images, a higher whiteness of a white area and a much improved static mark resistance, the photographic light-sensitive material of the invention employs the fluorescent brightener represented by the following Formula III.

Formula III:

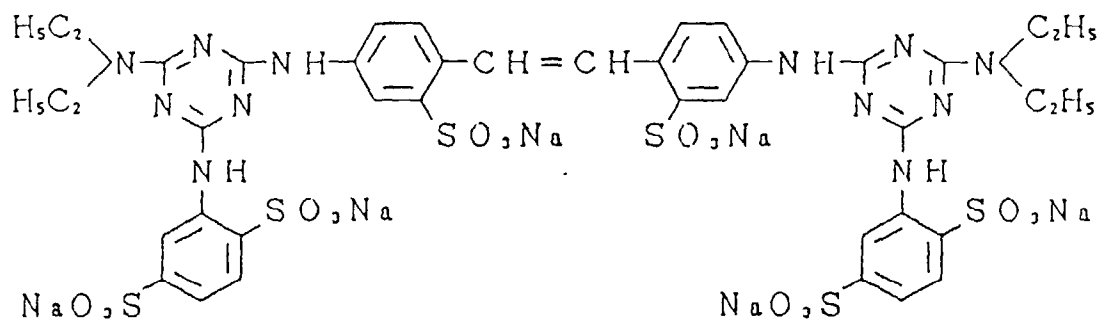


wherein A represents a -N=N- or a -C=; R₁, R₂, R₃ and R₄ may be the same or different from one another and each represent a substituted or unsubstituted alkyl group (e.g., 2-ethylamino-ethyl, ethyl), a substituted or unsubstituted alkylamino group (e.g., N,N-diethylamino, N,N-di-hydroxyethylamino), a substituted or unsubstituted arylamino group (e.g., phenylamino) or a substituted or unsubstituted aryloxy group (e.g., phenoxy); X₁ and X₂ each represent a hydrogen atom or a -SO₃M, where M is a hydrogen atom or an atom or a group to form a water-soluble salt (e.g., -NH₄, alkali metal such as Na, K).

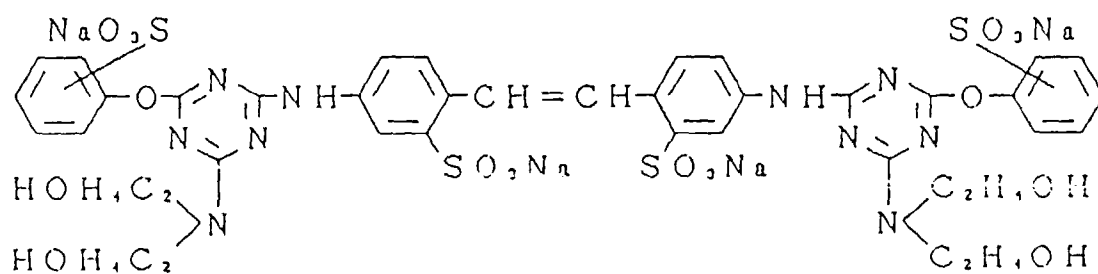
In the compound of Formula III, -SO₃M group is contained in a number of 1 to 6 including those which may be substituted in each of R₁ to R₄.

The examples of the fluorescent brightener of the invention are shown below.

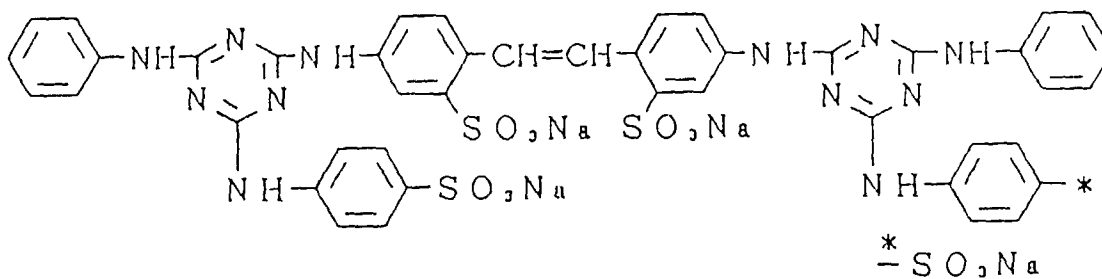
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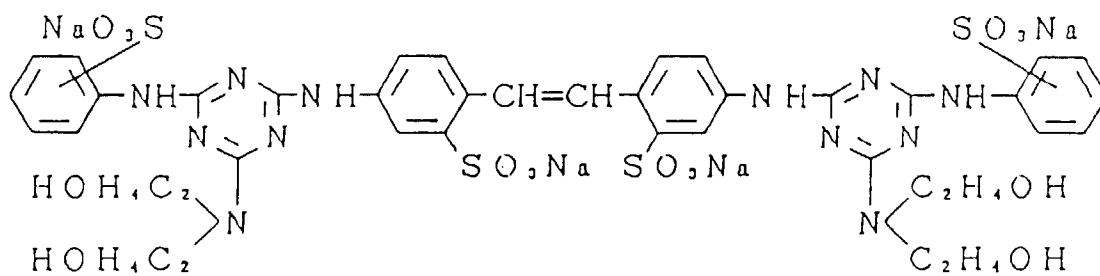
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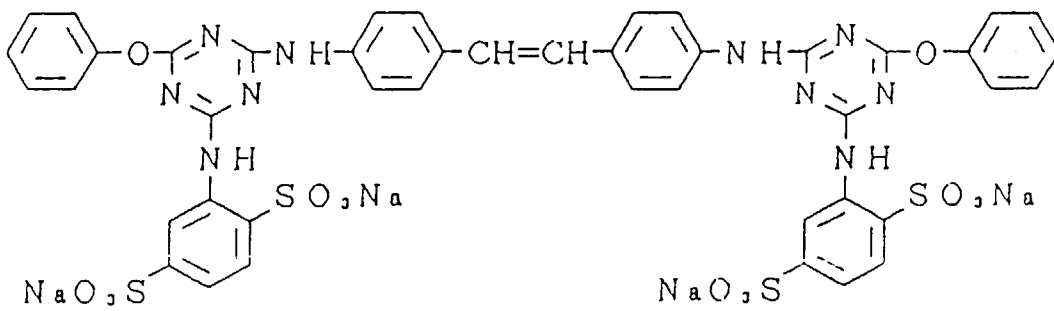
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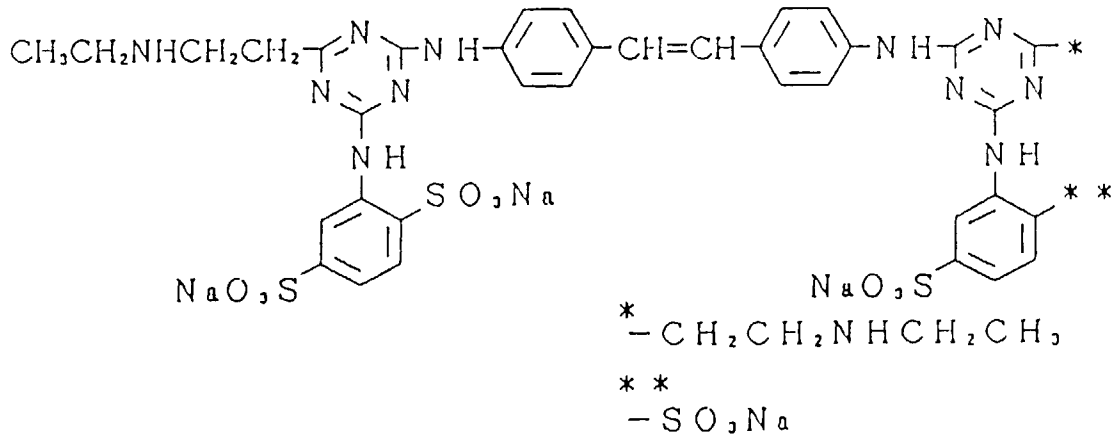
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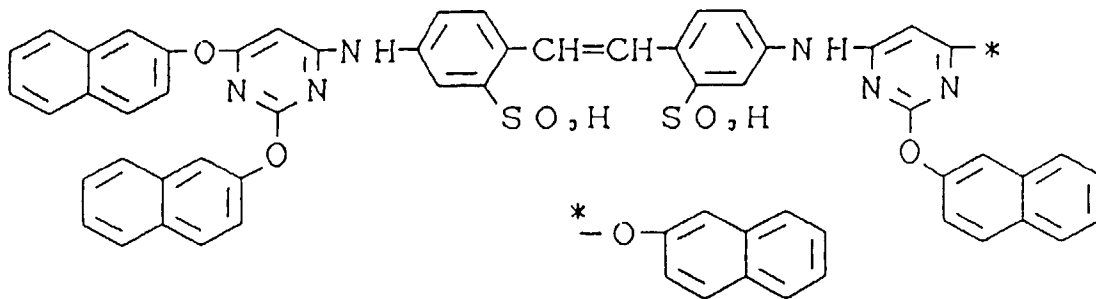
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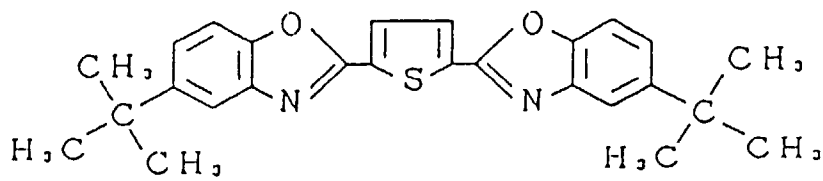
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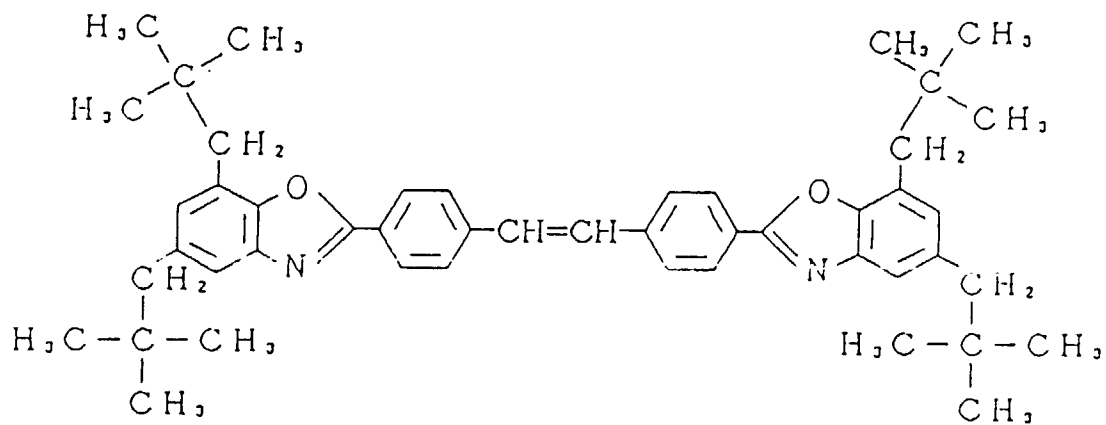
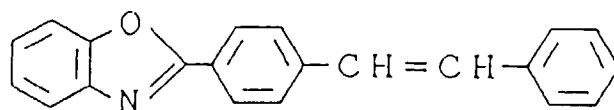
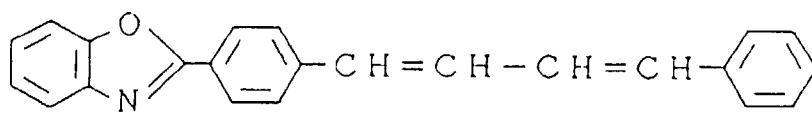
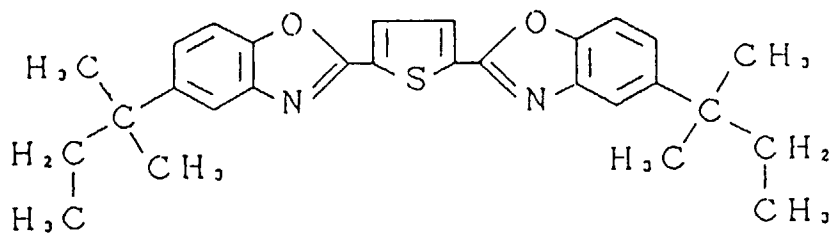


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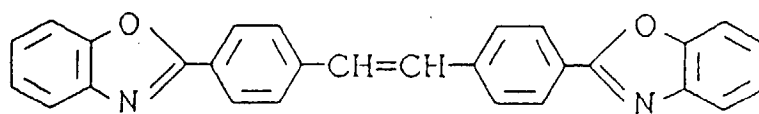


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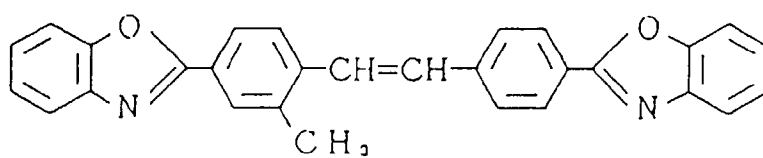




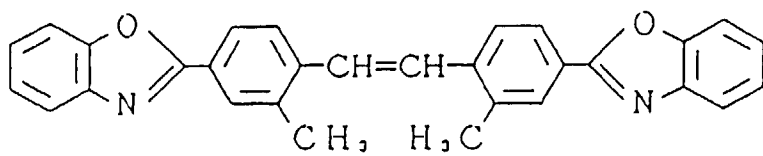
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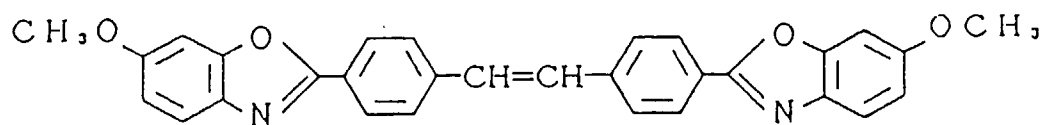
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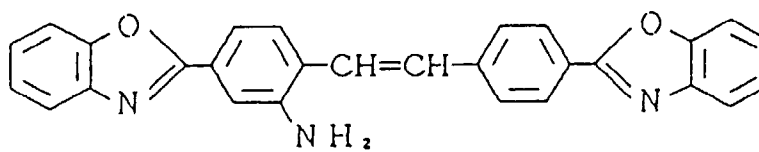
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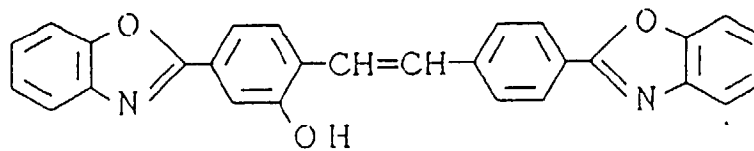
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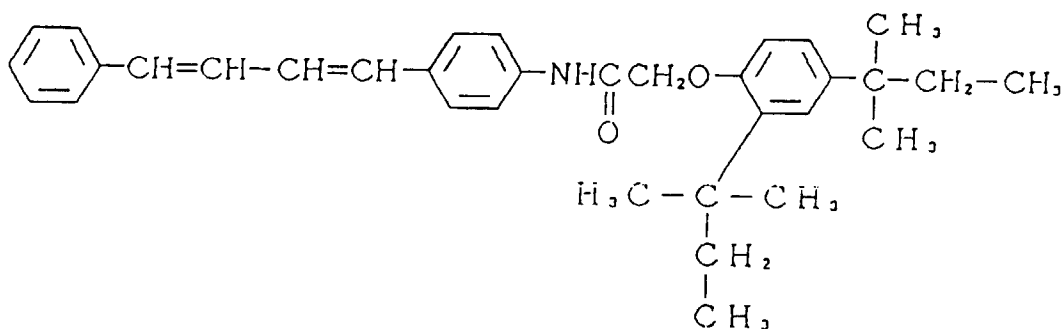


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The fluorescent brightener of the invention may be added in a light-sensitive layer and/or a nonlight-sensitive layer, or in a support of a silver halide photographic light-sensitive material. It can also be added as a supersensitizer to a silver halide emulsion. Further, it can be retained in a finished photographic constituent by being added to a developer bath or a stabilizer bath.

When the fluorescent brightener is contained in a photographic constituent in the invention, an addition amount is preferably 0.01 to 2 g/m², and more preferably 0.02 to 1 g/m²; when it is added to a developer bath, an addition amount is preferably 0.1 to 2 g per liter, more preferably 0.5 to 1.5 g per liter of developer; and when it is added to a stabilizer bath, an addition amount is preferably 0.1 to 2 g per liter, more preferably 1 to 2 g per liter of stabilizer.

In the invention, silver halide grains having a silver chloride content of more than 90 mol% are used at least in one silver halide light-sensitive layer. Said silver halide grains have preferably a silver chloride content of more than 90 mol%, and a silver bromide content of less than 10 mol%, and a silver iodide content of less than 0.5 mol%. More preferably, said silver halide is a silver chlorobromide containing 0.1 to 2 mol% of silver bromide.

The silver halide grains employed in the silver halide photographic light-sensitive material of the invention may be used singly or in combination with other silver halide grains of different composition. They may also be used together

with silver halide grains having a silver chloride content of less than 10 mol%.

In a silver halide emulsion layer containing the silver halide grains with a silver chloride content of more than 90 mol% according to the invention, said silver halide grains with a silver chloride content of more than 90 mol% account for more than 60 wt%, preferably more than 80 wt% of the total silver halide grains contained in said emulsion layer.

The composition of silver halide grains used in the invention may be uniform throughout the grain or different from inner portion to outer portion of the grain. In case of the grains whose composition is different from inner portion to outer portion, the composition may change continuously or discontinuously.

A grain size of the silver halide grains used in the invention is not particularly limited; but it is preferably 0.2 to 1.6 μm , and more preferably 0.25 to 1.2 μm taking photographic properties such as rapid processability and sensitivity into consideration. The grain size can be measured by various methods generally known in the photographic art. The typical methods are those described in "Analysis Method of Grain Size" (pp. 94-122, A.S.T.M. Symposium on Light Microscopy, 1955) or Chapter 2 of "The Theory of the Photographic Process" (by Mees and James, 3rd edition, published from Macmillan Company (1966)).

This grain size can be determined using a grain's projected area or directly from an approximate value. When grains have a substantially uniform shape, their grain size distribution can be expressed fairly accurately in diameters or projected areas.

The grain size distribution of the silver halide grains used in the invention may be either polydispersed or monodispersed; but it is preferred that a variation coefficient be less than 0.22 in the grain size distribution of silver halide grains, and monodispersed silver halide grains having a variation coefficient of less than 0.15 are much more preferred. This variation coefficient is a coefficient to indicate an extent of a grain size distribution and defined by the following expression:

$$\text{Variation coefficient } (S/\bar{r}) = \frac{\text{Standard deviation of grain size distribution}}{\text{Average grain size}}$$

$$\text{Standard deviation of grain size distribution } (S) = \sqrt{\frac{\sum (\bar{r} - r_i)^2 n_i}{\sum n_i}}$$

$$\text{Average grain size } (\bar{r}) = \frac{\sum n_i r_i}{\sum n_i}$$

wherein r_i represents a size of each grain and n_i represents the number of grains.

The term "grain size" used here means a diameter for a spherical silver halide grain, or a diameter of a circle converted into the same area from a projected image for a grain of cubic or nonspherical shape.

The silver halide grains used in an emulsion used in the invention may be prepared by any one of the acidic method, neutral method and ammonia method. Said gains may be grown in one step, or may be grown after preparing seed grains. The method of growing grains and that of preparing seed grains may be the same or different from each other.

As a method to react a soluble silver salt with a soluble halogen salt, there may be used any of the single jet method, reverse jet method and double jet precipitation method, but the jet precipitation method is preferred. The pAg controlled double jet method, which is described in Japanese Patent O.P.I. Publication No. 48521/1979 as a version of the jet precipitation method, is also usable.

If necessary, a silver halide solvent such as thioether may be used.

The silver halide grains used in the invention may be of any crystal form, but one of the preferred examples is a cube having (100) faces as a crystal face. There may also be used silver halide grains having a crystal form of octahedron, tetradehedron or dodecahedron, which are prepared by methods described in specifications such as U.S. Patent Nos. 4,183,756, 4,225,666, Japanese Patent O.P.I. Publication No. 26589/1980, Japanese Patent Examined Publication No. 42737/1980 and literatures such as The Journal of Photographic Science, 21, 39 (1973). Further, grains having twin faces may be used, too.

To the silver halide grains used in the invention, there may be added a cadmium salt, zinc salt, lead salt, thallium salt, iridium salt or complex thereof, rhodium salt or complex thereof, iron salt or complex thereof, in a process to form grains and/or in a process to grow grains, so that metal ions can be contained inside of the grains and/or on the surface thereof. Further, reduction sensitized specks can be formed inside of grains or the surface thereof by keeping the grains in an appropriate reducing environment.

The emulsion containing the silver halide grains used in the invention may be subjected to desalting process after the growth of silver halide grains to remove useless soluble salts, or such salts may be left in the emulsion. The desalting can be performed according to the method described in Research Disclosure No. 17643.

The silver halide grains used in the invention may be those in which latent images are mostly formed on the surface

of grains, or those in which latent images are mostly formed inside of grains; but, preferred grains are those in which latent images are mostly formed on the surface of grains.

The emulsion used in the invention can be chemically sensitized according to conventional methods; that is, there can be used singly or in combination of various methods such as sulfur sensitization using a sulfur containing compound capable of reacting with silver ions or an active gelatin, selenium sensitization with a selenium compound, reduction sensitization with a reducing compound and precious metal sensitization using a compound of gold or other precious metals.

In the invention, a chalcogen sensitizer can be used as a chemical sensitizing agent. "Chalcogen sensitizer" is a general term for sulfur sensitizers, selenium sensitizers and tellurium sensitizers; for photographic purpose, sulfur sensitizers and selenium sensitizers are preferred. Examples of the sulfur sensitizer include thiosulfates, allylthiocarbamide, thiourea, allylthiocyanate, cystine, p-toluenethiosulfonates and rhodanine. Other examples are sulfur sensitizers described in U.S. Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313, 3,656, 955, West Germany Patent Provisional Publication (OLS) No. 1,422,869 and Japanese Patent O.P.I. Publication Nos. 24937/1981, 45016/1980. An addition amount of the sulfur sensitizer varies considerably depending upon pH, temperature and size of silver halide grains, but a rough standard is preferably 10^{-7} to 10^{-1} mol per mol of silver halide.

In the invention, selenium sensitization can be used. Usable selenium sensitizers are aliphatic isoselenocyanates such as allylisoselenocyanate, selenoureas, selenoketones, selenoamides, selenocarboxylates, selenophosphates, diethylselenide, diethyldiselenide; details of which are described in U.S. Patent Nos. 1,574,944, 1,602,592 and 1,623,499.

Further, reduction sensitizing can be jointly used. Usable reducing agents are tin (II) chloride, dioxythiourea, hydrazine and polyamines.

Noble metals other than gold, such as palladium, can be used jointly.

It is preferred that the silver halide grains used in the invention contain a gold compound. The preferred gold compounds are those having a gold's oxidation number of +1 or +3, such as chloraurates, potassium chloraurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, pyridyltrichloro gold, gold sulfide and gold selenide.

The gold compound may be used to sensitize silver halide grains, or may be used in a way which does not substantially contribute to sensitizing.

An addition amount of the gold compound varies depending upon conditions, but it is usually 10^{-8} to 10^{-1} , preferably 10^{-7} to 10^{-2} mol per mol of silver halide. The addition may be made during silver halide grain formation, physical ripening or chemical ripening, or after chemical ripening.

The emulsion used in the invention can be spectrally sensitized to a desired wavelength region with a dye known as a sensitizing dye in the photographic art. The sensitizing dye may be used singly or in combination.

The silver halide photographic light-sensitive material containing the emulsion used in the invention can be a negative or positive film, or a color photographic paper, and is best suited to a color photographic paper for appreciation which displays the effect of the invention most conspicuously.

These light-sensitive materials including a color photographic paper may be for the use of black and white photography or for multicolor application. In the light-sensitive material for multicolor, plural silver halide emulsion layers containing magenta, yellow and cyan couplers as photographic couplers and plural nonlight-sensitive layers are usually provided on a support in an appropriate layer order. The number of layers and the layer order may be changed according to a primary performance and use.

The preferred layer structure of the multicolor photographic light-sensitive material of the invention is that in which a yellow dye image forming layer, intermediate layer, magenta dye image forming layer, intermediate layer, cyan dye image forming layer, intermediate layer and protective layer are sequentially provided on a support in this order.

In the emulsion layer of the photographic light-sensitive material containing the dispersion used in the invention, use is made of dye image forming couplers which react with an oxidation product of an aromatic primary amine developing agent to form dyes. Said dye forming couplers are normally selected so as to form dyes which absorb light-sensitive spectral light of respective emulsion layers; that is, a yellow dye forming coupler is used in a blue-sensitive emulsion layer, a magenta dye forming coupler in a green-sensitive emulsion layer, and a cyan dye forming coupler in a red-sensitive emulsion layer. However, the light-sensitive material may be prepared by a combination other than the above when a specific requirement arises.

It is preferred that the dye forming coupler used in the invention possess in the molecule a group called ballast group which has 8 or more carbon atoms and prevents the coupler to diffuse.

Preferred yellow dye forming couplers are of acylacetanilide type; benzoylacetanilide compounds and pivaloylacetanilide compounds are particularly preferred.

Examples of usable yellow couplers are those described in British Patent No. 1,077,874, Japanese Patent Examined Publication No. 40757/1970, Japanese Patent O.P.I. Publication Nos. 1031/1972, 26133/1972, 94432/1973, 87650/1975, 3631/1976, 115219/1977, 99433/1979, 133329/1979, 30127/1981 and U.S. Patent Nos. 2,875,057,

3,253,924, 3,265,506, 3,408,194, 3,551,155, 3,551,156, 3,664,841, 3,725,072, 3,730,722, 3,891,445, 3,900,483, 3,929,484, 3,933,500, 3,973,968, 3,990,896, 4,021,259, 4,022,620, 4,029,508, 4,057,432, 4,106,942, 4,133,958, 4,269,936, 4,286,053, 4,304,845, 4,314,023, 4,336,327, 4,356,258, 4,386,155, 4,401,752.

As the magenta dye forming coupler, pyrazolone couplers may be used, but pyrazolotriazole coupler are preferred.

Examples of usable magenta couplers are those described in Japanese Patent Application No. 166895/1988, U.S. Patent No. 3,725,065, and Japanese Patent O.P.I. Publication Nos. 99437/1984, 42045/1983, 162548/1984, 171956/1984, 33552/1985, 43659/1985, 172982/1985, 190779/1985.

As the cyan dye forming coupler, cyan dye forming couplers of phenol type or naphthol type are used.

Examples of these cyan dye forming couplers can be seen in U.S. Patent Nos. 2,306,410, 2,356,475, 2,362,598, 2,367,531, 2,369,929, 2,423,730, 2,474,293, 2,476,008, 2,498,466, 2,545,687, 2,728,660, 2,772,162, 2,895,826, 2,976,146, 3,002,836, 3,419,390, 3,446,622, 3,476,563, 3,737,316, 3,758,308, 3,839,044, British Patent Nos. 478,991, 945,542, 1,084,480, 1,337,233, 1,388,024, 1,543,040 and Japanese Patent O.P.I. Publication Nos. 37425/1972, 10135/1975, 25228/1975, 112038/1975, 117422/1975, 130441/1975, 6551/1976, 37647/1976, 52828/1976, 108841/1976, 109630/1978, 48237/1979, 66129/1979, 131931/1979, 32071/1980, 146050/1984, 31953/1984, 117249/1985.

The above dye forming couplers may be used in a silver halide emulsion layer in an amount of 1×10^{-3} to 1 mol, preferably 1×10^{-2} to 8×10^{-1} mol per mol of silver halide.

In the invention, the compound represented by Formula I and the compound represented by Formula II can be made into a dispersion by various dispersing methods such as oil protect dispersing, dispersing with a water-insoluble polymer and dispersing with a latex.

The useful compounds of the invention including the compound represented by Formula I and the compound represented by Formula II are dissolved in a high boiling organic solvent of 150°C or more, or in a mixture thereof with a low boiling organic solvent and/or a water-soluble organic solvent if necessary, then dispersed with the aid of surfactant in a hydrophilic binder such as aqueous gelatin solution using a dispersing means such as stirrer, homogenizer, colloid mill or supersonic apparatus, and subsequently added in an hydrophilic colloid layer. A process to remove the low boiling organic solvent may be provided after or during dispersing.

High boiling solvents used to disperse the compounds represented by Formula I or II are preferably those having a dielectric constant of 5.5 or less, such as phthalates, phosphates, amides of organic acids, ketones and hydrocarbons each having a dielectric constant of 5.5 or less. Much preferred high boiling organic solvents are those having a dielectric constant of 1.9 to 5.0 and a vapor pressure of 0.5 mmHg or less at 100°C. Among these solvents, phthalates and phosphates are more preferable. The most preferable solvent is dialkyl phthalate having alkyl groups of 9 or more carbon atoms. The high boiling solvent may be a mixture of two or more types.

The dielectric constant used here means a dielectric constant at 30°C.

Examples of preferred high boiling solvent are as follows:

- (1) Di-2-ethylhexyl phthalate
- (2) Dioctyl phthalate
- (3) Di-isononyl phthalate
- (4) Di-isodecyl phthalate
- (5) Didodecyl phthalate
- (6) Tri-isononyl phosphate
- (7) Tri-isodecyl phosphate
- (8) Tri-isododecyl phosphate
- (9) Di-2-ethylhexyl azelate
- (10) Di-2-ethylhexyl azelate
- (11) Di-2-ethylhexyl sebacate
- (12) Octyl-decyl phthalate
- (13) Oleyl benzoate
- (14) Benzyl benzoate

As a binder used in the photographic light-sensitive material containing the dispersion used in the invention, gelatin is advantageously used. Other usable compounds are gelatin derivatives, graft polymers between gelatin and other polymers, proteins, sugar derivatives, cellulose derivatives and hydrophilic colloids such as synthetic hydrophilic homopolymers and copolymers.

The photographic emulsion layers and other hydrophilic colloid layers containing the dispersion of the invention are hardened by employing, singly or in combination, a hardener which cross-links binder molecules to enhance the layer strength. The hardener is preferably added in these layers in an amount large enough to dispense with addition of the hardener to a processing solution, but the addition to a processing solution is also allowed.

In the photographic light-sensitive material containing the dispersion used in the invention, there may be provided auxiliary layers such as a filter layer, antihalation layer and/or anti-irradiation layer. These layers and/or emulsion layers may contain a dye which is washed away from the color light-sensitive material or bleached in the developing process.

In applying a light-sensitive coating solution using the silver halide emulsion used in the invention, a thickener may be employed in order to improve coating performance. Extrusion coating and curtain coating, which can coat two or more layers simultaneously, are particularly useful.

Developing agents used in the color developer used in the invention include conventional ones widely employed in various color photographic processes.

In the invention, color developing is immediately followed by a processing with a solution having a bleaching capability, and said solution with a bleaching capability may be a processing solution having a fixing capability concurrently (what is called a bleach-fixer).

As a bleaching agent used in said bleaching process, a metal complex salt of organic acid is employed.

EXAMPLES

The invention will be hereunder described with the examples.

Example 1

There was dissolved 50 g of magenta coupler M-A in a mixed solvent of 80 ml of high boiling solvent DNP and 200 ml of ethyl acetate, the solution was added to a 5%-aqueous gelatin solution containing tri-isopropyl naphthalene sulfonic acid as a dispersing aid, and then the mixture was dispersed with a homogenizer. After making up the dispersion prepared to 1,500 ml, it was kept at 35°C. This dispersion was then added to 1,000 ml of a 3%-aqueous gelatin solution, and further 400 g of a green-sensitive silver chlorobromide emulsion (a monodispersed emulsion containing 80 mol% of silver bromide, weight of silver 30 g) was added thereto, so that a coating solution for a third layer was prepared. Similarly, coating solutions for other layers were prepared.

Then, the following layers were formed on a corona-treated polyethylene-coated paper support (polyethylene on the emulsion layer side contains titanium dioxide and a bluing agent) in sequence to obtain color light-sensitive material sample 1.

1st layer: blue-sensitive emulsion layer

Coating weights were regulated to 0.8 g/m² of yellow coupler Y-1, 0.3 g/m² of antifading agent ST-1, 0.3 g/m² silver equivalent of a blue-sensitive silver chlorobromide emulsion (containing 20 mol% of silver chloride and 80 mol% of silver bromide), 0.3 g/m² of high boiling solvent DNP and 1.2 g/m² of gelatin.

2nd layer: intermediate layer

Coating weights were regulated to 0.05 g/m² of hydroquinone derivative HQ-1 and 1.0 g/m² of gelatin.

3rd layer: green-sensitive emulsion layer

Coating weights were regulated to 0.4 g/m² of magenta coupler M-A, 0.2 g/m² silver equivalent of a green-sensitive silver chlorobromide emulsion (containing 20 mol% of silver chloride and 80 mol% of silver bromide), 0.4 g/m² of high boiling solvent DIDP, 0.01 g/m² of Al-3 and 1.4 g/m² of gelatin.

4th layer: intermediate layer

Coating weights were regulated to 0.3 g/m² of UV absorbent UV-1, 0.3 g/m² of UV absorbent UV-2, 0.4 g/m² of DNP, 0.05 g/m² of hydroquinone derivative HQ-1, 0.02 g/m² of Al-1, 1.0 g/m² of gelatin and a trace of an oil-soluble bluing agent.

5th layer: red-sensitive emulsion layer

Coating weights were regulated to 0.2 g/m² of cyan coupler C-1, 0.2 g/m² of cyan coupler C-2, 0.2 g/m² of antifading agent ST-1, 0.4 g/m² of DOP, 0.3 g/m² silver equivalent of a red-sensitive silver chlorobromide emulsion (containing 20 mol% of silver chloride and 80 mol% of silver bromide) and 1.4 g/m² of gelatin.

6th layer: intermediate layer

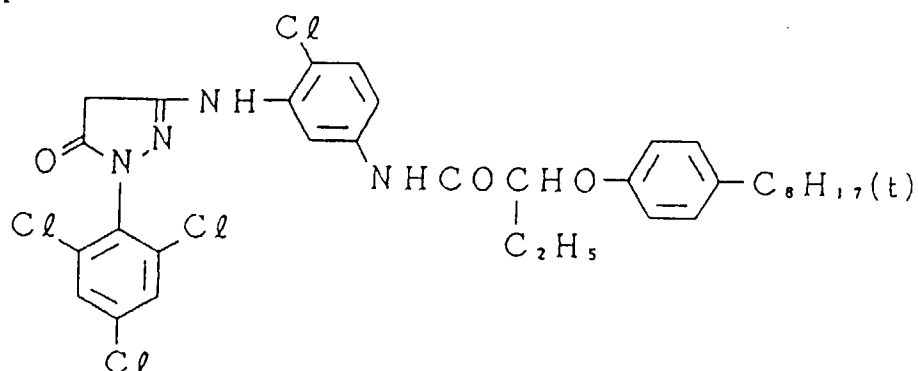
Coating weights were regulated to 0.1 g/m² of UV absorbent UV-1, 0.1 g/m² of UV absorbent UV-2, 0.02 g/m² of HQ-1, 0.1 g/m² of polyvinylpyrrolidone, 0.2 g/m² of DNP and 0.4 g/m² of gelatin.

7th layer: protective layer

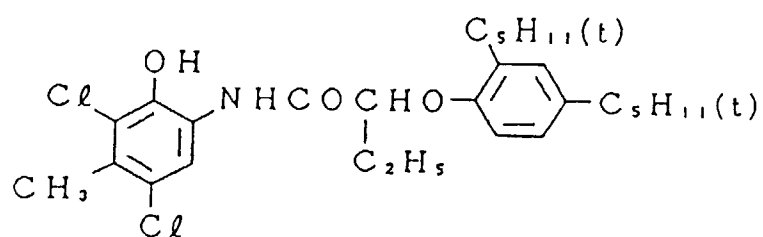
Coating weight was regulated to 0.9 g/m² of gelatin.

Sample 1 was prepared as the above. Similar samples were prepared in the same manner as the above, except that UV absorbents, cyan couplers and yellow couplers used in the 4th, 5th and 6th layers were varied as shown in Table 1.

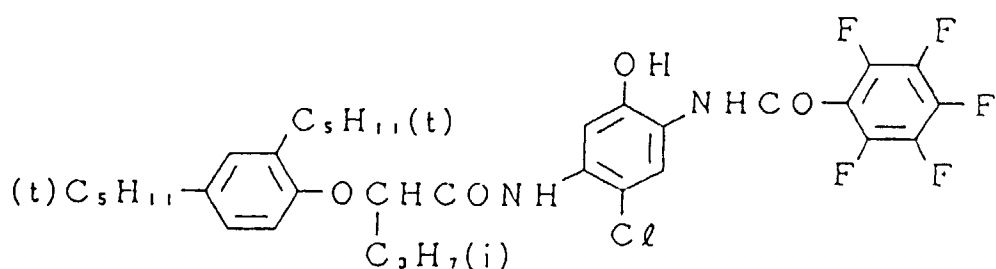
M - A



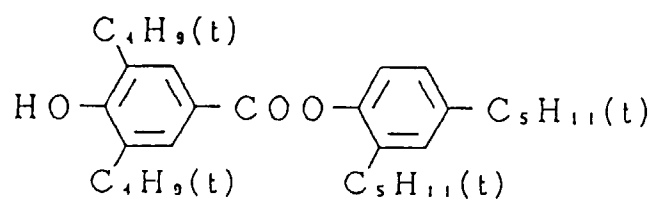
C - 1



C - 2



S T - 1

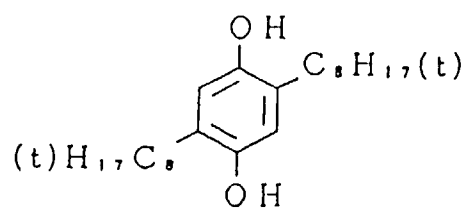


DOP (dioctyl phthalate)

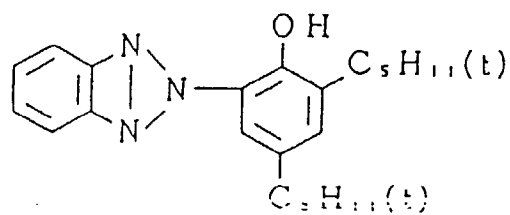
DNP (dinonyl phthalate)

DIDP (di-isodecyl phthalate)

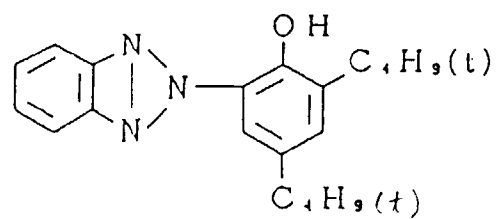
H Q - 1



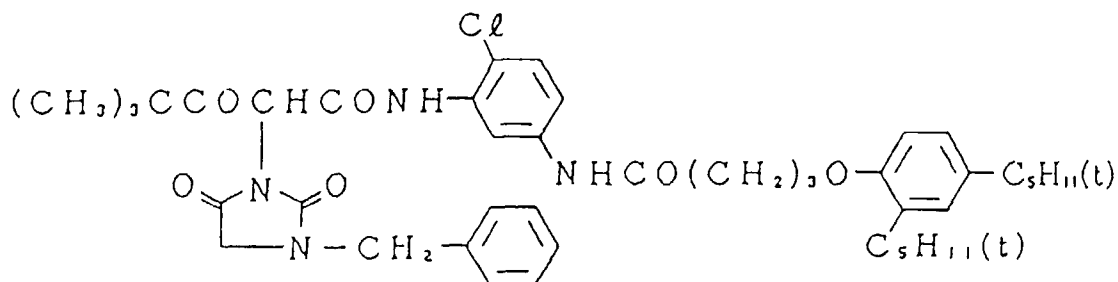
U V - 1



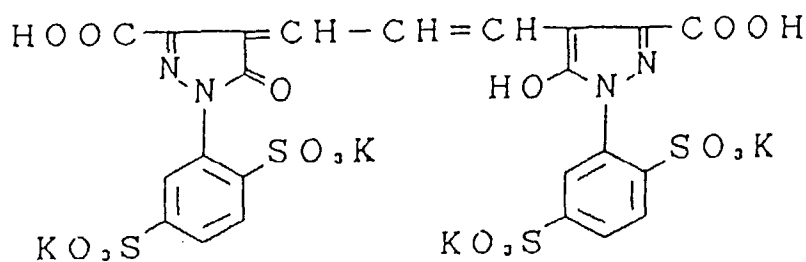
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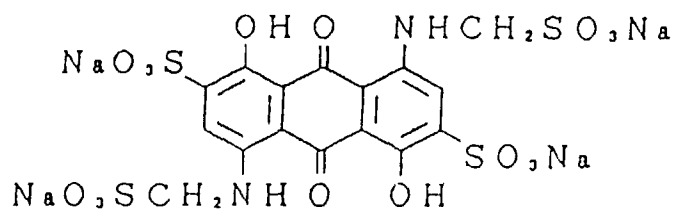
Y-1



A-1



AI-3



In addition to the above, sodium 2,4-dihydroxy-6-chloro-S-triazine was used as a hardener.

The samples prepared as above were subjected to wedge exposure with red light and blue light using a sensitizer model KS-7 (product of Konica Corp.), and then processed under the following conditions:

Processing	Processing Temp.	Processing Time
Color developing	32.8°C	3 min. and 30 sec.
Bleach-fixing	32.8°C	1 min. and 30 sec.
Stabilizing	32.8°C	3 min. and 30 sec.

(Composition of the developer)

The following were contained in one liter of the developer.

N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.0 g
Hydroxylamine sulfate	2.0 g

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(continued)

Potassium carbonate	25.0 g
Sodium chloride	0.1 g
Sodium bromide	0.2 g
Anhydrous sodium sulfite	2.0 g
Benzyl alcohol	10.0 ml
Polyethylene glycol (average molecular weight : 400)	3.0 ml
pH was adjusted to 10.0 with sodium hydroxide.	

(Composition of the bleach-fixer)

The following were contained in one liter of the bleach-fixer.

Sodium ferric ethylenediamine tetraacetate	60.0 g
Sodium thiosulfate	100.0 g
Sodium bisulfite	20.0 g
Sodium metabisulfite	5.0 g
pH was adjusted to 7.0 with sulfuric acid.	

(Composition of the stabilizer)

The following were contained in one liter of the stabilizer.

5-Chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediamine tetraacetate	1.0 g
Ammonium hydroxide (20% aqueous solution)	3.0 g
Ammonium sulfite	3.0 g
pH was adjusted to 7.0 with sulfuric acid and sodium hydroxide.	

The processing was carried out after running 50 m² of a light-sensitive material with an automatic processor having a stabilizing unit of multistage counterflow type.

After processing, each sample was subjected to a light-fastness test of cyan and yellow dye images and measurement of whiteness and sweating resistance.

Light-fastness test

Reflection densities of red light and blue light were measured on each sample before and after a 30-day exposure to the sunlight using an under-glass outdoor exposing stand. The degree of color fading caused by light (color fading rate) was determined by the following expression:

$$\text{Color fading rate} = \frac{D - D_0}{D_0} \times 100 \%$$

D₀ = density before fading

D = density after fading

Measurement of whiteness

The unexposed area (white area) of each sample was evaluated with a color analyzer model 607 made by Hitachi, and then a* and b* values were calculated (a larger b* value indicates a higher yellowing).

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Sweating resistance

After storing each of cyan colored samples in a thermostatic chamber of 85°C, 60% RH, degree of sweating of an oily component on the sample surface was visually evaluated.

5 The results are shown in Table 1.

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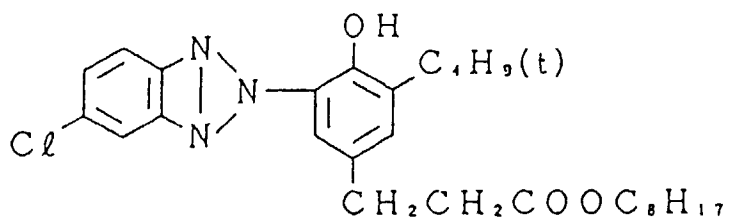
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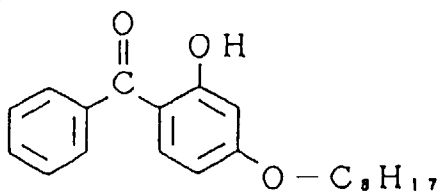
Tabl: 1

Sample No.	1st layer yellow coupler	5th layer Cyan coupler	4th, 6th layers UV absorbent	4th and 6th layers addition amount (g/m ²)	5th layer UV absorbent (J/m ²)	Light-fastness Yellow image fading rate (g/m ²)	Light-fastness Cyan image fading rate (g/m ²)	a*	b*	Whiteness Visual observation	Sweating resistance
1	Y-1	C-1, C-2	UV-1 UV-2	0.4 0.4	-	10	14	0.45	-1.61	Light yellow	Δ ₁
2	Y-1	C-1, C-2	UV-3	0.8	-	11	15	0.44	-1.03	Yellow	Δ ₁
3	Y-1	C-1, C-2	UV-4	0.8	-	21	29	0.43	-1.59	Light yellow	x
4	Y-1	C-1, C-2	I-1	0.8	-	8	11	0.43	-1.82	White	o
5	Y-1	C-1, C-2	I-2	0.8	-	7	10	0.44	-1.81	White	o
6	Y-1	C-1, C-2	I-3	0.8	-	8	11	0.44	-1.84	White	o
7	Y-1	C-1, C-2	I-18	0.8	-	9	12	0.44	-1.84	White	o
8	Y-1	C-1, C-2	I-1	0.8	I-1, 0.1	8	9	0.43	-1.84	White	o
9	Y-1	C-3	UV-1 UV-2	0.4 0.4	-	10	13	0.45	-1.61	Light yellow	Δ ₁
10	Y-1	C-3	UV-3	0.8	-	11	14	0.43	-1.02	Yellow	Δ ₁
11	Y-1	C-3	UV-4	0.8	-	21	29	0.43	-1.58	Light yellow	x
12	Y-1	C-3	I-1	0.8	-	8	9	0.44	-1.84	Light yellow	o
13	Y-1	C-3	I-1	0.8	I-1, 0.1	8	8	0.44	-1.84	Light yellow	o
14	Y-2	C-3	UV-1 UV-2	0.4 0.4	-	10	13	0.45	-1.84	Light yellow	Δ ₁
15	Y-2	C-3	UV-3	0.8	-	11	14	0.44	-1.02	Yellow	Δ ₁
16	Y-2	C-3	UV-4	0.8	-	21	29	0.43	-1.58	Light yellow	x
17	Y-2	C-3	I-1	0.8	-	7	9	0.45	-1.84	Light yellow	o
18	Y-2	C-3	I-2	0.8	-	6	8	0.45	-1.84	Light yellow	o

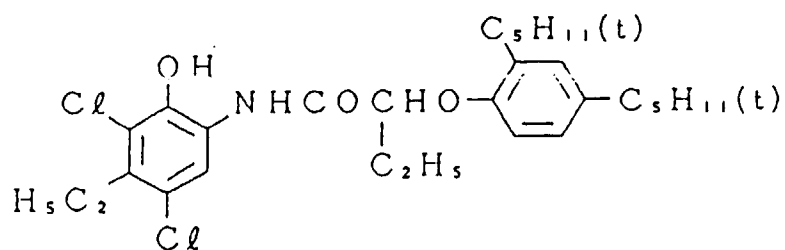
UV - 3



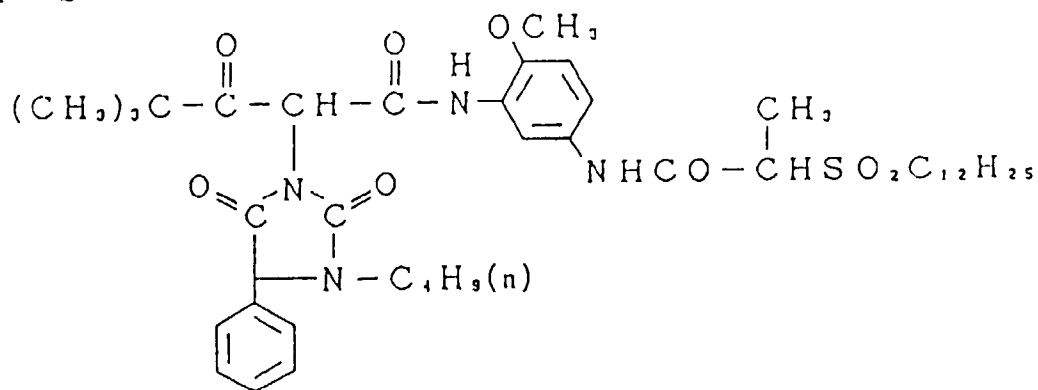
UV - 4



C - 3



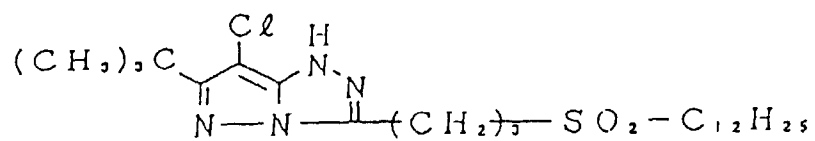
Y - 2



Example 2

Samples were prepared in the same manner as in Example 1, except that the magenta coupler used in the 3rd layer of Example 1 was replaced by M-B and the antifading agent in the 3rd layer was changed as shown in Table 2. Further, samples were also prepared by changing the UV absorbents in the 4th and 6th layers and the magenta coupler and antifading agent in the 3rd layer as shown in Table 2. Each sample was exposed through a green optical wedge to obtain magenta dye images and then subjected to the evaluation in the same manner as that in Example 1.

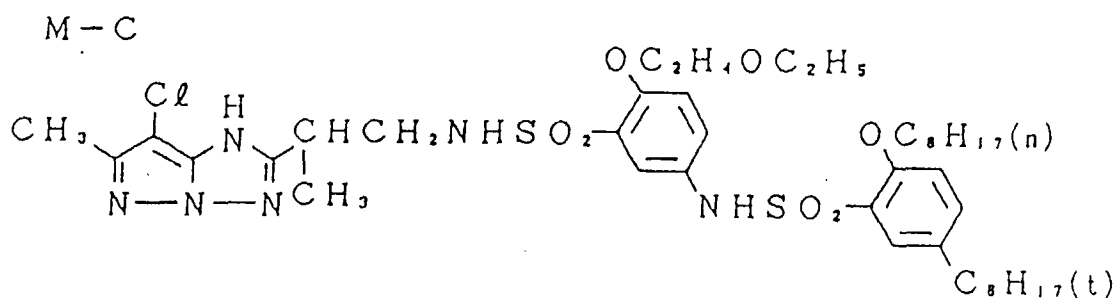
M-B



The results are shown in Table 2.

Table 2

Sample No.	3rd layer Magenta coupler	Antifading agent	4th, 6th layers UV absorbent	4th and 6th layers addition amount (g/m ²)	Light-fastness Magenta image fading rate	a*	b*	Whiteness Visual observation	Sweating resistance
19	M-B	-	UV-1 UV-2	0.4 0.4	31	0.45	-1.61	Light yellow	Δ
20	M-B	-	UV-3	0.8	30	0.44	-1.02	Yellow	Δ
21	M-B	-	UV-4	0.8	52	0.43	-1.58	Light yellow	x
22	M-B	-	I-1	0.8	24	0.43	-1.81	White	o
23	M-B	-	I-2	0.8	22	0.44	-1.80	White	o
24	M-B	-	I-3	0.8	23	0.43	-1.82	White	o
25	M-B	-	I-18	0.8	25	0.42	-1.82	White	o
26	M-B	ST-5 (0.1 g/m ²) ST-6 (0.1 g/m ²)	I-1	0.8	11	0.42	-1.81	White	o
27	M-B	ST-5 (0.1 g/m ²) ST-6 (0.1 g/m ²)	I-1	0.8	11	0.42	-1.81	White	⊙
28	M-C	ST-7 (0.2 g/m ²)	I-1	0.8	13	0.42	-1.80	White	o



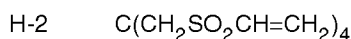
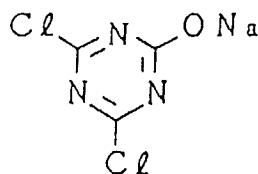
Coating solution for 3rd layer

Sixty ml of ethyl acetate was added to 35 g of magenta coupler M-A, 1.0 g of antistain agent HQ-1 and 30 g of high boiling solvent DNP to dissolve them. Next, the solution was dispersed in 200 ml of a 10% aqueous gelatin solution with a homogenizer to prepare a magenta coupler dispersion. This dispersion was then mixed with a green-sensitive silver halide emulsion (containing 27 g of silver) prepared under the following conditions, so that a coating solution for the 3rd layer was obtained.

Coating solutions for other layers were prepared in the similar manner as that for the 3rd layer.

Subsequently, similar light-sensitive material samples were prepared in the similar manner as in sample 29, except that the UV absorbent in the 4th and 6th layers and the antifading agent in the 3rd layer were changed as shown in Table 3. As hardeners, the following H-1 and H-2 were used.

H-1



Preparation of blue-sensitive silver halide emulsion

The following solutions A and B were simultaneously added to 1,000 ml of a 2% aqueous gelatin solution at 40°C over a period of 30 minutes, while maintaining pAg at 6.5 and pH at 3.0. Next, the following solutions C and D were simultaneously added thereto over a period of 180 minutes, while maintaining pAg at 7.3 and pH at 5.5.

In the above procedure, pAg was controlled according to the method described in Japanese Patent O.P.I. Publication No. 45437/1984, and pH was controlled with addition of sulfuric acid or an aqueous solution of sodium hydroxide.

Solution A

Sodium chloride	3.42 g
Potassium bromide	0.03 g
Water to make	200 ml

Solution B

Silver nitrate	10 g
Water to make	200 ml

Solution C

Sodium chloride	102.7 g
Potassium bromide	1.0 g
Water to make	600 ml

Solution D

Silver nitrate	300 g
Water to make	600 ml

After the addition, desalting was carried out using a 5% aqueous solution of Demol N (product of Kao Atlas) and a 20% aqueous solution of magnesium sulfate. Then, the silver halide grains obtained were mixed with an aqueous gelatin solution. Thus, monodispersed cubic emulsion EMP-1 was prepared, the emulsion had an average grain size of 0.85 μm , a variation coefficient ($\sigma/\bar{r}$) of 0.07 and a silver chloride content of 99.5 mol%.

Emulsion EMP-1 was then chemically sensitized for 90 minutes at 50°C using the following compounds to obtain a blue-sensitive silver halide emulsion (EmA).

Sodium thiosulfate	0.8 mg/mol AgX
Chloroauric acid	0.5 mg/mol AgX
Stabilizer SB-5	6×10^{-4} mol/mol AgX
Sensitizing dye D-1	5×10^{-4} mol/mol AgX

Preparation of green-sensitive silver halide emulsion

A monodispersed cubic emulsion (EMP-2) having an average grain size of 0.43 μm , a variation coefficient ($\sigma/\bar{r}$) of 0.08 and a silver chloride content of 99.5 mol% was prepared in the same manner as in emulsion EMP-1, except that the addition of solutions A and B as well as that of solutions C and D were changed.

Emulsion EMP-2 was subjected to chemical sensitization for 120 minutes at 55°C with the addition of the following compounds to obtain a green-sensitive silver halide emulsion (EmB).

Sodium thiosulfate	0.5 mg/mol AgX
Chloroauric acid	1.0 mg/mol AgX
Stabilizer SB-5	6×10^{-4} mol/mol AgX
Sensitizing dye D-2	4×10^{-4} mol/mol AgX

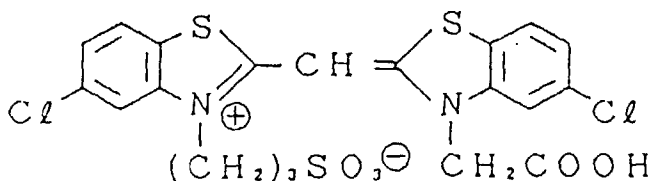
Preparation of red-sensitive silver halide emulsion

A monodispersed cubic emulsion (EMP-3) having an average grain size of 0.50 μm , a variation coefficient ($\sigma/\bar{r}$) of 0.08 and a silver chloride content of 99.5 mol% was prepared in the same manner as in emulsion EMP-1, except that the addition time of solutions A and B as well as the addition time of solutions C and D were changed.

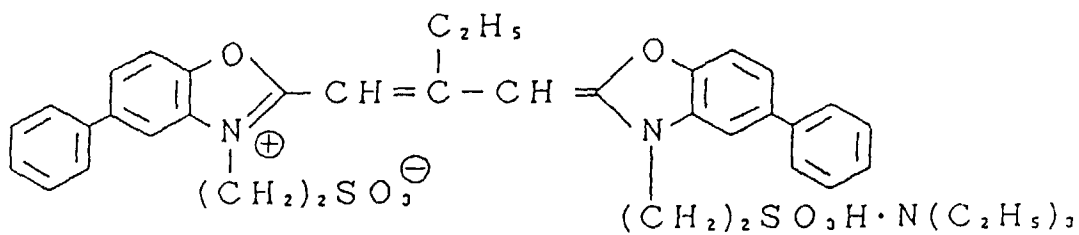
Then, emulsion EMP-3 was chemically sensitized for 90 minutes at 60°C with the addition of the following compounds to obtain a red-sensitive silver halide emulsion (EmC).

Sodium thiosulfate	1.8 mg/mol AgX
Chloroauric acid	2.0 mg/mol AgX
Stabilizer SB-5	6×10^{-4} mol/mol AgX
Sensitizing dye D-3	8×10^{-5} mol/mol AgX

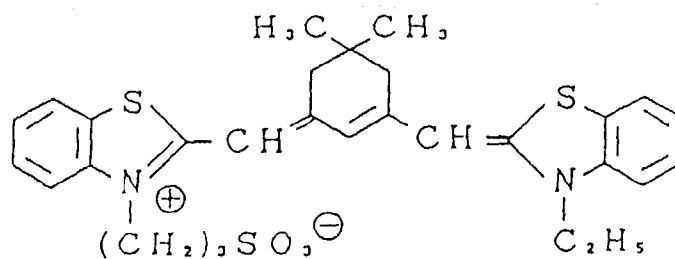
D - 1



D - 2



D - 3



SB - 5

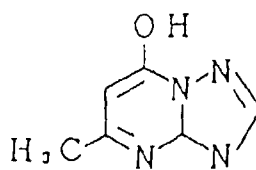
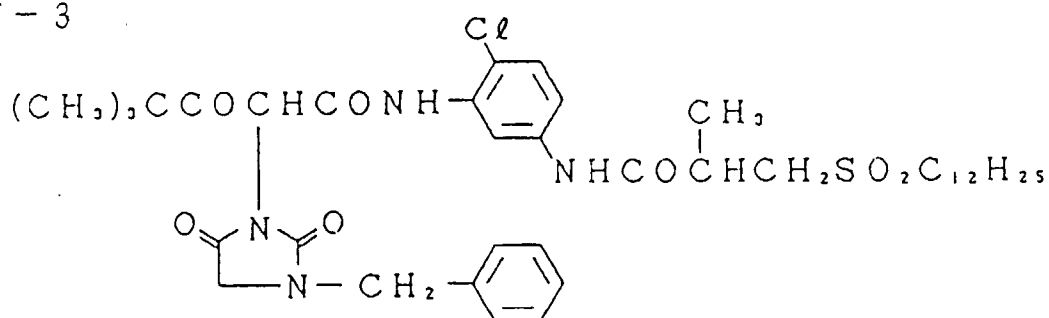


Table 3

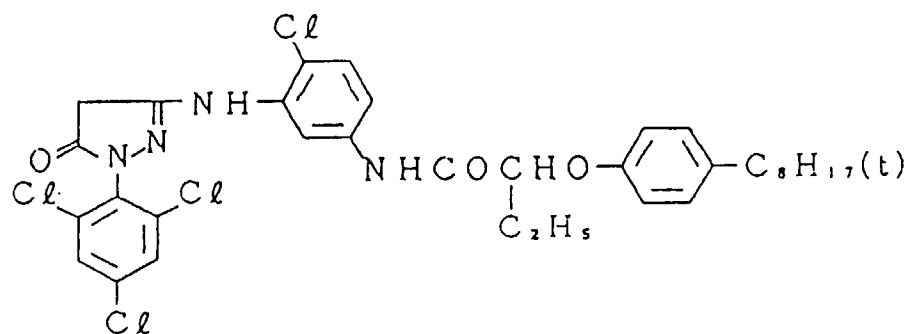
	Layer	Constitution	Coating weight (g/m ²)
5			
	7th layer (protective layer)	Gelatin	0.9
10			
	6th layer	Gelatin	0.4
		Antistain agent (HQ-1)	0.01
15		DNP	0.2
		PVP	0.03
20		Anti-irradiation dye (AI-2)	0.02
		UV absorbent (UV-1)	0.2
		UV absorbent (UV-2)	0.1
25			
	5th layer (red- sensitive)	Gelatin	1.4
		Red-sensitive silver halide emulsion (EmC) in terms of silver	0.24
30		Cyan coupler (C-1)	0.17
		Cyan coupler (C-2)	0.25
35		Dye image stabilizer (ST-1)	0.20
		High boiling solvent (HB-1)	0.10
		Antistain agent (HQ-1)	0.01
40		DOP	0.30
	4th layer	Gelatin	1.0
45		Antistain agent (HQ-1)	0.03
		DNP	0.40
		UV absorbent (UV-1)	0.6
50		UV absorbent (UV-2)	0.2
55			

Layer	Constitution	Coating weight (g/m ²)
3rd layer (green-sensitive)	Gelatin	1.40
	Green-sensitive silver halide emulsion (EmB) in term of silver	0.27
	Magenta coupler (M-A)	0.35
	Antistain agent (HQ-1)	0.01
	DNP	0.30
	Anti-irradiation dye (AI-1)	0.01
2nd layer (intermediate)	Gelatin	1.0
	Antistain agent (HQ-1)	0.12
	DIDP	0.15
1st layer (blue-sensitive)	Gelatin	1.20
	Blue-sensitive silver halide emulsion (EmA) in terms of silver	0.30
	Yellow coupler (Y-3)	0.80
	Dye image stabilizer (ST-1)	0.30
	Dye image stabilizer (ST-2)	0.20
	Antistain agent (HQ-1)	0.02
	DNP	0.20
Support	Polyethylene-laminated paper	

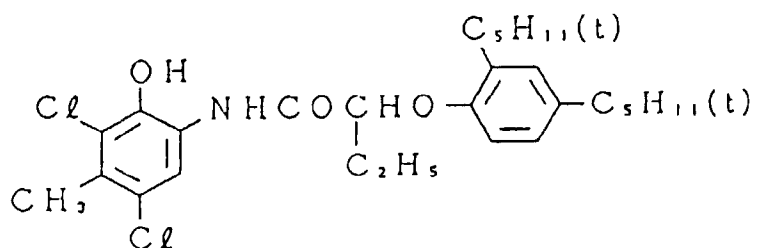
Y - 3



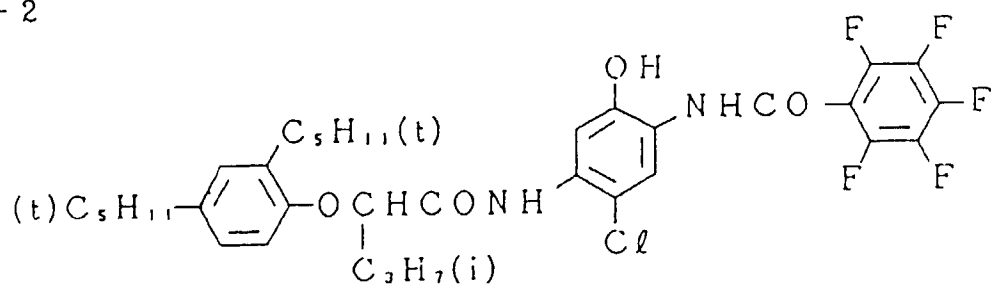
M - A



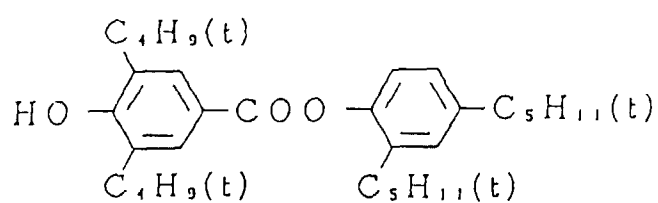
C - 1



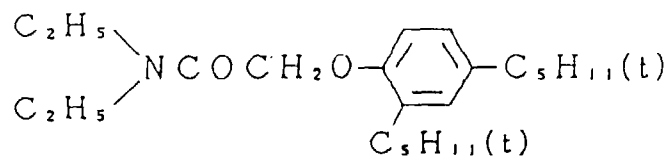
C - 2



ST - 1

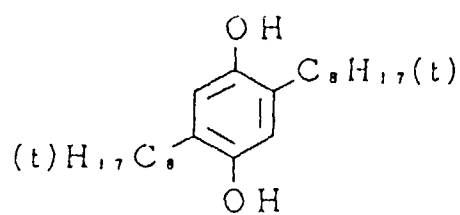


ST - 2

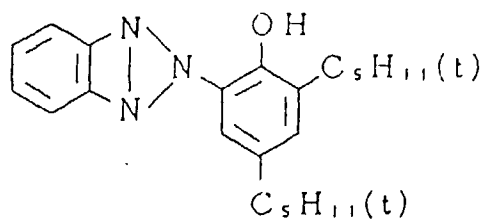


55 DOP: dioctyl phthalate
 DNP: dionyl phthalate
 DIDP: di-isodecyl phthalate
 PVP: polyvinylpyrroladone

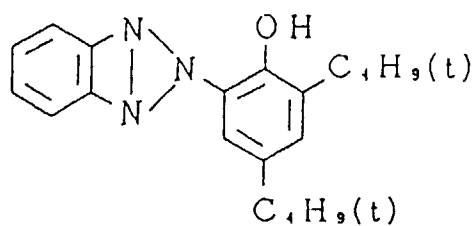
HQ - 1



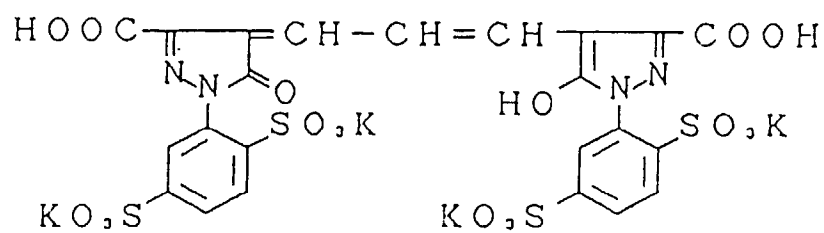
UV - 1



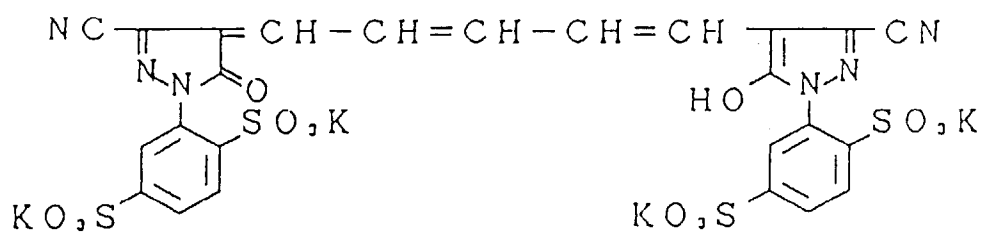
UV - 2



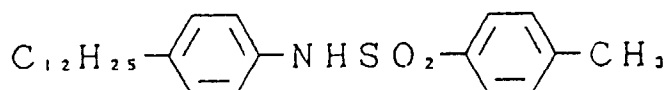
AI - 1



AI - 2



H B - 1



These samples were exposed to green light through an optical wedge with a sensitometer model KS-7 made by Konica Corp. and then processed according to the following procedure.

Processing	Processing Temp.	Processing Time
Color developing	35.0 ± 0.3°C	45 sec.
Bleach-fixing	35.0 ± 0.5°C	45 sec.
Stabilizing	30 - 34°C	90 sec.
Drying	60 - 80°C	60 sec.

Color developer composition	
Pure water	800 ml
Triethanolamine	10 g
N,N-diethylhydroxylamine	5 g
Potassium bromide	0.02 g
Potassium chloride	2 g
Potassium sulfite	0.3 g
1-Hydroxyethylidene-1,1-diphosphonic acid	1.0 g
Ethylenediaminetetraacetate	1.0 g
Disodium catechol-3,5-disulfonic acid	1.0 g
N-Ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Potassium carbonate	27 g
Water was added to make the total volume 1 liter. pH was adjusted to 10.10.	

Bleach-fixer composition	per liter
Ammonium ferric ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetate	3 g
Ammonium thiosulfate (70% aqueous solution)	100 ml
Ammonium sulfite (40% aqueous solution)	27.5 ml
pH was adjusted to 5.7 with potassium carbonate or glacial acetic acid.	

Stabilizer composition	per liter
5-Chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediaminetetraacetate	1.0 g
Ammonium hydroxide (20% aqueous solution)	3.0 g
Ammonium sulfite	3.0 g
pH was adjusted to 7.0 with sulfuric acid or sodium hydroxide.	

The processing was carried out in an automatic developing machine having a stabilizing unit of multistage counterflow type, after a running treatment using 100 m² of sample 29.

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Light fastness of magenta dye images, yellow stain caused by exposure to light and static mark resistance were measured on the processed samples in the following manner.

Light fastness test

Reflection densities of green light were measured after and before exposing each sample to the sunlight for 30 days on an under-glass outdoor-exposing stand. The degree of color fading caused by exposure to light (color fading rate) was determined by the following expression.

$$\text{Color fading rate} = \frac{D - D_0}{D_0} \times 100$$

D_0 : density before fading

D : density after fading

Measurement of yellow stain caused by exposure to light

An increase of blue light reflection density was measured at a white portion of each of the samples used in the light fastness test.

Measurement of static mark resistance

The static mark resistance was rated by the number of static-mark-carrying prints per 100 prints when processed with a high speed printer operating at a speed of 20 million E-sized sheets per minute under a low humidity condition.

The evaluation results are shown in Table 4.

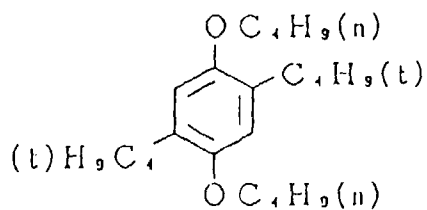
Table 4

Sample No.	UV absorbent in 4th and 6th layers	Coating weight of UV absorbent in 4th and 6th layers (g/m ²)	Antifading agent in 3rd layer	Light fastness (color fading rate %)	Yellow stain by caused light	Static mark resistance (sheets/100 sheets)
29	UV-1 UV-2	0.8 0.3	-	21	0.06	2
30	UV-3	1.1	-	20	0.06	2
31	UV-4	1.1	-	32	0.08	3
32	I-1	1.1	-	17	0.04	1
33	I-2	1.1	-	15	0.04	1
34	I-3	1.1	-	18	0.04	1
35	I-18	1.1	-	18	0.04	1
36	I-1	1.1	ST-3 (0.2 g/m ²) ST-4 (0.1 g/m ²)	9	0.03	1
37	I-1*	1.1	ST-3 (0.2 g/m ²) ST-4 (0.1 g/m ²)	9	0.03	0
38**	I-1	1.1	-	18	0.05	5

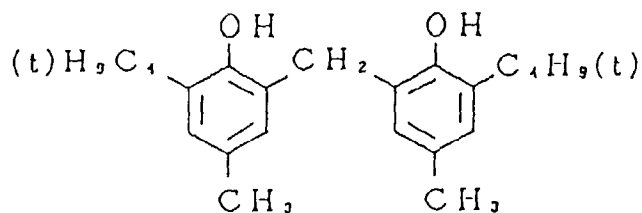
* : The addition amount of dinonyl phthalate in the 4th and 6th layers of sample 9 was 0 g/m².

** : A silver chlorobromide containing 20 mol% of silver chloride was used in sample 10 as the silver halide.

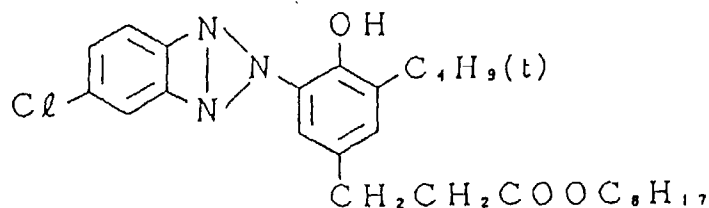
ST - 3



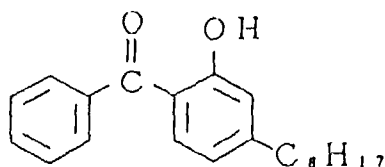
ST - 4



UV - 3



UV - 4



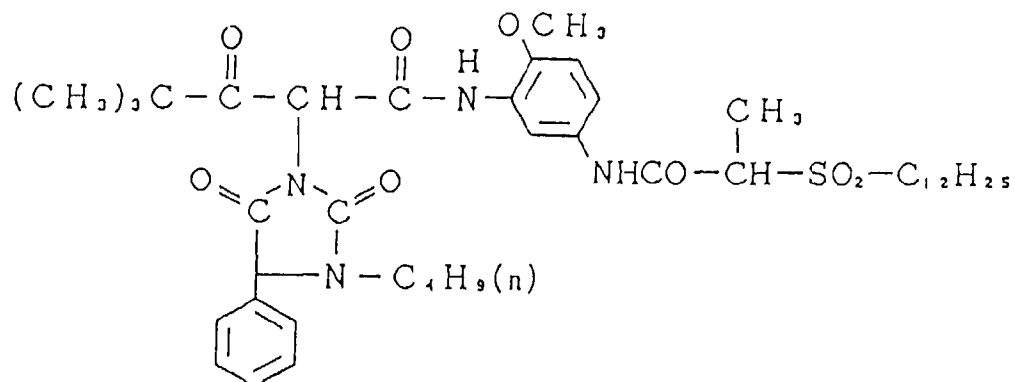
As apparent from Table 4, the samples of the invention were high in both light fastness and static mark resistance, and low in yellow stain attributable to light. Further, sample 36, which contained an antistain agent in the 3rd layer, exhibited a much higher light fastness and a much lower yellow stain by light. Sample 37 exhibited a much higher static mark resistance.

Example 4

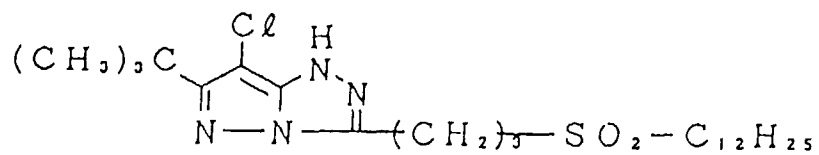
Samples were prepared by the same procedure as in Example 3, except that the couplers in sample 29 were replaced by the following Y-2, M-B, C-3 and the UV absorbents and antistain agents were used in varied combinations as shown in Table 5. Then, the samples were evaluated as in Example 3.

The results are shown in Table 5.

Y - 2



M - B



C - 3

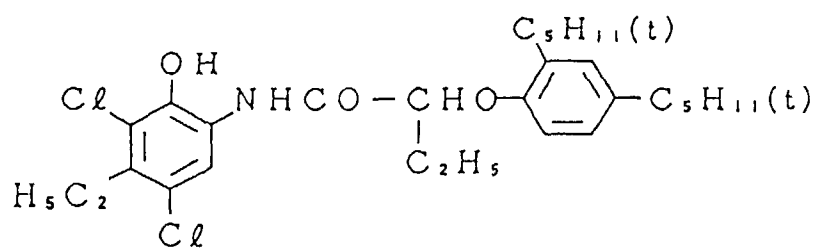


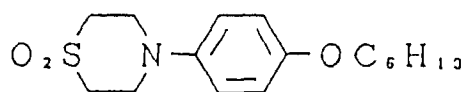
Table 5

Sample No.	UV absorbent in 4th and 6th layers	Coating weight of UV absorbent in 4th and 6th layers (g/m ²)	Antifading agent in 3rd layer	Light fastness (color fading rate %)	Yellow stain by caused light	Static mark resistance (sheets/100 sheets)
39	UV-1 UV-2	0.8 0.3	-	59	0.04	2
40	UV-3	1.1	-	57	0.04	2
41	UV-4	1.1	-	87	0.06	3
42	I-1	1.1	-	39	0.02	1
43*	UV-1 UV-2	0.8 0.3	-	60	0.05	5
44*	I-1	1.1	-	44	0.03	5
45	I-1	1.1	ST-5 (0.1 g/m ²) ST-6 (0.1 g/m ²)	28	0.02	1
46	I-2	1.1	ST-5 (0.1 g/m ²) ST-6 (0.1 g/m ²)	26	0.02	1
47	I-3	1.1	ST-5 (0.1 g/m ²) ST-6 (0.1 g/m ²)	29	0.02	1
48	I-18	1.1	ST-5 (0.1 g/m ²) ST-6 (0.1 g/m ²)	29	0.02	1
49	I-1**	1.1	ST-5 (0.1 g/m ²) ST-6 (0.1 g/m ²)	27	0.02	0

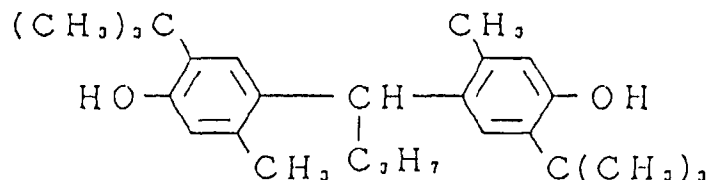
* : Samples 43 and 44 used a silver chlorobromide containing 20 mol% of silver chloride.

** : The coating weights of dinonyl phthalate in the 4th and 6th layers of sample 49 were 0 g/m², respectively.

ST-5



ST-6



As seen in Table 5, the samples of the invention were high in light fastness and static mark resistance and less in yellow stain caused by exposure to light.

These effects can be obtained only by the constitution according to the invention.

Example 5

Sample 50 was prepared in the same manner as in sample 29 of Example 3, except that antistain agents ST-3 and ST-4 were further added in the 3rd layer in amounts of 0.2 and 0.1 g/m², respectively.

Samples 51 to 70 were prepared in the same manner as in sample 41, except that the UV absorbents used in the 4th and 6th layers were changed and a fluorescent brightener was added in the 2nd layer as shown in Table 6. An addition amount of the fluorescent brightener was 0.1 g/m².

Samples prepared as above were processed in the same way as that of Example 3, and were evaluated for whiteness instead of yellow stains caused by exposure to light.

Measurement of whiteness: intensity of fluorescence

Spectral reflection densities at an unexposed area (white area) were measured on each sample with a color analyzer model 607 made by Hitachi, and the intensity of fluorescence was given by a difference in reflection densities at 440 nm between measurements with and without a UV absorbing filter.

The results are shown in Table 6.

Table 6

Sample No.	Fluorescent brightener in 2nd layer	UV absorbent in 4th and 6th layers (g/m ²)	Magenta image light fastness (color fading rate)	Intensity of fluorescence	Static mark resistance (sheets/100 sheets)
50	-	UV-1 (0.8)	21	0.000	2
		UV-2 (0.3)		0.000	
51	-	UV-3 (1.1)	20	0.000	2
52	-	UV-4 (1.1)	32	0.000	3
53	-	I-1 (1.1)	17	0.000	1
54	-	I-2 (1.1)	15	0.000	1
55	-	I-3 (1.1)	18	0.000	1
56	-	I-18 (1.1)	18	0.000	1
57	-	- (0.0)	43	0.000	28
58	3	UV-1 (0.8)	22	0.007	2

Table 6 (continued)

Sample No.	Fluorescent brightener in 2nd layer	UV absorbent in 4th and 6th layers (g/m ²)	Magenta image light fastness (color fading rate)	Intensity of fluorescence	Static mark resistance (sheets/100 sheets)
59	3	UV-2 (0.3)	22	0.005	2
60	3	UV-3 (1.1)	34	0.010	2
61	3	UV-4 (1.1)	16	0.012	1
62	3	I-1 (1.1)	15	0.012	1
63	3	I-2 (1.1)	17	0.011	1
64	3	I-3 (1.1)	17	0.012	1
65	2	I-18 (1.1)	16	0.011	1
66	4	I-1 (1.1)	16	0.011	1
67	8	I-1 (1.1)	16	0.013	1
68	13	I-1 (1.1)	16	0.014	1
69	7*	I-1 (1.1)	16	0.010	1
70	14+22**	I-1 (1.1)	16	0.023	1

*: In sample 69, the fluorescent brightener was used in 5th layer as a supersensitizing agent.

**: In sample 70, the fluorescent brightener was added in the polyethylene coated on the emulsion side of a paper support.

As apparent from Table 6, the samples of the invention using specific UV absorbents and fluorescent brighteners had high fluorescent intensities and were low in deterioration of both light fastness and static mark resistance.

Example 6

Sample 71 was prepared in the similar manner as in Example 5, except that the yellow coupler, magenta coupler, cyan coupler and antifading agents ST-3 and ST-4 in the 3rd layer in sample 50 were changed to Y-2, M-B, C-3 and ST-5 and ST-6.

Similarly, samples 71 to 85 were prepared by changing the combination of UV absorbents used in the 4th and 6th layers as shown in Table 7.

The samples prepared as above were processed, as in Example 5, with combinations of developers and stabilizers shown in Table 7, and then evaluated for the light fastness of a magenta image and intensity of fluorescence in a white area. The developers and stabilizers shown in Table 7 were as follows:

Developer A : the same as the color developer used in Example 5

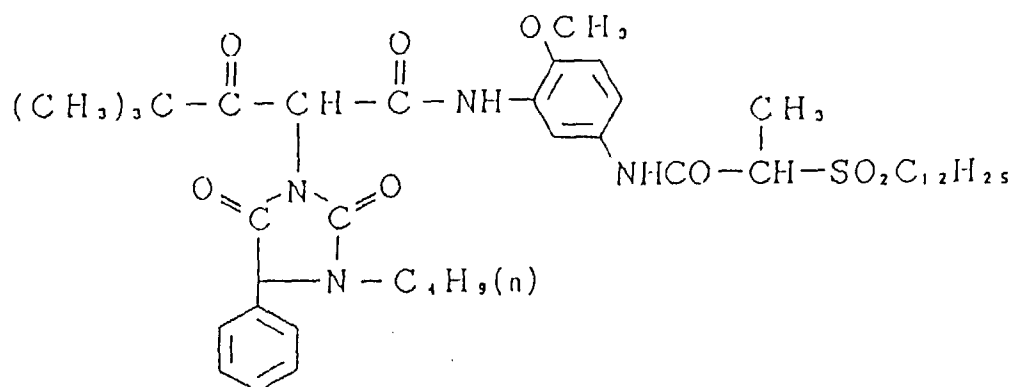
Developer B : developer A to which 1.0 g/l of a fluorescent brightener (exemplified compound 1) was added.

Stabilizer A: the same as the stabilizer used in Example 5

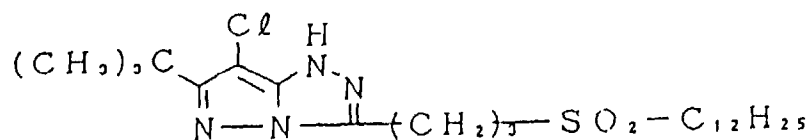
Stabilizer B: stabilizer A to which 1.5 g/l of a fluorescent brightener (exemplified compound 1) was added.

The evaluation results are shown in Table 7.

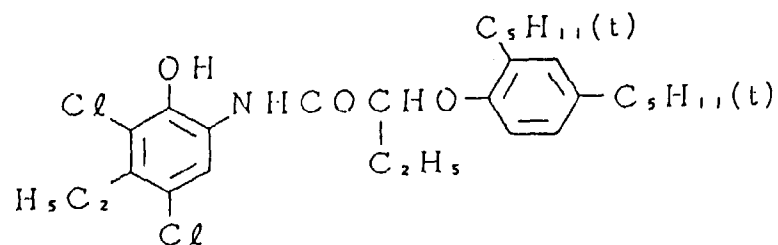
Yellow coupler Y-2



Magenta coupler M-B

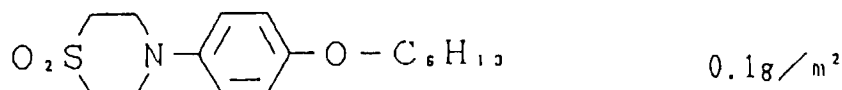


Cyan coupler C-3



Antifading agents in the 3rd layer

ST-5



ST-6

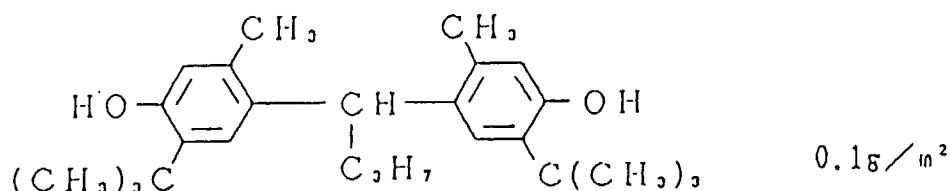


Table 7

Sample No.	UV absorbent in 4th and 6th layers (g/m ²)	Color developer	Stabilizer	Light fastness (color fading rate)	Intensity of fluorescence
71	UV-1 (0.8)	A	A	21	0.000
	UV-2 (0.3)				
72	UV-3 (1.1)	A	A	20	0.000
73	UV-4 (1.1)	A	A	32	0.000
74	I-1 (1.1)	A	A	17	0.000
75	I-2 (1.1)	A	A	15	0.000
76	I-3 (1.1)	A	A	18	0.000
77	I-18 (1.1)	A	A	18	0.000
78	- (0.0)	A	A	43	0.000
79	UV-1 (0.8)	B	B	22	0.008
	UV-2 (0.3)				
80	UV-3 (1.1)	B	B	22	0.007
81	UV-4 (1.1)	B	B	34	0.009
82	I-1 (1.1)	B	B	16	0.012
83	I-2 (1.1)	B	B	15	0.012
84	I-3 (1.1)	B	B	16	0.011
85	I-11 (1.1)	B	B	16	0.011

As shown in Table 7, samples 82 to 85 could form sharp images high in intensity of fluorescence, light fastness and whiteness.

Example 7

On the emulsion layer side of Konica photographic paper (Konica Color QA Paper Type A II), coating solutions each containing UV absorbent I-1 or UV-3 were coated and hardened to give a coating weight of 1.0 g/m² for I-1 and UV-3, respectively. The samples obtained were exposed, processed and evaluated in the same manner as in Example 2. The sample containing I-1 could form sharp images higher than those obtained from the sample containing UV-3 in intensity of fluorescent, whiteness and light fastness.

Example 8

In order to examine the storage stability and light-fastness enhancing capability of the dispersion of the invention containing UV absorbents respectively represented by Formulas I and II, dispersions were prepared by varying the combination of two types of UV absorbents as shown in Table 8.

Table 8

Sample No.	UV absorbent composition	High boiling solvent	Remarks
101	UV-5 : UV-6 (1 : 1)	DNP	UV absorbent described in Example 3 of J.P. Examined Pub. No. 30493/1973
102	UV-7 : UV-1 (1 : 1)	DNP	UV absorbent described in Example 1 of J.P. O.P.I. Pub. No. 85425/1978
103	UV-2 : UV-1 (1 : 1)	DNP	UV absorbent described in Example 1 of J.P. O.P.I. Pub. No. 215378/1979
104	I-1 : II-1 (1 : 1)	DNP	
105	I-1 : II-1 (1 : 1)	TINP	
106	I-1 : II-1 (1 : 1)	DBP	
107	I-2 : II-1 (1 : 1)	DNP	
108	I-3 : II-1 (1 : 1)	DNP	
109	I-1 : II-1 (1 : 1)	None	
110	I-3 : I-15 (1 : 1)	DNP	
*: TINP indicates triisononyl phosphate. Other abbreviations for high boiling solvents are explained in the foregoing Examples.			

The dispersions were prepared by the following procedure:

- (a) Ten g of a UV absorbent mixture having a composition shown in Table 8, 10 g of a high boiling solvent and 20 g of ethyl acetate were mixed and dissolved at 60°C.
- (b) Fifteen g of gelatin for photography was mixed with 200 ml of pure water and then allowed to swell for 20 minutes. After dissolving the gelatin at 60°C, 20 ml of a 5% aqueous solution of Alkanol B (product of Dupont) was added thereto and stirred for thorough mixing.
- (c) Solutions obtained in (a) and (b) were mixed and then dispersed for 20 minutes with a supersonic homogenizer to obtain a dispersion, which was subsequently made up to 300 ml with pure water.

The above procedure was repeated while varying the UV absorbent composition as shown in Table 8, so that 10 types of dispersions were obtained.

Each dispersion was then subjected to the following storage stability test.

(Storage stability test of the dispersion)

Containers holding respective dispersion samples 101 to 110 were stoppered and allowed to stand for 48 hours at 40°C. After standing, the degree of crystal deposition in a dispersion was examined. The results are shown in Table 9.

The degree of crystal deposition was measured by steps of diluting 100 ml of a dispersion with 100 ml of warm water, filtering the diluted dispersion under a reduced pressure with a filter paper No. 5A (product of Toyo Filter Paper), washing, drying and weighing deposits.

Further, to examine the light fastness of the dispersion, multilayered silver halide photographic light-sensitive materials were prepared by employing each of the foregoing dispersions in the 4th and 6th layers by the procedure described below.

The layers described in Table 9 were formed on the right side of a paper support coated on the right side with

polyethylene containing titanium dioxide and a bluing agent and on the opposite side with polyethylene. Sample 111 of multilayered silver halide color photographic light-sensitive material was thus obtained. Coating solutions were prepared in the following manner.

5 Preparation of coating solution for 3rd layer

Sixty ml of ethyl acetate was added to 35 g of magenta coupler M-A, 1.0 g of antistain agent HQ-1 and 30 g of high boiling solvent DNP to dissolve them. The solution was dispersed in 200 ml of a 10% aqueous gelatin solution with a supersonic homogenizer to prepare a magenta coupler dispersion.

10 The dispersion was then mixed with a green-sensitive silver halide emulsion (containing 27 g of silver) prepared under the following conditions, so that a coating solution for the 3rd layer was prepared.

Samples similar to sample 111 were prepared likewise, except that the UV absorbents in the 4th and 6th layers were varied as shown in Table 9. Emulsions Em-A, Em-B and Em-C used were the same as those employed in Example 3. Photographic processing was also carried out in the same way as in Example 3.

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Table 9

	Layer	Constitution	Coating weight (g/m ²)
5			
	7th layer (protective layer)	Gelatin	0.9
10			
	6th layer	Gelatin	0.4
		Antistain agent (HQ-1)	0.01
15		DNP	0.2
		PVP	0.03
20		Anti-irradiation dye (AI-2)	0.02
		UV absorbent (UV-5)	0.15
25		UV absorbent (UV-6)	0.15
	5th layer (red-sensitive)	Gelatin	1.40
		Red-sensitive silver halide emulsion (EmC) in terms of silver	0.24
30		Cyan coupler (C-1)	0.17
		Cyan coupler (C-2)	0.25
35		Dye image stabilizer (ST-1)	0.20
		High boiling solvent (HB-1)	0.10
40		Antistain agent (HQ-1)	0.01
		DOP	0.30
	4th layer	Gelatin	1.0
45		Antistain agent (HQ-1)	0.03
		DNP	0.40
50		UV absorbent (UV-5)	0.4
		UV absorbent (UV-6)	0.4
55			

	Layer	Constitution	Coating weight (g/m ²)
5	3rd layer (green-sensitive)	Gelatin	1.40
		Green-sensitive silver halide emulsion (EmB) in term of silver	0.27
10		Magenta coupler (M-A)	0.35
		Dye image stabilizer (ST-3)	0.2
15		Dye image stabilizer (ST-4)	0.1
		Antistain agent (HQ-1)	0.01
		DNP	0.30
20	2nd layer (intermediate)	Anti-irradiation dye (AI-1)	0.01
		Gelatin	1.0
25		Antistain agent (HQ-1)	0.12
		Diaminostilbene type brightener	0.10
		DIDP	0.15
30	1st layer (blue-sensitive)	Gelatin	1.20
		Blue-sensitive silver halide emulsion (EmA) in terms of silver	0.30
35		Yellow coupler (Y-1)	0.80
		Dye image stabilizer (ST-1)	0.30
40		Dye image stabilizer (ST-2)	0.20
		Antistain agent (HQ-1)	0.02
		DNP	0.20
45	Support	Polyethylene-laminated paper	

After processing, each sample was evaluated for the light fastness of magenta dye images by the following method.

Light fastness test

Reflection densities of green light were measured after and before exposing each sample to the sunlight for 30 days on an under-glass outdoor-exposing stand. The degree of color fading caused by exposure to light (color fading rate) was determined by the following expression.

$$\text{Color fading rate} = \frac{D - D_0}{D_0} \times 100$$

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Do: density before fading

D: density after fading

Similarly, each sample was also exposed to light of a daylight fluorescent lamp (20,000 lux) for 60 days.

The degree of crystal deposition was measured by weighing deposits obtained through procedure of diluting 100 ml of a dispersion with 100 ml of warm water, filtering it under a reduced pressure with a filter paper No. 5A (product of Toyo Filter Paper), washing and drying.

The evaluation results are shown in Table 10.

Table 10

Sample No.	UV absorbent	High boiling solvent	Stability of dispersion weight of depositions (mg)	Light stability	
				Sunlight	Fluorescent lamp
111	UV-5 UV-6	DNP	18	35	32
112	UV-7 UV-1	DNP	19	21	20
113	UV-2 UV-1	DNP	15	21	20
114	I-1 II-1	DNP	3	14	13
115	I-1 II-1	TINP	3	14	14
116	I-1 II-1	DBP	6	15	16
117	I-2 II-1	DNP	3	13	13
118	I-3 II-1	DNP	6	15	19
119	I-2 II-1	None	1	11	12
120	I-3 I-15	DNP	13	16	16

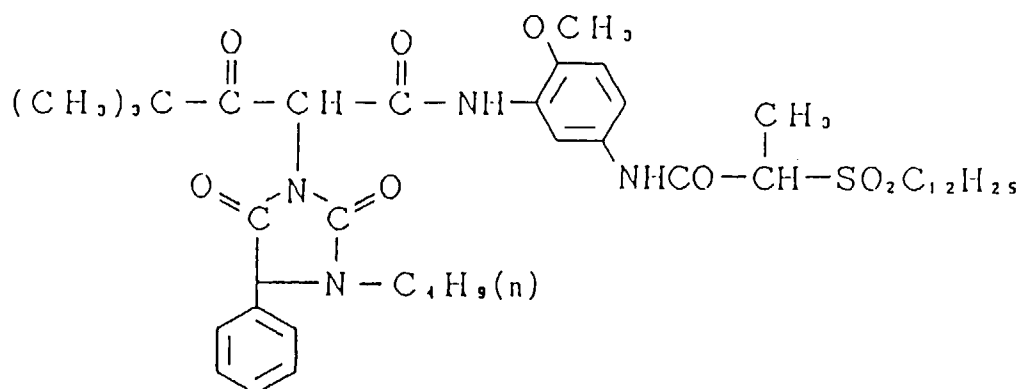
As apparent from the results in Table 10, the samples of the invention were not only good in dispersibility but also high in light fastness to either of the light sources.

Example 9

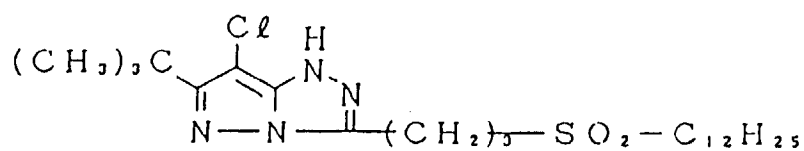
The procedure of Example 8 was repeated, except that the yellow coupler, magenta coupler, cyan coupler of sample 121, dye image stabilizers ST-3 and ST-4 used in the 3rd layer thereof and the UV absorbents in the 4th and 6th layers were varied as shown in Table 11.

The evaluation results of these samples are shown in Table 11.

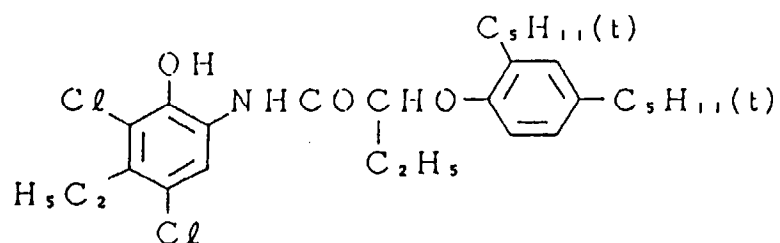
Yellow coupler Y-2



Magenta coupler M-B

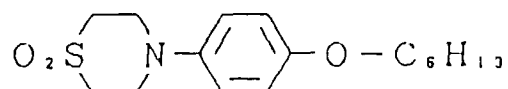


Cyan coupler C-3



Dye image stabilizers used in the 3rd layer

ST-5

0.1 g/m²

ST-6

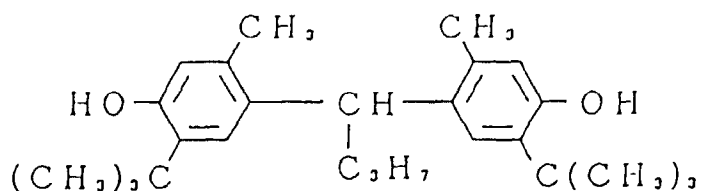
0.1 g/m²

Table 11

Sample No.	UV absorbent	Stability of dispersion weight of depositions (mg)	Light stability	
			Sunlight	Fluorescent lamp
121	UV-1 UV-2	18	36	34
122	UV-3 UV-4	19	20	21
123	UV-5 UV-4	15	22	22
124	I-3 II-1	3	15	14
125	I-4 II-1	3	14	14
126	I-5 II-1	6	16	15
127	I-3 II-7	1	14	13
128	I-3 II-9	1	15	14
129	I-3 II-9*	0	15	14
130	I-5 II-17	13	17	20

*: In sample 19, an addition amount of DNP was 0.0 g/m².

As seen in Table 11, the samples of the invention had a high dispersion stability, besides being capable of forming images with a good light fastness to either of the light sources.

Example 10

Color photographic light-sensitive materials were prepared by forming the following 1st to 9th layers on the right side and the 10th layer on the opposite side of a paper support coated with polyethylene on both sides (thickness: 145 μm). The polyethylene on the right side of the support contained titanium white as a white pigment.

Emulsions used were prepared in the same manner as in emulsion EM-11.

(Compositions of photographic structural layers)

Compositions of the photographic structural layers are shown in the specification below, where the coating weight is mg/dm^2 , and that of a silver halide emulsion is a value converted into silver.

In coating these layers, SA-1 and SA-2 were used as coating aids, and H-1 and H-3 as hardeners.

Preparation of emulsion EM-11

While maintaining an aqueous solution of ossein gelatin at 40°C, an aqueous solution containing ammonia and silver nitrate and an aqueous solution containing potassium bromide and sodium chloride (molar ratio of KBr to NaCl was 95:5) were simultaneously added thereto by the control double jet method, so that a cubic silver bromide emulsion having an average grain size of 0.45 μm was prepared. In this process, pH and pAg were controlled to give a cubic grain shape. Further, to the emulsion obtained were simultaneously added an aqueous solution containing ammonia and silver nitrate and an aqueous solution containing potassium bromide and sodium chloride (molar ratio of KBr to NaCl was 40:60) by the control double jet method till the average grain size became 0.6 μm , in order to form shells. In this addition process, pH and pAg were also controlled to give a cubic grain shape. After washing the emulsion to remove soluble salts, gelatin was added thereto to obtain emulsion EM-1 (extent of grain size distribution was 8%).

$$\text{Extent of distribution (\%)} = \frac{\text{Standard deviation of grain size}}{\text{Average grain size}} \times 100$$

The grain sizes and core sizes of the silver halide grains used were as follows:

Grain sizes after shelling (μm)	Core sizes (μm)
0.18	0.135
0.30	0.225
0.55	0.413
0.75	0.563

1st layer (red-sensitive layer)

0.18- μm cubic silver chlorobromide emulsion spectrally sensitized by red-sensitive sensitizing dyes (RD-1 and RD-2)	0.6
0.30- μm cubic silver chlorobromide emulsion spectrally sensitized by red-sensitive sensitizing dyes (RD-1 and RD-2)	0.9
0.55- μm cubic silver chlorobromide emulsion spectrally sensitized by red-sensitive sensitizing dyes (RD-1 and RD-2)	1.5
Gelatin	13.8
Cyan coupler (CC-1)	2.1
Cyan coupler (CC-2)	2.1
Image stabilizer (AO-2)	2.2
Solvent (SO-1)	3.3
Stabilizers (ST-11, ST-12, ST-13)	

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2nd layer (intermediate layer)

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Gelatin	7.5
Antistain agent (HQ-1)	0.55
Solvent (SO-2)	0.72

3rd layer (green-sensitive layer)

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0.18- μ m cubic silver chlorobromide emulsion spectrally sensitized by green-sensitive sensitizing dye (GD-1)	0.6
0.30- μ m cubic silver chlorobromide emulsion spectrally sensitized by green-sensitive sensitizing dye (GD-1)	0.9
0.55- μ m cubic silver chlorobromide emulsion spectrally sensitized by green-sensitive sensitizing dye (GD-1)	1.5
Gelatin	13.0
Magenta coupler (MC-1)	2.4
Image stabilizer (AO-1)	2.4
Image stabilizer (AO-2)	1.2
Solvent (SO-3)	3.1
Antistain agent (HQ-2)	0.15
Stabilizers (ST-11, ST-12, ST-13)	

4th layer (intermediate layer)

The same as the 2nd layer

30

5th layer (yellow filter layer)

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45

Gelatin	4.2
Yellow colloidal silver	1.0
UV absorbent (UV-5)	0.5
UV absorbent (UV-6)	1.4
Antistain agent (HQ-1)	0.4

Solvent (SO-2)	0.8
----------------	-----

6th layer (antistain layer)

50

55

Gelatin	4.0
Antistain agent (HQ-1)	0.27
Solvent (SO-2)	0.36

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7th layer (blue-sensitive layer)

0.31-μm tetradecahedral silver chlorobromide emulsion spectrally sensitized by blue-sensitive sensitizing dye (BD-1)	1.2
0.55-μm cubic silver chlorobromide emulsion spectrally sensitized by blue-sensitive sensitizing dye (BD-1)	1.8
0.75-μm cubic silver chlorobromide emulsion spectrally sensitized by blue-sensitive sensitizing dye (BD-1)	3.0
Gelatin	13.5
Yellow coupler (Y-1)	8.4
Image stabilizer (AO-3)	2.5
Solvent (SO-1)	5.2
Stabilizers (ST-11, ST-13, ST-14)	

8 th layer (ultraviolet adsorption layer)

Gelatin	5.4
UV absorbent (UV-5)	1.0
UV absorbent (UV-6)	2.8

Solvent (SO-3)	1.2
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9th layer (protective layer)

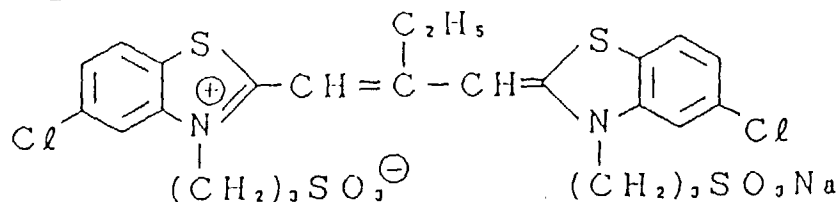
Gelatin	12.3
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10th layer

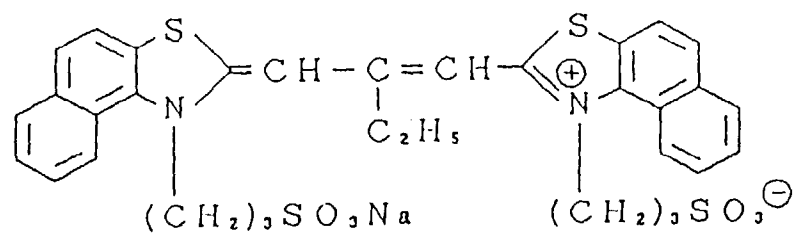
Gelatin	40.0
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Separately, a sample of the invention was prepared in the same manner as in the foregoing color photographic light-sensitive material, except that exemplified compounds I-1 and II-9 were employed in the 5th and 8th layers instead of UV-5 and UV-6 used in the above 5th and 8th layers.

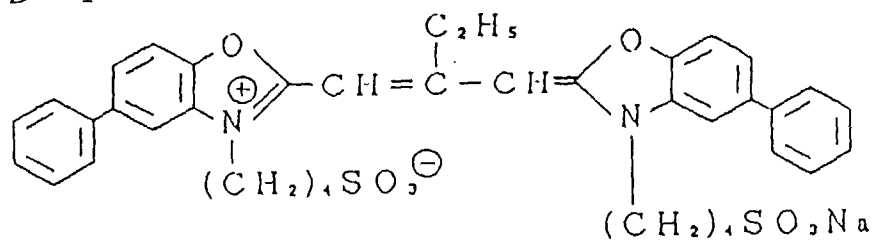
RD - 1



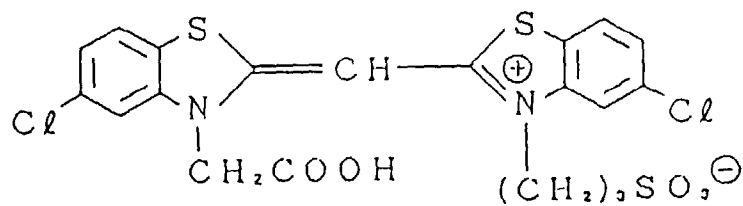
RD - 2



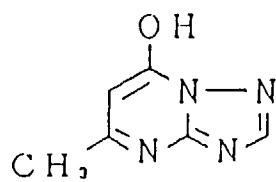
GD - 1



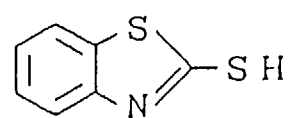
BD - 1



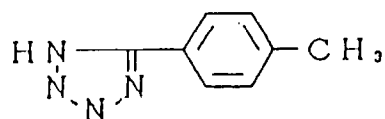
ST-11



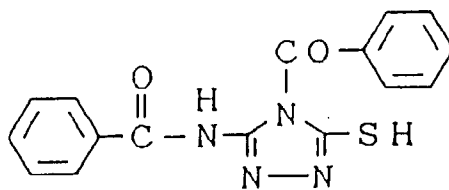
ST-12



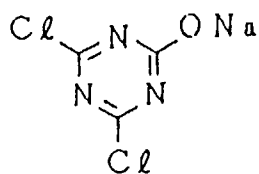
ST-13



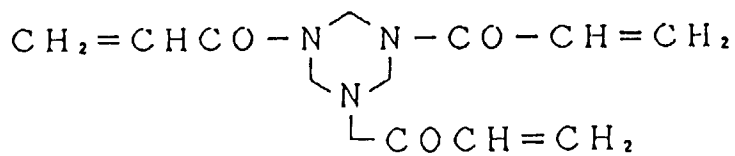
ST-14



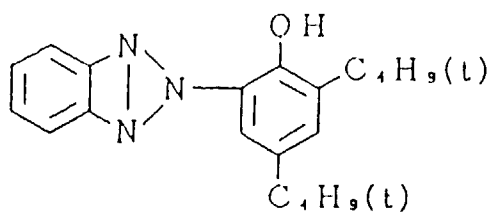
H-1



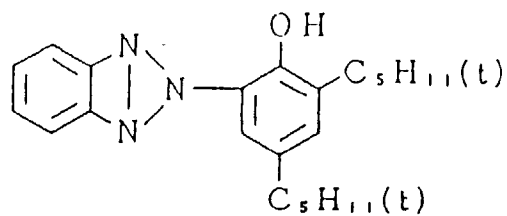
H-3



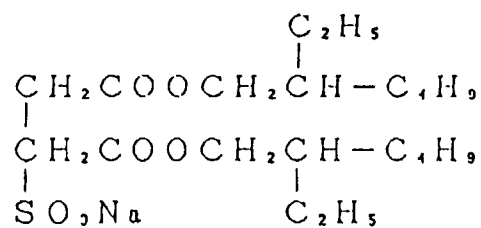
UV - 1



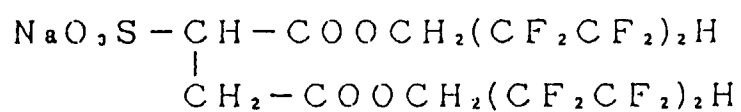
UV - 2



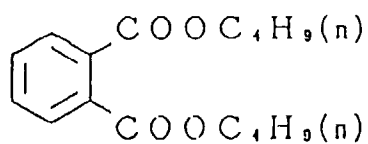
S A - 1



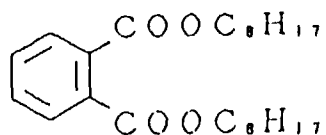
S A - 2



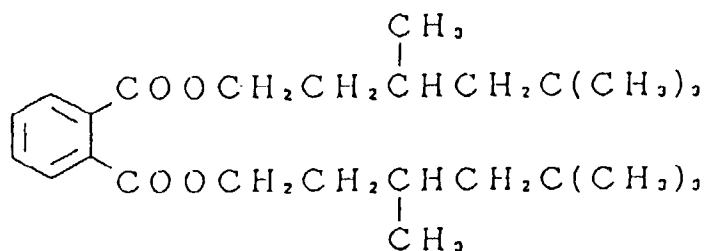
S O - 1



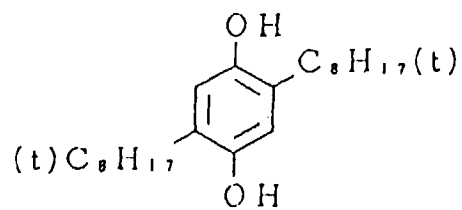
S O - 2



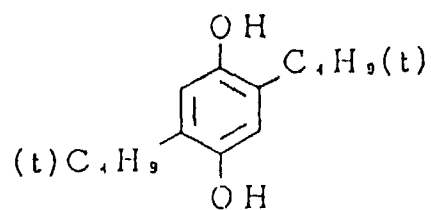
S O - 3



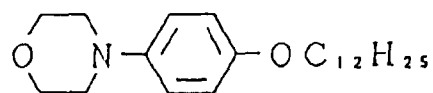
HQ-1



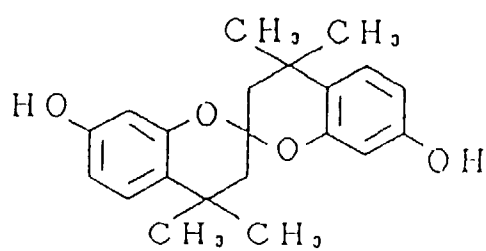
HQ-2



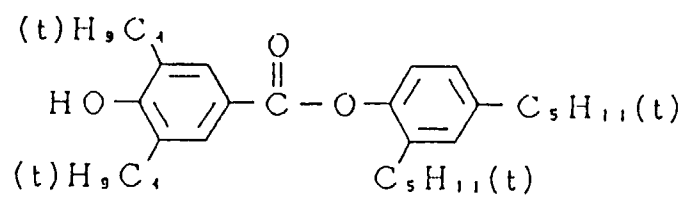
AO-1



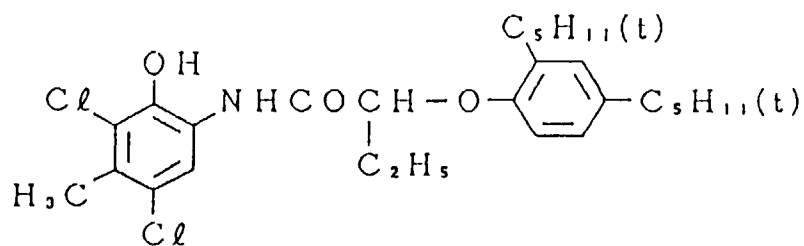
AO-2



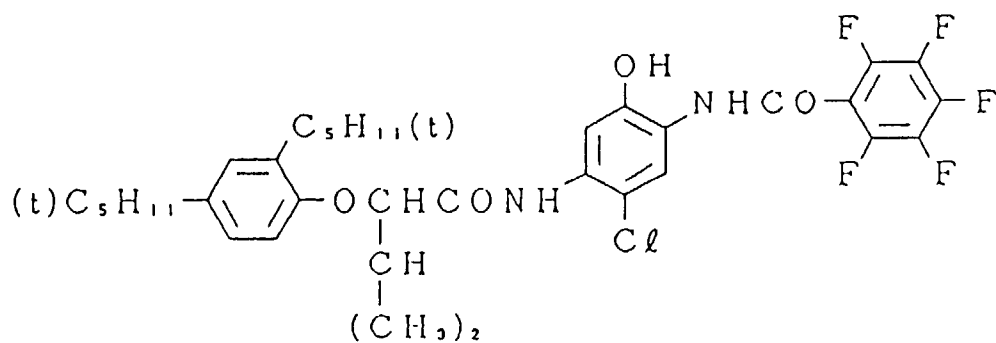
AO-3



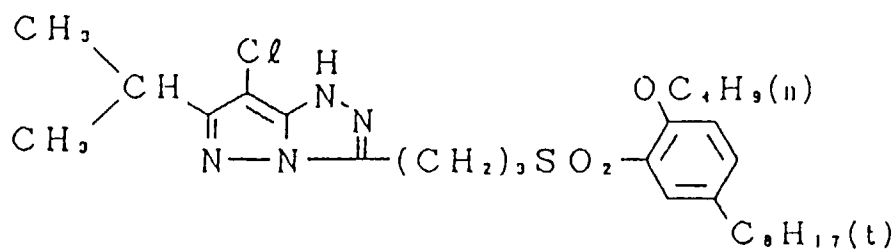
C-1



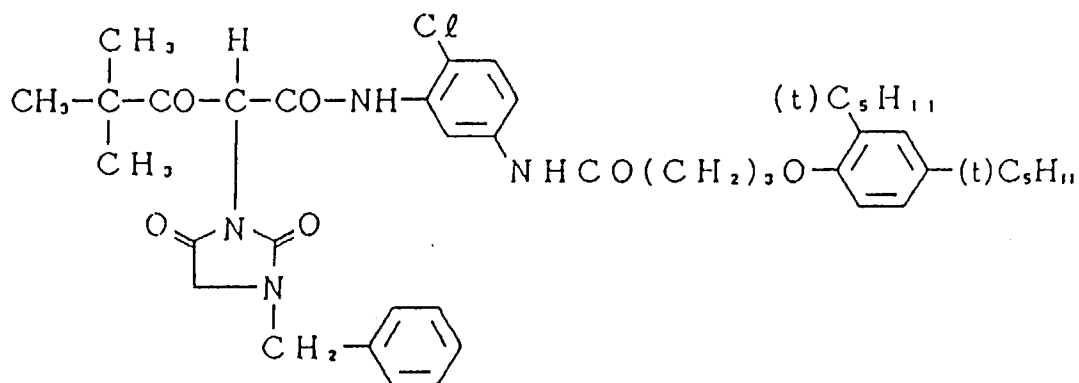
C-2



M-1



Y-1



EP 0 451 813 B1

Two direct positive silver halide color photographic light-sensitive materials of internal latent image type prepared as above were exposed through an optical wedge. The exposed samples were then processed by the following procedure.

Processing	Temperature	Time
(1) Dipping (color developer)	37°C	12 sec.
(2) Exposure for fogging		(1 lux) 12 sec.
(3) Color developing	37°C	1 min. and 35 sec.
(4) Bleach-fixing	35°C	45 sec.
(5) Stabilizing	25 - 30°C	1 min. and 30 sec.
(6) Drying	75 - 80°C	45 sec.

Processing solution compositions

Color developer

Benzyl alcohol	15 ml
$\text{Ce}_2(\text{SO}_4)_3$	0.015 g
Ethylene glycol	8 ml
Potassium sulfite	2.5 g
Potassium bromide	0.6 g
Sodium chloride	0.2 g
Potassium carbonate	25.0 g
ST-4	0.1 g
Hydroxylamine sulfate	5.0 g
Sodium diethylenetriamine pentacetate	2 g

Developing agent (N-ethyl-N- β -methanesulfonamidoethyl-
 3-methyl-4-aminoaniline sulfate) 1.5×10^{-2} mol
 Fluorescent brightener (4,4'-diaminostilbene
 disulfonic acid derivative) 1.0 g
 Potassium hydroxide 2.0 g
 Diethylene glycol 15 ml
 Water was added to make 1 liter. pH was adjusted to
 10.15.

Bleach-fixer		
	Ammonium ferric diethylenetriamine pentacetate	90 g
	Diethylenetriamine pentaacetate	3 g
	Ammonium thiosulfate (70% solution)	180 ml
	Ammonium sulfite (40% solution)	27.5 ml
	3-Mercapto-1,2,4-triazole	0.15 g
pH was adjusted to 7.1 with potassium carbonate or glacial acetic acid, then water was added to make the total volume 1 liter.		

Stabilizer

o-Phenylphenol 0.3 g
 Potassium sulfite (50% solution) 12 ml
 Ethylene glycol 10 g
 1-hydroxyethylidene-1,1-diphosphonic acid 2.5 g
 Bismuth chloride 0.2 g
 Zinc sulfate heptahydrate 0.7 g

Ammonium hydroxide (28% solution) 2.0 g

Polyvinylpyrrolidone (K-17) 0.2 g

Fluorescent brightener (4,4'-diaminostilbene
disulfonic acid derivative) 2 g

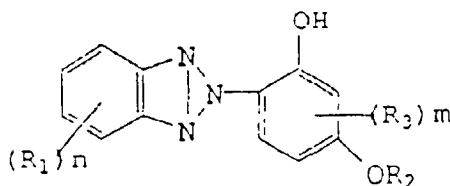
Water was added to make 1 liter, and pH was adjusted to
7.5 with ammonium hydroxide or sulfuric acid.

The two samples processed as above were evaluated as in Example 8. The sample with a specific combination of UV absorbents according to the invention did not cause coating troubles and provided images having a light fastness higher than those of the sample using UV-1 and UV-2.

Claims

1. A photographic material having a support and a light sensitive silver halide emulsion layer, wherein the photographic material contains a compound represented by a formula I in a light sensitive silver halide emulsion layer or a non-light-sensitive layer:

I



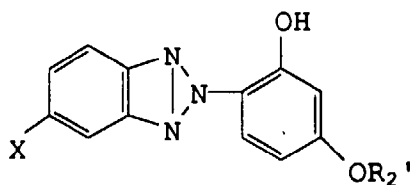
wherein R_1 represents a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group or a substituted or unsubstituted aryloxy group; R_2 represents a substituted or unsubstituted alkyl group having a total number of carbon atoms of eight or more, a cis-9-octadecenyl group or a substituted or unsubstituted aryl group; R_3 represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group or a substituted or unsubstituted aryloxy group; n represents an integer of 0 to 4, and m represents an integer of 0 to 3, provided that in case

- a) R_1 being a substituted alkyl or aryloxy group or
- b) R_2 being a substituted alkyl or aryl group

the substituent cannot be a quaternary ammonium moiety.

2. A photographic material according to claim 1, wherein R_2 represents 2-ethyl-hexyl, sec-dodecyl, iso-tridecyl, cis-9-octadecenyl, or octyloxycarbonylethyl.
3. A photographic material according to claim 1, wherein R_2 represents 2-ethyl-hexyl, sec-dodecyl, iso-tridecyl or cis-9-octadecenyl.
4. A photographic material according to claim 1, wherein the compound is represented by a formula I-A;

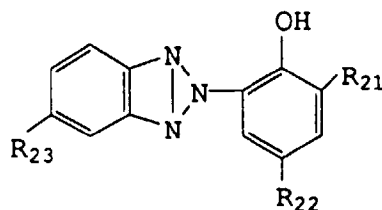
I-A



wherein X represents a hydrogen atom or a halogen atom; R_2' represents a substituted or unsubstituted alkyl group having a total number of carbon atoms of eight or more.

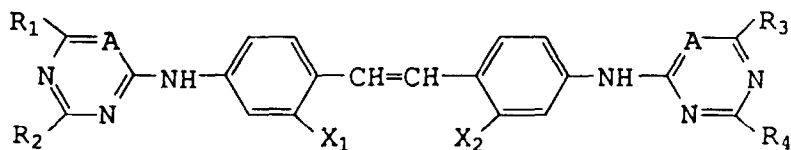
5. A photographic material according to claim 4, wherein R_2' represents a branched alkyl group; X represents a hydrogen atom or a chlorine atom.
6. A photographic material according to claim 1, wherein the silver halide emulsion has a silver chloride content of more than 90 mol%.
7. A photographic material according to claim 1, wherein the light sensitive silver halide emulsion layer or the non-light-sensitive layer contains a compound represented by a formula II:

II



wherein R_{21} , R_{22} , and R_{23} each represent a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryloxy group, a substituted or unsubstituted alkenyl group, a nitro group or a hydroxyl group.

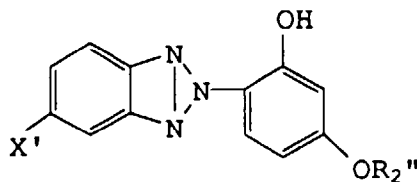
8. A photographic material according to claim 1, which further comprises a fluorescent brightener.
9. A photographic material according to claim 8, wherein the fluorescent brightener is represented by a formula III:



wherein A represents a -N=N- or -C=; R_1 , R_2 , R_3 and R_4 may be the same or different from one another and each represent a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkylamino group, a substituted or unsubstituted arylamino group or a substituted or unsubstituted aryloxy group; X_1 , and X_2 each represent a hydrogen atom or a $-SO_3M$, where M is a hydrogen atom or an atom or a group to form a water-soluble salt.

10. A photographic material according to Claim 1, wherein the compound of formula I is represented by formula I-B and the light sensitive silver halide emulsion has a silver chloride content of more than 90 mol%, a silver bromide content of less than 10 mol% and a silver iodide content of less than 0.5 mol%:

I-B

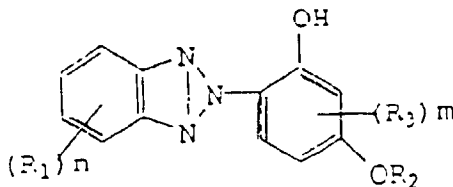


wherein X' represents a chlorine atom and R₂ is an i-octyl group.

Patentansprüche

1. Photographisches Aufzeichnungsmaterial mit einem Schichtträger und einer lichtempfindlichen Silberhalogenidemulsionsschicht, welches in einer lichtempfindlichen Silberhalogenidemulsionsschicht oder nichtlichtempfindlichen Schicht eine Verbindung der Formel (I):

I



worin bedeuten:

R₁ ein Halogenatom, eine substituierte oder unsubstituierte Alkylgruppe, eine substituierte oder unsubstituierte Arylgruppe, eine substituierte oder unsubstituierte Alkoxygruppe oder eine substituierte oder unsubstituierte Aryloxygruppe;

R₂ eine substituierte oder unsubstituierte Alkylgruppe mit einer Gesamtzahl an Kohlenstoffatomen von 8 oder mehr, eine cis-9-Octadecenylgruppe oder eine substituierte oder unsubstituierte Arylgruppe;

R₃ eine substituierte oder unsubstituierte Alkylgruppe, eine substituierte oder unsubstituierte Arylgruppe, eine substituierte oder unsubstituierte Alkoxygruppe oder eine substituierte oder unsubstituierte Aryloxygruppe;

n eine ganze Zahl von 0 bis 4 und

m eine ganze Zahl von 0 bis 3,

wobei gilt, daß im Falle

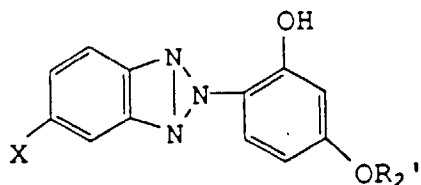
a) daß R₁ für eine substituierte Alkoxy- oder Aryloxygruppe oder

b) R₂ für eine substituierte Alkyl- oder Arylgruppe steht, der Substituent nicht aus einer quaternären Ammoniumeinheit bestehen kann,

enthält.

2. Photographisches Aufzeichnungsmaterial nach Anspruch 1, wobei R₂ für 2-Ethylhexyl, sek.-Dodecyl, Isotridecyl, cis-9-Octadecenyl oder Octyloxycarbonylethyl steht.
3. Photographisches Aufzeichnungsmaterial nach Anspruch 1, wobei R₂ für 2-Ethylhexyl, sek.-Dodecyl, Isotridecyl oder cis-9-Octadecenyl steht.
4. Photographisches Aufzeichnungsmaterial nach Anspruch 1, wobei die Verbindung der Formel I-A:

I-A



worin bedeuten:

X ein Wasserstoffatom oder ein Halogenatom und

R₂' eine substituierte oder unsubstituierte Alkylgruppe mit einer Gesamtzahl an Kohlenstoffatomen von 8 oder mehr,

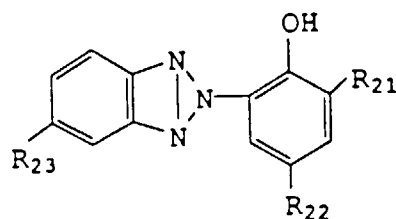
entspricht.

5. Photographisches Aufzeichnungsmaterial nach Anspruch 4, wobei R₂' für eine verzweigt-kettige Alkylgruppe steht und X ein Wasserstoffatom oder ein Chloratom darstellt.

6. Photographisches Aufzeichnungsmaterial nach Anspruch 1, wobei die Silberhalogenidemulsion einen Silberchloridgehalt von mehr als 90 Mol-% aufweist.

7. Photographisches Aufzeichnungsmaterial nach Anspruch 1, wobei die lichtempfindliche Silberhalogenidemulsionsschicht oder die nichtlichtempfindliche Schicht eine Verbindung der Formel II:

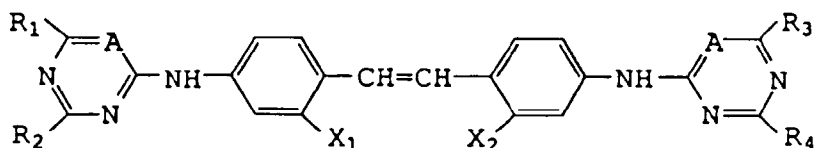
II



worin R₂₁, R₂₂ und R₂₃ jeweils ein Wasserstoffatom, ein Halogenatom, eine substituierte oder unsubstituierte Alkylgruppe, eine substituierte oder unsubstituierte Arylgruppe, eine substituierte oder unsubstituierte Alkoxygruppe, eine substituierte oder unsubstituierte Aryloxygruppe, eine substituierte oder unsubstituierte Alkenylgruppe, eine Nitrogruppe oder eine Hydroxylgruppe darstellen, enthält.

8. Photographisches Aufzeichnungsmaterial nach Anspruch 1, welches zusätzlich einen fluoreszierenden Aufheller enthält.

9. Photographisches Aufzeichnungsmaterial nach Anspruch 8, wobei der fluoreszierende Aufheller der Formel III:



worin bedeuten:

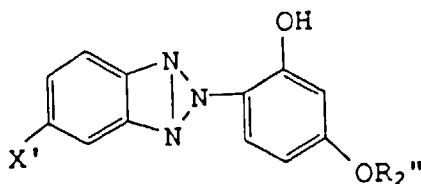
A -N=N- oder -C=;

R_1 , R_2 , R_3 und R_4 , die gleich oder voneinander verschieden sein können, jeweils eine substituierte oder unsubstituierte Alkylgruppe, eine substituierte oder unsubstituierte Alkylaminogruppe, eine substituierte oder unsubstituierte Arylaminogruppe oder eine substituierte oder unsubstituierte Aryloxygruppe;

X_1 und X_2 jeweils ein Wasserstoffatom oder einen Rest $-SO_3M$ mit M gleich einem Wasserstoffatom oder einem Atom oder einer Gruppe zur Bildung eines wasserlöslichen Salzes,

entspricht.

10. Photographisches Aufzeichnungsmaterial nach Anspruch 1, wobei die Verbindung der Formel I aus einer solchen der Formel I-B:

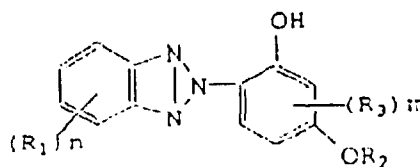


worin X' für ein Chloratom steht und R_2 eine Isooctylgruppe darstellt, besteht und die lichtempfindliche Silberhalogenidemulsion einen Silberchloridgehalt von mehr als 90 Mol-%, einen Silberbromidgehalt von weniger als 10 Mol-% und einen Silberjodidgehalt von weniger als 0,5 Mol-% aufweist.

Revendications

1. Matériau photographique ayant un support et une couche d'une émulsion d'halogénure d'argent sensible à la lumière, où le matériau photographique contient un composé représenté par la formule I dans une couche d'émulsion d'halogénure d'argent sensible à la lumière ou dans une couche non sensible à la lumière :

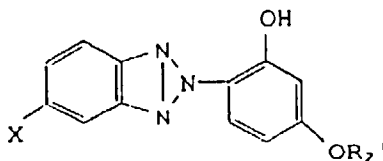
I



dans laquelle R_1 représente un atome d'halogène, un groupe alkyle substitué ou non, un groupe aryle substitué ou non, un groupe alcoxy substitué ou non, ou un groupe aryloxy substitué ou non; R_2 représente un groupe alkyle substitué ou non, ayant un nombre total d'atomes de carbone de huit ou plus, un groupe cis-9-octadécényle ou un groupe aryle substitué ou non; R_3 représente un groupe alkyle substitué ou non, un groupe aryle substitué ou non, un groupe alcoxy substitué ou non ou un groupe aryloxy substitué ou non; n représente un nombre entier de 0 à 4 et m représente un nombre entier de 0 à 3, à condition que, dans le cas où a) R_1 est un groupe aryloxy ou alcoxy substitué ou b) R_2 est un groupe aryle ou alkyle substitué, le groupe substituant ne puisse être un groupe ammonium quaternaire.

2. Matériau photographique selon la revendication 1, où R_2 représente un groupe 2-éthyl-hexyle, sec-dodécyle, iso-tridécyle, cis-9-octadécényle ou octyloxycarbonyléthyle.
3. Matériau photographique selon la revendication 1, où R_2 représente un groupe 2-éthyl-hexyle, sec-dodécyle, iso-tridécyle ou cis-9-octadécényle.
4. Matériau photographique selon la revendication 1, où le composé est représenté par la formule

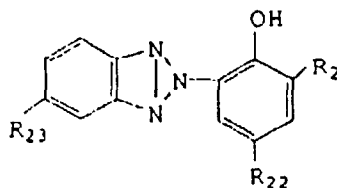
I-A



où X représente un atome d'hydrogène ou un atome d'halogène; R_2' représente un groupe alkyle substitué ou non ayant un nombre total d'atomes de huit ou plus.

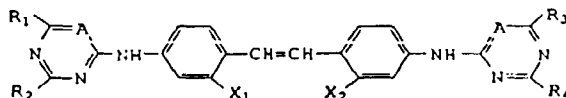
5. Matériau photographique selon la revendication 4, où R_2' représente un groupe alkyle ramifié; X représente un atome d'hydrogène ou un atome de chlore.
6. Matériau photographique selon la revendication 1, où l'émulsion d'halogénure d'argent a une teneur en chlorure d'argent supérieure à 90% en moles.
7. Matériau photographique selon la revendication 1, où la couche d'émulsion d'halogénure d'argent sensible à la lumière, ou la couche non sensible à la lumière contient un composé représenté par une formule II :

II



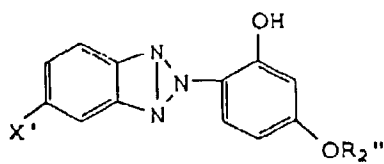
où R_{21} , R_{22} et R_{23} représentent chacun un atome d'hydrogène, un atome d'halogène, un groupe alkyle substitué ou non, un groupe aryle substitué ou non, un groupe alcoxy substitué ou non, un groupe aryloxy substitué ou non, un groupe alcényle substitué ou non, un groupe nitro ou un groupe hydroxyle.

8. Matériau photographique selon la revendication 1, qui contient en outre un agent optique fluorescent.
9. Matériau photographique selon la revendication 8, où l'agent optique fluorescent est représenté par la formule III :



où A représente -N=N- ou -C=; R_1 , R_2 , R_3 et R_4 peuvent être les mêmes ou différents l'un de l'autre et ils représentent chacun un groupe alkyle substitué ou non, un groupe alkylamino substitué ou non, un groupe arylamino substitué ou non, un groupe aryloxy substitué ou non; X_1 et X_2 représentent chacun un atome d'hydrogène ou un groupe -SO₃M, où M est un atome d'hydrogène ou un atome ou un groupe permettant de former un sel hydrosoluble.

10. Matériau photographique selon la revendication 1, où le composé de la formule I est représenté par la formule I-B et l'émulsion d'halogénure d'argent sensible à la lumière a une teneur en chlorure d'argent qui ne dépasse pas 90% en moles, une teneur en bromure d'argent inférieure à 10% en moles et une teneur en iodure d'argent inférieure à 0,5% en moles



où X' représente un atome de chlore et R₂ est un groupe i-octyle.