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(54) Silver halide photographic emulsions with reduced dye desensitisation

(57) The present invention concerns a silver halide emulsion, and more particularly a silver halide emulsion which resolves the problem of desensitisation which can be caused by the spectral sensitising dye.

This emulsion is an emulsion of the core/shell type having a particular grain structure which has been chemically sensitised by means of thiourea compounds and a gold (I) compound which does not contain a labile sulphur atom.

The emulsions of the present invention make it possible to reduce the dye desensitisation.

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Description

The present invention concerns a silver halide emulsion, and more particularly a silver halide emulsion which resolves the problem of desensitisation which can be caused by the spectral sensitising dye.

Silver halide photographic emulsions have a natural photosensitivity region which is limited to ultraviolet, violet and blue. In order to obtain an acceptable colour rendering, it is necessary to use compounds which have the property of being adsorbed on the silver halide grains and making these grains sensitive to a wavelength region extending, in the visible spectrum, beyond the intrinsic photosensitivity region of the silver halides. The photosensitivity of the emulsion depends on the quantity of spectral sensitisers adsorbed on the silver halide grains. It increases with the increase in the quantity of spectral sensitising dyes up to a maximum sensitivity value. Beyond this maximum, when the quantity of spectral sensitising dyes is increased a reduction in sensitivity is observed. The quantity of dye which enables maximum sensitivity to be obtained may vary according to the spectral sensitising dye and the size, shape or composition of the halide grains.

The effect of the spectral sensitisers may therefore be reversed. In general, this reversed effect, known as desensitisation, appears when the quantity of sensitisers adsorbed on the surface of the halide grains exceeds a certain threshold. For certain particular silver halide grains, this desensitisation appears as soon as the spectral sensitiser covers 50% of the surface of the silver halide grains.

It is therefore important to be able to increase the quantity of spectral sensitisers adsorbed on the silver halide grains without desensitisation resulting therefrom. In photography, it is known that emulsions can be chemically sensitised in the presence of one or more compounds of sulphur, gold and/or selenium in order to increase the overall sensitivity of the photosensitive products obtained. Examples of chemical sensitising compounds were described in Research Disclosure, No 308119, December 1989, Section III.

In European patent 428,041, the emulsions are chemically sensitised in the presence of conventional sulphur and gold compounds and a selenium compound having a labile selenium atom.

In US patent 4,810,626, the silver halide emulsions were sensitised with a compound of the tetrasubstituted selenourea or thiourea type.

In US patent 5,049,485, photographic products were sensitised by means of gold (I) compounds (degrees of oxidation equal to 1) of formulae AUL^+X^- or $AUL(L_1)^+X^-$ in which L is a mesoionic group, X is an anion and L_1 is a donor ligand of the Lewis base type. Such compounds have improved properties compared with conventional gold compounds. In the examples, the chemical sensitisation was implemented using the gold (I) compound in combination either with a conventional sulphur compound ($Na_2S_2O_3$) or with a substituted thiourea. The sensitometric results show that the use of a gold (I) compound in combination with a thiourea has no advantage compared with the use of a gold (I) compound with $Na_2S_2O_3$ as disclosed in the patent cited above.

As the prior art set out above shows, it is known that the sensitivity of photographic products can be improved by using sulphur compounds and gold compounds. However, none of the documents cited above mentions the problems of desensitisation by a spectral sensitising dye (hereinafter referred to as "dye desensitisation").

The object of the present invention is to obtain an emulsion having high sensitivity whilst eliminating the problem of dye desensitisation.

In fact, we discovered that the problem of dye desensitisation which arose with some emulsions could be resolved by associating these particular emulsions with a chemical sensitisation by means of gold compounds with a degree of oxidation equal to 1 (hereinafter referred to as gold (I)) which do not contain a labile sulphur atom and by means of a thiourea.

The photographic emulsion according to the invention has improved sensitivity which results from increasing the quantity of spectral sensitisers adsorbed on the silver halide grains without causing dye desensitisation.

Although the combination of a thiourea and a gold (I) compound was described in US patent 5,049,485, it was not known that this combination would make it possible to avoid the dye desensitisation which occurs with certain types of silver halide emulsion.

The photographic emulsion of the present invention consists of silver halide grains comprising a central zone (the core) consisting of at least two silver halides and an outer zone (the shell) having a silver halide composition different from the composition of the central zone, characterised in that

(1) the molar percentage of at least one of the silver halides which constitutes the core with respect to the total number of moles of silver halides in the core decreases between the centre of the grains and the core/shell interface,

(2) the chemical sensitisation of the grain was effected by means of at least one thiourea and at least one gold (I) compound not containing any labile sulphur atom.

According to one embodiment, the proportion of at least one of the halides forming the core decreases continuously between the centre of the grains and the core/shell interface so that the difference between the molar percentage of each of the silver halides between the centre of the grain and the core/shell interface is at least 10%, the percentages being calculated from the total number of moles of silver halides constituting the core.

The silver halide emulsion forming the core of the invention comprises at least two silver halides chosen from amongst silver chloride, bromide and iodide.

The process for preparing such decreasing-profile emulsions consists of precipitating successive regions having different silver halide compositions whilst simultaneously introducing a solution of a silver salt and a solution of alkali metal halide(s), hereinafter referred to as "halide solution" or "halide jet" containing one or more alkaline halides. The process according to the invention is characterised in that, during the precipitation of the core, a halide solution is used which comprises at least two different halides, the concentrations of which are caused to vary inversely, between initial values and predetermined final values. These variations are preferably practically linear.

In order to avoid abrupt variations in the halide composition of the grain at the core/shell interface, the final values of the concentration in the halide solution used for the core are preferably equal to the concentrations of said halides in the halide solution at the start of precipitation of the shell immediately adjacent to the core.

The core of the silver halide grains of the emulsions of the invention preferably consists of silver bromoiodide, silver chloroiodide or silver chlorobromoiodide with a molar percentage of silver iodide which decreases between the centre of the grains and the core/shell interface. In order to obtain such an emulsion having a bromoiodide core, the silver bromoiodide core is precipitated whilst linearly decreasing the concentration of iodide and linearly increasing the concentration of bromide in the halide jet consisting of alkaline iodide and alkaline bromide. In this case, the iodide content in the grain varies from a maximum value at the centre of the grain to a zero value at the core/shell interface. The shell, which may consist of one or more silver halides other than iodide, is then precipitated.

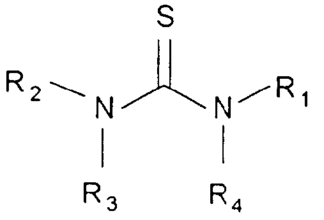
The overall quantity of silver iodide in the core is, within the framework of the invention, between 10 and 30% molar with respect to the total number of moles of silver halide contained in the core, and this proportion of iodide can vary between 36% at the centre of the grain and 0% at the core/shell interface.

The shell of the grains constituting the emulsion may be formed by one or more layers having identical or different silver halide compositions. According to one embodiment, this shell does not contain any silver iodide.

The ratio of the number of moles of silver halide constituting the core to the number of moles of silver halide constituting the shell is between 0.2 and 2. According to one embodiment, the core of the grains is formed by silver bromoiodide, the shell of the grains is formed by silver bromide and the core/shell molar ratio is 0.5.

The grains may have different morphologies, for example tabular, octahedral (faces 111), cubo-octahedral or cubic (faces 100). In one embodiment of the invention, the grains are cubo-octahedral with a size of between 0.1 and 3.0 µm, and preferably 0.3 and 2.0 µm.

The thioureas which can be used in the present invention are tetrasubstituted thioureas of formula:

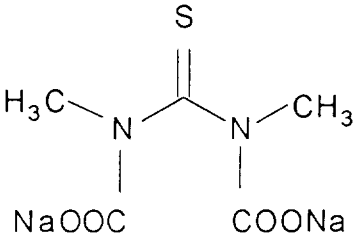


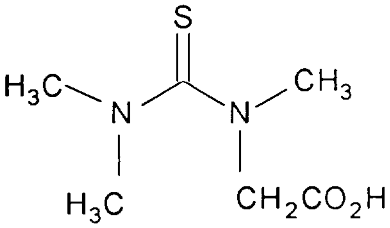
in which each R_1, R_2, R_3 and R_4 group represents either separately a hydrogen atom, an alkyl, cycloalkyl or carbocyclic or heterocyclic aryl radical, or an aralkyl radical, or R_2-R_3, R_3-R_4 or R_4-R_1 are combined to represent a heterocycle with 5 to 7 linkages, provided that at least one of the R_1, R_2, R_3 or R_4 groups contains or is a nucleophilic group of the carboxylic, sulphinic, sulphonic, hydroxamic, mercapto, sulphonamido or primary or secondary amino group.

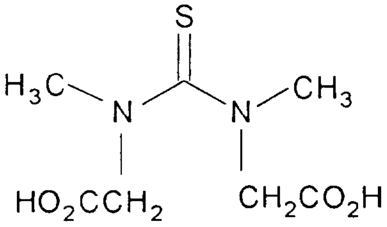
The thioureas which can be used in the scope of this invention are described in detail in US patent 4,810,626.

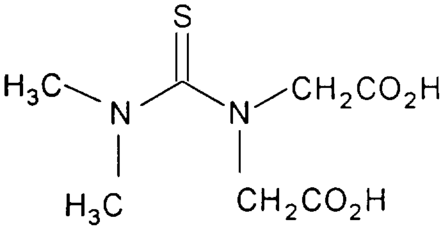
The radicals R_1, R_2, R_3 and R_4 which contain a nucleophilic group are, for example, chosen from amongst -COOH, $-CH_2COOH$, C_2H_4COOH, $-CH_2SO_2H$, $-CH_2SO_3H$, $-C_2H_4SO_2H$, $-C_2H_4NHOH$, $-C_2H_4SH$, $-(CH_2)_2NHSO_2CH_3$, $-C_2H_4NHCH_3$ and the corresponding salts.

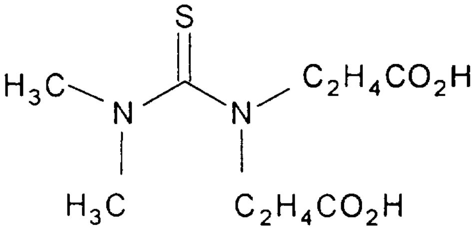
The preferred thioureas of the invention are the 1,1,3,3-tetrasubstituted 2-thioureas of formulae:

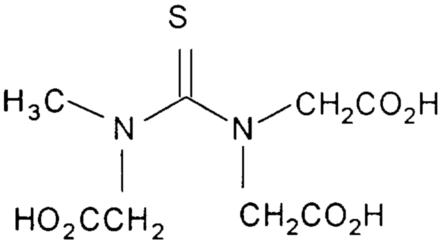


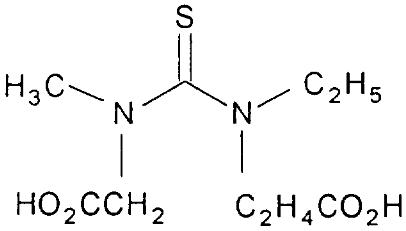


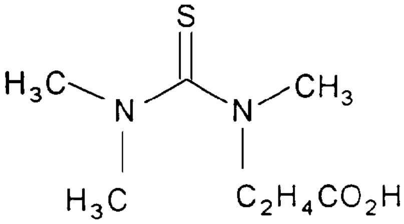


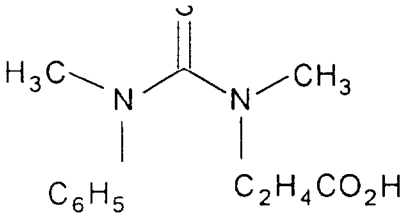


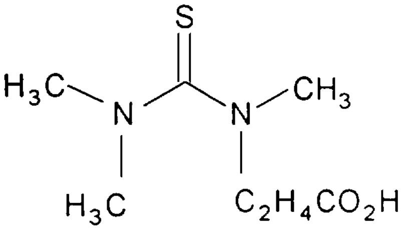


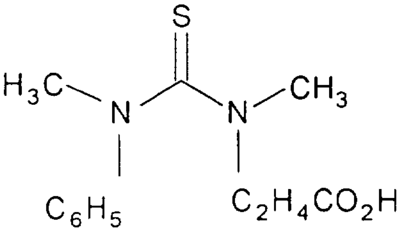


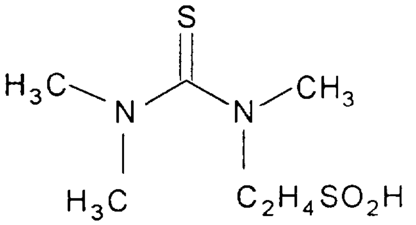


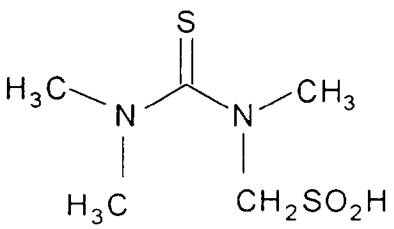










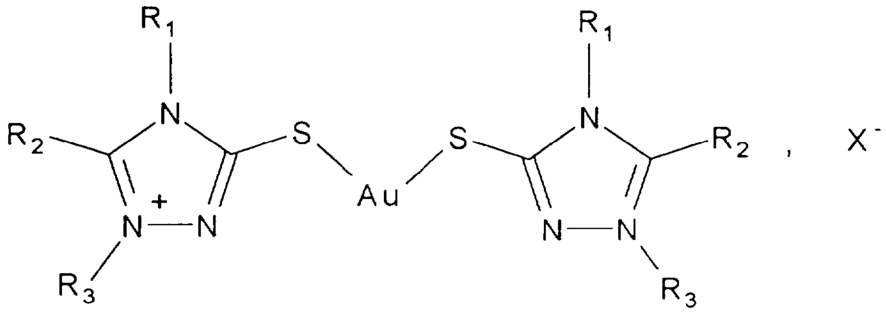


The thioureas of this invention may be synthesised using the method described in US patent 4,810,626. One method, for example, consists of reacting an aliphatic monoaminocarboxylic acid with a dialkylthiocarbamoyl halide.

The quantities of thioureas may be between 10^{-6} and 10^{-1} mmole per mole of silver halide and preferably between 10^{-4} and 10^{-2} mmole per mole of silver halide.

The gold (I) containing no labile sulphur atom of the present invention are compounds which are sufficiently stable to be used in the photographic emulsions without causing undesirable secondary reactions. In particular, in the scope of the present invention, the gold (I) compounds must not contain a labile sulphur atom which would react with the silver present in the medium so as to form silver sulphide, which would interfere with the chemical sensitisation of the emulsion. In addition, the gold (I) compounds of the present invention must be easily dispersable in the aqueous compositions used in photography. The gold (I) compounds which may be used within the scope of the invention were described in US patent 5 049 484 and 5 049 485.

According to one embodiment, these gold (I) compounds have the following structure:



in which R^1, R^2 and R^3 are each separately a hydrogen atom, or an alkyl, alkylene, alkyloxy, aryl or amino group, substituted or otherwise, and X is an anion.

The quantity of gold (I) compounds which may be added to a silver halide emulsion is between 10^{-6} and 10^{-1} mmol/mol of silver and preferably between 10^{-4} and 10^{-2} mmol/mol of silver.

Although the quantity of each of the chemically sensitising compounds differs widely according to the conditions of use, the thioureas and gold (I) compounds are, according to the invention, such that the molar ratio between the quantity of sulphur contained in the thiourea and the quantity of gold (I) is between 1 and 4 and preferably 2 and 3.

The compounds described above may be used alone or in combination with conventional sensitising agents known for the chemical sensitisation of photographic emulsions.

The thioureas and gold (I) compounds of the invention may be added to the silver halide emulsion together or separately and at different stages of the sensitisation of the emulsion. The addition of these chemical sensitisers to the emulsion may be effected in the presence of a solvent for silver halides such as thioethers or thiocyanates.

The conditions for sensitising the silver halide grains, such as the pH, the pAg, the temperature, etc, are not particularly limited when the compounds described here are used. The pH is generally between 1 and 9, and generally between 5 and 7, and the pAg is generally between 5 and 12 and preferably between approximately 7 and 10. The silver halide grains may be sensitised at a temperature between approximately 30 and 90°C, and it is preferred to use a temperature between approximately 35 and 70°C. The silver halide emulsion can be spectrally sensitised with spectral sensitising dyes and in accordance with the chromating methods as described for example in Research Disclosure, December 1989, No 308119, Section IV (hereinafter referred to as Research Disclosure). These dyes may for example be cyanine, merocyanine, composite cyanine, composite merocyanine and hemioxodol dyes. The dyes which are particularly useful belong to the merocyanine class. These dyes contain, as a heterocyclic core, any core generally used in cyanine dyes.

Within the scope of the invention, the spectral sensitising dyes are added to the emulsion after the chemical sensitisation stage.

The emulsions of the present invention may be used in colour photographic products of different types, such as negative, positive or reversal photographic products.

According to the invention, the colour photographic products comprise, in a conventional manner, at least three elements which are respectively blue-, green- and red-sensitive and which supply respectively the yellow, magenta and cyan components of the subtractive synthesis of the colour image.

Colour photographic products generally comprise a support carrying at least one blue-sensitive silver halide emulsion layer with which a yellow dye forming coupler is associated, at least one green-sensitive silver halide emulsion layer with which a magenta dye forming coupler is associated, and at least one red-sensitive silver halide emulsion layer with which a cyan dye forming coupler is associated.

These products may contain other layers which are conventional in photographic products, such as spacing layers, filter layers, anti-halo layers and immobilisation layers. The support may be any suitable support used with photographic products. Conventional supports comprise polymer films, paper (including polymer-coated paper), glass and metal. Research Disclosure Section XVII supplies details concerning supports and auxiliary layers for photographic products.

The silver halide emulsions of the invention and other layers on the photographic products of this invention may contain, as a vehicle, hydrophilic colloids, used alone or in combination with other polymer substances (for example latexes). Suitable hydrophilic substances comprise natural substances such as proteins, protein derivatives, cellulose derivatives, for example cellulose esters, gelatin, for example gelatin treated with a base (cattle bone or tanned gelatin) or gelatin treated with an acid (pigskin gelatin), gelatin derivatives, for example acetylated gelatin, phthylated gelatin, etc, polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, collodion, agar-agar and albumin.

Surfactants may be incorporated in a layer of photographic emulsion or in another hydrophilic colloidal layer as a coating additive to prevent the accumulation of static charges, to improve the lubrication properties, to improve the dispersion of the emulsion, to prevent adhesion and to improve the photographic characteristics such as rapid access development, or increase in contrast or sensitisation.

The photographic emulsion of the present invention may contain dye image forming couplers, that is to say compounds capable of reacting with an oxidation product of an aromatic amine (generally a primary amine) to form a dye. Non-diffusible couplers containing a ballast group are desirable. It is possible to use either couplers with four equivalents or couplers with two equivalents. In addition, it is possible to use couplers enabling the colours to be corrected, or couplers releasing a development inhibiter in the course of development (referred to as a DIR coupler).

The photographic products of the invention may contain, inter alia, optical brighteners, anti-fogging compounds, surfactants, plasticisers, lubricants, hardening agents, stabilising agents, or absorption and/or diffusion agents as described in Sections V, VI, VIII, XI, XII and XVI of the above-mentioned Research Disclosure.
The methods of adding these various compounds and the coating and drying methods are described in Sections XIV and XV of the same Research Disclosure.

The products of the invention, after being exposed, undergo photographic processing to develop the latent silver image and a colour image, in the presence of a coupler, which, in certain cases, may be incorporated in the photographic product.

The photographic products are then washed and processed in a stabilising bath.

Development is effected by means of a reducing compound which makes it possible to transform the exposed silver halide grains into metallic silver grains. This reducing compound oxidises and its oxidised form reacts with the coupler to form a dye. These compounds are chosen from amongst the aromatic primary amines such as paraphenylene diamines, aminophenols, etc. These compounds may be used alone or in a mixture, or with auxiliary developers. This bath may in addition contain a stabiliser such as sulphites, a buffer such as carbonates, boric acid, borates or alkanolamines.

The following examples illustrate the invention and show that the emulsions according to the invention have improved sensitivity without any problem of desensitisation by the sensitiser.

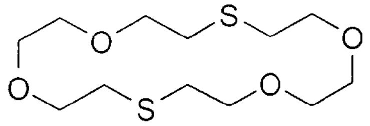
EXAMPLES

A. PRECIPITATION OF EMULSIONS

EXAMPLE 1 :Control Core/Shell emulsions Without silver halide Profile in the core (CSWP)

Using the double jet precipitation technique, an AgBrI cubo-octahedral emulsion of the core/shell type is prepared as follows:

In a 20 litre reacting vessel under strong agitation containing an aqueous solution of gelatin, NaBr and a growth modifier (M1) assisting the formation of cubo-octahedral grains, nucleation is effected at 60°C and at a pH of 5.1 by introducing, over 70 seconds by the double jet method, a 0.5 M solution of $AgNO_3$ and a 0.5 M solution of NaBr. The flow of $AgNO_3$ is constant and the flow of NaBr is adjusted so that the pAg remains equal to 9. (The pAg is the reciprocal of the logarithm of the silver ion concentration in the vessel.)



After a waiting period, growth is effected in order to precipitate the AgBrI core on the AgBr nuclei. To do this, in the solution maintained at 60°C, a solution of $AgNO_3$, 2M is introduced over 48 minutes using the double jet method with a flow of the type a + bt (a and b being constants and t the time in minutes) and the flow of halide containing NaBr, NaI, 2M is adjusted to 18% mole NaI so that the pAg is constant and equal to 9. 3.33 moles of AgBrI are precipitated.

The AgBr shell is then formed by introducing a solution of $AgNO_3$, 2M and a solution of NaBr, 2M at 60°C using the double jet method over 43 minutes. The flow of $AgNO_3$ is constant and the flow of NaBr is adjusted so that the pAg remains constant and equal to 9. 6.67 moles of AgBr are precipitated.

Finally the emulsion is washed at 40°C and at a pH of 3.8.

A control emulsion with cubo-octahedral grains is obtained, having a core of AgBrI with a uniform iodide content of 18% molar and an AgBr shell. The total iodide content of the grains is 3% molar. The size of this emulsion is determined by volumetric analysis of the silver halide grains, which is carried out by electrolytic reduction. Such a method is described by A Holland and A Feinerman in J. Applied Photo. Eng. 8, 165 (1982). This method makes it possible to obtain the volumetric distribution of the grains. From this distribution, it is possible to calculate the equivalent spherical diameter (ESD).

$$ESD = 2(3V/4\pi)^{1/3} \text{ in micrometres}$$

The emulsion obtained above has a grain size of approximately 1.2 µm.

EXAMPLE 2 :Core/Shell emulsions with Decreasing iodide Profile in the core (Invention CSDP)

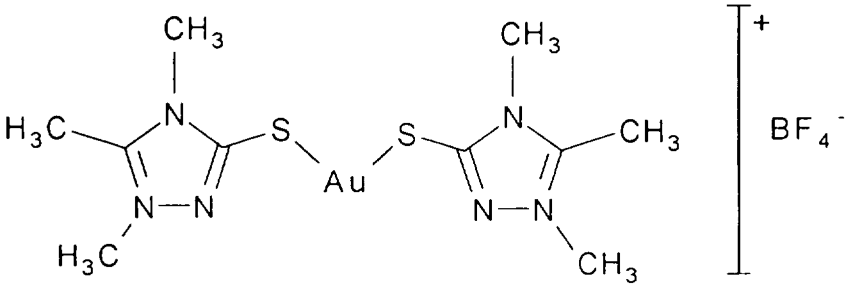
The operating method of Example 1 is repeated except, during the core precipitation step, the iodide concentration in the halide jet decreases linearly over time between an initial concentration of 36% and a final concentration of 0%. Conversely, the bromide concentration varies linearly between 64% at the start of the precipitation and 100% at the end of the precipitation of the core.

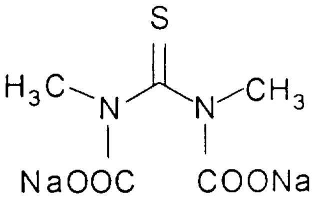
The emulsion thus obtained consists of silver halide grains of the core/shell type with an iodide content in the core which gradually reduces to a nil value at the interface. The core/shell molar ratio is 0.5 with an iodide content in the core of 18%, the total iodide content being 6%. The mean size of the grains is 1.16 µm.

B. SENSITISATION OF THE EMULSIONS

EXAMPLE 3

The emulsion of Example 2 is chemically sensitised by means of the gold (I) compound of formula (A) (0.73 mg/mol Ag) and the thiourea of formula (B) (0.83 mg/mol Ag) in the presence of sodium thiocyanate (150 mg/mol Ag) in accordance with the method described below.

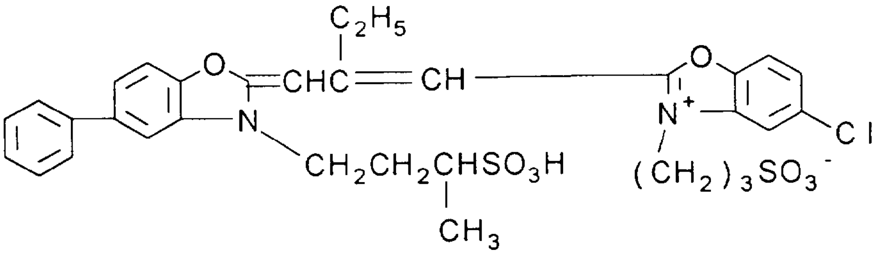

(A)


(B)

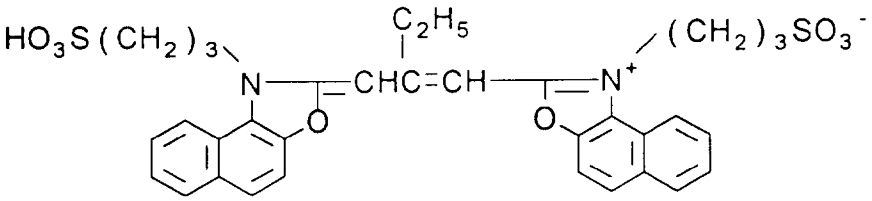
The chemical sensitisers are added to the emulsion maintained at 40°C, the pH being adjusted to 6.4 and the pAg to 8.25.

After introduction of the chemical sensitisers, the emulsion is maintained at 70°C for 25 min.

There is then added to this chemically sensitised emulsion maintained at 40°C, a mixture of spectral sensitising dyes of formula:



(I)

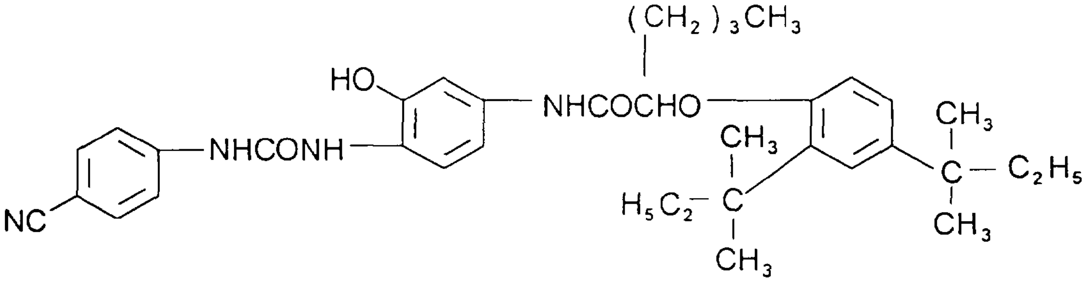


(II)

The molar ratio of the sensitising dyes (I)/(II) is 3/1.

The quantity of spectral sensitising dyes is such that the coverage of the grains is 55%, the coverage of the grain by the dye being defined as the surface area of the grain covered by the dye compared with the total surface of the grain, expressed as a percentage. This percentage is determined from the molecular dimension of the dye when it is adsorbed on the grain (the impression of the dye) and from the surface area of the grain.

The chemically and spectrally sensitised emulsion is coated on a cellulose triacetate support with a silver content of 0.807 g/m^2, a gelatin content of 3.23 g/m^2 and coupler (C1) with a content of 1.05 g/m^2. This emulsion layer is covered with a gelatin top layer (2.15 g/m^2) containing a hardening agent.



(C1)

The sample thus obtained is exposed by means of a Kodak sensitometer equipped with a lamp with a colour temperature of 5500°K for 1/100 seconds. The sensitometer is fitted with a Wratten 9 filter.

The sample is then developed using a standard Kodak Flexicolor C41® process which comprises the following steps:

- development using a chromogenic developer,
- bleaching,
- first washing,
- fixing,
- second washing,
- stabilisation, and
- drying.

The sensitivity of the sample is assessed by the formula:

$$\text{Sensitivity} = 100(1-\text{Log } E)$$

in which E represents the photographic exposure required to obtain a density D = Dmin + 0.4.

The desensitisation by the dye (Δ) is assessed by means of the difference between the intrinsic sensitivity of the emulsion and the sensitivity of the same emulsion spectrally sensitised to the optimum extent.

"Intrinsic sensitivity" means the sensitivity of the emulsion before spectral sensitisation. This intrinsic sensitivity is determined on a sample obtained from the emulsion chemically sensitised according to the method described above, which is exposed at 365 nm and processed using the Kodak Flexicolor C41^R process. The sensitivity as defined above is measured.

The granularity is the granularity normalised by the contrast, that is to say the granularity measured for a maximum contrast.

The contrast (γ) is determined by the slope of the sensitometric curve measured between Dmin + 0.4 and Dmin + 1.4.

EXAMPLE 4 (comp)

The CSDP emulsion of Example 2 is processed as described in Example 3 except that the chemical sensitisation is effected by means of sodium thiosulphate pentahydrate (0.70 mg/mol Ag) and potassium tetrachloroaurate (0.47 mg/mol Ag) in the presence of sodium thiocyanate (150 mg/mol Ag) and acetamidophenyltetramercaptol (50 mg/mol) which acts as an anti-fogging agent. After introduction of the chemical sensitisers, the emulsion is maintained at 70°C for 25 min.

The emulsion is then coated, exposed and developed according to the method of Example 3.

EXAMPLE 5 (comp)

The CSDP emulsion of Example 2 is processed as described in Example 3 except that the chemical sensitisation is effected by means of sodium thiosulphate pentahydrate (1.3 mg/mol Ag) and potassium tetrachloroaurate (0.43 mg/mol Ag).

After introduction of the chemical sensitisers, the emulsion is maintained at 70°C for 25 min.

The emulsion is then coated, exposed and developed according to the method of Example 3.

EXAMPLE 6 (comp)

The CSDP emulsion of Example 2 is processed as described in Example 3 except that the chemical sensitisation is effected by means of sodium thiosulphate pentahydrate (0.09 mg/mol Ag) and a gold (I) compound of formula $Na_3[Au(S_2O_3)_3]2H_2O$ (0.65 mg/mol Ag) in the presence of sodium thiocyanate (150 mg/mol Ag) and acetamidophenyltetramercaptol (50 mg/mol), which acts as an anti-fogging agent.

After introduction of the chemical sensitisers, the emulsion is maintained at 70°C for 25 min.

The emulsion is then coated, exposed and developed according to the method of Example 3.

In this case, the addition of sulphur is effected by means of the thiosulphate and the gold (I) compound, which contains labile sulphur atoms.

EXAMPLE 7 (comp)

The CSDP emulsion of Example 2 is processed as described in Example 3 except that the chemical sensitisation is effected by means of sodium thiosulphate pentahydrate (0.73 mg/mol Ag) and a gold (I) compound of formula $Na_3[Au(S_2O_3)_3]2H_2O$ (0.60 mg/mol Ag). In this case, the addition of sulphur is effected by means of the thiosulphate and the gold (I) compound, which contains labile sulphur atoms.

After introduction of the chemical sensitisers, the emulsion is maintained at 70°C for 25 min.

The emulsion is then coated, exposed and developed according to the method of Example 3.

EXAMPLE 8 (Control)

The CSWP emulsion of Example 1 is processed as described in Example 3 except that the chemical sensitisation is effected by means of sodium thiosulphate pentahydrate (0.39 mg/mol Ag) and a gold (I) compound of formula $Na_3[Au(S_2O_3)_3]2H_2O$ (2.88 mg/mol Ag) in the presence of sodium thiocyanate (200 mg/mol Ag).

The quantity of spectral sensitising dyes (S-1) used with such an emulsion is such that the coverage of the grains is 80%. After introduction of the sensitising dyes, the emulsion is maintained at 70°C for 20 min.

The emulsion is then coated, exposed and developed according to the method of Example 3.

EXAMPLE 9 (Control)

The CSWP emulsion of Example 1 is processed according to the method of Example 8 except that the chemical sensitisation is effected by means of the gold (I) compound of formula (A) (2.03 mg/mol Ag) and the thiourea of formula (B) (2.22 mg/mol Ag) in the presence of sodium thiocyanate (50 mg/mol Ag).

C. SENSITOMETRIC RESULTS

The sensitometric results of Examples 3 to 7 are set out in Table 1 below.

TABLE 1

	Dmin	Sens.	Δ	γ	1000.Granu
Ex.3 (Inv)	0.10	118	2	0.84	24
Ex.4 (Comp)	0.09	100	29	0.74	26
Ex.5 (Comp)	0.11	107	15	0.87	26
Ex.6 (Comp)	0.12	99	30	0.75	26
Ex.7 (Comp)	0.10	109	15	0.83	25

The results show that the sensitivity and the dye desensitisation of the emulsions of the present invention are improved compared with the same emulsion sensitised in a conventional manner.

In addition, with the emulsions of the present invention, it is no longer necessary to add an anti-fogging agent when the emulsion is sensitised in the presence of sodium thiocyanate, which is a compound much used in photography.

Examples 6 and 7 show that the use of a conventional sulphur sensitiser and a gold (I) compound containing labile sulphur atoms does not improve the dye desensitisation.

In addition, it should be noted that, when an emulsion is chemically sensitised by means of a thiourea and a gold (I) compound containing labile sulphur atoms, silver sulphide is formed in the emulsion, which amounts to sensitising the silver halide emulsion in a conventional manner.

The sensitometric results of Examples 8 and 9 are set out in Table 2 below.

TABLE 2

	Dmin	Sens.	Δ	γ	1000.Granu
Ex.8	0.07	100	0	1.10	20
Ex.9.	0.06	102	0	1.29	18

These results show that, when the silver halide emulsion is a core/shell emulsion without a halide profile in the core, there is no problem of dye desensitisation. In addition, it is clear from these results that the special chemical sensitisation of the invention does not significantly increase the sensitivity of such an emulsion.

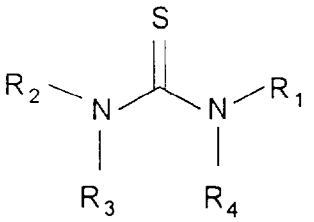
Claims

1. Photographic emulsion consisting of silver halide grains comprising a central zone (the core) consisting of at least two silver halides and an outer zone (the shell) having a silver halide composition different from the composition of the core, characterised in that

(1) the molar percentage of at least one of the silver halides of the core with respect to the total number of moles of silver halides in the core decreases between the centre of the grains and the core/shell interface,

(2) the chemical sensitisation of the grain is effected by means of a thiourea and a gold (I) compound not containing any labile sulphur atom.

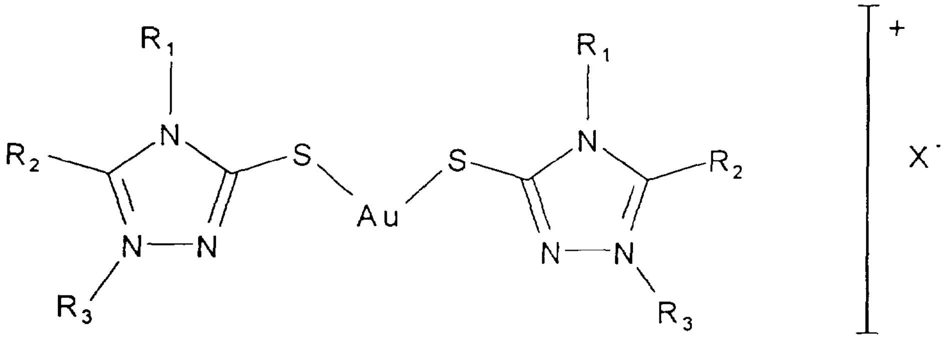
2. Photographic emulsion according to Claim 1, in which the thiourea corresponds to the formula



in which each R_1, R_2, R_3 and R_4 group represents either separately a hydrogen atom, an alkyl, cycloalkyl or carbocyclic or heterocyclic aryl radical, or an aralkyl radical, or R_2-R_3, R_3-R_4 or R_4-R_1 are combined to represent a heterocycle with 5 to 7 linkages, provided that at least one of the R_1, R_2, R_3 or R_4 groups contains or is a nucleophilic group of the carboxylic, sulphinic, sulphonic, hydroxamic, mercapto, sulphonamido or primary or secondary amino group.

3. Emulsion according to Claim 2, in which the nucleophilic groups are chosen from amongst $-COOH$, $-CH_2COOH$, $-C_2H_4COOH$, $-CH_2SO_2H$, $-CH_2SO_3H$, $-C_2H_4SO_2H$, $-C_2H_4NHOH$, $-C_2H_4SH$, $-(CH_2)_2NHSO_2CH_3$, $-C_2H_4NHCH_3$ and the corresponding acid salts.

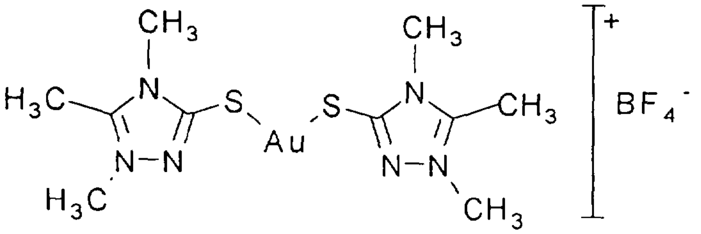
4. Emulsion according to Claim 1, in which the gold (I) compound corresponds to the formula



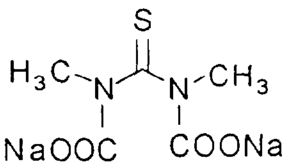
in which R^1, R^2 and R^3 are each separately a hydrogen atom, or an alkyl, alkylene, alkyloxy, aryl or amino group, substituted or otherwise, and X is an anion.

5. Photographic emulsion according to Claim 1, in which the quantities of thiourea and gold (I) compound are such that the molar ratio between the quantity of sulphur contained in the thiourea and the quantity of gold (I) compound is between 1 and 4 and preferably 2 and 3.

6. Photographic emulsion according to Claim 4, in which the gold (I) compound is



7. Photographic emulsion according to Claim 2, in which the thiourea is



8. Photographic emulsion according to Claim 1, in which difference between the molar percentage of each of the silver halides constituting the core between the centre of the grains and the core/shell interface is at least 10%.

9. Photographic emulsion according to Claim 1, in which the core consists of silver bromoiodide, silver chloroiodide or silver chlorobromoiodide.

10. Emulsion according to Claim 8, in which the core consists of silver bromoiodide and the molar percentage of silver iodide in the core, with respect to the total number of moles of silver halide in the core, decreases continuously between the centre of the grains and the core/shell interface and the shell does not contain any silver iodide.

11. Photographic emulsion according to Claim 8, in which the total molar percentage of silver iodide in the core is between 10 and 30%, with respect to the total number of moles of silver halide in the core.

12. Photographic emulsion according to Claim 8, in which the shell consists of several layers having different halide compositions.

13. Photographic emulsion according to Claim 8, in which the ratio of the number of moles of silver halide constituting the core to the number of moles of silver halide constituting the shell is between 0.2 and 2.

14. Emulsion according to Claim 8, in which the core of the grains consists of silver bromoiodide, the shell of silver bromide and the core/shell molar ratio is equal to 0.5.

15. Photographic emulsion according to Claim 14, in which the molar percentage of silver iodide in the core varies between 36% at the centre and 0% at the interface, with respect to the total number of moles of silver halide in the core.

16. Process for preparing a photographic emulsion comprising silver halide grains with a core/shell structure, which consists of precipitating successive zones having different halide compositions by introducing simultaneously a solution of silver salt and a solution of halide(s) of an alkali metal and chemically sensitising the grains obtained, the process characterised in that:

(1) at least during the precipitation of the central zone (the core), the halide solution contains at least two different halides, the concentrations of which in the halide solution vary practically linearly between predetermined initial values and final values which are equal to the concentrations of these halides in the halide solution at the start of the precipitation of the immediately adjacent zone of the shell, and in that

(2) the chemical sensitisation is effected by means of a thiourea and a gold (I) compound not containing any labile sulphur atome ;

the photographic emulsion and the spectral sensitising compounds being as defined in any one of the preceding claims.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 42 0278

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y A	EP-A-0 618 484 (KODAK) * page 4, line 57 - page 5, line 2; claims 1-14 * ---	1-6,8-16 7	G03C1/09 G03C1/035
D,Y A	US-A-5 049 485 (DEATON) * column 3; example 1 * * column 9; example S1 * * column 10; example S4; table II * -----	1-6,8-16 7	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 December 1995	Magrizos, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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