

19



Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number: **0 498 302 A1**

12

EUROPEAN PATENT APPLICATION

21 Application number: **92101544.2**

51 Int. Cl.⁵: **G03C 1/035, G03C 5/50**

22 Date of filing: **30.01.92**

30 Priority: **31.01.91 US 648262**

43 Date of publication of application:
12.08.92 Bulletin 92/33

84 Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IT LI LU MC
NL PT SE**

71 Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650-2201(US)

72 Inventor: **Chen, Benjamin Teh-Kung, c/o**
EASTMAN KODAK COMPANY
Patent Department, 343 State Street
Rochester, New York 14650-2201(US)
Inventor: **Reed, Kenneth Joseph, c/o**
EASTMAN KODAK COMPANY
Patent Department, 343 State Street
Rochester, New York 14650-2201(US)
Inventor: **Roussilhe, Jacques, c/o EASTMAN**
KODAK COMPANY
Patent Department, 343 State Street
Rochester, New York 14650-2201(US)

74 Representative: **Brandes, Jürgen, Dr.Rer.Nat.**
Wuesthoff & Wuesthoff, Patent- und
Rechtsanwälte, Schweigerstrasse 2
W-8000 München 90(DE)

54 **Silver halide emulsions for use in processing involving solution physical development.**

57 Formation of an image in a silver halide photographic material that includes a processing step in a developing solution wherein solution physical development occurs is improved by the incorporation in the photographic material of a silver halide emulsion layer comprising silver halide grain substrates having protrusions thereon, the protrusions having a different halide composition than the substrates such that solubility of the protrusions in the developing solution is greater than the solubility of the substrates in the developing solution.

EP 0 498 302 A1

This invention is related to photography. In particular, the invention is related to silver halide emulsions and the processing of photographic materials containing silver halide emulsions.

Silver halide is one of the most widely-used radiation-sensitive components in photographic materials. Silver halide is usually incorporated in photographic materials in the form of microscopic grains dispersed in a carrier medium, such as gelatin. This is referred to as a silver halide emulsion. Silver halide grains are known to exist in a wide variety of configurations or crystal structures. These include cubes, hexagonal or wurtzite structures, tetradecahedral structures, octahedral structures, and the like.

Silver halide grains having composite crystal structures are also known. For example, GB 1,027,146 describes a technique for forming composite silver halide grains. This reference teaches the formation of silver halide core or nuclei grains, which are then covered with one or more contiguous layers of silver halide having a different halide composition than the core. U.S. Patent 4,463,087 describes silver halide grains having epitaxially-grown silver salts thereon where epitaxial growth is controlled by the use of an adsorbed site director. U.S. Patent 4,814,264 describes a silver halide emulsion wherein at least 50 weight percent of the silver halide grains comprise a silver halide grain matrix having thereon 10 to 10,000 protrusions per square micrometer of grain matrix surface. The protrusions have an average projected diameter of up to 0.15 μm and a halogen composition different from that of the grain matrix. The emulsion is chemically and spectrally sensitized after formation is chemically and spectrally sensitized after formation of the protrusions. U.S. Patent 4,888,272 describes silver halide emulsions similar to those of U.S. 4,814,264, but the silver halide is chemically sensitized prior to formation of the protrusions.

Imaging methods utilizing radiation-sensitive silver halide emulsions generally utilize a developing step where silver halide grains that have been exposed to light (i.e., a latent image) are reduced to metallic silver during processing with a chemical developing agent. During this process, development may occur by direct chemical development, solution physical development, or both. In direct chemical development, a chemical developing agent reacts directly with silver halide in the grains carrying the latent image to reduce the silver ions to metallic silver. In solution physical development, silver ions from the silver halide grains pass into solution and subsequently diffuse to a nucleus (usually an exposed silver halide grain undergoing direct chemical development) where they are reduced to metallic silver. The occurrence of solution physical development is usually associated with processing solutions containing a developing agent along with one or more silver solvents, such as sulfite or thiocyanate.

The utilization during development processing of solution physical development can offer a number of advantages. For example, one typical utilization of solution physical development is in color reversal processing. Color reversal processing generally involves a first black and white development step followed by fogging of undeveloped silver halide and then a color development step. In such a process, dissolution of silver halide grains during the first development step leads to less silver halide per crystal available for the dye-forming development reaction that takes place during the color development step, thus leading to improved granularity performance of the material.

However, one problem associated with emulsions that are subjected to solution physical development during processing is that greater photographic speed is desired. Additionally, for reversal photographic materials, which as described above are usually subjected to solution physical development during processing, it is highly desirable to provide sharpening of the sensitometric curve in the toe region, which produces improved highlight portions of images recorded on such materials. It is toward these objectives that the present invention is directed.

According to the present invention, a method of forming an image in a silver halide photographic material that includes a processing step in a developing solution wherein solution physical development occurs is improved by the incorporation in the photographic material of a silver halide emulsion layer comprising silver halide grain substrates having protrusions thereon, the protrusions having a different halide composition than the substrates such that the solubility of the protrusions in the developing solution is greater than the solubility of the substrates in the developing solution.

The invention provides photographic materials that can be subjected to processing involving solution physical development, and that will exhibit improved speed. This is accomplished with little degradation of the material's granularity characteristics. The invention also provides photographic materials that exhibit general gamma increases as well as toe sharpening of the reversal sensitometric curve with little degradation of speed/fog position.

Solution physical development most often occurs in processes where conditions during development tend to favor the dissolution of silver halide, thus providing the necessary dissolved silver ions. Well-known compounds for promoting silver halide solubility in processing solutions (i.e., silver halide solvents) include sulfite salts (e.g., potassium sulfite) and thiocyanate salts (e.g., sodium thiocyanate). Bromide ion in the developer can affect the rate of solution of silver halide, with the rate of solution typically at a minimum at

bromide less than 1 g/l. The pH of the developing solution can also affect solution physical development, with the relative amount of solution physical development decreasing as pH increases. Also the polyethylene oxides and their derivatives can also increase the rate of solution physical development in certain iodide-containing emulsions where a silver halide solvent is present.

5 The substrate silver halide grains are of the type commonly employed in silver halide photography. They exhibit isomorphic face centered cubic rock salt type crystal structures. The substrate grains can comprised of silver bromide, silver chloride, silver chlorobromide, silver chloriodide, silver bromiodide, silver chlorobromiodide, or mixtures thereof. When iodide is present in the grains, it is limited to that which can be accommodated by the cubic crystal lattice. In a cubic silver bromide crystal lattice up to about 40
10 mole percent iodide can be incorporated, depending upon the temperature of precipitation. It is specifically contemplated to employ silver halide substrate grains containing below about 15 mole percent iodide. For ordinary photographic applications iodide concentrations are typically less than about 18 mole percent, and these are particularly preferred. The iodide distribution may be homogeneous (e.g., as resulting from run iodide precipitation) or discreet (e.g., core/shell emulsions, double and multiple structures, on emulsions
15 resulting from dump iodide precipitation). The substrate grains can include coarse, medium, or fine silver halide grains bounded predominantly by {100} or {111} crystal planes and can be regular or irregular in shape, including, for example, cubic and octahedral shapes. The grains can be cubic, octahedral, or tabular. In one preferred embodiment of the invention, the silver halide grain population is monodisperse having a coefficient of dispersion of less than 30% and more preferably less than 15%.

20 Typically the substrate grains are most conveniently prepared as a separate silver halide emulsion prior to the addition of the epitaxially deposited silver salt forming the overall, composite grain structure. The substrate grain emulsions can be prepared by a variety of techniques - e.g., single-jet, double-jet (including continuous removal techniques), accelerated flow rate, and interrupted precipitation techniques, as illustrated by Trivvelli and Smith, *The Photographic Journal*, Vol. LXXIX, May, 1939, pp. 330-338, T. H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapter 3, U.S. Patent 2,222,264,
25 German OLS No. 2,107,118, U.K. Patents 1,335,925, 1,430,465, and 1,469,480, U.S. Patents 3,650,757, 3,917,485, 3,979,213, Research Disclosure, Item 17643, Vol. 176, Dec. 1978, and Research Disclosure Item 22434, Vol. 225, January 1983. Research Disclosure and its predecessor, Product Licensing Index, are publications of Industrial Opportunities Ltd.; Homewell, Havant; Hampshire, P09 1EF, United Kingdom.

30 Modifying compounds can be present during substrate grain precipitation. Such compounds can be initially in the reaction vessel or can be added along with one or more of the salts according to conventional procedures. Modifying compounds, such as compounds of copper, thallium, lead, mercury, bismuth, cadmium, zinc, middle chalcogens (i.e., sulfur, selenium, and tellurium), gold, and Group VIII noble metals (e.g., iridium), can be present during silver halide precipitation, as illustrated by U.S. Patents 1,195,432,
35 1,951,933, 2,448,060, 2,628,167, 2,950,972, 3,488,709, 3,737,313, 3,772,031, 4,269,927, and Research Disclosure, Vol. 134, June 1975, Item 13452.

The formation of the protrusion is preferably carried out by adding a water-soluble silver salt and water-soluble halogen salts which correspond to the composition of the protrusions to be formed. The addition of the water-soluble silver salt for the formation is preferably carried out at such a speed that formation of a
40 separate nuclei population does not occur.

It is desired that the formation of the protrusions is carried out at a high silver potential level of at least preferably about +110 mV or more, more preferably about +120 mV to +500 mV, most preferably about +350 mV to +500 mV, although the level may vary somewhat depending on the halogen composition of the protrusions to be formed, the procedure for deposition such as double-jet or single-jet (with single jet,
45 the above preferred silver potentials represent the potentials at the end of the run), and/or the temperature during the formation, and/or the additives to be added during the formation, etc. In the present invention, the silver potential is measured by a saturated calomel electrode (SCE) hereinafter, unless specifically stated otherwise.

The temperature during the step of the formation of the protrusions is preferably low and is generally
50 below 80 °C, preferably below 65 °C, and more preferably below 30 °C, although this may vary somewhat depending on the other conditions during the formation.

Although the presence of a silver halide solvent during the formation of the protrusions is not preferable, a solvent can be used in an amount such that the protrusions are not intermingled with each other more than necessary.

55 The protrusions formed on the grain substrates of the present invention can be of any size and present of any coverage level. The protrusions will generally cover from 0.1 to 100% of the substrate surface area, and preferably at least 25% of the substrate surface area.

According to the present invention, the halide composition of the substrate grain and the protrusion are

chosen so that the aqueous solubility of the protrusion is greater than that of the substrate grain. Useful combinations of halide compositions for the substrate and protrusion are shown below:

substrate	protrusion
bromide	chloride
bromide	chlorobromide
chlorobromide	chloride
chloriodide	chloride
chloriodide	chlorobromide
bromiodide	chloride
bromiodide	chlorobromide
bromiodide	bromide
bromiodide	chlorobromiodide
iodide	chloride
iodide	bromide
iodide	chlorobromide
iodide	chloriodide
iodide	bromiodide
iodide	chlorobromiodide

Of these, the most preferred combinations are:

substrate	protrusion
bromide	chloride
bromide	chlorobromide
bromiodide	chloride
bromiodide	chlorobromide
bromiodide	bromide
bromiodide	chlorobromiodide
iodide	chloride
iodide	bromide
iodide	chlorobromiodide

The deposition of the protrusion onto the substrate grain can be directed or non-directed. By directed, it is meant that the growth of the protrusion is substantially confined to selected surface sites on the substrate grain. This may be accomplished through the use of an adsorbed site director (e.g., an aggregating spectral sensitizing dye,) on the substrate grain, as described in U.S. Patents 4,435,501 and 4,463,087, by use of iodide in the substrate grain as described in U.S. Patents 4,094,684 and 4,142,900, or by choosing nonisomorphic crystal lattice silver salts for deposition at selected sites on face centered cubic rock salt type crystal lattice silver halide substrate grains. The disclosures of U.S. Patents 4,094,684, 4,142,900, 4,435,501, and 4,463,087 are incorporated herein by reference.

Chemical sensitization can be undertaken prior to, during, or after deposition of the protrusion on the substrate grain or as a following step. For example, when silver thiocyanate is deposited on silver bromiodide, a large increase in sensitivity is realized merely by selective site deposition of the silver salt. Thus, further chemical sensitization steps of a conventional type may not be necessary to obtain photographic speed. On the other hand, an additional increment in speed can generally be obtained when further chemical sensitization is undertaken. The quantity of sensitizers can be reduced, if desired, where (1) protrusion deposition itself improves sensitivity or (2) sensitization is directed to protrusion deposition sites. Spectral sensitization is contemplated before, during, or following chemical sensitization.

Any conventional technique for chemical sensitization can be employed. Chemical sensitization may be undertaken based on the composition of the silver salt deposited or on the composition of the substrate grains.

The silver halide emulsions of the present invention can be chemically sensitized before, during, or after protrusion deposition with active gelatin, as illustrated by T. H. James, The Theory of the Photographic Process, 4th Ed., Macmillan, 1977, pp. 67-76, or with sulfur, selenium, tellurium, gold, platinum, palladium,

iridium, osmium, rhodium, rhenium, or phosphorus sensitizers or combinations of these sensitizers, such as at pAg levels of from 5 to 10, pH levels of from 5 to 8 and temperatures of from 30 to 80 ° C, as illustrated by Research Disclosure, Vol. 120, April 1974, Item 12008, Research Disclosure, Vol. 134, June 1975, Item 13452, U.S. Patents 1,623,499, 1,673,522, 2,399,083, 2,642,361, 3,297,447, 3,297,446, U.K. Patent 1,315,755, U.S. Patents 3,772,031, 3,761,267, 3,857,711, 3,565,633, 3,901,714 and 3,904,415 and U.K. Patent 1,396,696; chemical sensitization being optionally conducted in the presence of thiocyanate compounds, preferably in concentrations of from 2×10^{-3} to 2 mole percent, based on silver, as described in U.S. Patent 2,642,361; sulfur containing compounds of the type disclosed in U.S. Patents 2,521,926, 3,021,215, and 4,054,457. It is specifically contemplated to sensitize chemically in the presence of finish (chemical sensitization) modifiers--that is, compounds known to suppress fog and increase speed when present during chemical sensitization, such as azaindenes, azapyridazines, azapyrimidines, benzothiazolium salts, and sensitizers having one or more heterocyclic nuclei. Exemplary finish modifiers are described in U.S. Patents 2,131,038, 3,411,914, 3,554,757, 3,565,631, 3,901,714, Canadian Patent 778,723, and Duffin Photographic Emulsion Chemistry, Focal Press (1966), New York, pp. 138-143. Additionally or alternatively, the emulsions can be reduction sensitized--e.g., with hydrogen, as illustrated by U.S. Patents 3,891,446 and 3,984,249, by low pAg (e.g., less than 5) and/or high pH (e.g., greater than 8) treatment or through the use of reducing agents, such as stannous chloride, thiourea dioxide, polyamines and amineboranes, as illustrated by U.S. Patent 2,983,609, Research Disclosure, Vol. 136, August 1975, Item 13654, U.S. Patents 2,518,698, 2,739,060, 2,743,182, 2,743,183, 3,026,203, 3,361,564. Surface chemical sensitization, including sub-surface sensitization, illustrated by U.S. Patents 3,917,485 and 3,966,476, is specifically contemplated.

In addition to being chemically sensitized the silver halide emulsions of the present invention are preferably also spectrally sensitized. This may be done before, during, or after protrusion deposition. It is specifically contemplated to employ spectral sensitizing dyes that exhibit absorption maxima in the blue and minus blue--i.e., green and red, portions of the visible spectrum. In addition, for specialized applications, spectral sensitizing dyes can be employed which improve spectral response beyond the visible spectrum. For example, the use of infrared absorbing spectral sensitizers is specifically contemplated.

The silver halide emulsions of this invention can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines (i.e., tri-, tetra- and polynuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls and streptocyanines.

The cyanine spectral sensitizing dyes include, joined by a methine linkage, two basic heterocyclic nuclei, such as those derived from quinolinium, pyridinium, isoquinolinium, 3H-indolium, benz[e]indolium, oxazolium, oxazolinium, thiazolium, thiazolinium, selenazolium, selenazolinium, imidazolium, imidazolinium, benzoxazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthoxazolium, naphthothiazolium, naphthoselenazolium, dihydronaphthothiazolium, pyrylium, and imidazopyrazinium quaternary salts.

The merocyanine spectral sensitizing dyes include, joined by a double bond or methine linkage, a basic heterocyclic nucleus of the cyanine dye type and an acidic nucleus, such as can be derived from barbituric acid, 2-thiobarbituric acid, rhodanine, hydantoin, 2-thiohydantoin, 4-thiohydantoin, 2-pyrazolin-5-one, 2-isoxazolin-5-one, indan-1,3-dione, cyclohexane-1,3-dione, 1,3-dioxane-4,6-dione, pyrazolin-3,5-dione, pentane-2,4-dione, alkylsulfonylacetonitrile, malononitrile, isoquinolin-4-one, and chroman-2,4-dione.

One or more spectral sensitizing dyes may be used. Dyes with sensitizing maxima at wavelengths throughout the visible spectrum and with a great variety of spectral sensitivity curve shapes are known. The choice and relative proportions of dyes depends upon the region of the spectrum to which sensitivity is desired and upon the shape of the spectral sensitivity curve desired. Dyes with overlapping spectral sensitivity curves will often yield in combination a curve in which the sensitivity at each wavelength in the area of overlap is approximately equal to the sum of the sensitivities of the individual dyes. Thus, it is possible to use combinations of dyes with different maxima to achieve a spectral sensitivity curve with a maximum intermediate to the sensitizing maxima of the individual dyes.

Combinations of spectral sensitizing dyes can be used which result in supersensitization--that is, spectral sensitization that is greater in some spectral region than that from any concentration of one of the dyes alone or that which would result from the additive effect of the dyes. Supersensitization can be achieved with selected combinations of spectral sensitizing dyes and other addenda, such as stabilizers and antifoggants, development accelerators or inhibitors, coating aids, brighteners and antistatic agents. Any one of several mechanisms as well as compounds which can be responsible for supersensitization are discussed by Gilman, "Review of the Mechanisms of Supersensitization", Photographic Science and Engineering, Vol. 18, 1974, pp. 418-430.

Spectral sensitizing dyes also affect the emulsions in other ways. Spectral sensitizing dyes can also

function as antifoggants or stabilizers, development accelerators or inhibitors, and halogen acceptors or electron acceptors, as disclosed in U.S. Patents 2,131,038 and 3,930,860.

The emulsions used in the present invention may be used in color or black-and-white photographic materials. Such materials, which generally comprise a support having thereon at least one silver halide emulsion layer and, in the case of a color material, having associated therewith one or more dye-forming
5 couplers, may be prepared, exposed, and processed by techniques well-known in the art.

The silver halide emulsions used in the practice of the invention may be advantageously stabilized with stabilizers such as acetophenylmercaptotetrazole. This can be provide the emulsions with lower fog and better keeping characteristics.

10 The invention is further described in the following examples.

Emulsion A

A 20 liter kettle was charged with 4.0 liters of DW, 60 g/l of deionized gelatin and brought to 40° C. An
15 antifoaming agent and a thioether ripener were added before adjusting vAg to 0 mV with NaBr solution. A stable population of AgBr microcrystals was nucleated by flowing 0.1035 moles of AgNO₃ and NaBr via a double jet method over a time period of 3.0 minutes using 0.5 M/l reagents. The excess bromide was maintained such as to give a vAg = 0 mV at a temperature of 40° C. This nucleation was followed by a growth period lasting 69 minutes in which the following reagents - AgNO₃ (1.5 m/l), NaBr (1.455 M/l), KI
20 (0.045 M/l) - were introduced via an accelerated double jet technique while the temperature and vAg were maintained at 40° C and 0 mV respectively. The emulsion was then washed by an ordinary flocculation method. The final emulsion had an octahedral shape, edge length = 0.72 micron, and bulk iodide of 3 percent.

Emulsion B

A 20 liter kettle is charged with 6.6 liters of DW, 34 g/l of phthalated deionized gelatin, and brought to
70° C. An anti-foaming agent a thioether ripener were added before adjusting vAg to 50 mV with NaBr solution. A stable population of AgBr microcrystals is nucleated by flowing 0.075 moles of AgNO₃ and a
30 mixed solution of NaBr and KI via a double jet method over a time period of 2.0 minutes using 0.3 M/l AgNO₃ and a mixed solution of NaBr (0.28 M/l) and KI (0.015 M/l). The salt excess is maintained such as to give a vAg = 50 mV at a temperature of 70° C.

This nucleation is followed by an initial growth period lasting 45 minutes in which the following reagents
- AgNO₃ (1.5 M/l), mixed solution of NaBr (1.425 M/l) and KI (0.075 M/l) - were introduced via an
35 accelerated double jet technique while the temperature and vAg were maintained at 70° C and 50mV respectively. This initial growth segment is followed by a second growth segment lasting 20 minutes in which the following reagents - AgNO₃ (1.5 M/l and NaBr (1.5 M/l) - were introduced via the same technique as above with the temperature and vAg maintained at the same values as above. An iridium dopant is added during the growth stages. The emulsion is then washed by an ordinary flocculation method. The final
40 emulsion has an octahedral shape, edge length = 0.75 micron, and bulk iodide of 3.7 percent.

Emulsion C

A 20 liter kettle was charged with 4.0 liters of distilled water, 60 g/l of phthalated deionized gelatin, and
45 brought to 40° C. An antifoaming agent and a thioether ripener were added before adjusting vAg to 0 mV with NaBr solution. A stable population of AgBr microcrystals was was nucleated by flowing 0.122 moles of AgNO₃ and NaBr via a double jet method over a time period of 2.0 minutes using 0.5 M/l reagents. The excess bromide was maintained such as to give a vAg = 0 mV at a temperature of 40° C.

This nucleation was followed by a hold period of 2 minutes. This hold period was followed by an initial
50 growth period lasting 42 minutes in which AgNO₃ (2 M/l), NaBr (2 M/l) and KI (2.0 M/l) were introduced via a double jet method such as to produce an iodide profile within the precipitated phase while the temperature and vAg were maintained at the same values as above. A final growth segment was precipitated lasting 38 minutes in which AgNO₃ (2.0 M/l) and NaBr (2.0 M/l) were introduced via a double jet method while the temperature and vAg were maintained at the same values as above. The emulsion was
55 then washed by an ordinary flocculation method. The final emulsion had an octahedral shape, edge length = 0.67 micron, and bulk iodide of 3%.

Emulsion D

An 18 liter vessel was charged with 5.2 liters of distilled water, 2 g/l of gelatin, and 6.4 g/l of NaBr (pBr=1.3), and brought to 40°C. A stable population of AgBr microcrystals was nucleated by flowing 0.0284 moles of AgNO₃ as a single jet over a time period of 1.5 minutes using 0.25 N silver nitrate at 70°C.

This nucleation was followed by a growth period lasting 40 minutes in which 2.0M AgNO₃ and 2.75M NaBr were introduced by an accelerated double jet technique while the pBr was maintained 1.5 and the temperature at 70°C. 6.38 moles of AgX were precipitated.

This growth was followed by an addition of 1.75 moles of NaBr followed by the addition of 0.72 moles of AgI.

A subsequent growth segment lasting 17 minutes precipitated 3.6 moles of silver halide at 70°C. The kettle environment was changed to a pBr of 2.4 and a final 10 minute growth precipitated 0.46 moles under these conditions.

The emulsion was washed by an ordinary flocculation method. The emulsion had a tabular shape 1.44 x 0.107 μm with a bulk iodide of 6%.

15 Example 1

Emulsion A was sensitized with 800 mg/mole sodium thiocyanate, 2.67 mg/mole tetrachloroaurate, 4 mg/mole sodium thiosulfate, heated for 20 minutes at 70°C and dyed at 0.39 mmoles of dye D-1 per silver mole.

20 Example 2

The chemical sensitization was the same as example 1 except that a protrusion deposition was performed. 0.18 moles of sensitized emulsion was melted at 40°C and the vAg was adjusted with 0.01 M AgNO₃ to 140 mV. Then NaCl was added to the extent of 7.8 mole % of the total host emulsion. Finally 0.1 M/l AgNO₃ was run in over a period of 20 minutes such that a total of 6% was added relative to the amount of host emulsion. This emulsion was dyed with 0.39 mmole of dye D-1 per silver mole as in example 1.

30 Example 3

Emulsion B was sensitized with 75 mg/mole sodium thiocyanate, 4.25 mg/mole tetrachloroaurate, 8.5 mg/mole sodium thiosulfate, heated for 20 minutes at 70°C and dyed at 0.34 mmoles dye D-1 per silver mole.

35 Example 4

The chemically-sensitized emulsion described in Example 3 (without the dye) was then subjected to a 6% AgCl deposition with subsequent dyeing at 0.34 mmoles per silver mole of dye D-1 in exactly the same manner as Example 2.

40 Example 5

The Example 3 procedure was followed, only after the final dye addition, 80 mg/mole of acetamido phenylmercaptotetrazole was added to the melt.

45 Example 6

The Example 4 procedure was followed, only 12% AgCl was deposited (14% NaCl was added and the deposition featured 0.02 M AgNO₃). Finally, 80 mg/mole of acetamido phenylmercaptotetrazole was added to the melt.

Example 7

Emulsions C was sensitized with 50 mg/mole sodium thiocyanate, of 0.45 mmoles/Ag mole dye D-1, 2.77 mg/Ag mole tetrachloroaurate, 5.55 mg/Ag mole sodium thiosulfate, 5 mg/Ag mole of a benzothiazolium finish-modifier, and heated for 10 minutes at 70°C. In these examples, the dye was therefore present at the time of the deposition.

Example 8

A 6% AgCl deposition on Emulsion b was performed using the procedure outlined in Example 2, only since the dye was present at the time of epitaxy, no further dye was added.

5

Example 9

To one mole of emulsion D was added 100 mg of NaSCN, 1.67 mg of potassium tetrachloroaurate, 5.5 mg of sodium thiosulfate, 1.0 millimole of dye D-1 and 0.38 mmole of dye D-2. This was then heated for 15 minutes at 60° C.

10

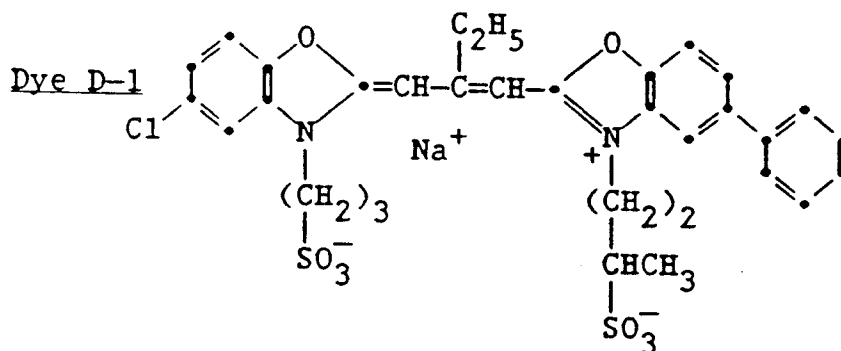
Example 10

The spectrochemically sensitized emulsion in example 9 was adjusted to 140 mV with 0.1M AgNO₃ and 0.006M KI. An excess of 10.1% NaCl was added based on the moles of host emulsion. 8 mole percent AgCl was precipitated onto this host over a period of 12 minutes using 0.3M AgNO₃.

15

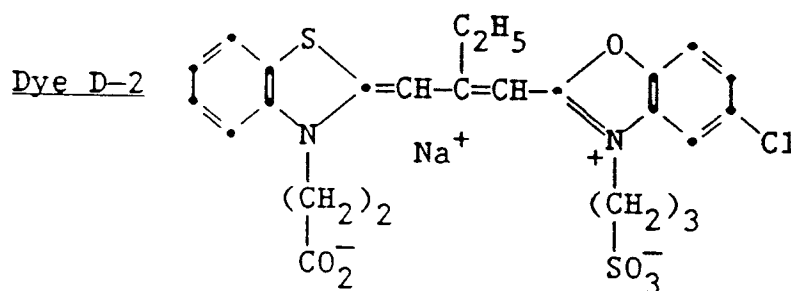
The emulsions were coated at 8.07 mg/dm² of silver halide, 23.68 mg/dm² of gelatin, 16.15 mg/dm² of coupler C-1, with a 23.68 mg/dm² gelatin overcoat on an acetate support with gel pad. The gelatin layers were hardened with 1.55% bis(vinylsulfonyl methane) hardener.

20



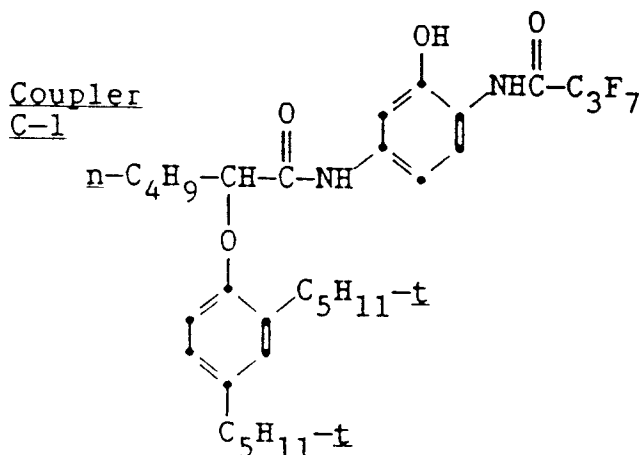
25

30



35

40



45

50

55

The coated materials were exposed for 1/100 sec at 5500K equivalent color temperature filtered with a Wratten 9 and 1.246 neutral density filter, and processed in well-known standard Kodak E-6 ® color reversal processing, which utilizes 65.8 g/l potassium sulfite and 0.995 g/l sodium thiocyanate in the first developer to stimulate solution physical development. For comparison, identical materials were exposed and processed in Kodak C-41 ® color negative processing, in which essentially no solution physical development occurs.

The results in the following table clearly demonstrate the difference in behavior of the protrusion-containing emulsions in the reversal process involving solution physical development compared to the negative process.

TABLE 1

Example	Emulsion	NEGATIVE PROCESS		REVERSAL PROCESS	
		Log Threshold Speed Δ	Gamma	Log Threshold Speed Δ	Gamma
1	A	-	2.17	-	-1.74
2	A	0	1.93	+ .20	-2.00
3	B	-	2.21	-	-2.00
4	B	+ .14	1.63	+ .20	-2.32
5	B	-	2.49	-	-2.185
6	B	.06	2.07	+ .25	-2.465
7	B	-	2.10	-	-1.92
8	B	+ .19	1.85	+ .25	-2.07
9	D	-	1.36	-	-1.64
10	D	-18	1.50	-15	-2.03

The addition of protrusions provided gamma increases in the reversal process compared to gamma decreases in the negative process, and greater speed increases (or smaller speed decreases) in the reversal process compared to the negative process.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. In a method of forming an image in a photographic material comprising a support having thereon at least one silver halide emulsion layer, said method including a processing step in a developing solution wherein solution physical development occurs, the improvement wherein the silver halide emulsion layer comprises silver halide grain substrates having protrusions thereon, the protrusions having a different halide composition than the substrates such that the solubility of the protrusions in said developing solution is greater than the solubility of the substrates in said developing solution.
2. A method according to claim 1 wherein said process is a reversal process.
3. A method according to claim 2 wherein said processing step in a developing solution wherein solution physical development occurs is the first development step of said reversal process.
4. A method according to any of claims 1-3 wherein the halide composition of the substrate and protrusion is selected from the following pairs:

substrate	protrusion
bromide	chloride
bromide	chlorobromide
chlorobromide	chloride
chloriodide	chloride
chloriodide	chlorobromide
bromiodide	chloride
bromiodide	chlorobromide
bromiodide	bromide
bromiodide	chlorobromiodide
iodide	chloride
iodide	bromide
iodide	chlorobromide
iodide	chloriodide
iodide	bromiodide
iodide	chlorobromiodide

5

10

15

20

5. A method according to claim 4 wherein the halide composition of the substrate and protrusion is selected from the following pairs:

substrate	protrusion
bromide	chloride
bromide	chlorobromide
bromiodide	chloride
bromiodide	chlorobromide
bromiodide	bromide
bromiodide	chlorobromiodide
iodide	chloride
iodide	bromide
iodide	chlorobromiodide

25

30

35

6. A method according to any of claims 1-3 wherein said developing solution includes at least one of: sulfite ion or thiocyanate ion

40

7. A method according to any of claims 1-3 wherein the silver halide grain substrates are octahedral, cubo/octahedral, tabular, or cubic grains.

8. A method according to any of claims 1-3 wherein said substrates comprise less than 18% iodide, said iodide distributed in the substrate homogeneously or discreetly.

45

9. A method according to any of claims 1-3 wherein said substrates have sensitization sites covered by said protrusions.

10. A method according to any of claims 1-3 wherein at least 25 weight percent of silver halide grains in said emulsion have at least 0.1 percent of their surface covered by protrusions.

50

11. A reversal photographic material comprising a support having thereon at least one silver halide emulsion layer comprising silver halide grain substrates having protrusions thereon, the protrusions having a different halide composition than the substrates such that the solubility of the protrusions is greater than the solubility of the substrates.

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 1544

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.5)
D,A	US-A-4 888 272 (S. KISHIDA ET AL.) * claims * ---	1-11	G03C1/035 G03C5/50
D,A	US-A-4 814 264 (S. KISHIDA ET AL.) * claims, abstract, figures * ---	1-11	
A	EASTMAN KODAK COMPANY 'Black-and-White Processing Using KODAK Chemicals' 1985 , KODAK , NEW YORK, US * page 7, left column, line 30 - line 48 * -----	1-11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 MAY 1992	Examiner BUSCHA A. J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P0401)