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(54) **Process of preparing a monodispersed tabular silver halide grain emulsion**

Verfahren zur Herstellung von Emulsionen mit monodispersen Silberhalogenidtafelkörnen

Procédé de préparation d'un émulsion à grain tabulaire à l'halugénure d'argent monodisperse

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EP-A- 0 518 066 **US-A- 5 258 276**

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a process for preparing monodispersed tabular silver halide emulsion useful in light-sensitive photographic materials.

BACKGROUND OF THE INVENTION

[0002] Tabular silver halide grains, their preparation and use in photographic emulsions, are widely known. Tabular silver halide grains are crystals possessing two major faces that are substantially parallel. They have been extensively studied in the literature since photographic emulsions containing these grains appeared to offer some significant advantages over photographic emulsions containing round or globular or cubic grains. Tabular grains usually have polygonal (i.e., triangular or hexagonal) parallel crystal faces, each of which is usually greater than any other crystal face of the grain and are conventionally defined by their aspect ratio (namely AR) which is the ratio of the diameter of the grain to the thickness. Tabular grains offer significant technical and commercial advantages apparent to those skilled in the art. The most important advantages of tabular grains can be summarized as follows:

1. Tabular grains have a high surface to volume ratio so that a large amount of sensitizing dye can be adsorbed on the surface, and a high development rate and covering power can be obtained.
2. Tabular grains tend to lie parallel to the surface of the support base when emulsions containing them are coated and dried so that it is possible to reduce the thickness of the coated layer and accordingly to increase sharpness.
3. When a sensitizing dye is added to tabular grains, the extinction coefficient of the dye is greater than the extinction coefficient for the indirect transition of the silver halide so that in X-ray materials it is possible to obtain a relevant reduction in cross-over, thereby preventing any worsening of quality.
4. Tabular grains are usually very thin and so the amount of radiation absorbed per grain (proportional to the thickness) is low and there is low fogging due to natural radiation on aging.
5. Tabular grains show low light scattering and the images obtained from them have a high resolution.

[0003] In spite of all these advantages, tabular grain emulsions tend toward more dispersed grain populations than can be achieved in the preparation of conventional silver halide grains. This has been a concern since reducing grain dispersion or variation in grain size within an emulsion is a basic approach to increasing the imaging consistency of the emulsion. Grain dispersion concern relates to (1) the presence of non-conforming grain shapes, such as, for example, octahedral, cubic, or rod shapes and (2) to the variance of the grain size distribution. Non-conforming grains can interact differently with light and exhibit some undesirable properties. For example, faces of non-tabular grains are randomly oriented with respect to the support base, octahedral grains exhibit lower covering power and greater thickness, and rod grains can self develop in the absence of light, thereby increasing fog.

[0004] On the other hand, even a population of grains having a common shape can have a high dispersion in terms of grain size distribution. A common method for quantifying grain size distribution is to extract a sample of individual grains, calculate the corresponding diameter for each grain ($D_{1\rightarrow n,}$ wherein n is the number of extracted grains), calculate the average diameter ($Dm=\Sigma_{1\rightarrow n}D/n$), calculate the standard deviation of the grain population diameters (S), divide the standard deviation (S) by the average diameter (Dm) and multiply by 100, thereby obtaining the coefficient of variation (COV) of the grain population as a percentage.

[0005] It is known in the art that emulsions having a low COV (e.g., lower than 30%) can be optimally sensitized as a result of their similar surface areas, have low light scattering and therefore a high image sharpness as a result of the reduction of the finer grain population, have a low granularity as a result of the reduction of the larger grain population, and have a higher contrast.

[0006] Accordingly, various solutions have been proposed in the art to reduce the COV of tabular grain emulsions. Monodispersed tabular grain emulsions and methods to prepare them are disclosed for example in US 4,150,994, US 4,184,877, US 4,184,878, US 4,301,241, US, 4,386,156, US 4,400,463, US 4,425,426, US 4,797,354, US, 4,977,074, US 4,945,037, US 5,215,879, US 4,798,775, S 4,722,886, US 4,801,522, US 5,013,641, US 5,254,453, EP 503,700, EP 569,075, EP 577,886, EP 588,338, EP 600,753. These patents and patent applications attempt to obtain monodispersed tabular grains by controlling various parameters during nucleation and ripening of the silver halide emulsion. The most important nucleation conditions to be kept under control for obtaining monodispersed tabular grain emulsions are temperature, gelatin concentration, addition rates of silver salt aqueous solution, addition rates of alkali halide aqueous solution, stirring rate, iodide content in the alkali halide solution, amount of silver halide solvent, pH of the dispersing medium, concentration of bromide ions in the reaction vessel, molecular weight of dispersing medium, iodide content in the vessel at the start, and the like. Similarly, the most important ripening conditions are temperature, dispersing

medium concentration, silver halide solvent concentration, pBr, and addition rates of silver salt aqueous solution.

[0007] Maternaghan in US 4,150,994, US 4,184,877, and US 4,184,878 describes the formation of thick monodispersed tabular grain emulsion from seed crystals having at least 90%mol of iodide.

[0008] Saito in US 4,301,241 describes a process for forming a silver halide emulsion containing multiple twin crystal grains and a narrow grain size distribution. The examples report multiple twin crystal grain silver bromoiodide emulsions having an average grain size from 0.86 to 1.023 μm and a coefficient of variation of from 11.6% to 13.6%.

[0009] Mignot in US 4,386,156 describes silver bromide tabular grain emulsions having an aspect ratio of at least 8.5:1 and a COV of less than 30. The tabular grains described by Mignot are bounded by (100) crystal faces and are square or rectangular.

[0010] Abbot et al. in US 4,425,426 disclose a radiographic element comprising a tabular grain emulsion in which grains having thickness lower than 0.2 μm and average aspect ratio from 5:1 to 8:1 account for at least 50% of the total projected area. During precipitation of silver halide grains the rate of introduction of silver and halide salts is maintained below the threshold level at which the formation of new grain nuclei is favored in order to obtain relatively monodispersed thin tabular grains with COV lower than 30%.

[0011] Saitou et al. in US 4,797,354 disclose a silver halide emulsion comprising hexagonal tabular grains with an "adjacent edge ratio" of from 2/1 to 1/1 accounting for 70% to 100% of the projected area of all the grains, and further that said hexagonal tabular grains are monodisperse and have an average aspect ratio from 2.5:1 to 20:1. The term "adjacent edge ratio" is referred to as the ratio of the longest edge length to the shortest edge length of each hexagonal tabular grain. Accordingly, the definition of "adjacent edge ratio" is a measure of the hexagon regularity.

[0012] Saitou et al. US 4,977,074 disclose and claim a silver halide emulsion comprising substantially circular tabular grains with a "linear ratio" equal to or lower than 2/5 accounting for from 70% to 100% of the projected area of all the grains, and further that said circular tabular grains are monodispersed. The term "linear ratio" is defined as the ratio of the total length of the linear portion in the substantially circular tabular grain divided by the total length of the extrapolated hexagonal tabular grain. The lower the linear ratio value, the more circular the grain.

[0013] US 4,945,037 discloses a process to produce a tabular silver halide grain emulsion in which at least 60% of the total projected area is covered by tabular grains having a core portion and an outer portion, the iodide content of the core portion being from 7 mol% to the solid solution limit. The process is characterized by specific nucleating condition, that is, a gelatin concentration of from 0.1 to 20% by weight, an addition rate of silver and halide salts of from 6*10-4 to 2.9*10-1 mol/minute per liter, and a pBr value of from 1.0 to 2.5.

[0014] US 4,798,775 discloses a process to obtain monodispersed tabular grains comprising the steps of forming silver halide nuclei with a silver iodide content of from 0 to 5% in the mother liquor, by maintaining the pBr in the reaction vessel between 2.0 and -0.7 for at least the initial half of the nucleation time, ripening the nuclei formed in the nucleation step by maintaining the concentration of silver halide solvent from 10^{-4} to 5 moles per liter of mother liquor, and growing the seed grains by addition of silver and halide soluble salts or by addition of fine silver halide grains.

[0015] US 4,801,522 discloses a process to form tabular silver halide grains having a thickness of from 0.05 to 0.5 μm, average grain volume of from 0.05 to 1.0 μm^3 and a mean aspect ratio higher than 2:1 comprising the steps of adding silver nitrate to a reaction vessel comprising a bromide ion concentration of from 0.08 to 0.25 N (pBr= 1,1-0,6), adding ammonia solution to achieve 0.002 to 0.2N after at least 2% of the total silver has been added to the vessel, and adding silver and halide (Br or BrI) salts by balanced double jet.

[0016] US 4,722,886 describes a process to form a monodispersed tabular silver halide grain emulsion comprising the steps of adding silver nitrate to a reaction vessel comprising a bromide ion concentration of from 0.08 to 0.25 N to form silver halide nuclei, adding a basic silver halide solvent (e.g., ammonia solution) to achieve 0.02 to 0.2N after at least 2% by weight of the total silver has been added to the vessel, stopping silver nitrate addition for a time period of from 0.5 to 60 minutes at a Br ion concentration of from 0.005 to 0.05 N, neutralizing at least part of the present solvent, and growing the formed silver halide grains by adding silver and halide (Br or BrI) soluble salts by balanced double jet.

[0017] US 5,013,641 describes a process of forming monodispersed silver halide emulsions comprising (a) combining silver nitrate and sodium bromide in gelatin solution, (b) adding NaOH to adjust the pH to greater than 9, (c) allowing digestion of the nucleated particles, (d) adjusting the pH to below 7 by acid addition, and (e) adding silver nitrate and sodium halide to grow the nucleated particles.

[0018] US 5,254,453 discloses a process for forming monodispersed silver bromide or bromoiodide grains with COV lower than 25%, thickness of from 0.05 to 0.5 μm, mean aspect ratio higher than 2, and diameter of from 0.2 to 3 μm comprising the following steps: (a) digesting the nucleated particles in a basic silver halide solvent at a concentration of from 0.0015 to 0.015 N and (b) neutralizing said basic solvent after digestion and before growing.

[0019] EP 503,700 discloses a process of forming monodispersed silver bromide or bromoiodide tabular emulsions with a COV lower than or equal to 15% characterized by the addition of an aminoazaindene at any stage of the preparation, but before 50% of the total silver halide is precipitated.

[0020] EP 569,075 discloses a process of forming monodispersed silver bromide or bromoiodide tabular emulsions with average aspect ratio higher than 2, an average thickness of from 0.15 and 0.30 μm, and a COV of from 0.15 to 0.45

wherein the process is characterized by (a) providing a gelatin/bromide solution at a pBr of from 1.0 to 2.0, (b) nucleating by consuming less than 10% of the total silver nitrate used, (c) a first double jet growth (consuming at least 10% of the total silver nitrate used) at a pBr value of from 1.0 and 2.5, and (d) a second double jet growth (consuming at least 40% of the total silver nitrate used) at a pBr value higher than 2.7

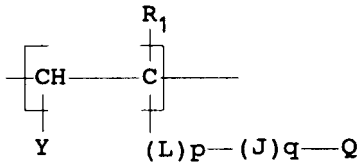
[0021] EP 577,886 describes a process of forming monodispersed silver bromide or bromoiodide tabular emulsions with average aspect ratio of from 2 to 8, and a COV lower than 30. The process comprises the following steps: (a) performing a nucleation step by balanced double jet by precipitating at most 5% of the total silver halide, (b) ripening the formed nuclei, (c) performing at least one growing step by balanced double jet at pBr lower than 2, (d) ultrafiltrating the reaction mixture during the precipitation steps with an ultrafiltration flux equal to or greater than the sum of the flow rates of the silver and halide ion solutions.

[0022] Grzeskowiak, in US 5,028,521, discloses a process for preparing monodispersed tabular silver halide grain emulsions having an aspect ratio from 3:1 to 12:1 consisting in (a) preparing a bromide/gelatin mixture at pBr of from 0.7 to 1.0, (b) adding silver nitrate and further halide to maintain excess of bromide, (c) adding ammonia to achieve at least 0.05N after at least 20% by weight of the total silver is added, (d) adding further silver nitrate and halide by balanced double jet, by maintaining an ammonia concentration of at least 0.03N.

[0023] EP 588,338 describes a process characterized by specific nucleating condition, that comprises (a) adding from 0.30 to 9.0% by weight of the total amount of soluble silver salt to a vessel containing 0.08 to 0.25 M aqueous soluble halide salt (b) adding a solution of ammoniacal base when 0.30 to 9% by weight of the total amount of soluble silver salt has been added, (c) adding soluble silver salt to obtain growth pBr of from 1.3 to 2.3, and (d) adding soluble silver and halide salts to grow tabular grains

[0024] Other recent patents and patents applications attempt to obtain monodispersed silver halide tabular emulsion by adding a specific polymeric surfactant during nucleation and/or ripening.

[0025] US 5,215,879 describes a process to obtain monodispersed silver halide emulsions in which a polymer having the following formula is added during the ripening step.



wherein Y is H or carboxyl group; R_1 is H, a halogen atom, an alkyl group or CH_2COOM, where M is H or an alkali metal atom; L is -CONH-, -NHCO-, -COO-, OCO-, -CO- or -O-; J is an alkylene group, an arylene group, or $(CH_2CH_2O)m(CH_2)n$-, where m is an integer from 0 to 40 and n is an integer from 0 to 4; and Q is H, alkyl group, a N-containing heterocyclic group, a quaternary ammonium group, a dialkylamino group, -OM, $-NH_2$, $-SO_3M$, $-O-PO_3M_2$ and -CO-R.

[0026] EP 513,722, EP 513,723, EP 513,724, and EP 513,725 describe a process in which monodispersed tabular emulsions are obtained by adding, during nucleation, polymers having the following general formulas (1) to (4), respectively.

LAO-HAO-LAO (1)

HAO-LAO-HAO (2)

HAO-LAO-L-LAO-HAO (3)

LAO-HAO-L-HAO-LAO (4)

wherein LAO is a lipophilic alkylene oxide block unit, HAO is a hydrophilic alkylene oxide block unit, and L is a trivalent or tetravalent organic group comprising nitrogen.

SUMMARY OF THE INVENTION

[0027] The present invention relates to a process for preparing monodispersed tabular silver halide grain emulsions, said process comprising the following steps:

(a) forming a population of silver halide nuclei in a dispersing medium,
(b) ripening said population of silver halide nuclei, and
(c) growing said population of silver halide nuclei to form tabular silver halide grains,

characterized in that a polyalkylene oxide-polyalkylsiloxane copolymer is added during at least one of said steps (a), (b), and (c).

[0028] The presence of the polyalkylene oxide-polyalkylsiloxane copolymer during the formation process of tabular silver halide grains enable the growth of tabular silver halide grain emulsions having a reduced amount of non-conforming grains and a lower coefficient of variation (COV).

DETAILED DESCRIPTION OF THE INVENTION

[0029] The present invention relates to a process for preparing monodispersed tabular silver halide grain emulsions, said process comprising the following steps:

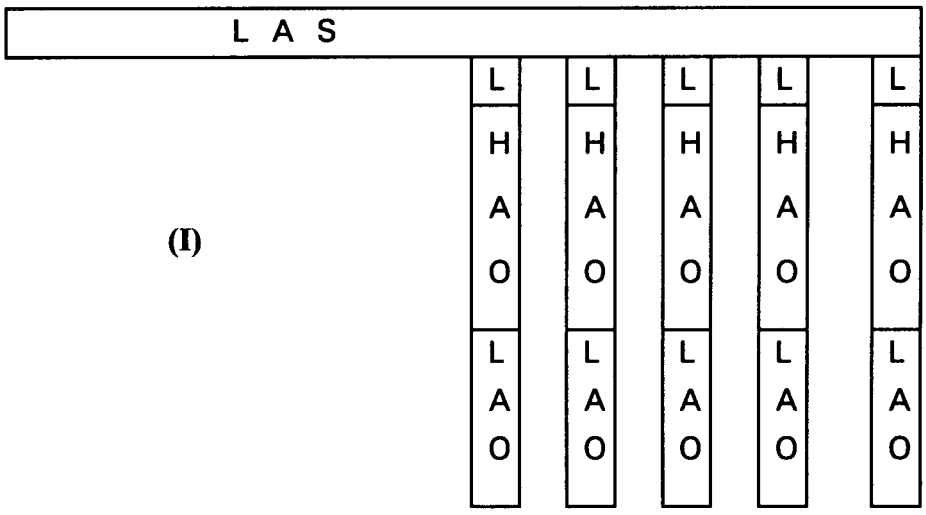
(a) forming a population of silver halide nuclei in a dispersing medium,
(b) ripening said population of silver halide nuclei, and
(c) growing said population of silver halide nuclei to form tabular silver halide grains,

characterized in that a polyalkylene oxide-polyalkylsiloxane copolymer is added during at least one of said steps (a), (b), and (c).

[0030] According to a more preferred embodiment of the present invention, the polyalkylene oxide-polyalkylsiloxane copolymer is added to the reaction vessel before the start of the nucleation step (a).

[0031] The polyalkylene oxide-polysiloxane copolymer of the present invention is a block, graft, or randomly copolymerized polymer having units in the polymer backbone chain(s) which are polyalkylene oxides and polyalkylsiloxane. The polymers must contain at least 10% of each of these types of units on a molar basis of the total polymer composition to be within this class. It is preferred that each of the two moieties comprise from 10 to 90 molar percent of the total polymer, preferably from 20 to 80 molar percent of the total polymer, and there may be additional moieties of up to 30 molar percent copolymerized therewith, as long as the required minimums for each moiety of the basic two moieties are present in the copolymer.

[0032] According to a first embodiment, the polyalkylene oxide-polyalkylsiloxane copolymer of the present invention can be represented by the following formula (I):

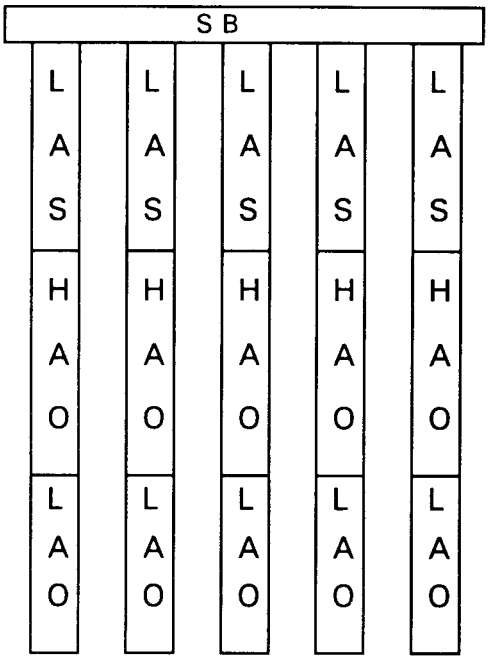


(I)

wherein LAS represents a lipophilic alkylene siloxane block unit, HAO represents a hydrophilic alkylene oxide block unit, LAO represents a terminal lipophilic alkylene oxide block unit, and L is a lipophilic hydrocarbon system.

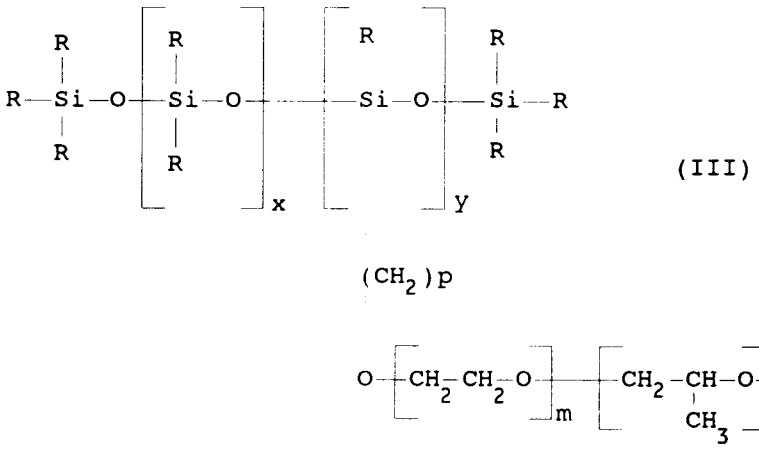
[0033] According to a second embodiment the polyalkylene oxide-polyalkylsiloxane copolymer of the present invention can be represented by the following formula (II):

(II)



wherein LAS represents a lipophilic alkylene siloxane block unit, HAO represents a hydrophilic alkylene oxide block unit, LAO represents a terminal lipophilic alkylene oxide block unit, and SB is a silicone backbone.

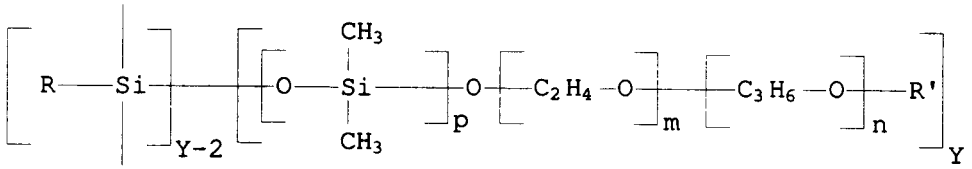
[0034] The polyalkylene oxide-polyalkylsiloxane copolymer according to formula (I) is a linear polyalkylsiloxane having polyalkylene oxide groups attached thereto through a short hydrocarbon chain which can also be represented by the following general formula (III):



(III)

wherein R is a methyl group, R' can be either hydrogen or a lower alkyl radical of from 1 to 4 carbon atoms, x is an integer from 0 to 100, y is an integer from 1 to 50, m is an integer from 1 to 50, n is an integer from 1 to 50, and p is an integer from 2 to 6.

[0035] The polyalkylene oxide-polyalkylsiloxane copolymer according to formula (II) is a branched polyalkylsiloxane in which the polyalkylene oxide block units are joined to a silicone backbone through an alkylsiloxane block unit, and can also be represented by the following general formula (IV):



(IV)

wherein R is a methyl group, R' can be either hydrogen or a lower alkyl radical of from 1 to 4 carbon atoms, y is an integer from 3 to 50, m is an integer from 1 to 50, n is an integer from 1 to 50, and p is an integer from 1 to 50.

[0036] Typical examples of polyalkylene oxide-polyalkylsiloxane copolymers according to the above formulae (I) and (IV) are listed in the following table A:

TABLE A

Compound	Formula	Ratio m/n	R'	Molecular Weight
Silwet™ L-720	IV	1:1	Butyl	12,000
Silwet™ L-7001	III	2:3	Methyl	20,000
Silwet™ L-7002	III	1:1	Butyl	8,000
Silwet™ L-7200	III	3:1	H	19,000
Silwet™ L-7210	III	1:5	H	13,000
Silwet™ L-7230	III	2:3	H	29,000

[0037] Silwet is a registered trademark of Union Carbide Chemicals and Plastics Company. The polyalkylene oxide-polyalkylsiloxane copolymer according to the present invention is added to the reaction vessel in an amount ranging from 5 to 200 mg per mole of total silver added during tabular silver halide grain formation.

[0038] The presence of the polyalkylene oxide-polyalkylsiloxane copolymer during the formation process of tabular silver halide grains enable the growth of tabular silver halide grain emulsions having a reduced amount of non-conforming grains and a lower coefficient of variation (COV). The term "reduced amount of non-conforming grains" means that silver halide grains having a crystal shape different from the tabular shape, such as, for example, cubic shape, octahedral shape, rod shape and the like, are present in a percentage lower than 5%, preferably lower than 1% based on the total number of the silver halide grains of the resulting emulsion. The term "lower coefficient of variation" means that the COV of the emulsion obtained with the method of the present invention is lower than the COV of a corresponding emulsion prepared in absence of the polyalkylene oxide-polyalkylsiloxane copolymer. A COV reduction of 5 point percentage, preferably of 10 point percentage is obtained with the method of the present invention.

GRAIN PREPARATION

[0039] Tabular silver halide grains contained in the silver halide emulsions of the present invention have an average diameter:thickness ratio (often referred to in the art as aspect ratio) of at least 2:1, preferably 2:1 to 20:1, more preferably 2:1 to 14:1, and most preferably 2:1 to 8:1. Average diameters of the tabular silver halide grains suitable for use in this invention range from about 0.3 to about 5 μm, preferably 0.5 to 3 μm, more preferably 0.8 to 1.5 μm. The tabular silver halide grains suitable for use in this invention have a thickness of less than 0.4 μm, preferably less than 0.3 μm and more preferably within 0.1 to 0.3 μm. The projected area of the tabular silver halide grains obtained with the process of the present invention accounts for at least 50%, preferably at least 80% and more preferably at least 90% of the projected area of all the silver halide grains of the emulsion.

[0040] The tabular silver halide grain dimensions and characteristics described above can be readily ascertained by procedures well known to those skilled in the art. The term "diameter" is defined as the diameter of a circle having

an area equal to the projected area of the grain. The term "thickness" means the distance between two substantially parallel main planes constituting the tabular silver halide grains. From the measure of diameter and thickness of each grain the diameter:thickness ratio of each grain can be calculated, and the diameter:thickness ratios of all tabular grains can be averaged to obtain their average diameter:thickness ratio. By this definition the average diameter:thickness ratio is the average of individual tabular grain diameter:thickness ratios. In practice, it is simpler to obtain an average diameter and an average thickness of the tabular grains and to calculate the average diameter:thickness ratio as the ratio of these two averages. Whatever the method used, the average diameter:thickness ratios obtained do not greatly differ.

[0041] In the present invention, commonly employed halogen compositions of the silver halide grains can be used. Typical silver halides include silver chloride, silver bromide, silver iodide, silver chloroiodide, silver bromoiodide, silver chlorobromoiodide and the like. However, silver bromide and silver bromoiodide are preferred silver halide compositions for tabular silver halide grains with silver bromoiodide compositions containing from 0 to 10 mol% silver iodide, preferably from 0.2 to 5 mol% silver iodide, and more preferably from 0.5 to 1.5% mol silver iodide. The halogen composition of individual grains may be homogeneous or heterogeneous.

[0042] Silver halide emulsions containing tabular silver halide grains can be prepared by various processes known for the preparation of photographic materials.

[0043] Silver halide emulsions can be prepared using a single-jet method, a double-jet method, or a combination of these methods and can be ripened using, for instance, an ammonia method, a neutralization method, or an acid method. Features which may be adjusted to control grain growth include pH, pAg, temperature, shape and size of reaction vessel, and the reaction method (e.g., accelerated or constant flow rate precipitation, interrupted precipitation, ultrafiltration during precipitation, reverse mixing process and combinations of those). A silver halide solvent, such as ammonia, thioethers, thioureas, etc., may be used, if desired, for controlling grain size, form of the grains, particle size distribution of the grains, and the grain-growth rate. References can be found in Trivelli and Smith, The Photographic Journal, Vol. LXXIX, May 1939, pp. 330-338, T.H. James, The Theory of The Photographic Process, 4th Edition, Chapter 3, US Patent Nos. 2,222,264, 3,650,757, 3,917,485, 3,790,387, 3,716,276, 3,979,213, Research Disclosure, Dec. 1989, Item 308119 "Photographic Silver Halide Emulsions, Preparations, Addenda, Processing and Systems", and Research Disclosure, Sept. 1976, Item 14987.

[0044] Preparation of silver halide emulsions containing tabular silver halide grains is described, for example, in de Cugnac and Chateau, "Evolution of the Morphology of Silver Bromide Crystals During Physical Ripening", Science and Industries Photographiques, Vol. 33, No.2 (1962), pp.121-125, in Gutoff, "Nucleation and Growth Rates During the Precipitation of Silver Halide Photographic Emulsions", Photographic Science and Engineering, Vol. 14, No. 4 (1970), pp. 248-257,in Berry et al., "Effects of Environment on the Growth of Silver Bromide Microcrystals", Vol.5, No.6 (1961), pp. 332-336, in US Pat. Nos. 4,063,951, 4,067,739, 4,184,878, 4,434,226, 4,414,310, 4,386,156, 4,414,306 and in EP Pat. Appln. No. 263,508.

[0045] The preparation process of a silver halide emulsion generally comprises a nucleation step, in which silver halide grain seeds are formed, followed by one or more growing steps, in which the grain seeds achieve their final dimension, and a washing step, in which all soluble salts are removed from the final emulsion. A ripening step is usually present between the nucleation and growing step and/or between the growing and the washing steps.

GRAIN PREPARATION BEST MODE

[0046] According to a preferred embodiment, the process of this invention will be explained in more detail by the following general procedure.

[0047] Into a conventional reaction vessel for silver halide precipitation equipped with a stirring apparatus is introduced a dispersing medium aqueous solution comprising a bromide salt at an initial bromide ion concentration ranging from 0.01 to 0.5N. The bromide salt is usually a soluble alkali metal salt, e.g., KBr, NaBr, a soluble alkaline earth metal salt, e.g., $MgBr_2$, $CaBr_2$, or an ammonium salt.

[0048] According to a preferred embodiment of the invention at least one polyalkylene oxide-polyalkylsiloxane copolymer according to the above general formulae (I) to (IV) is present in the reaction vessel before the start of the nucleation. The polyalkylene oxide-polyalkylsiloxane copolymer is present in the dispersing medium at a concentration ranging from 5 to 200 mg per mole of the total silver nitrate added during the overall process of tabular silver halide grain formation. However, the polyalkylene oxide-polyalkylsiloxane copolymer can also be added at any subsequent step of the tabular silver halide grain formation, as well as two or more additions can be performed at different steps, provided that the total amount added does not exceed the above mentioned range.

[0049] The dispersing medium initially present in the reaction vessel can be chosen among those conventionally employed in the silver halide emulsions. Preferred dispersion media include hydrophilic colloids, such as proteins, protein derivatives, cellulose derivatives (e.g. cellulose esters), gelatin (e.g. acid or alkali treated gelatin), gelatin derivatives (e.g. acetylated gelatin, phthalated gelatin and the like), polysaccharides (e.g. dextran), gum arabic, casein and the like. It is also common to employ said hydrophilic colloids in combination with synthetic polymeric binders and pep-

tizers such as acrylamide and methacrylamide polymers, polymers of alkyl and sulfoalkyl acrylates and methacrylates, polyvinyl alcohol and its derivatives, polyvinyl lactams, polyamides, polyamines, polyvinyl acetates, and the like.

[0050] The temperature of the reaction vessel content is preferably in the range of from 30°C to 80°C, more preferably from 40°C to 70°C. The pH of the starting solution usually ranges from 2.0 to 8.0, preferably from 3.0 to 7.0. pH values lower than 7 can be obtained by addition of organic or inorganic acids, such as, for example, nitric acid, sulfuric acid, acetic acid, and the like. The pBr of the starting solution ranges from 0.3 to 2.0, preferably from 0.5 to 1.5.

[0051] The silver halide nuclei can be formed either by double jet addition of silver nitrate and bromide salt aqueous solutions or by single jet addition of a silver nitrate aqueous solution. During the nucleation step, the aqueous solutions can be either added at a steady rate or at an accelerated rate. The addition rate can range from 5 to 120 ml/min, preferably from 5 to 75 ml/min, by maintaining the temperature constant. An amount of silver nitrate ranging from 1% to 10% by weight of the total silver nitrate is usually added during the nucleation step. The term "total silver nitrate" means the amount of silver nitrate employed during the overall emulsion making process, that is, from the nucleation step to the final growing step.

[0052] At the end of the nucleation step, the addition of silver nitrate and bromide salt is stopped and the obtained silver halide nuclei can be ripened for a period of time of from 30 seconds to 30 minutes. The ripening step can be performed in the presence of a silver halide solvent, e.g., thiourea, ammonia, thioether, thiosulfate or thiocyanate, which can be added either before or during the ripening step. The concentration of the silver halide solvent into the reaction vessel can range from 0.002 to 0.2N. At the end of the ripening step, the pH of the resulting solution is eventually corrected to a value within 6 to 8 by addition of organic or inorganic acid, such as, for example, nitric acid, sulfuric acid, acetic acid, and the like.

[0053] After that the silver halide seed grains are grown by double jet addition of a silver nitrate aqueous solution and a bromide salt aqueous solution at an accelerated flow rate. The growing step can also be stopped to allow a pBr correction by single jet addition of a silver nitrate or bromide salt aqueous solution. In this case, the growing step may be deemed to be split in two or more sub-growing steps. The pBr value is usually controlled in the range of from 1 to 3, preferably from 1.5 to 2.5. During the growing step, a soluble iodide salt can also be added together with the bromide salt. In this case the amount of the iodide present in the final emulsion ranges from 0.01 to 10%mol, preferably from 0.05 to 5%mol based on the total halide. An amount of silver nitrate ranging from 50% to 80% by weight of the total silver nitrate is usually added during the growing step(s).

[0054] At the end of the growing step(s), the tabular grains can be further ripened for a period of time of from 1 to 20 minutes by addition of a silver halide solvent in an amount of from 0.1 to 30 g per mole of silver halide. Useful ripening agents include silver halide solvents such as, for example, thiourea, ammonia, thioether, thiosulfate or thiocyanate.

[0055] In order to reach the proper final size, the tabular silver halide grain obtained at the end of the growing step are usually further grown by double jet addition of a silver nitrate aqueous solution and a bromide salt aqueous solution at steady or accelerated flow rate. An amount of silver nitrate ranging from 20% to 40% by weight of the total silver nitrate is usually added during this final growing step.

[0056] At the end of the tabular silver halide grain formation, water soluble salts are removed from the emulsion by procedures known in the art. Suitable cleaning arrangements are those wherein the dispersing medium and soluble salts dissolved therein can be removed from the silver halide emulsion on a continuous basis, such as, for example, a combination of dialysis or electrodialysis for the removal of soluble salts or a combination of osmosis or reverse osmosis for the removal of the dispersing medium.

[0057] In a particularly preferred embodiment, among the known techniques for removing the dispersing medium and soluble salts while retaining silver halide grains in the remaining dispersion, ultrafiltration is a particularly advantageous cleaning arrangement for the practice of this process. Typically, an ultrafiltration unit comprising membranes of inert, non-ionic polymers is used as a cleaning arrangement. Since silver halide grains are large in comparison with the dispersing medium and the soluble salts or ions, silver halide grains are retained by said membranes while the dispersing medium and the soluble salts dissolved therein are removed.

[0058] The action mechanism of preferred membranes is described in GB 1,307,331. The membranes used in the ultrafiltration comprise a very thin layer of extremely fine pore texture supported upon a thicker porous structure. Suitable membranes consist of polymers such as polyvinylacetate, polyvinylalcohol, polyvinylformate, polyvinylethers, polyamides, polyimides, polyvinyl chloride and polyvinylidene chloride, aromatic polymers, such as aromatic polyesters, polytetrafluoroethylene, regenerated cellulose, cellulose esters, such as cellulose acetate, or mixed cellulose esters. The membranes in question have anisotropic, semipermeable properties, show considerable mechanical, thermal and chemical stability and are photographically inert. The membranes are preferably permeable to molecules having molecular weights of up to about 300,000 and, more especially, of up to about 50,000.

CHEMICAL SENSITIZATION

[0059] Prior to use, the tabular silver halide grain emulsion prepared according to the method of the present inven-

tion is generally fully dispersed and bulked up with gelatin or other dispersion of peptizer and subjected to any of the known methods for achieving optimum sensitivity.

[0060] Chemical sensitization is performed by adding chemical sensitizers and other additional compounds to the silver halide emulsion, followed by the so-called chemical ripening at high temperature for a predetermined period of time. Chemical sensitization can be performed by various chemical sensitizers such as gold, sulfur, reducing agents, platinum, selenium, sulfur plus gold, and the like. The tabular silver halide grains for use in the present invention, after grain formation and desalting, are chemically sensitized by at least one gold sensitizer and at least one thiosulfonate sensitizer. During chemical sensitization other compounds can be added to improve the photographic performances of the resulting silver halide emulsion, such as, for example, antifoggants, stabilizers, optical sensitizers, supersensitizers, and the like.

[0061] Gold sensitization is performed by adding a gold sensitizer to the emulsion and stirring the emulsion at high temperature of preferably 40°C or more for a predetermined period of time. As a gold sensitizer, any gold compound which has an oxidation number of +1 or +3 and is normally used as gold sensitizer can be used. Preferred examples of gold sensitizers are chloroauric acid, the salts thereof and gold complexes, such as those described in US 2,399,083. It is also useful to increase the gold sensitization by using a thiocyanate together with the gold sensitizer, as described, for example, in T.H. James, The Theory of the Photographic Process, 4th edition, page 155, published by MacMillan Co., 1977. Specific examples of gold sensitizers include chloroauric acid, potassium chloroaurate, auric trichloride, sodium aurithiosulfate, potassium aurithiocyanate, potassium iodoaurate, tetracyanoauric acid, 2-aurosulfobenzothiazole methochloride and ammonium aurothiocyanate.

[0062] Thiosulfonate sensitization is performed by adding a thiosulfonate sensitizer to the tabular silver halide emulsion and stirring the emulsion at a high temperature of 40°C or more for a predetermined period of time.

[0063] The amounts of the gold sensitizer and the thiosulfonate sensitizer for use in the present invention change in accordance with the various conditions, such as activity of the gold and thiosulfonate sensitizer, type and size of tabular silver halide grains, temperature, pH and time of chemical ripening. These amounts, however, are preferably from 1 to 20 mg of gold sensitizer per mol of silver, and from 1 to 100 mg of thiosulfonate sensitizer per mol of silver. The temperature of chemical ripening is preferably 45°C or more, and more preferably 50°C to 80°C. The pAg and pH may take arbitrary values.

[0064] During chemical sensitization, addition times and order of gold sensitizer and thiosulfonate sensitizer are not particularly limited. For example, gold and thiosulfonate sensitizers can be added at the initial stage of chemical sensitization or at a later stage either simultaneously or at different times. Usually, gold and thiosulfonate sensitizers are added to the tabular silver halide emulsion by their solutions in water, in a water-miscible organic solvent, such as methanol, ethanol and acetone, or as a mixture thereof.

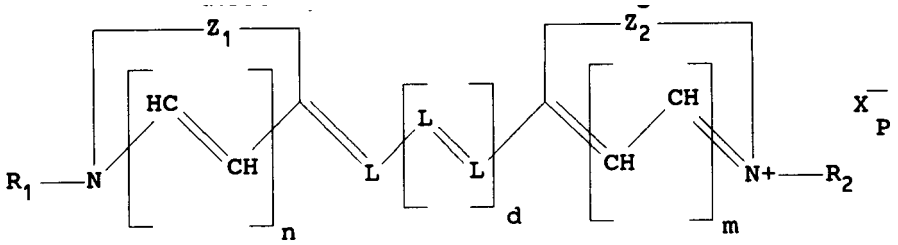
SPECTRAL SENSITIZATION

[0065] The tabular silver halide emulsions of the present invention are preferably spectrally sensitized. It is specifically contemplated to employ in the present invention, in combination with the tabular silver halide emulsions, spectral sensitizing dyes having absorption maxima in the blue, minus blue (i.e., green and red) and infrared portions of the electromagnetic spectrum. Spectral sensitizing dyes for use in the present invention include polymethine dyes, such as cyanine and complex cyanine dyes, merocyanine and complex merocyanine dyes, as well as other dyes, such as oxonols, hemioxonols, styryls, merostyryls and streptocyanines as described by F.M. Hamer, The Cyanine and Related Compounds, Interscience Pulishers, 1964.

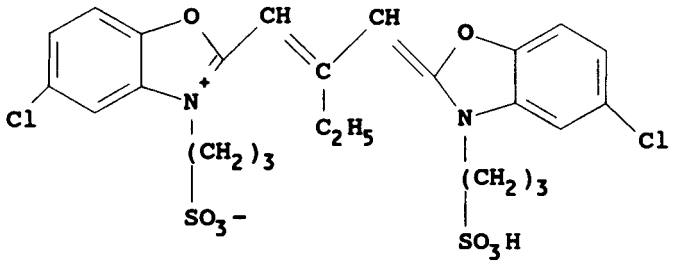
[0066] The cyanine dyes include, joined by a methine linkage, two basic heterocyclic nuclei, such as pyrrolidine, oxazoline, thiazoline, pyrrole, oxazole, thiazole, selenazole, tetrazole and pyridine and nuclei obtained by fusing an alicyclic hydrocarbon ring or an aromatic hydrocarbon ring to each of the above nuclei, such as indolenine, benzindolenine, indole, benzoxazole, naphthoxazole, benzothiazole, naphthothiazole, benzoselenazole, benzimidazole and quinoline. These nuclei can have substituents groups.

[0067] The merocyanine dyes include, joined by a methine linkage, a basic heterocyclic nucleus of the type described above and an acid nucleus, such as a 5- or 6-membered heterocyclic nucleus 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, and isoquinolin-4-one.

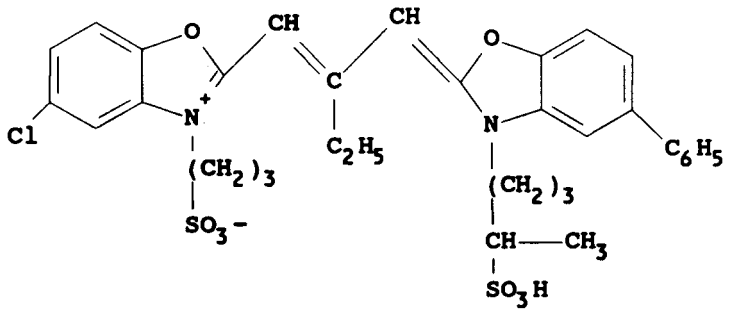
[0068] Of the above dyes, dyes most effectively used in the present invention are cyanine dyes, such as those represented by the following formula:



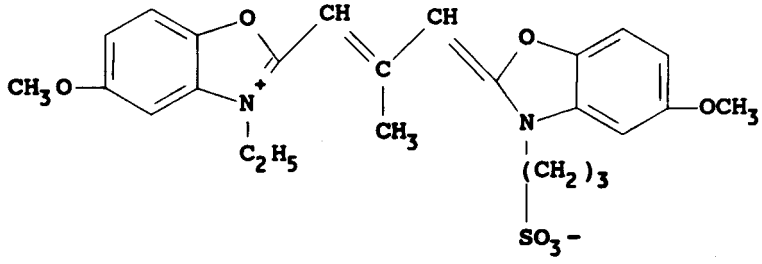
wherein n, m, p and d each independently represents 0 or 1, L represents a methine linkage, e.g., =CH-, ≡C(C_2H_5), etc., R_1 and R_2 each represents a substituted or unsubstituted alkyl group, preferably a lower alkyl group of from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, butyl, cyclohexyl and dodecyl, a hydroxyalkyl group, e.g., β-hydroxyethyl and Ω-hydroxybutyl, an alkoxyalkyl group, e.g., β-methoxyethyl and Ω-butoxyethyl, a carboxyalkyl group, e.g., β-carboxyethyl and Ω-carboxybutyl, a sulfoalkyl group, e.g., β-sulfoethyl and Ω-sulfobutyl, a sulfatoalkyl group, e.g., β-sulfatoethyl and Ω-sulfatobutyl, an acyloxyalkyl group, e.g., β-acetoxyethyl, γ-acetoxypropyl and Ω-butyryloxybutyl, an alkoxycarbonylalkyl group, e.g., β-methoxycarbonylethyl and Ω-ethoxycarbonylbutyl, benzyl, phenethyl, or an aryl group of up to 30 carbon atoms, e.g., phenyl, tolyl, xylyl, chlorophenyl and naphthyl, X represents an acid anion, e.g., chloride, bromide, iodide, thiocyanate, sulfate, perchlorate, p-toluenesulfonate and methylsulfate; said methine linkage forming an intramolecular salt when p is 0; Z_1 and Z_2, the same or different, each represents the non metallic atoms necessary to complete the same simple or condensed 5- or 6-membered heterocyclic nucleus, such as a benzothiazole nucleus (e.g., benzothiazole, 3-, 5-, 6- or 7-chloro-benzothiazole, 4-, 5- or 6-methylbenzothiazole, 5- or 6-bromobenzothiazole, 4- or 5-phenylenzothiazole, 4-, 5- or 6-methoxybenzothiazole, 5,6-dimethyl-benzothiazole and 5- or 6-hydroxy-benzothiazole), a naphthothiazole nucleus (e.g., α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5-ethoxy-α-naphthothiazole and 8-methoxy-α-naphthothiazole), a benzoselenazole nucleus (e.g., benzoselenazole, 5-chloro-benzoselenazole and tetrahydrobenzoselenazole), a naphthoselenazole nucleus (e.g., α-naphtho-selenazole and β-naphthoselenazole), a benzoxazole nucleus (e.g., benzoxazole, 5- or 6-hydroxy-benzoxazole, 5-chloro-benzoxazole, 5- or 6-methoxy-benzoxazole, 5-phenyl-benzoxazole and 5,6-dimethyl-benzoxazole), a naphthoxazole nucleus (e.g., α-naphthoxazole and β-naphthoxazole), a 2-quinoline nucleus (e.g., 2-quinoline, 6-, 7, or 8-methyl-2-quinoline, 4-, 6- or 8-chloro-2-quinoline, 5-, 6- or 7-ethoxy-2-quinoline and 6- or 7-hydroxy-2-quinoline), a 4-quinoline nucleus (e.g., 4-quinoline, 7- or 8-methyl-4-quinoline and 6-methoxy-4-quinoline), a benzimidazole nucleus (e.g., benzimidazole, 5-chloro-benzimidazole and 5,6-dichloro-benzimidazole), a thiazole nucleus (e.g., 4- or 5-methyl-thiazole, 5-phenyl-thiazole and 4,5-di-methyl-thiazole), an oxazole nucleus (e.g., 4- or 5-methyl-oxazole, 4-phenyl-oxazole, 4-ethyl-oxazole and 4,5-dimethyl-oxazole), and a selenazole nucleus (e.g., 4-methyl-selenazole and 4-phenyl-selenazole. More preferred dyes within the above class are those having an internal salt group and/or derived from benzoxazole and benzimidazole nuclei as indicated before. Typical methine spectral sensitizing dyes for use in the present invention include those listed below.



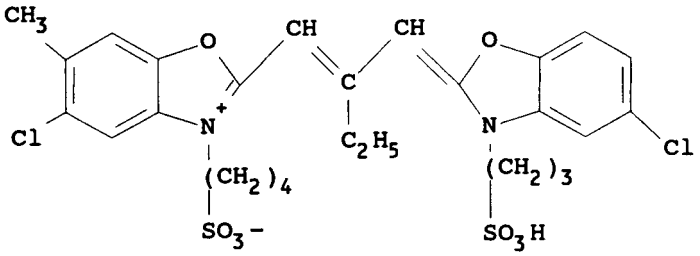
Dye A



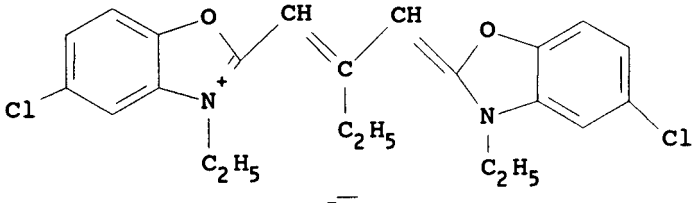
Dye B



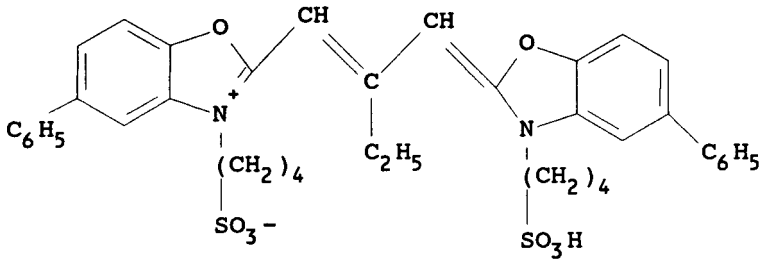
Dye C



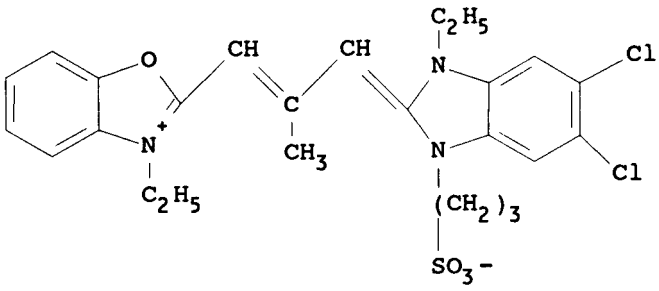
Dye D



Dye E



Dye F



Dye G

[0069] The methine spectral sensitizing dyes for use in this invention are generally known in the art. Particular reference can be made to US Pat. Nos. 2,503,776, 2,912,329, 3,148,187, 3,397,060, 3,573,916 and 3,822,136 and FR Pat. No. 1,118,778. Also their use in photographic emulsions is very known wherein they are used in optimum concentrations corresponding to desired values of sensitivity to fog ratios. Optimum or near optimum concentrations of spectral sensitizing dyes in the emulsions of the present invention generally go from 10 to 500 mg per mol of silver, preferably from 50 to 200, more preferably from 50 to 100.

[0070] Spectral sensitizing dyes can be used in combinations which result in super-sensitization, i.e., spectral sensitization which is greater in a spectral region than that from any concentration of one dye alone or which would result from an additive effect of the dyes. Supersensitization can be obtained with selected combinations of spectral sensitizing dyes and other addenda, such as stabilizers and antifoggants, development accelerators and inhibitors, optical brighteners, surfactants and antistatic agents, as described by Gilman, Photographic Science and Engineering, 18, pp. 418-430, 1974 and in US Pat. Nos. 2,933,390, 3,635,721, 3,743,510, 3,615,613, 3,615,641, 3,617,295 and 3,635,721.

[0071] Preferably, spectral sensitizing dyes are used in supersensitizing combination with polymeric compounds containing an aminoallylidenemalononitrile (>N-CH=CH-CH=$(CN)_2$) moiety, as those described in US 4,307,183. Said polymeric compounds are preferably obtained upon copolymerization of an allyl monomer which has an ethylenically condensed aminoallylidenemalononitrile moiety (such as dilallylaminoallylidenemalononitile monomer therein with an ethylenically unsaturated monomer, said monomer being preferably a water-soluble monomer; said copolymerization being preferably a solution polymerization said polymeric compound being preferably a water-soluble polymer; said

monomer more preferably being an acrylic or methacrylic monomer, most preferably being acrylamide or acrylic acid.

[0072] Examples of polymeric compounds which can be used in supersensitizing combination with spectral sensitizing dyes are preferably the polymeric compounds described in the following Table B wherein the monomer is copolymerized (in solution in the presence of a polymerization initiator) with a diallylaminoallylidenemalononitrile monomer, as well as a weight percent quantity of aminoallylidenemalononitrile moieties (AAMN) within the polymers themselves are indicated.

TABLE B

Compound	Monomer	% AAMN
1	Acrylamide	9
2	Methacrylic acid	11
3	Acrylamide	10.5
4	Acrylic acid	23
5	Acrylamide	44
6	Vinylpirrolidone	44
7	Vinyloxazolidone	14.5
8	Vinyloxazolidone	37
9	Methacrylamide	8
10	Acrylamide-Allylamide.HCl	10
11	Acrylamide-Diallylamide.HCl	7

[0073] Methods of preparation of said polymeric compounds are described in the above mentioned US 4,307,183. The optimum concentrations of said polymeric compounds generally go from 10 to 1,000 mg per mol of silver, preferably from 50 to 500, more preferably from 150 to 350, the weight ratio of the polymeric compound to the spectral sensitizing dye normally being of 10/1 to 1/10, preferably 5/1 to 1/5, more preferably 2.5/1 to 1/1 (such a ratio of course depending upon the aminoallylidene-malononitrile moiety content of the polymeric compound: the higher such content, the lower such ratio).

[0074] Spectral sensitization can be performed at any stage of silver halide preparation. It can be performed subsequent to the completion of chemical sensitization or concurrently with chemical sensitization, or can precede chemical sensitization, or even can commence prior to the completion of silver halide precipitation. In the preferred form, spectral sensitizing dyes can be incorporated in the tabular grain silver halide emulsions prior to chemical sensitization.

PHOTOGRAPHIC MATERIAL

[0075] The tabular silver halide grain emulsions are useful in light-sensitive photographic materials. A light-sensitive silver halide photographic material can be prepared by coating the above described silver halide emulsion on a photographic support. There is no limitation with respect to the support. Examples of materials suitable for the preparation of the support include glass, paper, polyethylene-coated paper, metals, cellulose nitrate, cellulose acetate, polystyrene, polyesters such as polyethylene terephthalate, polyethylene, polypropylene and other well known supports.

[0076] Said light-sensitive silver halide photographic material specifically is applicable to light-sensitive photographic color materials such as color negative films, color reversal films, color papers, etc., as well as black-and-white light-sensitive photographic materials such as X-ray light-sensitive materials, lithographic light-sensitive materials, black-and-white photographic printing papers, black-and-white negative films, etc.

[0077] Preferred light-sensitive silver halide photographic materials are X-ray light-sensitive materials comprising the above described silver halide emulsion coated on one surface, preferably on both surfaces of a support, preferably a polyethylene terephthalate support. Preferably, the silver halide emulsion is coated on the support at a total silver coverage comprised in the range of 3 to 6 grams per square meter. Usually, the X-ray light-sensitive materials are associated with intensifying screens so as to be exposed to radiation emitted by said screens. The screens are made of relatively thick phosphor layers which transform the X-rays into light radiation (e.g., visible light). The screens absorb a portion of X-rays much larger than the light-sensitive material and are used to reduce the X-ray dose necessary to obtain a useful image. According to their chemical composition, the phosphors can emit radiation in the blue, green or

red region of the visible spectrum and the silver halide emulsions are sensitized to the wavelength region of the light emitted by the screens. Sensitization is performed by using spectral sensitizing dyes adsorbed on the surface of the silver halide grains as known in the art.

[0078] The exposed light-sensitive materials of this invention can be processed by any of the conventional processing techniques. The processing can be a black-and-white photographic processing for forming a silver image or a color photographic processing for forming a dye image depending upon the purpose. Such processing techniques are illustrated for example in Research Disclosure, 17643, December 1978. Roller transport processing in an automatic processor is particularly preferred, as illustrated in US Pat. Nos. 3,025,779, 3,515,556, 3,545,971 and 3,647,459 and in UK Pat. No. 1,269,268. Hardening development can be undertaken, as illustrated in US Pat. No. 3,232,761.

[0079] The silver halide emulsion layer containing the tabular silver halide grain emulsion obtained with the method of this invention can contain other constituents generally used in photographic products, such as binders, hardeners, surfactants, speed-increasing agents, stabilizers, plasticizers, optical sensitizers, dyes, ultraviolet absorbers, etc., and reference to such constituents can be found, for example, in Research Disclosure, Vol. 176 (December 1978), pp. 22-28. Ordinary silver halide grains may be incorporated in the emulsion layer containing the tabular silver halide grains as well as in other silver halide emulsion layers of the light-sensitive silver halide photographic material of this invention. Such grains can be prepared by processes well known in the photographic art.

[0080] The present invention is now illustrated by reference to the following examples, which are not intended to limit the scope of the invention.

EXAMPLES

Example 1

Control emulsion A

[0081] An aqueous gelatin solution consisting of 5124 ml of water, 45 g of deionized gelatin, 92.85 g of potassium bromide, and 1.83 g of sodium thiocyanate was put in a 10 liter reaction vessel.

Nucleation: 72 ml of a 2N silver nitrate aqueous solution were added over a period of 8 minutes at a constant flow rate, while keeping the temperature constant at 56°C. The starting pBr was 0.8.

Growth: 1172 ml of a 2N silver nitrate aqueous solution and 1172 ml of a 2N potassium bromide aqueous solution were added to the vessel by accelerated double jet method, with a linear addition ramp rising from 9.00 ml/min to 77.85 ml/min. At the end of the growing step, the pAg value was raised to about 7.8 by a single jet addition of 120 ml of a 2N silver nitrate aqueous solution at a constant rate of 60 ml/min, followed by a single jet addition of a 2N silver nitrate aqueous solution at a constant rate of 14.25 ml/min over a maximum period of 30 minutes.

Thickening: 75 ml of a 12 N aqueous solution of ammonia were added in the vessel over a period of a minute. After that, 495 ml of a 2N silver nitrate aqueous solution and the corresponding amount of a 1.94N potassium bromide and 0.06N potassium iodide aqueous solution were added over a period of about 30 minutes. The pAg of the reaction vessel was kept constant at a value of about 9.6.

[0082] At the end of the tabular silver halide grain formation, water soluble salts were removed from the emulsion by procedures known in the art.

Invention emulsion B

[0083] The procedure of emulsion A was repeated, except that Silwet™ L7001 was additionally present in the reaction vessel prior to the nucleation step. The amount of Silwet™ L7001 was about 15.5 mg per mole of silver introduced into the emulsion. Silwet™ L7001 is the trade name of a surfactant satisfying the general formula (III) described above wherein R' is a methyl and having a molecular weight of 20,000 Dalton, which is manufactured and sold by the Union Carbide Company.

Invention emulsion C

[0084] The procedure of emulsion A was repeated, except that Silwet™ L7001 was additionally present in the reaction vessel prior to the nucleation step, and that the pAg value of the thickening step was kept constant at 9.7. The amount of Silwet™ L7001 was about 24 mg per mole of silver introduced into the emulsion. Silwet™ L7001 is the trade name of a surfactant satisfying the general formula (III) described above wherein R' is a methyl and having a molecular weight of 20,000 Dalton, which is manufactured and sold by the Union Carbide Company.

[0085] The resulting tabular grain emulsions A to C showed the characteristics exposed in the following Table 1.

TABLE 1

	Control Emulsion A	Invention Emulsion B	Invention Emulsion C
Average Diameter	1.33 μm	1.29 μm	1.18 μm
Average Thickness	0.23 μm	0.22 μm	0.20 μm
Average Aspect Ratio	5.78	5.86	5.90
Standard Deviation	0.51 μm	0.42 μm	0.39 μm
COV	38	32	33

[0086] The data of Table 1 clearly show the action of the polyalkylene oxide-polyalkylsiloxane copolymer in reducing the COV of the resulting emulsion. Also, emulsion B and C showed a lower amount of non-conforming grains than the control emulsion A.

Example 2

Control emulsion D

[0087] An aqueous gelatin solution consisting of 4443 ml of water, 57 g of deionized gelatin, 85 g of potassium bromide, and 2.19 g of sodium thiocyanate was put in a 10 liter reaction vessel.

Nucleation: 63 ml of a 4.32N silver nitrate aqueous solution were added over a period of 4,5 minutes at a constant flow rate, while keeping the temperature constant at 55°C. The starting pBr was 0.8.
Growth: 584 ml of a 4.32N silver nitrate aqueous solution and 584 ml of a 4.00N potassium bromide aqueous solution were added to the vessel by accelerated double jet method, with a linear addition ramp rising from 14.02 ml/min to 58.98 ml/min. At the end of this first growing step, 49 ml of a 4N potassium bromide aqueous solution were added to the resulting emulsion by single jet at a constant rate of about 60 ml/min. After that, 1298 ml of a 4.32N silver nitrate aqueous solution and the corresponding amount of a 4.00N potassium bromide aqueous solution were added to the vessel by double jet method over a period of about 22 minutes to obtain a pAg value of about 8.6.
Thickening: 50 ml of a 12 N aqueous solution of ammonia were added in the vessel over a period of a minute. After that, 722 ml of a 4.32N silver nitrate aqueous solution and the corresponding amount of a 3.87N potassium bromide and 0.13N potassium iodide aqueous solution were added over a period of about 30 minutes. The pAg of the reaction vessel was kept constant at a value of about 8.95. At the end, 12 ml of a 4.00N aqueous solution of potassium bromide were added over a period of 30 seconds.

[0088] At the end of the tabular silver halide grain formation, water soluble salts were removed from the emulsion by procedures known in the art.

Invention emulsion E

[0089] The procedure of emulsion D was repeated, except that Silwet™ L7001 was additionally present in the reaction vessel prior to the nucleation step. The amount of Silwet™ L7001 was about 10 mg per mole of silver introduced into the emulsion. Silwet™ L7001 is the trade name of a surfactant satisfying the general formula (III) described above wherein R' is a methyl and having a molecular weight of 20,000 Dalton, which is manufactured and sold by the Union Carbide Company.

Invention emulsion F

[0090] The procedure of emulsion D was repeated, except that Silwet™ L720 was additionally present in the reaction vessel prior to the nucleation step. The amount of Silwet™ L720 was about 10 mg per mole of silver introduced into the emulsion. Silwet™ L720 is the trade name of a surfactant satisfying the general formula (IV) described above wherein R' is a butyl and having a molecular weight of 12,000 Dalton, which is manufactured and sold by the Union Carbide Company.

Invention emulsion G

[0091] The procedure of emulsion D was repeated, except that Silwet™ L7002 was additionally present in the reaction vessel prior to the nucleation step. The amount of Silwet™ L7002 was about 10 mg per mole of silver introduced into the emulsion. Silwet™ L7002 is the trade name of a surfactant satisfying the general formula (III) described above wherein R' is a butyl and having a molecular weight of 8,000 Dalton, which is manufactured and sold by the Union Carbide Company. The resulting tabular grain emulsions D to G showed the characteristics exposed in the following Table 2.

TABLE 2

	Control Emulsion D	Invention Emulsion E	Invention Emulsion F	Invention Emulsion G
Average Diameter	1.18 μm	1.06 μm	1.00 μm	1.18 μm
Average Thickness	0.23 μm	0.24 μm	0.23 μm	0.24 μm
Average Aspect Ratio	5.13	4.41	4.34	4.91
Non conforming grains*	100	0	25	40

*This is a value relative to the control emulsion D to which a value of 100 has been given.

[0092] The data of Table 2 clearly show the action of the polyalkylene oxide-polyalkylsiloxane copolymer in reducing the amount of non-conforming grains.

Example 3

Control emulsion H

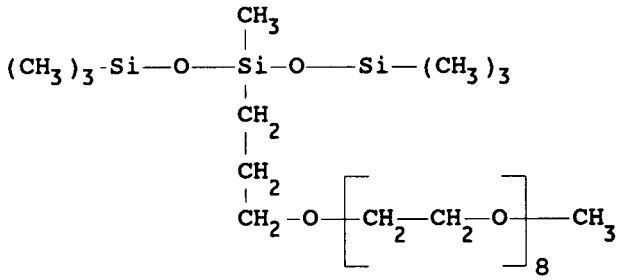
[0093] An aqueous gelatin solution consisting of 4443 ml of water, 57 g of deionized gelatin, 85 g of potassium bromide, and 2.19 g of sodium thiocyanate was put in a 10 liter reaction vessel.

Nucleation: 63 ml of a 4.32N silver nitrate aqueous solution were added over a period of 4,5 minutes at a constant flow rate, while keeping the temperature constant at 55°C. The starting pBr was 0.8.
Growth: 584 ml of a 4.32N silver nitrate aqueous solution and 584 ml of a 4.00N potassium bromide aqueous solution were added to the vessel by accelerated double jet method, with a linear addition ramp rising from 14.02 ml/min to 58.98 ml/min. 49 ml of a 4N potassium bromide aqueous solution were added to the resulting emulsion by single jet at a constant rate of about 60 ml/min. After that, 1062 ml of a 4.32N silver nitrate aqueous solution and the corresponding amount of a 4.00N potassium bromide aqueous solution were added to the vessel by double jet method over a period of about 18 minutes to obtain a pAg value of about 8.6.
Thickening: 50 ml of a 12 N aqueous solution of ammonia were added in the vessel over a period of a minute. After that, 722 ml of a 4.32N silver nitrate aqueous solution and the corresponding amount of a 3.87N potassium bromide and 0.13N potassium iodide aqueous solution were added over a period of about 30 minutes. The pAg of the reaction vessel was kept constant at a value of about 8.95. At the end, 12 ml of a 4.00N aqueous solution of potassium bromide were added over a period of 30 seconds.

[0094] At the end of the tabular silver halide grain formation, water soluble salts were removed from the emulsion by procedures known in the art.

Comparison emulsion I

[0095] The procedure of emulsion H was repeated, except that Silwet™ L77 was additionally present in the reaction vessel prior to the nucleation step. The amount of Silwet™ L77 was about 10 mg per mole of silver introduced into the emulsion. Silwet™ L77 is the trade name of a surfactant having the following formula:



and it is manufactured and sold by the Union Carbide Company. Silwet™ L77 has a structure similar to that of formula II but lacking the LAO blocks and with a very short LAS block.

Comparison emulsion L

[0096] The procedure of emulsion H was repeated, except that Silwet™ L7605 was additionally present in the reaction vessel prior to the nucleation step. The amount of Silwet™ L7605 was about 10 mg per mole of silver introduced into the emulsion. Silwet™ L7605 is the trade name of a surfactant similar to general formula (I) and (III) described above, but lacking the LAO block units, wherein R' is a methyl and having a molecular weight of 6,000 Dalton. It is manufactured and sold by the Union Carbide Company.

[0097] The resulting tabular grain emulsions H to L showed the characteristics exposed in the following Table 3.

TABLE 3

	Control Emulsion H	Comparison Emulsion I	Comparison Emulsion L
Average Diameter	1.07 μm	1.04 μm	1.05 μm
Average Thickness	0.245 μm	0.235 μm	0.24 μm
Average Aspect Ratio	4.37	4.42	4.37
Non-conforming grains*	100	100	120

*This is a value relative to the control emulsion D to which a value of 100 has been given.

[0098] The data of Table 3 clearly show that surfactants other than the present invention do not have the effect of the surfactant of the present invention.

Example 4

Control emulsion M

[0099] An aqueous gelatin solution consisting of 2160 ml of water, 12.5 g of deionized gelatin, 12.6 g of potassium bromide, and 7ml of a 4N HNO_3 solution was put in a 10 liter reaction vessel. The pBr was about 1.3 and the pH about 2.0.

Nucleation: 35 ml of a 1.96N silver nitrate aqueous solution and 35ml of a 1.96N potassium bromide aqueous solution were added by double jet addition over a period of 33 seconds at a constant flow rate, while keeping the temperature constant at 45°C.

Ripening: A solution of ammonia was added to give a pH of about 10.5. The silver halide nuclei were ripened at 70°C over 20 minutes under agitation. At the end the vessel content was neutralized to pH 6.85 with a 4N HNO_3 solution.

First Growth: A 1.96N silver nitrate aqueous solution was added to raise the pBr to a value of about 1.6. After that, 405 ml of a 1.96N silver nitrate aqueous solution and the corresponding amount of a 1.96N potassium bromide aqueous solution were added to the vessel by accelerated double jet method, with a linear addition ramp rising from 7.5 ml/min to 20.8 ml/min by keeping the pBr constant at 1.6.

Second Growth: A 1.96N silver nitrate aqueous solution was added to raise the pBr to a value of about 2.4. After that, 439 ml of a 1.96N silver nitrate aqueous solution and the corresponding amount of a 1.96N potassium bromide aqueous solution were added to the vessel by accelerated double jet method, with a linear addition ramp rising from 7.5 ml/min to 26.5 ml/min by keeping the pBr constant at 2.4.

Final Growth: 645 ml of a 1.96N silver nitrate aqueous solution and the corresponding amount of a 1.96N potassium bromide aqueous solution were added to the vessel by accelerated double jet method, with a linear addition ramp rising from 27 ml/min to 37.5 ml/min by keeping the pBr constant at 2.4.

[0100] At the end of the tabular silver halide grain formation, water soluble salts were removed from the emulsion by procedures known in the art.

Invention emulsion N

[0101] The procedure of emulsion M was repeated, except that Silwet™ L7001 was additionally present in the reaction vessel prior to the nucleation step and further added at the end of the ripening step. The total amount of Silwet™ L7001 was about 170 mg per mole of silver introduced into the emulsion. Silwet™ L7001 is the trade name of a surfactant satisfying the general formula (III) described above wherein R' is methyl and having a molecular weight of 20,000 Dalton, which is manufactured and sold by the Union Carbide Company.

Invention emulsion O

[0102] The procedure of emulsion M was repeated, except that Silwet™ L7001 was additionally present in the reaction vessel prior to the nucleation step. The total amount of Silwet™ L7001 was about 32 mg per mole of silver introduced into the emulsion.

Comparison emulsion P

[0103] The procedure of emulsion M was repeated, except that Pluronic™ 31R1 was additionally present in the reaction vessel prior to the nucleation step and further added at the end of the ripening step. The total amount of Pluronic™ 31R1 was about 115 mg per mole of silver introduced into the emulsion. Use of Pluronic™ 31R1 is disclosed in EP 513,722. Pluronic™ 31R1 is the tradename of a polyoxyethylene surfactant manufactured by BASF AG having the following formula

$$HO\text{-}(CH(CH_3)CH_2O)_x\text{-}(CH_2CH_2O)y\text{-}(CH_2CH(CH_3)O)_{x'}\text{-}H$$

wherein x equal to 25, x' equal to 25 and y equal to 7.

[0104] The resulting tabular grain emulsions M to P showed the characteristics resumed in the following Table 4.

TABLE 4

	Control Emulsion M	Invention Emulsion N	Invention Emulsion O	Comparison Emulsion P
Average Diameter	1.39 μm	0.81 μm	1.02 μm	1.36 μm
Average Thickness	0.184 μm	0.310 μm	0.195 μm	0.184 μm
Average Aspect Ratio	7.55	2.61	5.23	7.39
Standard Deviation	0.26	0.089	0.12	0.26
COV	19%	11%	11.5%	19%

[0105] The data of Table 4 clearly show that the prior art surfactant (other than the present invention) employed in comparison emulsion P does not have the effect of the surfactant of the present invention. On the contrary, emulsions N and O showed a lower COV and a lower amount of non-conforming grains than control emulsion M.

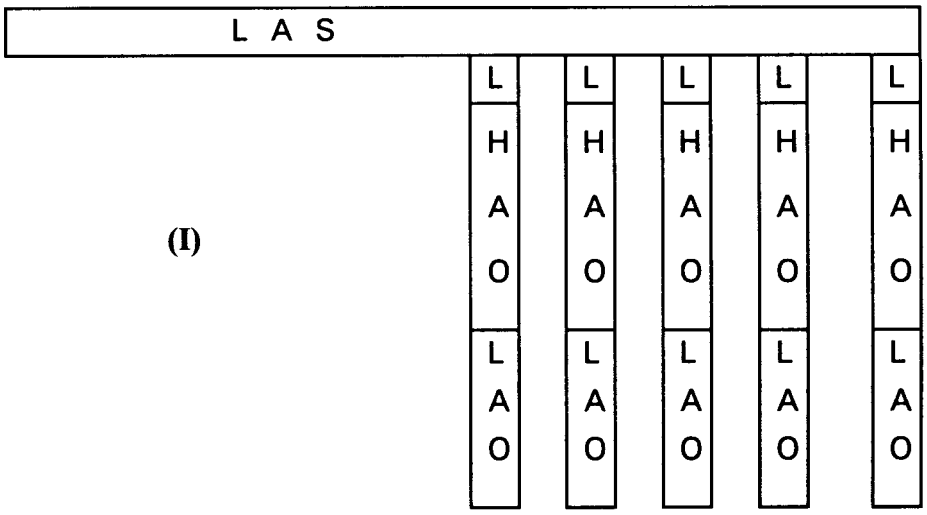
Claims

1. A process for preparing tabular silver halide grain emulsions, said process comprising the following steps:

(a) forming a population of silver halide nuclei in a dispersing medium,
(b) ripening said population of silver halide nuclei, and
(c) growing said population of silver halide nuclei to form tabular silver halide grains,

characterized in that a polyalkylene oxide-polyalkylsiloxane copolymer is added during at least one of said steps (a), (b), and (c).

2. The process for preparing tabular silver halide grain emulsions according to claim 1, wherein said polyalkylene oxide-polyalkylsiloxane copolymer has the following general formula (I):

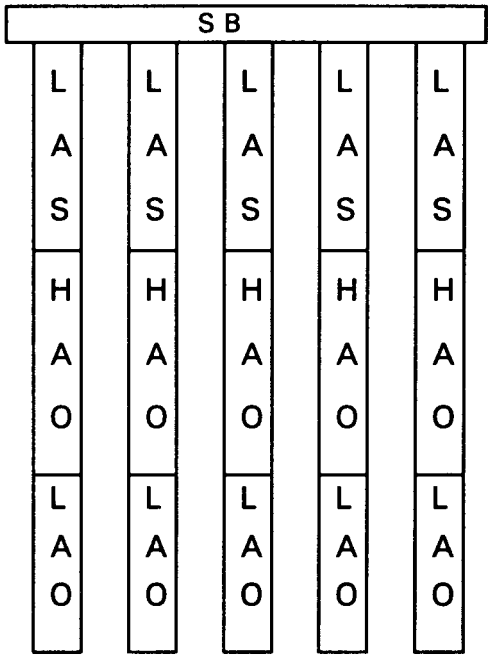


(I)

wherein LAS represents a lipophilic alkylene siloxane block unit, HAO represents a hydrophilic alkylene oxide block unit, LAO represents a terminal lipophilic alkylene oxide block unit, and L is a lipophilic hydrocarbon system.

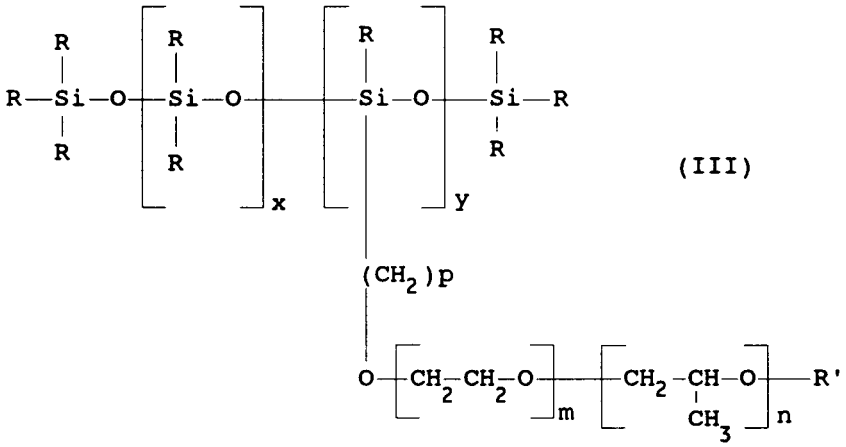
3. The process for preparing tabular silver halide grain emulsions according to claim 1, wherein said polyalkylene oxide-polyalkylsiloxane copolymer has the following general formula (II):

(II)



wherein LAS represents a lipophilic alkylene siloxane block unit, HAO represents a hydrophilic alkylene oxide block unit, LAO represents a terminal lipophilic alkylene oxide block unit, and SB is a silicone backbone.

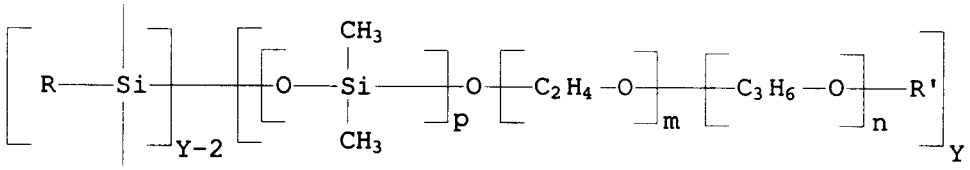
4. The process for preparing tabular silver halide grain emulsions according to claim 1, wherein said polyalkylene oxide-polyalkylsiloxane copolymer has the following general formula (III):



(III)

wherein R is a methyl group, R' can be either hydrogen or a lower alkyl radical of from 1 to 4 carbon atoms, x is an integer from 0 to 100, y is an integer from 1 to 50, m is an integer from 1 to 50, n is an integer from 1 to 50, and p is an integer from 2 to 6.

5. The process for preparing tabular silver halide grain emulsions according to claim 1, wherein said polyalkylene oxide-polyalkylsiloxane copolymer has the following general formula (IV):



wherein R is a methyl group, R' can be either hydrogen or a lower alkyl radical of from 1 to 4 carbon atoms, y is an integer from 3 to 50, m is an integer from 1 to 50, n is an integer from 1 to 50, and p is an integer from 1 to 50.

6. The process for preparing tabular silver halide grain emulsions according to claim 1, wherein said polyalkylene oxide-polyalkylsiloxane copolymer is added to the reaction vessel in an amount ranging from 5 to 200 mg per mole of total silver added during tabular silver halide grain formation.

7. The process for preparing tabular silver halide grain emulsions according to claim 1, wherein said polyalkylene oxide-polyalkylsiloxane copolymer is added to the reaction vessel before the start of the nucleation step (a).

Patentansprüche

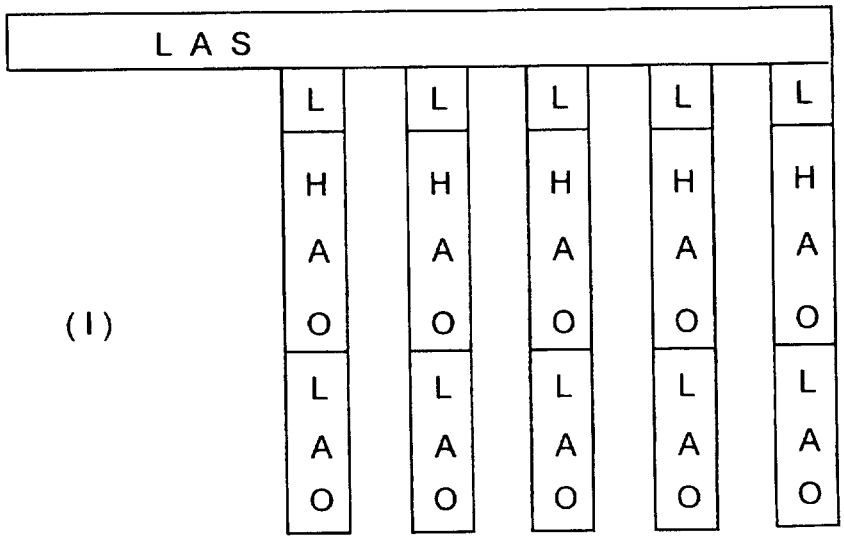
1. Verfahren zur Herstellung von Emulsionen tafelförmiger Silberhalogenidkörner, das folgende Schritte umfasst:

(a) Bildung einer Population von Silberhalogenidkeimen in einem Dispergiermittel,
(b) Reifung der Population von Silberhalogenidkeimen, und
(c) Wachstum der Population von Silberhalogenidkeimen unter Bildung tafelförmiger Silberhalogenidkörner,

dadurch gekennzeichnet, dass ein Polyalkylenoxid/Polyalkylsiloxan-Copolymer während mindestens einem der Schritte (a), (b) und (c) zugesetzt wird.

2. Verfahren zur Herstellung von Emulsionen tafelförmiger Silberhalogenidkörner nach Anspruch 1, dadurch gekennzeichnet, dass das Polyalkylenoxid/Polyalkylsiloxan-Copolymer die folgende allgemeine Formel (I) aufweist:

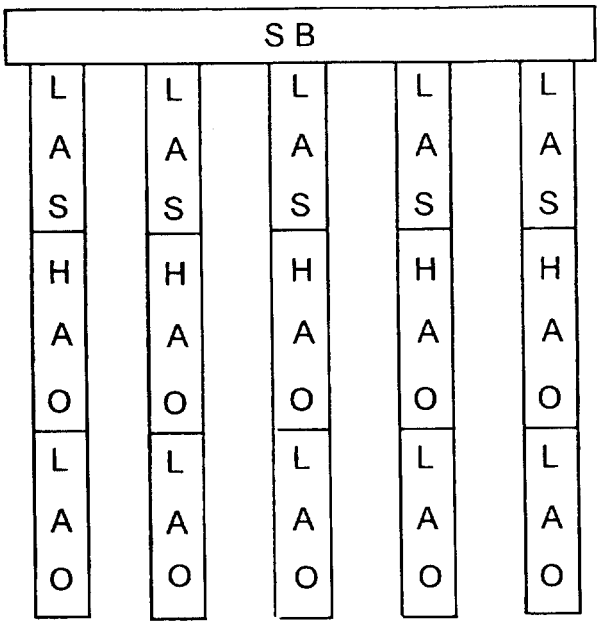
(I)



wobei LAS ein lipophiler Alkylensiloxan-Block ist, HAO ein hydrophiler Alkylenoxid-Block, LAO ein endständiger lipophiler Alkylenoxid-Block und L ein lipophiles Kohlenwasserstoffsystem.

3. Verfahren zur Herstellung von Emulsionen tafelförmiger Silberhalogenidkörner nach Anspruch 1, dadurch gekennzeichnet, dass das Polyalkylenoxid/Polyalkylsiloxan-Copolymer die folgende allgemeine Formel (II) aufweist:

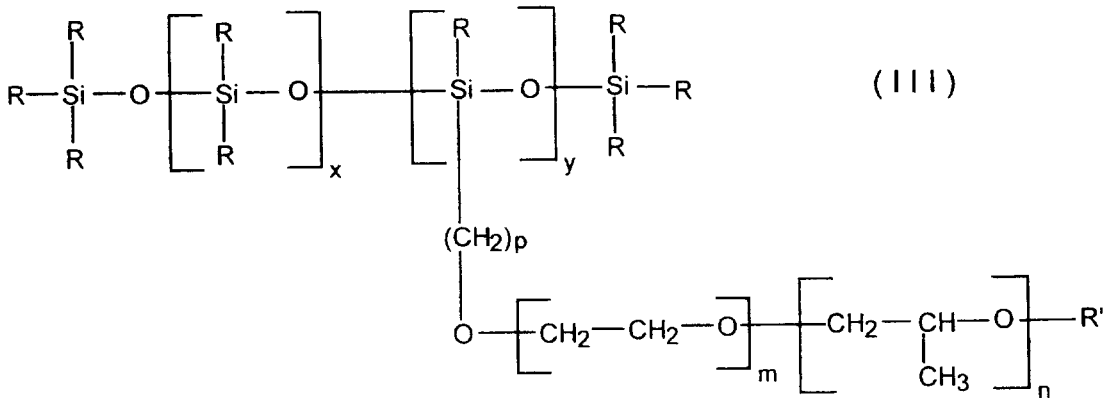
(II)



wobei LAS ein lipophiler Alkylensiloxan-Block ist, HAO ein hydrophiler Alkylenoxid-Block, LAO ein endständiger lipophiler Alkylenoxid-Block und SB ein Silicongerüst.

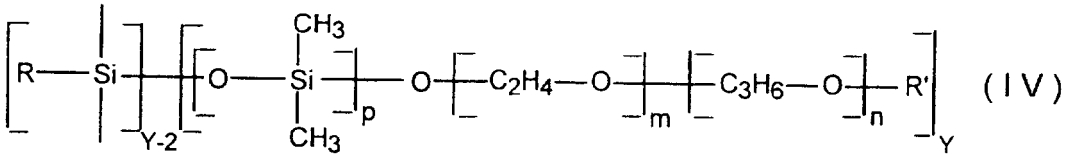
4. Verfahren zur Herstellung von Emulsionen tafelförmiger Silberhalogenidkörner nach Anspruch 1, dadurch gekennzeichnet, dass das Polyalkylenoxid/Polyalkylsiloxan-Copolymer die folgende allgemeine Formel (III) aufweist:

(III)



wobei R eine Methylgruppe ist, R' entweder Wasserstoff oder ein niederer Alkylrest mit 1 bis 4 Kohlenstoffatomen, x eine ganze Zahl zwischen 0 und 100, y eine ganze Zahl zwischen 1 und 50, m eine ganze Zahl zwischen 1 und 50, n eine ganze Zahl zwischen 1 und 50 und p eine ganze Zahl zwischen 2 und 6.

5. Verfahren zur Herstellung von Emulsionen tafelförmiger Silberhalogenidkörner nach Anspruch 1, dadurch gekennzeichnet, dass das Polyalkylenoxid/Polyalkylsiloxan-Copolymer die folgende allgemeine Formel (IV) aufweist:



(IV)

wobei R eine Methylgruppe ist, R' entweder Wasserstoff oder ein niederer Alkylrest mit 1 bis 4 Kohlenstoffatomen, y eine ganze Zahl zwischen 3 und 50, m eine ganze Zahl zwischen 1 und 50, n eine ganze Zahl zwischen 1 und 50 und p eine ganze Zahl zwischen 1 und 50.

6. Verfahren zur Herstellung von Emulsionen tafelförmiger Silberhalogenidkörner nach Anspruch 1, dadurch gekennzeichnet, dass das Polyalkylenoxid/Polyalkylsiloxan-Copolymer in den Reaktionsbehälter in Mengen von 5 bis 200 mg pro Mol des gesamten, während der Bildung der tafelförmigen Silberhalogenidkörner zugefügten Silbers eingegeben wird.

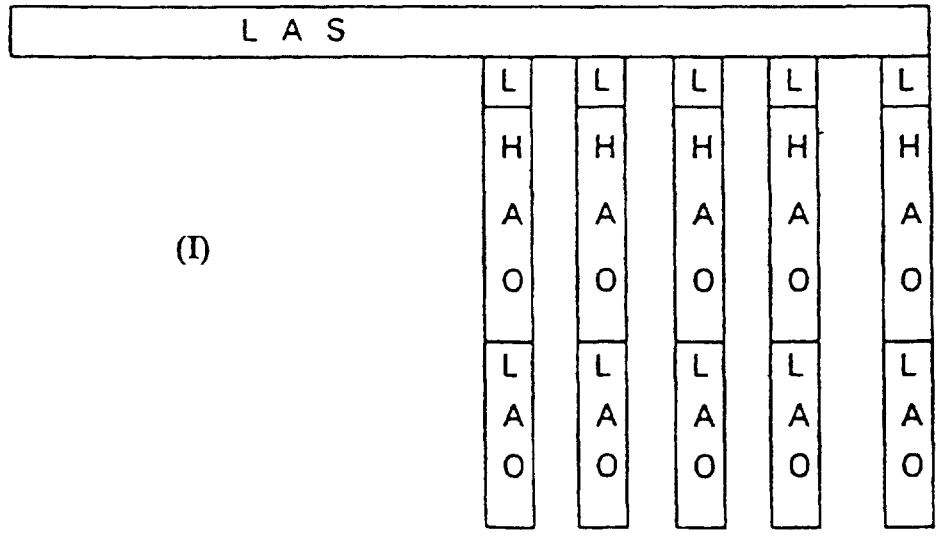
7. Verfahren zur Herstellung von Emulsionen tafelförmiger Silberhalogenidkörner nach Anspruch 1, dadurch gekennzeichnet, dass das Polyalkylenoxid/Polyalkylsiloxan-Copolymer vor Beginn des Keimbildungsschritts (a) in den Reaktionsbehälter eingegeben wird.

Revendications

1. Procédé de préparation d'émulsions à grains tabulaires d'halogénures d'argent, ledit procédé comprenant les étapes suivantes :

(a) formation d'une population de noyaux d'halogénures d'argent dans un milieu dispersant.
(b) maturation de ladite population de noyaux d'halogénures d'argent, et
(c) croissance de ladite population de noyaux d'halogénures d'argent pour former des grains tabulaires d'halogénures d'argent, caractérisé en ce qu'un copolymère d'oxyde de polyalkylène et de polyalkylsiloxane est ajouté pendant au moins l'une desdites étapes (a), (b) et (c).

2. Procédé de préparation d'émulsions à grains tabulaires d'halogénures d'argent selon la revendication 1, dans lequel ledit copolymère d'oxyde de polyalkylène et de polyalkylsiloxane a la formule générale (I) suivante :



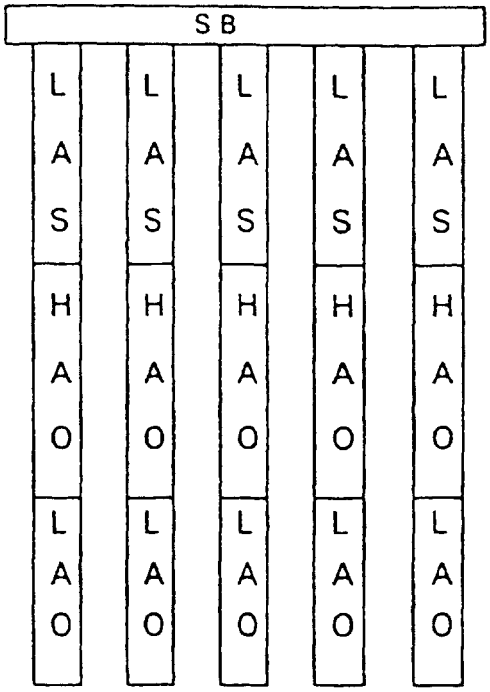
(I)

dans laquelle LAS représente une unité de bloc lipophile alkylènesiloxane, HAO représente une unité de bloc hydrophile oxyde d'alkylène, LAO représente une unité de bloc terminale lipophile oxyde d'alkylène et L représente

un système hydrocarboné lipophile.

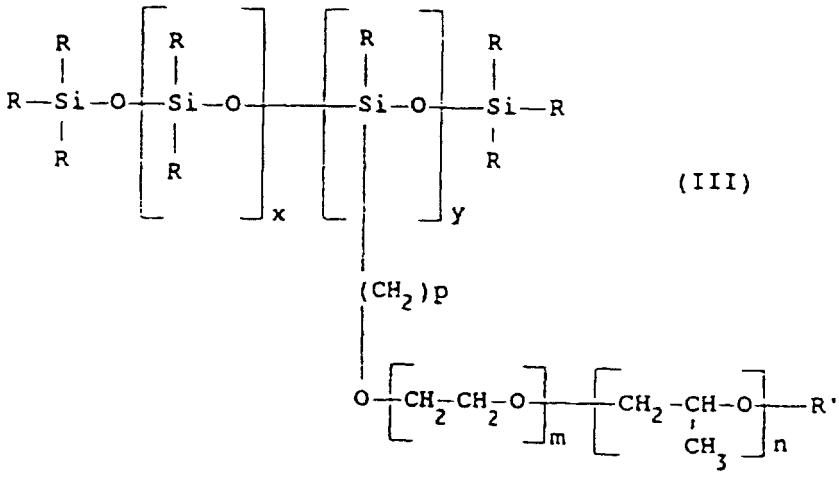
3. Procédé de préparation d'émulsions à grains tabulaires d'halogénures d'argent selon la revendication 1, dans lequel ledit copolymère d'oxyde de polyalkylène et de polyalkylsiloxane a la formule générale (II) suivante :

(II)



dans laquelle LAS représente une unité de bloc lipophile alkylènesiloxane, HAO représente une unité de bloc hydrophile oxyde d'alkylène, LAO représente une unité de bloc terminale lipophile oxyde d'alkylène et SB est un squelette silicone.

4. Procédé de préparation d'émulsions à grains tabulaires d'halogénures d'argent selon la revendication 1, dans lequel ledit copolymêre d'oxyde de polyalkylène et de polyalkylsiloxane a la formule générale (III) suivante :

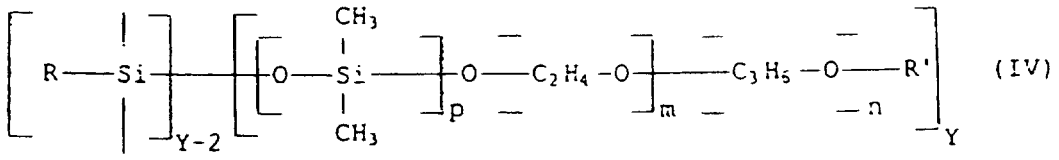


(III)

dans laquelle R est un groupe méthyle, R' peut être un hydrogène ou un radical alkyle inférieur ayant 1 à 4 atomes de carbone, x est un nombre entier compris entre 0 et 100, y est un nombre entier compris entre 1 to 50, m est un nombre entier compris entre 1 et 50, n est un nombre entier compris entre 1 et 50, et p est un nombre entier com-

pris entre 2 et 6.

5. Procédé de préparation d'émulsions à grains tabulaires d'halogénures d'argent selon la revendication 1, dans lequel ledit copolymère d'oxyde de polyalkylène et de polyalkylsiloxane a la formule générale (IV) suivante :



(IV)

dans laquelle R est un groupe méthyle, R' peut être un hydrogène ou un radical alkyle inférieur ayant 1 à 4 atomes de carbone, y est un nombre entier compris entre 3 to 50, m est un nombre entier compris entre 1 et 50, n est un nombre entier compris entre 1 et 50, et p est un nombre entier compris entre 1 et 50.

6. Procédé de préparation d'émulsions à grains tabulaires d'halogénures d'argent selon la revendication 1, dans lequel ledit copolymère d'oxyde de polyalkylène et de polyalkylsiloxane est ajouté au réacteur en une quantité allant de 5 à 200 mg par mole d'argent total ajouté pendant la formation des grains tabulaires d'halogénures d'argent.

7. Procédé de préparation d'émulsions à grains tabulaires d'halogénures d'argent selon la revendication 1, dans lequel ledit copolymère d'oxyde de polyalkylène et de polyalkylsiloxane est ajouté au réacteur avant le début de l'étape de nucléation (a).