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(54) Silver halide photographic emulsion comprising grains having faces (100) with cavities.

(57) The present invention concerns a silver halide photographic emulsion.

This emulsion comprises grains with faces (100) in which cavities are formed.

Application to the improvement of the sensitivity of the photographic emulsion.

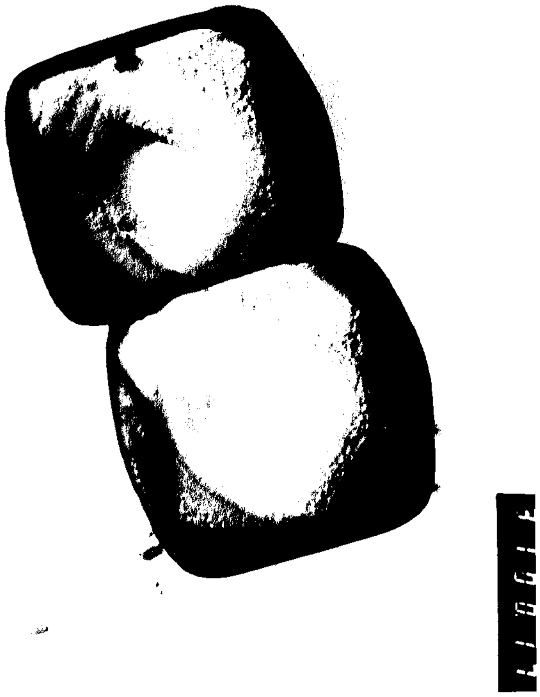

Fig. 1

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The present invention concerns silver halide photographic emulsions and particularly silver halide grains of the core/shell type, and a process for obtaining these grains and the corresponding photographic emulsions.

The process for forming the photographic image in silver halides comprises a stage of forming a latent image. At the time of exposure, electrons are produced and these electrons migrate in the grain and are trapped at specific sites where the latent image is formed. In ordinary, non-sensitised, silver halide grains, dispersion of the sites promotes a faster subsequent development but enables only low sensitivity levels to be achieved. The purpose of the sensitisation is to concentrate these sites in order to increase sensitivity. However, in doing this, the development speed is reduced.

Means have therefore been sought for improving the concentration and localisation of the latent image sites in silver halide grains. These means in the prior art consist of using compounds which are absorbed selectively on certain sites in the grains, introducing distortions in the grain or in the crystalline morphology of the grains, as is described in European patent 96 726 or US patent 5 045 443, modifying the grains by epitaxy, as is described in European patent 462 581, or again producing grains with a complex crystalline form, as is described in US patent 4 710 455. None of these different means is entirely satisfactory.

The present invention relates to silver halide grains with a sensitivity which is improved because of the better concentration of the latent image sites, resulting from the particular morphology of these grains, and a process for obtaining these grains.

The process according to the invention comprises the following stages:

(a) silver bromide grains are formed in a colloidal dispersion medium (such as a aqueous solution of gelatin); it is possible to proceed by nucleation from silver bromide nuclei or silver bromoiodide nuclei, at a pAg of between approximately 8.5 and 9.5 , a temperature of between 40 and 70°C and a pH of between 5.0 and 7.0,

(b) growth of the silver bromide grains obtained in stage (a) is achieved by maintaining the conditions of stage (a) until grains with a mean diameter of between 0.1 and 3.0 μm are obtained,

(c) the pAg is adjusted to a value between 7.5 and 8.0 and then to a value between 6.0 and 7.5, maintaining the temperature at approximately 60°C, and

(d) a silver chlorobromide shell is precipitated on the grains obtained at (c) in two successive stages, the first at an accelerated rate, the second at a constant rate, maintaining the pAg between 7.0 and 7.5, the temperature between 50 and 80°C and advantageously between 60 and 70°C, and the pH between 5.0 and 7.0, so as to achieve a preferential growth of silver chlorobromide on the edges adjacent to the faces (100) of the silver halide grains, and continuing this growth to the point where a cavity has been formed in the central region of the said faces (100).

In the above stage (c), the pAg is adjusted to between 7.5 and 8.0 by means of a silver nitrate solution and to between 7.5 and 6.0 by means of a simultaneous addition of chlorobromide and nitrate.

The photographic silver halide grains according to the invention are cubic or cubo-octahedral grains consisting of a core comprising silver bromoiodide or bromide and a silver chlorobromide shell; these grains have faces (100), 10 to 90% of the surface of which is occupied by a cavity.

The present invention is based on the concept that the morphology of the faces (100) of the grains can be modified to the point of forming holes or cavities on these faces by the controlled growth of silver halide on the edges delimiting these faces or on the faces (111). It will obviously be understood that this is only a hypothesis, that the cavities thus formed on the faces (100) constitute favoured centres for the subsequent deposition or adsorption of substances, for example sensitising dyes, which can then help to orientate the chemical sensitisation on favoured sites.

The emulsions according to the invention are cubo-octahedral emulsions obtained by precipitating, in a first stage, a first silver halide which constitutes the core of the grains, and then, in a second stage, a second silver halide which constitutes the shell of the grains. It is by modifying the conditions of precipitation of the shell that, under conditions described below, the cavities are obtained on the faces (100) of the grains. Consequently, the formation of these cavities on the faces (100) is also dependent on an appreciable variation in the crystalline phase between the core of the grain and its peripheral part, or shell.

The core consists of silver bromide or silver bromoiodide. The quantity of iodide may represent up to 30% molar and advantageously between 5 and 20% molar with respect to the total quantity of silver in the grains. The presence of iodide in the core of the grain, without being a necessary condition, assists the formation of the cavities in the faces (100) of the shell.

The shell contains silver chlorobromide. The chloride content is between 3 and 20% molar and advantageously between 5 and 15% molar with respect to the total quantity of silver in the grain. When the core consists of silver bromide, the optimum chloride content of the shell is between 10 and 15% molar, and when the core comprises silver bromoiodide, the optimum chloride content of the shell is between 3 and 25% molar with respect to the total quantity of silver.

As stated above, the present invention has the dual characteristic that the growth of the halide in the shell is modified and a modification of the crystalline phase between the core and the shell is created. This is achieved by modifying the parameters of the precipitation of the shell of the grains, namely the growth profile of the shell, the pAg, the agitation and the temperature.

The process for preparing the silver halide grains according to the invention comprises the following stages:

(a) silver bromide grains are formed in a colloidal dispersion medium (such as a solution of gelatin in water); it is possible to proceed by nucleation from silver bromide nuclei or silver bromoiodide nuclei, at a pAg of between approximately 8.5 and 9.5, a temperature of between 40 and 70°C and a pH of between 5.0 and 7.0,

(b) growth of the silver bromide grains obtained in stage (a) is achieved by maintaining the conditions of stage (a) until grains with a mean diameter of between 0.1 and 3.0 μm are obtained,

(c) the pAg is adjusted to a value between 7.5 and 8.0 and then to a value between 6.0 and 7.5, maintaining the temperature at approximately 60°C, and

(d) a silver chlorobromide shell is precipitated on the grains obtained at (c) in two successive stages, the first at an accelerated rate, the second at a constant rate, maintaining the pAg between 7.0 and 7.5, the temperature between 50 and 80°C and advantageously between 60 and 70°C, and the pH between 5.0 and 7.0, so as to achieve a preferential growth of silver chlorobromide on the ridges adjacent to the faces (100) of the silver halide grains and continuing this growth to the point where a cavity has been formed in the central region of the said faces (100).

According to one embodiment, in the growth stage (b), silver bromoiodide is precipitated. The core of the grains then consists of silver bromoiodide. The total quantity of iodide represents, in the core of the grains, up to 30% molar with respect to the total quantity of silver in the grain.

According to one embodiment, in stage (c), the pAg is adjusted to a value between 7.5 and 8.0 by means of silver nitrate and to a value between 6.0 and 7.5 with a simultaneous addition of silver nitrate and chlorobromide.

In stage (d), the flow rates of silver nitrate and sodium bromochloride are first accelerated, for example varying from 10 ml to 200 ml and advantageously from 20 ml to 100 ml. Then the flow rates of silver nitrate and sodium bromochloride are thereafter maintained constant, at a value between 50 and 200 ml and advantageously between 70 and 140 ml/min.

Proof that the silver halide grains according to the invention have cavities on the faces (100) is afforded by:

(A) conventional scanning electron microscopy, by direct observation, or by observation of carbon replicas, at a magnification of 250,000;

(B) analysis of the surface by tunnel-effect microscopy;

(C) X-ray diffraction.

Figure 1 shows an electron microscopy image of the carbon replica of a cubo-octahedral grain according to the invention with an ECD of 1.1 μm and a CoV (coefficient of variation) of 8% and with an edge adjacent to the face 100 of 0.53 μm, having a hole on one face (100), at a magnification of 250,000; the hole has an edge of 0.25 μm and a depth of 0.13 μm; the surface area of the hole represents 20% of the face (100) of the grain.

Figure 2 shows an electron microscopy image of the carbon replica of another cubo-octahedral grain according to the invention, at the same magnification.

Figure 3 shows the topography derived from a tunnel-effect microscopy photograph of a face (100) of a silver halide grain according to the invention, that is to say with a cavity; the depth of the cavity is 98.5 nm.

Figure 4 shows the topography, derived from a tunnel-effect microscopy photograph, of a face (100) of another grain according to the invention; the depth of the cavity is 132.7 nm.

Figure 5 shows the X-ray diffraction spectra of an emulsion having grains according to the invention, with holes on the faces (100), and of an emulsion having grains without a hole on the faces (100).

A process for increasing the size of the silver halide crystals formed by the process described here is to carry out the precipitation in the presence of a silver halide solvent. It is preferred that grain growth or ripening occur inside the reactor during grain formation. Known ripening agents can be used. These comprise ammonia or an excess of halide ions. Consequently, it appears that the halide salt solution run into the reactor can itself promote ripening. It is also possible to use other solvents or ripening agents which can be entirely contained within the dispersion medium in the reactor, before silver and halide salt addition or they can be introduced into the reactor with one or more halide or silver salts or peptizers. In another embodiment, the solvent or ripening agent may be introduced independently during the addition of the halide salts and silver salts.

The conventional silver halide solvents suitable for being used in the process of the present invention comprise ammonia, thiocyanates, thiosulphates and various thioethers and thioureas. The solvents based on thioethers comprise the solvents described in US patents 3 271 157, 3 531 289, 3 574 628, 3 767 413, 4 311 638 and 4 725 560. The useful solvents based on thiourea comprise the solvents described in US patents 4 284 717, 4 568 635, 4 695 534, 4 635 535, 4 713 322 and 4 749 646.

The silver halide grains produced according to the process of this invention have a bulk iodide content of between 2 and 15%. The size of the grains, as determined by the equivalent circular diameter of their projected surface area, is between 0.1 and 5.0 μm.

The various modifier compounds, such as the solvents for silver halides, the ripening agents, the spectral or sensitising dyes or the doping agents etc, may be present during the precipitation of the grains. Depending on the nature of some of these compounds, they may be absorbed within the cavities in the surfaces (100) of the grains.

In addition, it is believed that the photographically useful agents, such as developers, development accelerators, development inhibitors, dye image forming couplers, etc, or the precursors of such photographically useful agents, may be present during the precipitation of the grains so as to be incorporated within the cavities in the grain. Such agents are then easily available at the various grain development stages, in accordance with the environment in which they are situated.

The modifier compounds and the photographically useful agents may initially be in the reactor or they may be added either separately or with one or more of the salts, in accordance with conventional operating methods.

The chemical sensitisers and doping agents, such as compounds of copper, thallium, lead, bismuth, cadmium, zinc, the middle chalcogens (namely sulphur, selenium and tellurium), the group VIII noble metals and gold, may be present during the precipitation of the silver halides. US patents 1 195 432, 1 951 933, 2 448 060, 2 628 167, 2 950 972, 3 488 709, 3 737 313, 3 772 031 and 4 269 927 and Research Disclosure, Vol 134, June 1975, Article 13452, describe them. Research Disclosure and its predecessor, Product Licensing Index, are publications of Kenneth Mason Publications Limited, Emsworth, Hampshire, PO10 7DD, United Kingdom. The emulsions can be sensitised internally by reduction during precipitation, as described by Moisar et al, Journal of Photographic Science, Vol 25, 1977, pages 19-27.

The halide salts and silver salts individually may be added to the reactor by using surface or sub-surface delivery tubes, by gravity feed or by delivery apparatus for maintaining control of the rat of delivery, the pH, the pBr and/or the pAg of the reaction medium. US patents 3 821 002 and 3 031 304 and Claes et al, Photographische Korrespondenz, Vol 102, No 10, 1967, page 162, describe these methods. In order to obtain a rapid distribution of the reactants in the reactor, special mixing devices can be used. US patents 2 996 287, 3 342 605, 3 415 650, 3 785 777, 4 147 551 and 4 171 224, UK patent application 2 022 431A, German patent applications 2 555 364 and 2 556 885, and Research Disclosure, Vol 166, February 1978, Article 16662, describe such methods.

In order to form emulsions, a dispersion medium is initially introduced into the reactor. In a preferred form, the dispersion medium consists of an aqueous peptizer suspension. Peptizer concentrations are between approximately 0.2 and 10% by weight, based on the total weight of emulsion components in the reactor. It is usual practice to maintain the concentration of peptizer in the reactor at a value below approximately 6%, based on the total weight, before and during the formation of the silver halide, and to increase the emulsion vehicle concentration in order to obtain optimum coating characteristics by the delayed supplemetal addition of vehicle. It will be understood that the emulsion, as initially formed, contains approximately 5 to 50 g of peptizer per mole of silver halide and preferably approximately 10 to 30 g of peptizer per mole of silver halide. An additional quantity of vehicle can be added subsequently in order to obtain a concentration of up to 1000 g per mole of silver halide. The concentration of vehicle in the final emulsion is preferably greater than 50 g per mole of silver halide. When the final emulsion is coated and dried in forming a photographic element, the vehicle preferably represents approximately 30 to 70% by weight of the emulsion layer.

The vehicles (which comprise both binders and peptizers) can be chosen from amongst the vehicles generally used in silver halide emulsions. The preferred deflocculants are hydrophilic colloids, which can be used alone or in combination with hydrophobic substances. Suitable hydrophilic substances comprise gelatin, for example alkali-treated gelatin (hide gelatin or cattle bone gelatin) or acid-treated gelatin (pigskin gelatin), gelatin derivatives, for example acetylated gelatin, phthalylated gelatin, etc.

The vehicles, comprising particularly the hydrophilic colloids, as well as the hydrophobic substances used in combination with the latter, may be employed not only in the layers of emulsion on the photographic elements of this invention, but also in other layers, such as the top layers, the intermediate layers and the layers located below the emulsion layers.

The emulsions are preferably washed in order to eliminate the soluble salts. The soluble salts may be eliminated by decantation, filtration and/or chill setting and leaching, as described in US patents 2 316 845 and 3 396 027, by coagulation washing, as described in US patents 2 618 556, 2 614 928, 2 565 418, 3 241 969 and 2 489 341, by centrifugation and decantation of a coagulated emulsion, as described in US patents 2 463 794, 3 707 378, 2 996 287 and 3 498 454, by using hydrocyclones alone or in combination with centrifuges, as described in UK patents 1 336 692 and 1 356 573 and by Ushomirskii et al, Soviet Chemical Industry, Vol 6, No 3, 1974, pages 181-185. The emulsions can be dried and stored, with or without sensitisers, before using them, as described by Research Disclosure, Vol 101, September 1972, Article 10152. It is particularly advantageous to wash the emulsions after the completion of the precipitation.

The silver halide emulsions of the present invention may be sensitised chemically by means of active gelatin, as described by T H James, The Theory of the Photographic Process, 4th Ed., Macmillan, 1977, pp. 67-76, or by means of sulphur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, rhodium, rhenium, or phosphorous sensitisers or combinations or these sensitisers, at pAg levels between 5 and 10, pH values between 5 and 8 and temperatures between 30° and 80°C, as described in Research Disclosure, Vol 120, April 1974, Article 12008, Research Disclosure, Vol 134, June 1975, Article 13452, in the US patents 1 623 499 of Sheppard et al, 1 673 522 of Matthies et al, 2 399 083 of Waller et al, 2 642 361 of Damschroder et al, 3 297 447 of McVeigh and 3 297 446 of Dunn, in the UK patent 1 315 755 of McBride, in the US patents 3 772 031 of Berry et al, 3 761 267 of Gilman et al, 3 857 711 of Ohi et al, 3 565 633 of Klinger et al and 3 901 714 and 3 904 415 of Oftedahl, and in the UK patent 1 396 696 of Simons; the chemical sensitisation may optionally be conducted in the presence of thiocyanates, as described in the US patent 2 642 361 of Damschroder, compounds containing sulphur of the type described in the US patents 2 521 926 of Lowe et al, 3 021 215 of Williams et al and 4 054 457 of Bigelow, or derivatives of carboxylated thiourea as described in US patent 4 810 626. The emulsions can be sensitised chemically in the presence of modifiers finish (chemical sensitisation) - that is to say compounds known to eliminate fogging and increase speed when they are present during the chemical sensitisation, such as azaindenes, azapyradazines, azapyrimidines, benzothiazolium salts and sensitisers comprising one or more heterocyclic rings.

Examples of agents modifying the finish are described in the US patents 2 131 038 of Brooker et al, 3 411 914 of Dostes, 3 554 757 of Kuwahara et al, 3 565 631 of Oguchi et al and 3 901 714 of Oftadahl, in the Canadian patent 778 723 of Walworth and in Duffin, Photographic Emulsion Chemistry, Focal Press (1966), New York, pp 138-143. In addition, the emulsions can be sensitised by reduction - for example by means of hydrogen, as described in the US patents 3 891 446 of Janusonis and 3 984 249 of Babcock et al, by processing using a low pAg (for example less than 5) and/or a high pH (for example above 8) or by using reducing agents such as tin chloride, thiourea dioxide, polyamines and borane amines, as described in the US patent 2 983 601 of Allen et al, in the article by Oftadahl et al, Research Disclosure, Vol 136, August 1975, Article 13654, in the US patents 2 518 698 and 2 739 060 of Lowe et al, 2 743 182 and 2 743 183 of Roberts et al, 3 026 203 of Chambers et al and 3 361 564 of Bigelow et al. Surface chemical sensitisation or sub-surface sensitization below the surface, described in the US patents 3 917 485 of Morgan and 3 966 476 of Becker can be used. It is also possible to use associations of compounds of gold (I) and carboxylated N-methyl thiourea as described in US patents 5 049 485 and 5 049 484.

The silver halide emulsions used in this invention can be sensitised by conventional techniques described in Research Disclosure, Vol 178, December 1978.

The conventional techniques of sensitisation by means of noble metals (for example gold), the middle chalcogens (for example sulphur, selenium and/or tellurium) or sensitisation by reduction, as well as combinations of these techniques, are described in Research Disclosure, Article 17643, paragraph III, mentioned previously.

The silver halide emulsions record blue radiation, and need not to be spectrally sensitized in the blue part of the spectrum. The silver bromide and silver bromoiodide emulsions can be used for cording blue radiation without incorporating blue sensitisers, although their absorption efficiency is much higher when blue sensitisers are used. The silver halide emulsions, regardless of composition, intented to record radiation in the minus blue, are sensitised spectrally to green or red radiation by using spectral sensitising dyes.

The silver halide emulsions of this invention can be sensitised spectrally by using dyes of various classes, including the class of polymethine dyes, which comprise cyanines, merocyanines, complex cyanines and merocyanines (that is to say tri-, tetra- and polynuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls and streptocyanines.

One or more spectral sensitising dyes can be used. The dyes with the maximum sensitisation at wavelengths in the visible spectrum and having a wide variety of spectral sensitivity curve shapes are known. The choice and the relative proportions of the dyes depend on the region of the spectrum which it is desired to sensitise and on the shape of the spectral sensititivity curve desired.

The dyes with overlapping spectral sensitivity curves often yield, in combination, a curve in which the sensitivity at each wavelength in the overlap area 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 in order to obtain a spectral sensitivity curve with a maximum which is intermediate with respect to the sensitisation maxima of the individual dyes.

Combinations of spectral sensitising dyes can be used which result in supersensitisation, that is to say a spectral sensitisation greater in a certain spectral region than the one obtained by using any concentration of one of the dyes alone, or which would result from the additive effect of the dyes. Supersensitisation can be obtained by using selected combinations of spectral sensitising dyes and other additives, such as stabilisers and anti-fogging agents, accelerators or development inhibitors, coating additives, optical brighteners and antistatic agents. Gilman, "Review of the Mechanisms of Supersensitisation", Photographic Science and Engineering, Vol 18, 1974, pages 418-430, describes the different mechanisms as well as the compounds which can be responsible for supersensitisation.

The spectral sensitisation can be implemented at any stage in the preparation of the emulsion which is known up till now for being useful. The most usual spectral sensitisation is implemented in the art after ending the chemical sensitisation. However, the spectral sensitisation can be implemented either simultaneously with the chemical sensitisation or before the chemical sensitisation; it can even begin before the end of the precipitation of the silver halide grains, as described in US patent 3 628 960 and in the US patent 4 225 666 of Locker et al. The sensitisation can be enhanced by adjusting the pAg, including varying the pAg in one or more cycles, during the chemical and/or spectral sensitisation. Research Disclosure, Vol 181, May 1979, Article 18155 gives a specific example of adjustment of the pAg.

The additives, such as spectral sensitising dyes, in the grains of this invention may be added on all the faces or all the sides of the grains, which makes it possible to obtain a potential increase in the effects derived from these additives.

The sensitisation stage, whether it be chemical or spectral, may be implemented before the end of the formation of the grains according to the invention. This procedure allows both internal and external surfaces of the grain to be sensitized thereby providing, which enables a high surface/volume ratio and enhanced light absorption .

The photographic elements can use conventional additives, as described in Research Disclosure, Article 17643, cited previously and incorporated here by way of reference. Optical brighteners can be introduced, as described in paragraph V. Anti-fogging agents and sensitisers can be incorporated, as described in paragraph VI. Absorbent and scattering substances can be used in the emulsions of the invention and in the separate layers of the photographic elements, as described in paragraph VIII. Hardening agents can be incorporated, as described in paragraph X. Coating additives, as described in paragraph XI, and plasticisers and lubricants, as described in paragraph XII, may be present. Antistatic layers, as described in paragraph XIII, may be present. The methods of adding the additives are described in paragraph XIV. Matting agents can be incorporated, as described in paragraph XVI. Developers and development modifying agents can be incorporated, if desired, as described in paragraphs XX and XXI. The silver halide emulsion layers and the intermediate layers, top layers and substrate layers, if any, present in the photographic elements can be coated and dried as described in paragraph XV.

The layers on the photographic elements can be coated on various supports. Conventional photographic supports include polymer films, paper, metal sheets, glass and ceramic supporting elements, provided with one or more subbing layers to reinforce the adhesion properties, the antistatic, dimensional and abrasion properties, the hardness, friction and antihalation characteristics and/or the other properties of the surface of the support. The useful polymer film and paper supports are described in Research Disclosure, Article 17643 cited previously, paragraph XVII.

The photographic elements can be used to form dye images in these elements though the selective destruction for formation of dyes. The photographic elements can be used to form dye images by using developers containing dye image forming compounds, such as chromogenic couplers. In this form, the developer contains a color developping agent (for example a primary aromatic amine) which, in its oxidised form, is capable of reacting with the coupler (coupling) to form the image dye.

The dye-forming couplers can be incorporated in the photographic elements, as described in Research Disclosure, Vol 159, July 1977, Article 15930.

The dye-forming couplers and the other photographically useful compounds, such as inhibiters and development accelerators, can be incorporated in the hollow part of the grains of this invention. This can be achieved by adding the compounds to the precipitation vessel before completing the formation of the shell of the grains with the cavities and by eliminating therefrom, by washing, the photographically useful compounds which have not been incorporated, etc. These compounds can be released starting from the central part of the grains in the course of the photographic processing.

The dye-forming couplers are generally chosen to form subtractive primary image dyes (that is to say yellow, magenta and cyan) and they are non-diffusible colourless couplers, such as 2 and 4 equivalent couplers of the open chain ketomethylene, pyrazolone, pyrazolotriazole, pyrazolobenzimidazole, phenol and naphthol type hydrophobically ballasted for incorporation in the high boiling organic (coupler) solvents.

The dye-forming couplers, after coupling, are able to release photographically useful fragments, such as development inhibiters or accelerators, bleaching accelerators, reducing agents, solvents for silver halides, pigments, tanning agents, fogging agents, anti-fogging agents, competing couplers, etc.

EXAMPLE 1

This example illustrates the preparation of photosensitive silver halide grains with holes on the faces (100):

a) In a 20 l reactor, 57.8 g of deionised phthalylated gelatin and 4156 ml of distilled water were added; the solution obtained was heated to 60°C, the pH was adjusted to 5.1 and the pAg to 9.00, using 0.01 M NaBr; a 0.5 N NaBr solution and a 0.5 N $AgNO_3$ solution were added to the reactor by the double-jet technique, maintaining a controlled pAg of 9.00 and with a flow rate of 60 ml/min. In this way a stable population of AgBr microcrystals (0.026 moles) was obtained.

b) The growth of the crystals was continued for 30 minutes under the same conditions, using the double-jet technique with accelerated flow rates with a parabolic profile of $AgNO_3$ (2 N), NaBr (1.82 N) and KI (0.18 N) solutions, as indicated below:

Duration	Initial flow rate	Final flow rate
30 min	15 ml/min	114 ml/min

A mixed AgBrI phase was obtained (precipitation of 3.36 moles of silver).

c) After this growth stage, the pAg was adjusted to 7.75, by introducing 0.25 moles of $AgNO_3$ into the reactor over 143 seconds. The pAg was adjusted to 7.0 by introducing solutions of $AgNO_3$, NaBr and NaCl at 25 ml/min over 123 seconds.

d) The crystal growth was continued, using the following flow rate profiles:

Duration	Solution	Initial flow rate (ml/min)	Final flow rate (ml/min)
(I) 30 min	$AgNO_3$ 2.0 M	20 ml/min	100 ml/min
	NaBr 1.7 M	23.5 ml/min	117.7 ml/min
	NaCl 0.3 M	23.5 ml/min	117.7 ml/min
(II) 15 min	$AgNO_3$ 2.0 M	100 ml/min	100 ml/min
	NaBr 1.7 M	117.7 ml/min	117.7 ml/min
	NaCl 0.3 M	117.7 ml/min	117.7 ml/min

The pAg, pH and temperature were maintained at the values recorded at the end of stage (c), namely: pAg 7.0 temperature = 60°C, pH = 5.10. In phase (I), 3.57 moles of silver was precipitated, and in phase (II) 3.0 moles of silver.

At the end of stage (d), a chlorobromide shell has been obtained, the faces (100) of which have holes in them.

The emulsion was washed in a conventional manner by flocculation. The final emulsion consists of cubo-octahedral grains with an ESD (equivalent spherical diameter) of 1.06 μm, a COV (volume coefficient of variation) of 7.2% and a total iodide content of 3 moles %.

EXAMPLE 1A

An emulsion was prepared in accordance with the operating method of Example 1, with the following modifications.

Stage (d) was carried out by using the following flow rates (double jet):

Duration	Solution	Initial flow rate (ml/min)	Final flow rate (ml/min)
(I) 11.5 min	$AgNO_3$ 2.0 M	20 ml/min	49.8 ml/min
	NaBr 1.7 M	23.5 ml/min	58.8 ml/min
	NaCl 0.3 M	23.5 ml/min	58.6 ml/min
(II) 57.7 min	$AgNO_3$ 2.0 M	50 ml/min	50 ml/min
	NaBr 1.7 M	58.6 ml/min	58.6 ml/min
	NaCl 0.3 M	58.6 ml/min	58.6 ml/min

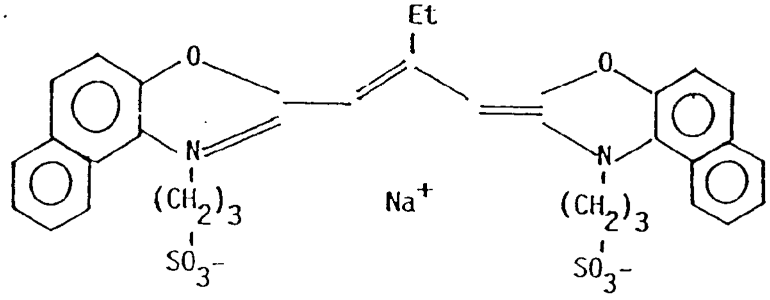
The emulsion was washed as in Example 1. The final emulsion consists of cubo-octahedral grains with an ESD of 1.04 µm, a COV of 7.3% and a total iodide content of 3 moles %. The electron microscopy photographs show that less than 5% of these grains have holes on their faces (100).

EXAMPLE 2

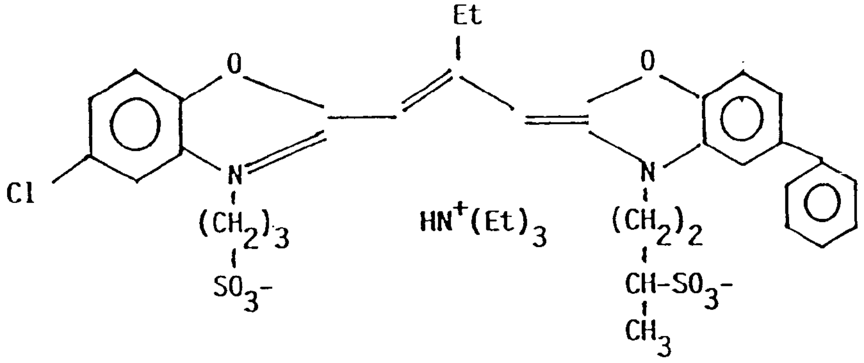
The emulsion prepared in accordance with the operating method of Example 1 was sensitised chemically and spectrally in the following manner. After precipitation of the shell and washing, the following were added successively:

- Potassium thiocyanate (5H20): 150 mg/mole Ag
- Sensitising dye (I): 186 mg/mole Ag
- Sensitising dye (II): 53.7 mg/mole Ag
- 10 min stage at 40°C
- Sodium thiosulphate: 0.27 mg/mole Ag
- $Na_2Au(S_2O_3)_2$: 2.03 mg/mole Ag
- Heating at 70°C for 20 minutes
- APMT: 50 mg/mole Ag

Dye (I)



Dye (II)



APMT: Aceto phenyl-5-mercaptotetrazole

The emulsion was applied to a cellulose triacetate support at 8.07 mg of silver, 32.3 mg of gelatin and 10.5 mg of the dye-forming coupler whose formula is given below, per dm^2. The gelatin was hardened with 1.75% bis(vinylsulphonylmethyl)ether. A top layer of gelatin (2.15 mg/dm^2) was coated on this layer. The product thus obtained was exposed for 1/100th of a second to a 3000°K light source through a Wratten 9 filter and processed using the Kodak C-41 process for developing colour negative films.

The sensitometric results are set out in Table I.

EXAMPLE 3 (Comparison)

The operating method of Example 2 was repeated, except that the emulsion prepared in Example 1A, the grains of which have practically no holes, was used. The product is then sensitised, coated, exposed and developed as indicated in Example 2.

The sensitometric results are set out in Table I.

TABLE I

Example	Dmax	Dmin	Contrast	Relative sensitivity	Δp
2 (invention)	2.04	0.13	1.33	112	O
3 (comparison)	2.9	0.10	1.41	100	+7

relative sensitivity: calculated at density = 0.3

Δp: loss of sensitivity under the effect of a pressure of 25 psi (175 kPa), exerted before exposure.

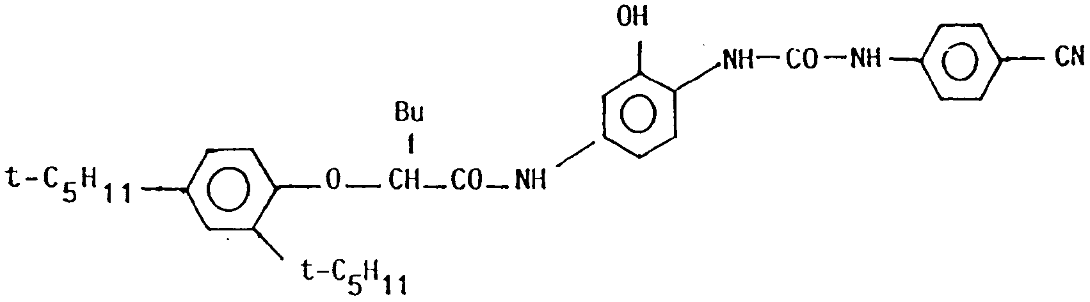
EXAMPLE 4

The emulsion prepared in accordance with the operating method of Example 1 is sensitised chemically and spectrally in the following manner. After precipitation of the shell and washing, the following are added successively:

- Potassium thiocyanate: 75 mg/mole Ag
- Sensitising dye (I): 186 mg/mole Ag
- Sensitising dye (II): 53.7 mg/mole Ag
- 10 min stage at 60°C
- Di(N-methyl-N-carboxymethyl)thiourea: 2.61 mg/mole Ag
- Gold (I) bis(1,4,5-trimethyl-1,3,4-triazolium-3-thiolate) tetrafluoroborate 1.8 mg/mole Ag
- Heating at 65°C for 15 minutes

The emulsion was coated on a support so as to form a product under the same conditions as in Example 2.

Coupler



The product obtained was processed using the Kodak C-41 process for developing colour negative films.

EXAMPLE 5 (Comparison)

The operating method of Example 4 was repeated, but using the emulsion prepared in Example 1A, in which the grains have practically no holes. The product is then sensitised, coated, exposed and processed as in Example 4.

The results obtained are set out in Table II.

TABLE II

	Dmax	Dmin	Contrast	Relative sensitivity	Δp
Example 4 (invention)	2.06	0.15	1.67	142	+2
Example 5	1.95	0.15	1.42 (comp)	136	+32

Claims

1. Process for preparing core/shell silver halide grains, sensitive to radiation, characterised in that it comprises the following stages:
   (a) forming silver bromide grains in a colloidal dispersion medium, by nucleation from silver bromide nuclei or silver bromoiodide nuclei, at a pAg of between 8.5 and 9.5, a temperature of between 40 and 70°C and a pH of between 5.0 and 7.0;
   (b) during a growth stage, maintaining the conditions of stage (a) until core grains with a mean diameter of between 0.1 and 2.0 μm are obtained;
   (c) modifying the growth environment of the core grains, by successively adjusting the pAg to a value between 7.5 and 8.0 and then to a value between 7.5 and 6.0, maintaining the temperature at approximately 60°C;
   (d) effecting the growth of a silver chlorobromide shell on the core grains by precipitating the silver chlorobromide in two successive stages, the first at an accelerated rate, the second at a constant rate, maintaining the pAg at a value between 7.0 and 7.5, at a temperature of between 50 and 80°C, and a pH of between 5.0 and 7.0, so as to achieve a preferential growth of silver chlorobromide on the ridges adjacent to the faces (100) of the silver halide grains and continuing this growth to the point where a cavity has been formed in the central region of the said faces (100).

2. Process according to Claim 1, characterised in that in stage (b) silver bromoiodide is precipitated.

3. Cubic or cubo-octahedral silver halide grains consisting of a core comprising silver bromoiodide and a silver chlorobromide shell, these grains having faces (100), 10 to 90% of the surface of which is occupied by a cavity.

4. Grains according to Claim 3, characterised in that they have faces (100), 10 to 40% of the surface of which is occupied by a cavity.

5. Grains according to one of Claims 3 or 4, characterised in that they have an equivalent circular diameter of between 0.1 and 5.0 μm.

6. Grains according to one of Claims 3 to 5, characterised in that the shell contains from 10 to 15 % molar chloride with respect to the total quantity of silver in the grain.

7. Grains according to Claim 6, characterised in that the shell contains 15 to 70% molar chloride with respect to the total quantity of silver in the grain.

8. Grains according to one of Claims 3 to 5, characterised in that they contain up to 30% molar iodide in the core with respect to the total quantity of silver in the grain.

9. Grains according to Claim 8, characterised in that the core contains between 5 and 15% molar iodide, and the shell at least 3% molar chloride, with respect to the total quantity of silver in the grain.

10. Grains according to one of Claims 3 to 9, characterised in that the shell/core molar ratio is between approximately 1:1 and 5:1.

11. Photographic product comprising at least one layer of emulsion which contains silver halide grains according to one of Claims 3 to 10.

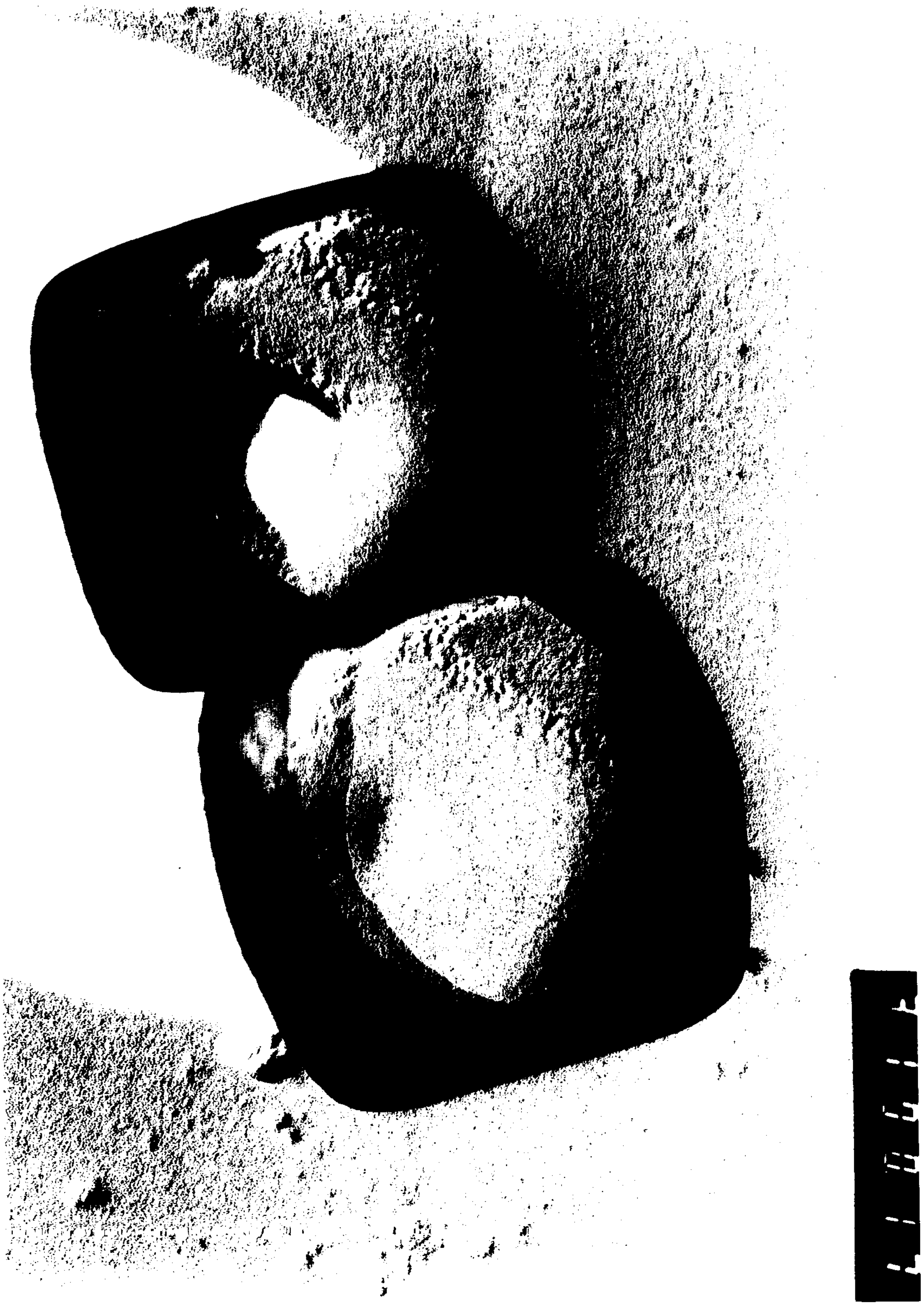


Fig. 1

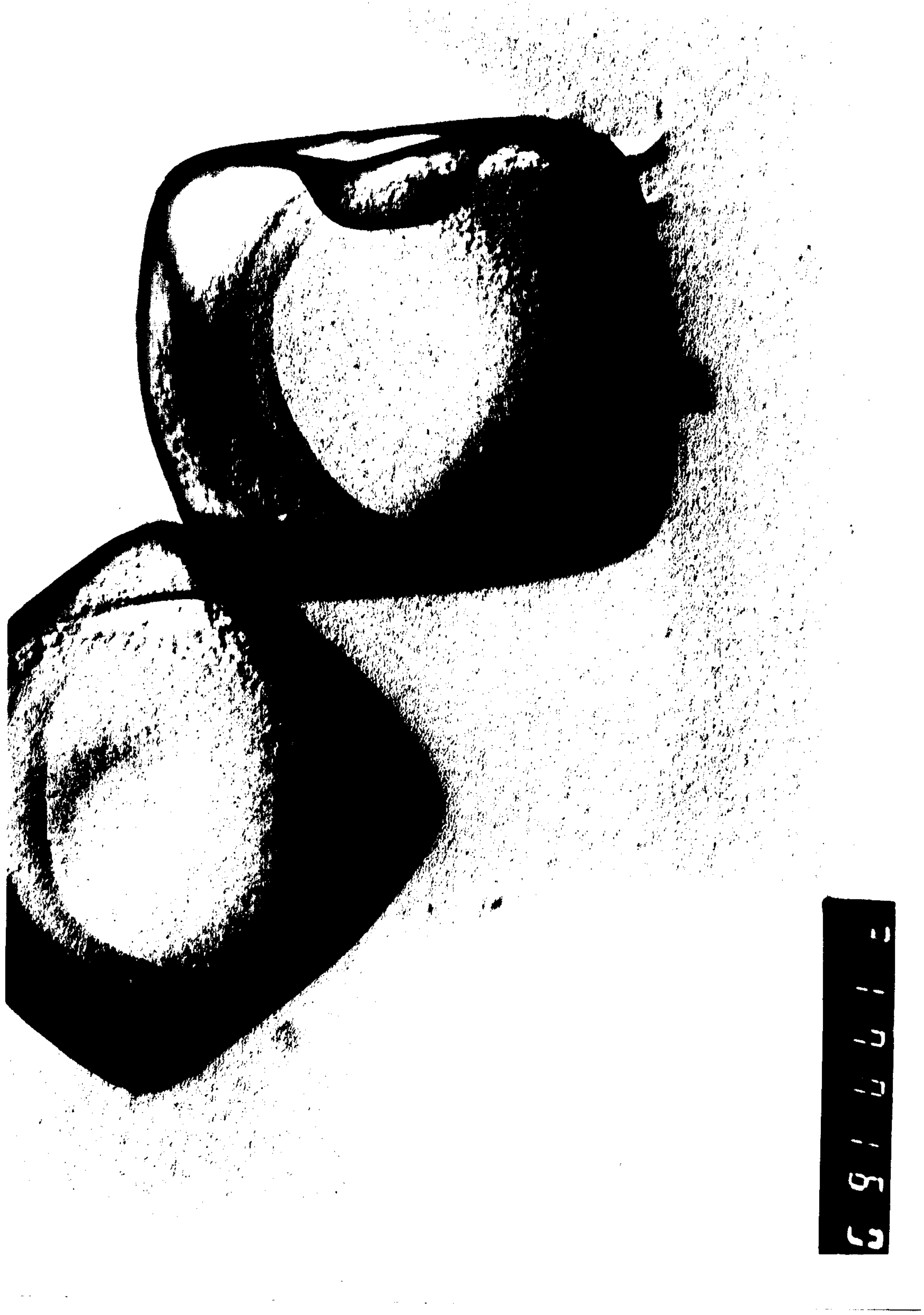


Fig. 2

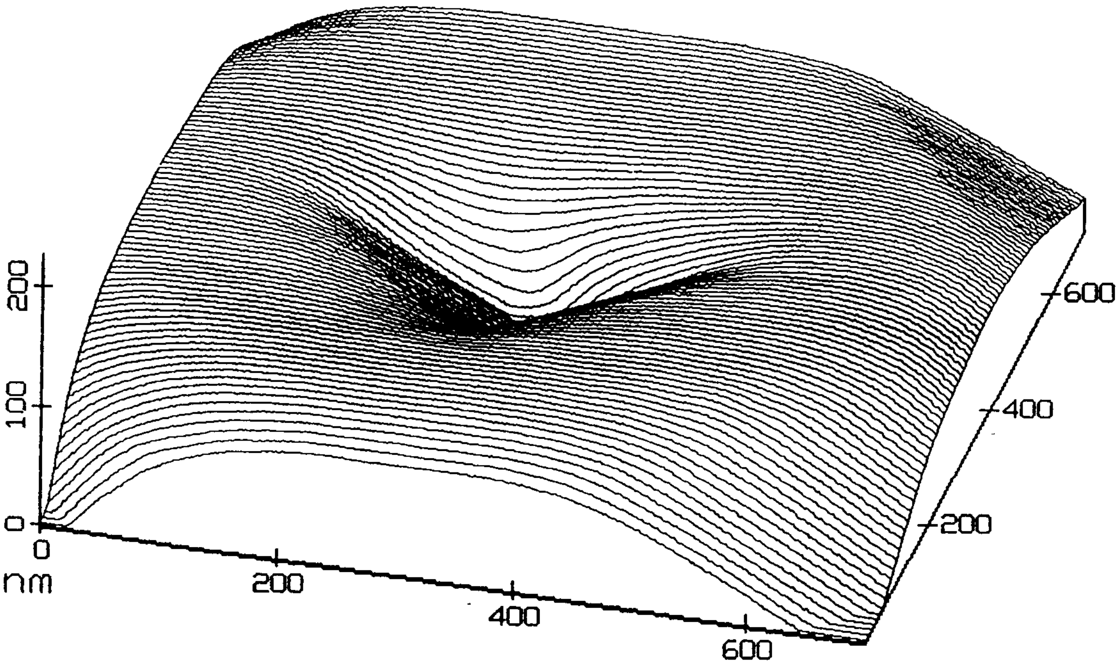

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Fig. 3

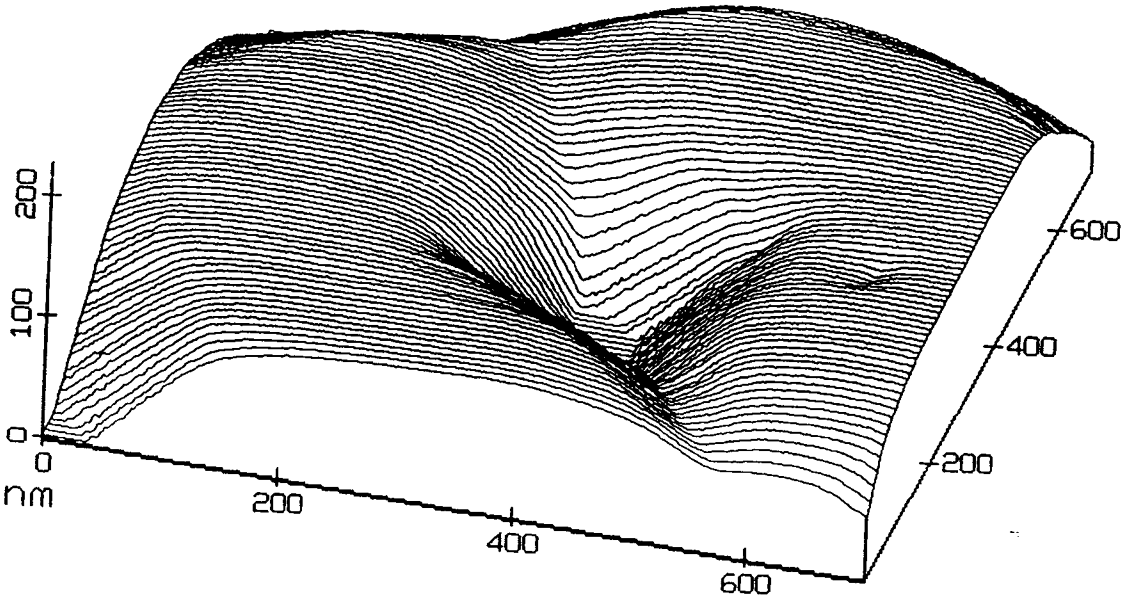
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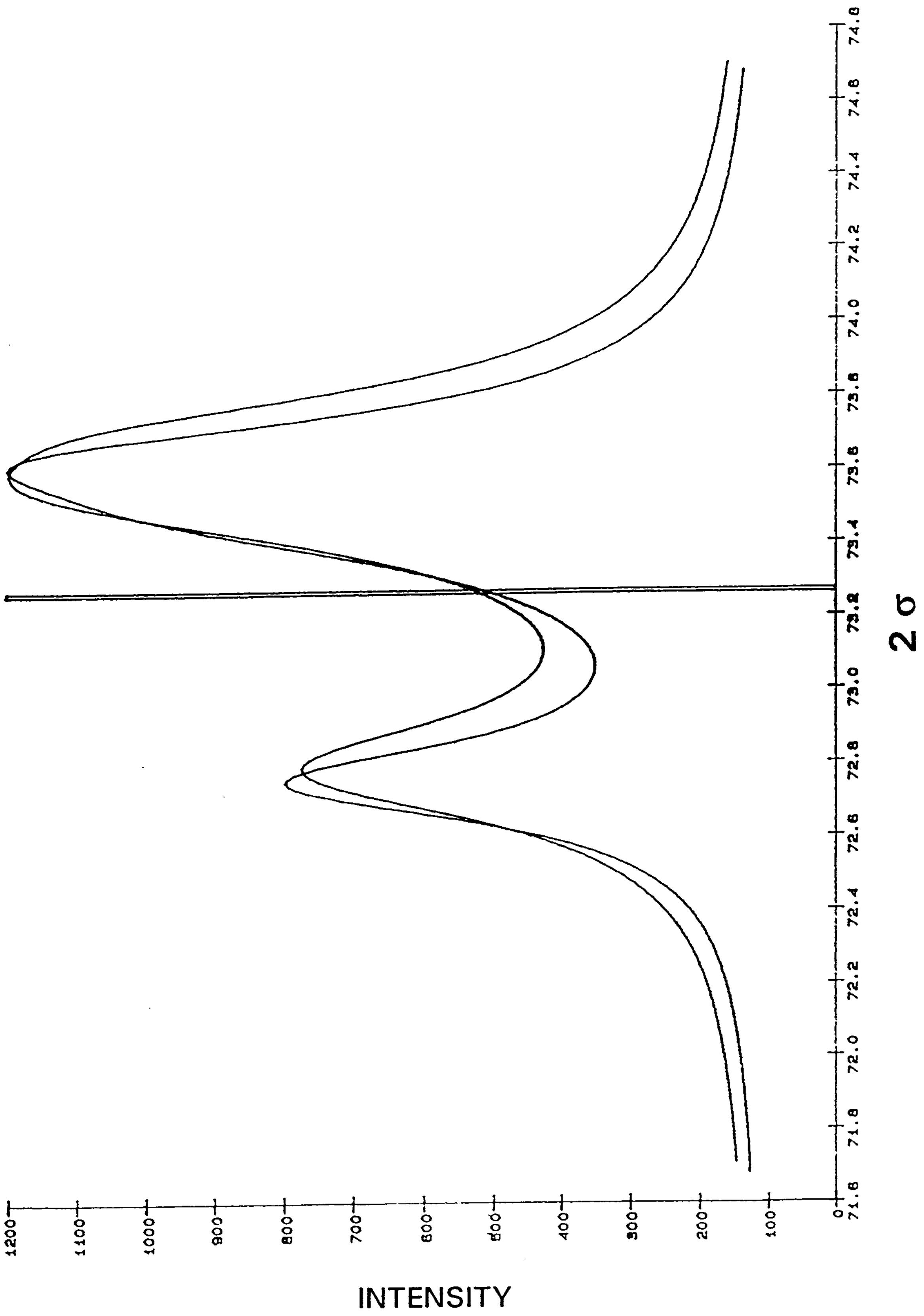
Fig. 4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900
800
700
600
500
400
300
200
100
0
INTENSITY
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71.8
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72.2
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72.6
72.8
73.0
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73.6
73.8
74.0
74.2
74.4
74.6
74.8
2σ

Fig. 5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 42 0275

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	US-A-4 710 455 (IGUCHI ET AL.) * column 4, line 6 - line 34; claims 1,11 *	3-11	G03C1/035
A		1,2	
X	EP-A-0 523 464 (MINNESOTA MINING AND MANUFACTURING COMPANY) * claims 1-5,9-19; examples 1,3-5 *	3-11	
A		1,2	
X	DATABASE WPI Section Ch, Week 8551, Derwent Publications Ltd., London, GB; Class E35, AN 85319311 & JP-A-60 221 320 (MITSUBISHI PAPER MILL) 6 November 1985 * abstract *	3-11	
A		1,2	
A	DATABASE WPI Week 8535, Derwent Publications Ltd., London, GB; AN 85213784 & JP-A-60 136 735 (MITSUBISHI PAPER MILL/MITSUBISHI PAPER MILLS LTD) 20 July 1985 * abstract *	1,2	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** G03C
A	EP-A-0 232 160 (KONISHIROKU PHOTO INDUSTRY COMPANY LTD) * claims 1-11; figures 1-7 *	1-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 January 1995	Buscha, A

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
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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