
# Silver halide emulsions of the Lippmann-type (Agfa-Gevaert)

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# Silver halide emulsions of the Lippmann-type

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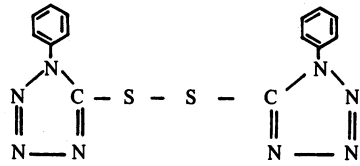
Lippmann-emulsions, normally having an average grain-size of less than 100 nm, are of particular importance for the preparation of photographic plates or films with high resolution, for use in micro-photography and in astrophotography, for recording nucleo-physical phenomenons, for the preparation of masks in the production of microelectronic integrated circuits, for use in holography, etc.

Lippmann-emulsions with an average grain-size smaller than usual i.e. smaller than about 65-70 nm would be of particular importance for reflection holograms where a high diffraction efficiency and a high signal to noise ratio are required; However, attempts to prepare such-like Lippmann-emulsions by varying the working conditions during the precipitation of the silver halide have not been successful.

It has been found that silver halide emulsions with very fine grain can be prepared by effecting the precipitation of the silver halide in an aqueous hydrophilic colloid medium in the presence of

a) aromatic or heterocyclic disulphides and diselenides such as the compounds having the following structural formulae:

1.



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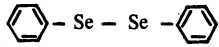

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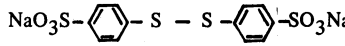

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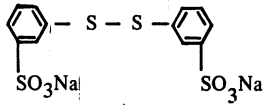

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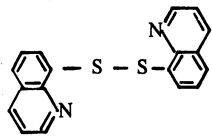
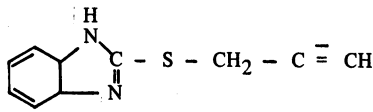


b) Selenocyanates such as

6.

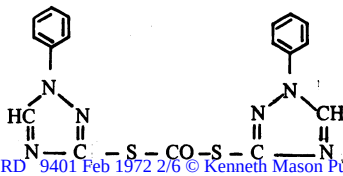
c) Acetylene compounds such as

7.



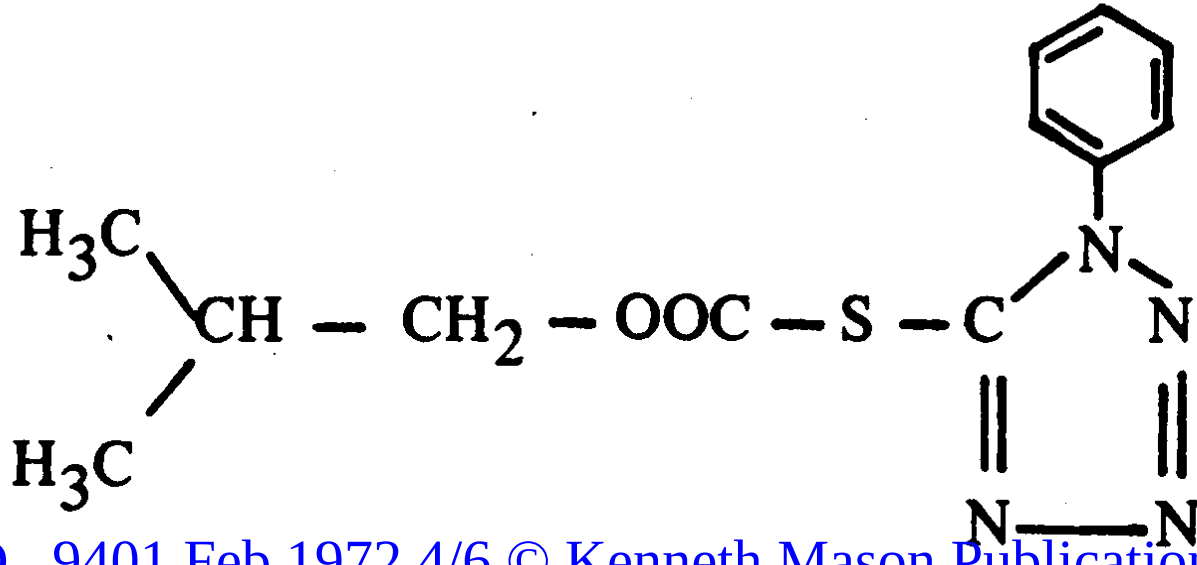
d) Heterocyclic dithioesters of carbonic acid such as

8.



e) Reaction products of heterocyclic mercaptans with esters of chloroformic acid such as the compound of the folllowing structural formula:

9.



By the use of the above compounds during the precipitation step of the silver halide, homogeneous Lippmann-emulsions can be prepared with an average size markedly smaller than in the absence of said compounds so that emulsions are obtained practically withiut scattering.

The compounds or solution of the compounds are generally incorporated into the aqueous hydrophilic colloid composition, more particularly aqueous gelatin, into which the silver halide is precipitated. They can be used in amounts varying between very wide limite, preferably between 2 g and 20 g per mole of silver halide.

The hydrophilic colloid used as the vehicle for the silver halide may be any of the common hydrophilic colloids employed in photographic light-sensitive emulsions, for example gelatin, albumin, zein, casein, alginic acid, collodion, a cellulose derivative such as carboxymethyl cellulose, a synthetic hydro-philic colloid such as polyvinyl alcohol and poly-N-vinyl pyrrolidone, etc. gelatin being however preferred. If desired compatible mixtures of two or more colloids may be employed for dispersing the silver halide.

The ratio of hydrophilic colloid binder to silver halide in the fine-grain emulsions is preferably comprised between 0.2 and 6.0.

Various silver salts may be used as the light-sensitive salt such as silver bromide, silver chloride or mixed silver halides such as silver chlorobromide, silver bromoiodide and silver chlorobromoiodide. Emulsions containing silver bromide or silver chloride or a mixture of silver chloride and silver bromide and such emulsions containing small amounts of silver iodide up to 8% are favoured.

The silver halide emulsions of the Lippmann type may be prepared according to methods well known in the art and described in the literature, see e.g. P. Glafkidès 'Photographic Chemistry' Vol. I, 1958, p.365-368; Mees/James 'The theory of the photographic Process' 3rd ed. (1966) p. 36 and National Physical Laboratory 'Notes on Applied Science' No. 20 : 'Small Scale preparation of fine-grain (colloidal) photographic emulsions' B'H' Crawford, London (1960). They may be prepared according to the technique described in our copending Application No. 15948/70.

After precipitation of the silver halide grains in the presence of the compounds of use according to the present invention the emulsion is washed in order to remove the water-soluble salts whereupon the emulsions may be chemically as well as spectrally sensitized.

They may be spectrally sensitized by any of the known spectral sensitizers such as cyanines and merocyanines for photographic silver halide materials. They may be chemically sensitized by means of sulphur compounds for example allyl thiocyanate, allyl thiourea, sodium thiosulphate, etc. They may also be sensitized by means of reductors for instance tin compounds, imino-amino methane sulphinic acids and derivatives thereof, cadmium salts, and small amounts of noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium. The emulsions according to the invention may also comprise compounds which sensitize the emulsion by development acceleration for example compounds of the polyoxyalkylene type e.g. alkylene oxide condensation products as described among others in US patent specification 2,531,832 and 2,533,990, in UK patent specifications 920,637 - 940,051 - 945,340 and 991,608 and in Belgian patent specification 648,710, as well as the known onium compounds including quaternary ammonium compounds quaternary phosphonium compounds and ternary sulphonium compounds.

Further, the emulsions may comprise antifoggants and stabilizers for

example heterocyclic nitrogen-containing thioxo compounds such as benzothiazoline-2-thione and 1-phenyl-2-tetrazoline-5-thione, compounds of the hydroxytriazolopyrimidine type such as 5-methyl-7-hydroxy-s-triazolo [1,5-a] pyrimidine and mercury compounds. They may also comprise light-absorbing dyes to reduce scattering and reflection of light within the photographic material as described in Belgian patent 699,375 and British co-pending Application 58,844/68.

Any of the hardening agents for hydrophilic colloids may be used in the emulsions according to the present invention for example formaldehyde, dialdehydes, diketones, halogen substituted aldehyde acids such as mucochloric acid and mucobromid acid, etc.

The emulsions may be coated on a wide variety of photographic emulsion supports. Typical supports include cellulose ester film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and related films of resinous materials as well as paper and glass. In order to promote adhesion of the silver halide emulsions to glass supports it may be advantageous to use silicone compounds of the kind described in British copending Application No. 54678/68.

Example

A silver bromide emulsion comprising 25 g of silver bromide and 65 g of gelatin was prepared by simultaneous addition of an aqueous silver nitrate solution and an aqueous potassium bromide solution to a 10% aqueous solution of gelatin. The conditions of precipitation were adjusted so that a Lippmann emulsion with an average grain size of 67 nm was obtained. Details as to the preparation of Lippmann-emulsions can be found amongst others in P. Glafkidès 'Photographic Chemistry' Vol. 1, 1958, Fountain Press, London.

Under completely analogous working conditions other emulsions were prepared with the difference that the 10% aqueous solution of gelatin into which the silver bromide was precipitated now contained one of the compounds listed in the table below in an amount of 8.5 g compound per mole of silver nitrate used.

The average silver bromide grain size was determined by turbimetry. The results attained are listed in the table below and show that the compounds of the above general formulae restrain growth of the silver halide grains.

Table

| Compound added | Average grain size in nm |
|---|---|
| none | 67 |
| 1 | 53 |
| 2 | 57.5 |
| 3 | 49.5 |
| 4 | 47.5 |
| 5 | 42.5 |
| 6 | 47.5 |
| 7 | 52.5 |
| 8 | 54.5 |
| 9 | 52.5 |

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