Sensitization of Tabular Silver Chloride Grains with Morphologically Stabilized {111} Crystal Planes.

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Abstract

The {111} crystal face of silver chloride crystals precipitated in aqueous gelatine solutions is thermodynamically unstable. The stability of this {111} crystal face can be increased by adsorption of organic habit modifiers.

Adenine has been reported as habit modifier for the precipitation of silver chloride crystals with {111} planes since the early seventies. By using adenine in the precipitation of tabular silver chloride grains it is possible to control the tabularity of these crystals by adjusting typical emulsion parameters such as pH, T, [gelatine], pAg,... .

Because adenine shows a high affinity for silver ions, it can only be used in limited amounts for optimizing the sensitivity of a silver halide emulsion in a typical sulphur/gold chemical sensitization. A method for preserving the high tabularity of silver chloride crystals at these low concentrations of adenine in the emulsions is presented, together with its analytical evidences.

The sensitometric value of these emulsions in green-sensitized film for medical radiography is demonstrated. Because of their high tabularity the spectral sensitization and the covering power are comparable with those of silver bromide materials.

Introduction

With the addition of adenine to an aqueous solution of gelatine, silver chloride {111} crystal faces are formed[1]. Conditions for tabular growth have been worked out. The quantitative influence of the parameters that control the tabularity and the crystal diameter have been experimentally determined.

These emulsions are not suited for photographic applications without a (partial) desorption of the habit modifier - adenine - from the crystal surface. The conditions of the desorption process are worked out in order to preserve the tabularity of the crystal and to create the optimum conditions for sensitization. The parameters that control this process are given.

Examples of the chemical sensitization of a tabular emulsion that is spectrally sensitized in green is worked out.

These sensitized emulsions are evaluated in film for medical radiography. Positioning against cubic silver chloride emulsions.

Stabilization of {111} crystal planes of silver chloride grains

Interaction of adenine with silver halide crystal faces.

Adenine interacts with silver ions through the nitrogen atoms in the 7,9 position on the imidazole[4]. The solubility product of silver adenate is strongly dependent on the pH[2,3]. At a pH of 5 or more the solubility of silver adenate is lower than the solubility of silver chloride. Under these conditions it is possible to convert the silver chloride at the surface to silver adenate.

Based on XRD measurements[4] it is concluded that the distance between the silver atoms in the silver adenate complex matches almost perfect the distance between the silver atoms at the {111} crystal plane of silver chloride. Chemisorption of adenine at the surface of a silver chloride crystal is possible.

The adsorption of adenine on the crystal surface is function of the pAg and of the halide composition of the crystal. Based on solubility product and on crystal parameters it is shown that the adsorption of adenine is very weak on a silver iodide surface, compared to a pure silver chloride surface[2,3].

Besides the halide composition of the crystal at the surface, the adsorption of other organic substances in the emulsion, e.g. gelatine, interferes with the interaction of adenine and the silver ions[3].

Parameter area for the precipitation of tabular {111} silver chloride crystals.

As recommended in literature, the pH of the precipitation reaction of silver chloride {111} tabular grains

is kept constant at pH = 6. The pAg range is chosen to guarantee more than 75 % adsorption of the adenine added to the silver chloride surface and therefore kept between pAg = 7.0 and pAg = 8.5. An experimental design study was used to optimize the concentrations of adenine and gelatine that control of the tabularity of the emulsion, together with the concentration of silver nitrate in the nucleation phase to control the volume of the tabular crystals.

For the study of the stabilization and the sensitization of the emulsions precipitated, a tabular grain with a crystal diameter of 0.65 microns and a tabular thickness of 0.14 microns (AR = 10) was selected.

Desorption of the habit modifier adenine from the crystal surface.

Through the chemisorption of adenine at the crystal surface the spectral and the chemical sensitization of the tabular silver chloride grains are strongly inhibited.

A method of desorption of the adenine from the {111} crystal surfaces is proposed that guarantees the control on the tabularity of the crystals[6].

The temperature is kept below 20C.

Under this condition desorption of adenine is only efficient after conversion of the surface with Br- ions, or more preferably, with iodide ions. A high reproducibility of the desorption process is possible if the concentration and the homogeneity of this I- conversion are strictly under control. Conversion and building-in of I-ions at the silver chloride crystal surface were studied with TEM and SIMS. Interaction with the adsorbed adenine was analysed.

A second important parameter for controlling the desorption of adenine is the pH of the emulsion. For adenine the pKa = 5.4. Because of the high solubility of the protonated adenine the desorption increases strongly at a pH = < 4. Flocculation of the photographic emulsion at this low pH makes it possible to decantate the adenine.

Redispersion of the flocculated emulsion at a temperature higher than 20C requires the addition of a spectral sensitizer to further control and stabilize the tabularity of the crystals. Spectral sensitizers that adsorb and form J-aggregates at the surface are especially preferred.

Using I- conversion in the desorption process of adenine from the silver chloride surface offers the opportunity to use spectral sensitizers for which J-aggregation is strongly induced with I-ions.

Sensitization of tabular {111} silver chloride grains.

Spectral sensitization.

Spectral sensitization of silver chloride {111} tabular grains with ethyloxacarbocyanines was studied. Examples are given for anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyloxacarbocyanine hydroxide as sensibilizer (dye 1). This sensibilizer shows a strong J-aggregate formation as a function of the I- concentration[5].

Concentrations of iodide in the chloride matrix of the crystal below 1 mol % are sensitometrically preferred.

For these low concentrations of iodide ions built-in at the silver chloride surface, the formation of the J-aggregate of dye 1 is inhibited by the adsorption of adenine at the crystal surface. Experimentally the maximum concentration of adenine and the optimum concentration of iodide that is acceptable to achieve optimum spectral and chemical sensitizations is determined. Below this concentration level no further improvement on sensitization is expected.

Chemical sensitization.

For the chemical sensitization of the tabular {111} silver chloride emulsions a conventional sulphur/gold system was applied. Further optimization through addition of labile selenium compound can be achieved.

Large amounts of adenine - the concentrations necessary for the precipitation - inhibit the photographic performance of the emulsion. Chemical sensitization at extremely high temperatures cannot overcome this problem.

Small quantities of adenine in the emulsion (cfr. supra) are a benefit for the chemical stability of the emulsion. Experimentally it is shown, from the relation between the concentration of adenine and the relation of fog to sensitivity of the emulsion, that those small amounts strongly improve the long term stability of the film materials.

Evaluation in X-ray screen/film systems.

A film support is coated on both sides with the stabilized and green-sensitized tabular emulsions for their evaluation in conventional medical radiography. Comparison is made with cubic silver chloride grains. The experimental results clearly show a higher covering power and a superior photographic sensitivity.

References

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