Senzitization and Stabilization of AgCl Tabular Crystals having Low Iodide Content.

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Abstract

The advantages of tabular grain emulsions are well known. Grains or crystals rich in silver bromide have already been explored intensively since the 80's but it is only since the 90's that the additional benefits of tabular crystals rich in silver chloride became evident.

Silver chloride crystals with major {111} planes are thermodynamically unstable in aqueous gelatin solutions. Although stabilization of the planes can be done with a crystal habit modifying agent (HMA), such as e.g. adenine, it is hitherto not possible yet to produce crystal populations that are as homogeneous as for AgBr. Typically still 20% of the {111} tabular crystals have a substantial thickness growth.

Moreover, the HMA adenine typically interferes with chemical and spectral sensitization and has to be removed during washing of the emulsion. In order to avoid recrystallization during the washing step, iodide has to be added in a substantial amount.

This paper presents a new method for improving the homogeneity and stabilization of silver chloride emulsion crystals having a low iodide content. Moreover the sensitometric influence and the importance of supersensitizing action in emulsions rich in silver chloride is discussed.

Introduction

The precipitation of silver chloride emulsions bounded by {111} major planes has a high degree of complexity. The {111} planes are not stable in an aqueous environment, implying that the precipitation should be done in the presence of a crystal habit modifying agent (HMA), such as e.g. adenine, which typically interferes with the chemical and spectral sensitization[1].

Moreover, the crystal population is not as homogeneous as for AgBr. About 20 % of the crystals usually have a significant thickness growth. These thick crystals contain 30 to 40% of the total amount of silver and result in a decrease in tabularity of the emulsion. A recent investigation has shown that presence of thick tabular grains can mainly be attributed to non-parallel twinning rather than to thickness growth at dislocations[2]. The difference between AgCl and AgBr is probably due to a higher twinning probability in case of AgCl crystals. Experiments on crystal formation from the vapour phase have shown that in case of AgCl more needle-shaped crystals with non-parallel twins and crystals with three twin planes are formed[3].

In this paper new concepts are presented in order to reduce the drawbacks of AgCl emulsion preparation technology. First of all a new concept is presented in order to decrease the number of non-parallel twins. The twinning frequency is reduced by the addition of a block-copolymer, leading to a more homogeneous tabular population. Moreover spectral sensitization is investigated for a specific carbocyanine dye and the mechanism of desensitization / supersensitization is compared with a recent study for AgBr[4].

Experimental

The AgCl(I)-tabular crystals are precipitated in the presence adenine. The scheme consists of a nucleation step at low temperature and high supersaturation, a physical ripening step and a growth step at high temperature and low supersaturation. Adenine is added during nucleation in amounts of 1.8 mmole/mole of Ag. Precipitation is performed in an aqueous solution of oxidized gelatin having 5 μ mole of methionine per g of gelatin. The population shows 80% of thin tabular grains with an average thickness of 140 nm and an iodide content of 1 mole %, based on silver. The remaining 20% are mainly thick tabular grains with a thickness of about 300 nm. The emulsion is spectrally sensitized with dye 1 and chemical sensitization with S and Au is optimized in order to get the best fog/speed relationship.

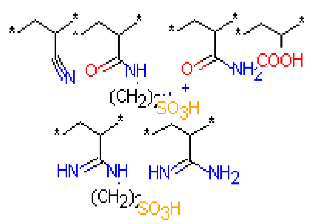
Dye 1: anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyloxacarbocyanine hydroxide.

Improvement of homogeneity

It is well known that the right choice of the type of peptizer is of utmost importance for the formation of AgCl tabular crystals. It has been shown that the crystal population changes from more or less non-tabular to more than 80%

tabular crystals if oxidized gelatin is used[4]. The use of non-oxidized gelatin obviously reduces the formation, and probably also the lateral growth, of the doubly twinned crystals.

In this study only oxidized gelatin is used as a peptizer. In accordance with the results of Maskasky [5], the crystal population consists of 80% tabular grains having a high aspect ratio. The remaining 20% are thick tabular grains having a low aspect ratio, which contain non-parallel twins[2]. Therefore conditions should be provided in order to reduce the twinning probability. As the type of peptizer has already been proven to be essential, the presence and concentration of different block-copolymers is investigated. Both polyalkylene oxides as well as acrylic multiblock co-polymers with following structural groups [6] are tested.



It is obvious that it is more critical to obtain the right nucleation conditions for AgCl- than for AgBr-precipitation. Apart from improving the homogeneity, also crystal habit stabilization should be maintained. This poses strong requirements on the action of the block-copolymers. On the one hand block-copolymers should adsorb at the AgCl-surface to alter the crystal population. On the other hand, said block-copolymers may not cause thickness growth, either by preventing adenine to adsorb, either by generating nucleation centers for thickness growth.

Table 1 shows the result obtained after having made use of Pluronic™ 17R1[7] as a polyalkylene oxide block-copolymer.

	Amount (g/l)	%Tabular Crystals	Thickness (µm)
Reference	0	86	0.12
Pluronics™17R1	1.5	83	0.27

Table 1: Percentage of tabular grains and their main thickness as a function of the amount of Pluronics™17R1.

It is clear that this block-copolymer causes an unwanted thickness growth. Furthermore it does not improve homogeneity.

However, by selecting the correct block-copolymer, a major improvement in homogeneity can be realized with only minor thickness growth. This is shown in figure 1 and 2 for the block-copolymer HYPAN®TC240[5].

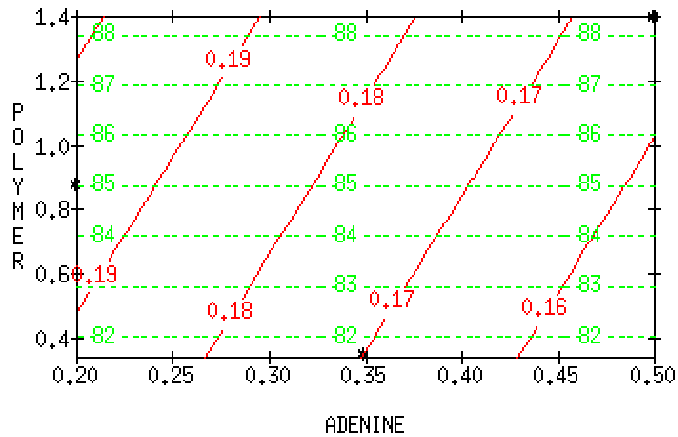


Figure 1: Percentage of tabular grains (dashed line, in %) and their thickness (solid line, in µ m) as a function of the amount of added polymer and adenine (in g/l).

Figure 1 indicates that adenine and the polymer are competitive in adsorption strength. Increasing the polymer content leads to thicker crystals, which suggests that adenine adsorption is less effective. An increasing adenine content can however compensate for this effect.

Figure 2 shows that increasing the amount of oxidized gelatin also leads to thinner tabular grains. Moreover it also improves the quality of the tabular population to the same extent as the polymer. The oxidized gelatin as well as the polymer seems to affect the twinning frequency. This can not be explained in terms of an increase in solubility as the polymer and the gelatin are not affecting solubility under the conditions used.

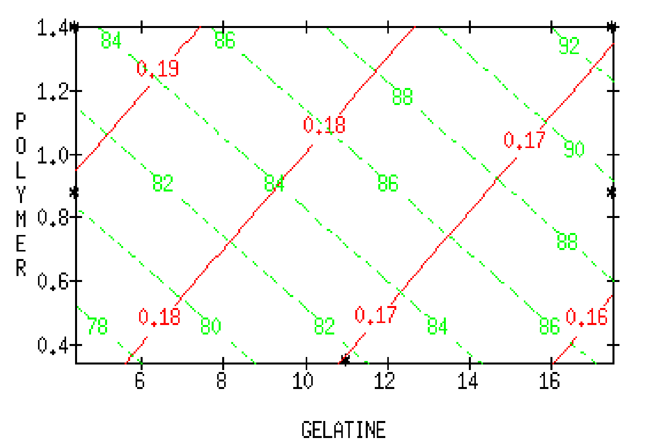


Figure 2: Percentage of tabular grains (dashed line, in %) and their thickness (solid line, in µ m) as a function of the amount of added polymer and oxidized gelatin (in g/l).

Sensitivity

If the AgCl-emulsions are sensitized with dye 1 at an optimized S/Au-level, sensitivity is very low and a desensitization mechanism is operative. This desensitization mechanism is studied as a function of supersensitization. The supersensitizer is added after spectral and chemical sensitization in amounts of 3 wt% with respect to dye 1. The supersensitizing dyes are all benzoxazolo- and benzimidazolocarbocyanine dyes and are selected on the basis of their oxidation potential in solution, measured with voltammetric analysis techniques. The oxidation potential varies between 0.5 and 0.9 V, measured versus a saturated calomel electrode, taken as a reference electrode. The spectral as well as the intrinsic sensitivity is determined and the change in spectral absorption at 550 nm is monitored. The latter is found to be small in all cases.

The spectral sensitivity can be enhanced with 0.35 Log E (E = Exposure = Ixt) by supersensitizing action and a close correlation exists with the oxidation potential of the spectral sensitizer (see figure 3). Moreover the intrinsic sensitivity increases substantially.

Similar to the reasoning in [4], these observations suggest that the supersensitizing action is mainly due to a reduced recombination on the dye as a consequence of a hole transfer to the supersensitizer. Part of the sensitizing action may of course also be due to an enhanced electron transfer.

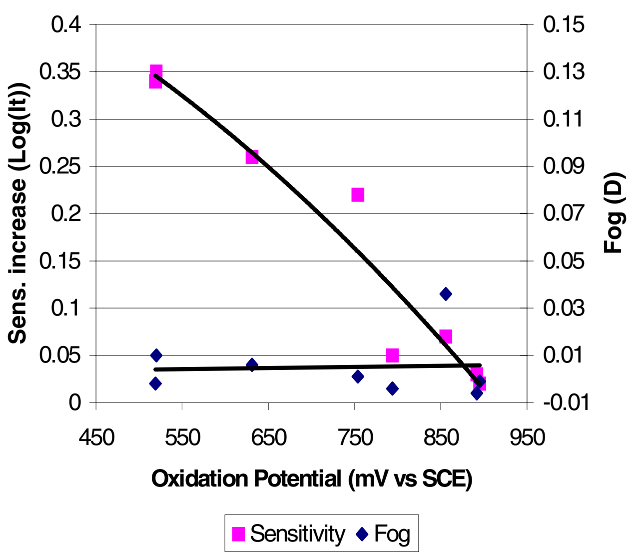


Figure 3: Sensitivity and fog as a function of the oxidation potential of the added supersensitizer. The data are normalized to the sensitivity and fog of the reference without supersensitizer.

Conclusions

In this study some drawbacks of precipitation technology of tabular AgCl are reduced. Homogeneity in the precipitation of tabular emulsion crystals rich in silver chloride is improved in the presence of a block-copolymer. Furthermore the sensitivity is increased by a supersensitizing action. The supersensitizing mechanism is attributed to a reduction of recombination on the dye hole, which is positioned on the supersensitizing dye.

References

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