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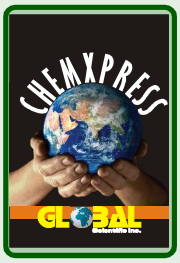

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Investigation of some factors affecting size and shape distribution of silver halide microcrystals in photographic emulsion

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Abstract: Influence of different mixing devices and surfactant Laprol 3603-2-12 on the formation of tabular silver halide microcrystals in the photographic emulsion has been investigated using scanning electron microscopy. Values of the Laprol concentrations for homogeneity increasing, obtaining of bimodal emulsion and for transformation crystals from tabular to octahedral one have been estimaited. Our experiments have shown that the Laprol is a powerful factor to control size distribution and the shape of the silver halide microcrystals in the gelatin solution.

Keywords: Gelatin photographic emulsion; Silver halide microcrystals; Surfactant.

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INTRODUCTION

The synthesis of photographic emulsions on the base homogeneous flat microcrystals (MC) or, as they are called, tabular T-crystals of the silver halide AgHal provided opportunity for the qualitative breakthrough in the technology of photographic films[1]. Granulometric homogeneity (C_V) is the ratio of the standard deviation of the MC equivalent diameter to its arithmetic mean. This statistical analysis should be performed for at least 300 particles. Granulometric homogeneity and crystals shape significantly depend on design features of the chemical reactor and the gelatin solution mixer, method of introducing of reagent solutions, the type of gelatin, etc. Modern synthesis of MC AgHal has 20 variables that must withstand at a well-defined algorithms[2]. This is difficult technological problem for industrial production. Therefore obtaining of desired properties of emulsions and providing their reproducibility is actual problem up to now.

Several years ago the effectiveness of high homogeneous ($C_V \leq 20\%$) and extrahomogeneous ($C_V \leq 10\%$) T-crystals in X-ray technical photographic films was shown by R. Dickerson and A. Tsor[3,4]. The silver consumption in film production was reduced up to 25% without loss of the photographic sensitivity compared with emulsions made of thickened or isometric MC. Surface-active agents (surfactants) under the trade mark Pluronic - two-functional polyols: polyoxy-propylene polyethylene glycols (PPG-PEG-PPG, $M_n \sim 3300$), polyoxyethylene poly-propylene glycols (PEG-PPG-PEG, $M_n \sim 2000$) and Tetronic - alkoxylated tetrafunctional ethylenediamine were proposed[3,5-7] for improving of the T-crystals uniformity. The optimal concentration of the surfactant was 1 - 5% of introduced into the reactor silver nitrate for emulsion nucleation stage. Unfortunately, this high surfactant concentrations increase the veil in the process of industrial production of films. Now new brands of surfactants were entered on the market of chemicals. Photographic films producers have practical interest in using of more effective surfactants for obtaining high homogeneous emulsions.

In this work the influence of three-functional copolymer of propylene oxide and ethylene oxide based on glycerol, namely brand Laprol (3603 -2-12, TU 2226-015-10488057-94 of JSC "Nizhnekamskneftekhim", Russia) on the synthesis of photographic emulsion with using different mixing devices has been investigated.

EXPERIMENTAL

Synthesis of photographic emulsions is carried out on the laboratory home made set-up for two-jet crystallization. The set-up consists of the chemical 2 liters reactor equipped with thermostat system and peristaltic pumps (for supply of reagents into the gelatin solution) controlled with the computer. We used two types of mixing devices – simple propeller stirrer and special home made stirrer[8]. Last model was settle down in the lower part of the reactor and consists of a turbine and the propeller inside tube case with conic bells. Liquid reagents were pumped from narrow silicone tubes under the turbine. The stream of the gelatin solution was directed upward. Therefore our reagents very quickly mix up and react with each other inside the tube case. Then they jump out in the volume of the reactor and repeatedly circulate via the mixing device. Temperature and pBr of the emulsion were regulated automatically using feedback of the corresponding pumps with the thermal sensors and ionomer. Operation of pumps and the data of all sensors were automatically recorded[2]. Such procedure provided high repeatability of the conditions for the emulsion synthesis. We varied only concentration of the surfactant addition (0; 0,005; 0,01; 0,05; 0,5% wt. of the Laprol per quantity of $AgNO_3$ entered into reactor at the nucleation stage).

Synthesis of the fine-grained emulsion for photographic film with high resolution was carried out according to the following scheme:

Loading of the reactor: 675 ml of initial gelatin solution in water with concentration of gelatin 0,8% wt.; Laprol of necessary concentration; water solution of KBr up to pBr = 1,3 in the final gelatin mixture (solution was mixed carefully and heated up to 40°Ñ).

The 1st stage - nucleation: solutions of 2,0 M $AgNO_3$ and 2,0 M KBr with rates of 6,75 ml/min and 10,7 ml/min, respectively were injected during 125 s. Rotation rate of the stirrer was around 600 rpm. After it the temperature of the emulsion was increased up to 50 °C during 20 min. pBr value was increased up to 1,6 by injection of 2,0 M of $AgNO_3$ solution with rate of 0,85 ml/min. Then pH of the emul-

sion was tuned up to 9,6 by addition of 25% wt. of ammonia water solution.

The 2nd stage - Ostwald ripening: this stage was carried out at 50 °C within 12 min. After it the emulsion was acidified to pH 5,5 by acetic acid injection. 100 ml of 13% wt. of water solution of gelatin was added into the reactor also.

The 3rd stage - crystallization of the 1st coat: solutions of 2,0 M $AgNO_3$ and 2,0 M KBr + 0,03 M KI were injected with equal rates 1,489 + 0,17t ml/min during t = 32 min at pBr = 1,6. The rotation rate of the stirrer was 800 rpm.

The 4th stage - crystallization of the 2nd coat: solutions of 2,0 M $AgNO_3$ and 2,0 M of KBr were injected with rates 6,008 + 0,13t ml/min during t = 30 min at pBr = 2,0. The rotation rate of the stirrer was 1000 rpm.

After ending of the synthesis MC were separated from gelatin by centrifugation and washing in the distilled water with ultrasound processing. About 5 µl of final water suspension of microcrystals were dried on a fresh plate of mica for the scanning electronic microscope (SEM) measurements. We used SEM Merlin (Carl Zeiss). Set of SEM images with magnification X10 000 of the mica plate surface was obtained. Magnification X20 000 was used for analyzing of a crystal shape.

Critical concentration of micelle formation (CCM) of Laprol was determined by the method[9] using the dependence of pyrene fluorescence intensity at 373 nm on Laprol's concentration. For fluorescence measurements Microplate reader Infinite 200 PRO (Tecan) was used (excitation wavelength was equal 339 nm).

RESULTS AND DISCUSSIONS

Above described synthesis scheme has been chosen by us because it guaranteed the obtaining of the fine-grained homogeneous $C_V \leq 30\%$ emulsion of tabular MC with the required average equivalent diameter about 0.5 µm, if a special mixing device is used[8]. The SEM image of such MC population is shown on Figure 1. First of all, experiment with simple propeller stirrer can show the role of a special mixing device in obtaining such high quality emulsion.

Figure 2a shows the MC of emulsion which was obtained using the simple propeller stirrer without surfactant. It is not quite homogeneous. Corresponding histogram illustrates that the population consists of a small fraction of relatively large T-crystals with equivalent diameter of 1.3 µm and a large number of small about 0.2 µm crystals of spherical shape. The thickness of the large MC varies from 0.15 to 0.28 µm. The granulometric homogeneity of such mixture of particles is very low $C_V = 84\%$.

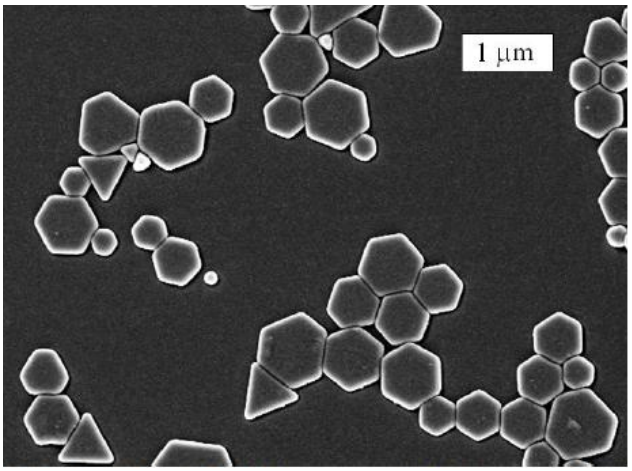

Figure 1 : The SEM image of MC population if special mixing device[8] is used for emulsion synthesis.

It not suitable for high-quality photographic films. It will be interesting to see the action of Laprol as a potential amplifier of T-crystals homogeneity in the conditions for obtaining of the low-grade emulsion. Successful result will be especially important for removing of any destabilizing factors which can appear during industrial synthesis.

Theoretically the effect of surfactants on the crystallization process is explained by formation of micelles around the MC nucleus. This shell smoothes fluctuations in the rate of increase of mass of single crystals due to the inevitable concentration and temperature gradients in the area of reagents injection and in the reactor value as a whole.

According to our measurements CCM of Laprol in deionized water at the temperature 40 °C is 0.042% wt. But content of 0.8% wt. gelatin in water solution reduces this value up to 0.007% wt. Reducing of CCM can be explained by the participation of the protein molecules in the formation of the colloidal system - composite micelles. Taking into account that 4.8 g of $AgNO_3$ is introduced into the reactor at the stage of nucleation and volume of gelatin solution

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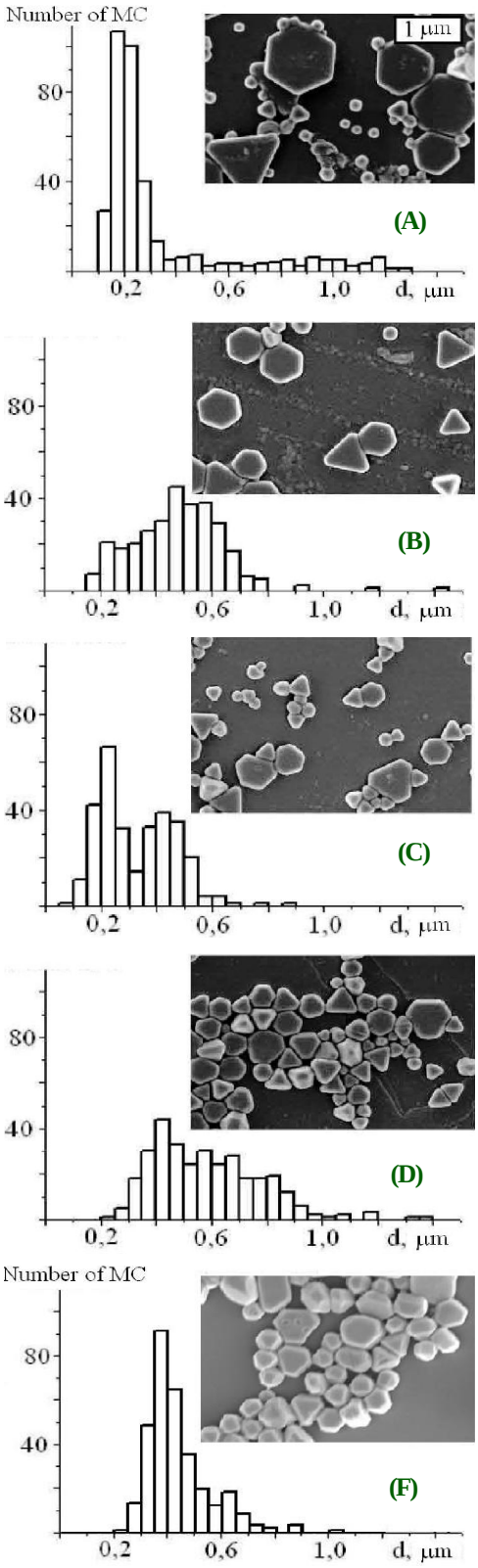

Figure 2 : The SEM images and size distributions (equivalent diameter) of microcrystals AgHal synthesized at different Laprol concentrations: a – 0; b - 0.005; c - 0.01; d - 0.05; f - 0,5% wt. of $AgNO_3$ which was used for the stage of nucleation. Magnification of all images is the same.

reaches about 700 ml at the end of this stage we can recalculate concentrations of the surfactant additions in our experiments on weight of final gelatin solution. It will be approximately $3,4 \times 10^{-5}$; $6,8 \times 10^{-5}$; 34×10^{-5}; 340×10^{-5}% wt. That is more than twice lower than CCM. However, the introduction of minimal addition of the surfactant changed the original emulsion significantly (Figure 2b). The number of small and large particles was considerably reduced. T-crystals are mainly formed with an average equivalent diameter 0,47 μm and a thickness of 0,16 ± 0,02 μm. Homogeneity was C_V = 32%. There are about 70% hexagonal T-crystals and ~ 25% of T-triangular crystals in the particle population. This emulsion is similar with emulsion on Figure 1 and hence acceptable to make high quality photographic films.

With twice increasing Laprol addition (Figure 2c) it is observed the formation of two groups of particles in roughly equal proportions: 1 - flat crystals with an equivalent diameter 0,35-0,55 μm and thickness 0.1 - 0.18 μm and 2 - isometric crystals having the size 0.1-0.3 μm. It is so-called bimodal emulsion. The symmetry of flat crystals is significantly disturbed. Irregular hexagons and triangles are observed. The trend of their transformation into isometric MC is observed. Homogeneity is deteriorated and equal C_V = 40%. Consequently the given concentration of Laprol already is not optimal for high quality photographic emulsion.

The third-largest addition caused a tendency to thicken the MC and to create octahedral particles (Figure 2d). Fine fraction about 0.2 μm almost disappeared. The number of large crystals increased again. The average size of the MC reached 0.58 μm. The relative share of the triangular MC increased. There are not only the deterioration of grain size (C_V = 302%) but the transformation of the crystal form in this case.

Fourth Laprol concentration turns the whole emulsion into octahedral shape 0.3 - 0.8 μm with sharp maximum near 0.4 μm on the size distribution curve (Figure 2f). In this case, speaking about the synthesis of T-crystals is impossible. The homogeneity of the emulsion C_V = 26% but it is not suitable for the manufacture of high-quality photographic films.

It is known hypothesis that T-crystals are formed by self-assembly of AgHal nuclei in flat associates and their subsequent stacked coalescence. We could con-

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firm it, having processed water suspension of microcrystals by ultrasound. Results of such intensive processing are shown on Figure 3. Ultrasound begins to destroy tabular crystals and to bare initial structure of growing together small particles. Apparently, determined in this work minimal micro addition of surfactant is optimal for regulation of this process. It's increasing only on one order changes the dynamics of crystal growth dramatically. Octahedral MC instead T-crystals were obtained, that are no suitable for the manufacture of high-quality photographic films.

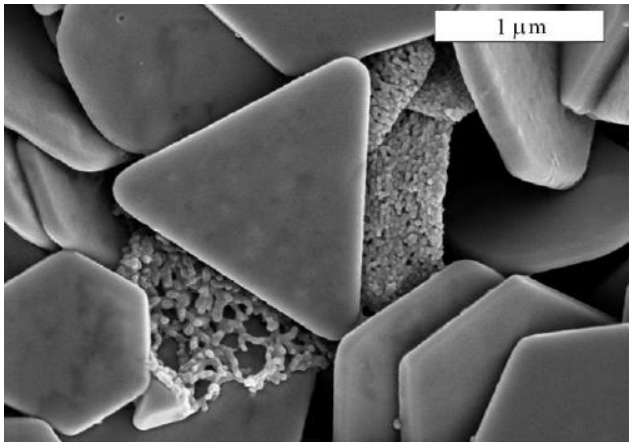

Figure 3 : Revealing of initial structure of tabular AgHal microcrystals consisting of accrete small particles.

CONCLUSION

In summary our experiments have shown that special mixing device and surfactant Laprol additions are a powerful factors to control size distribution and crystallographic structure of the silver halide microcrystals in gelatin solution. On the one hand Laprol can significantly increase the homogeneity of plane MC. This is observed when the surfactant concentration is 200 times smaller than the CCM. In terms of the initial gelatin solution it is 34×10^{-6}% wt., i.e. very small, microscopic addition to the final photographic emulsion. Therefore it is unlikely to be a source of negative influences on the subsequent processing and the properties of the photographic film. On the other hand it was found that the properties of the final emulsion are sensitive to small (two-time) change of the micro-concentration of Laprol that significantly impairs the homogeneity. Consequently a precise calculation of optimal surfactant addition is required.

ACKNOWLEDGEMENTS

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