Feature of Emulsion Ripening with Octahedral Habit Microcrystals.

I.L. Kolesnicova, N.S. Zvidentsova, S.A. Sozinov.
Kemerovo State University
Kemerovo, Russia.

Introduction.

This paper presents data on the investigation of emulsion photographic characteristics with octahedral habit microcrystals (MC) (111) with the size d=0.19-1.8 μm in different regimes of chemical ripening, tabular microcrystals (T-MC) AgBrI (111), senthesized by controlled double-jet crystallization (CDJC) and small grained emulsion ripening. Data on MC AgBr (100) are also given. The process of sensitivity formation under emulsion ripening synthesized at pBr < 2.5 without the introduction of photographically active admixtures is discussed. Sensitivity formation characteristics are dealt with taking into account synthesis conditions and ionic conductivity change in the process of MC ripening.

Experimental.

The process of photoemulsions chemical ripening is usually conducted at pBr=3.0; synthesis of octahedral microcrystals is carried out at pBr=1.6; synthesis of T-MC AgBrI (111) is performed at pBr=2.3, cubic ones being conducted at pBr=3.2. Microcrystals AgBr (111) ripening should be exacted to differ from the process of MC AgBr (100) ripening. This is connected with ionic equilibrium change in the solution under ripening, microcrystals surface energy and ionic conductivity in the process of MC modification.

MC AgBr (111) (d=0.19-1.8 μm) were synthesized in the conditions: T=45-60^{0}C, pBr=1.6, $W_{CRYST.}$=1.9-25 ml/min. Chemical ripening was carried out at T=52^{0}C, pBr=3.0, $t_{RIPEN.}$=0-3 hr. MC AgBr (100) and T-MC AgBrI (111) ripening were performed under the same conditions.

From the data obtained earlier [1,2], the following ripening regimes were chosen to confirm the received results:

1. Spontaneous sensitization (ripening without photographically active admixtures),
2. Spontaneous sensitization with further addition of triazaindolizine (TAI) at the end of ripening,
3. Spontaneous sensitization at different values of pBr in the process of second ripening (pBr=1.6, pBr=3.0),
4. Sulphury sensitization,
5. Sulphury sensitization with the addition of TAI at the end of ripening.

In the process of emulsion ripening samples were selected for sensitometric tests, dielectric loss measurement and electron-microscopy analysis.

Results and Discussions.

The data given at fig.1 shows that light sensitivity increases with the increase of MC sizes up to 1.5 μm, and then sensitivity decrease is observed. TAI introduction at the end of ripening leads to the additional sensitivity growth. These results were checked on gelatin of three types using water of different purity degree. The character of observed dependence a quality level is preserved in all cases. This allows us to make a conclusion that on the emulsions with MC silver halides, synthesized at pBr=1.6 a considerable share of sensitivity under chemical sensitization can be shaped without photographically active admixtures.

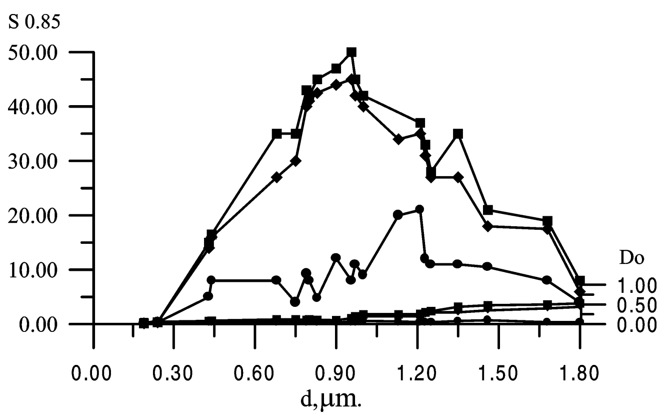

Figure.1. The dependence of light sensitivity and fog level upon average equivalent size of microcrystals ● the change of light sensitivity and fog level of nonsensibilized emulsion, ◆ the change of light sensitivity and fog level in ripening regime 1, ■ the change of light sensitivity and fog level in ripening regime 2.

Figure 2 presents results showing that light sensitivity of MC octahedral habit increases in chemical sensitization kinetics at pBr=3.0 without fog level increase. Light sensitivity and fog level at pBr=1.6 didn't exceed the initial level during 3 hours ripening.

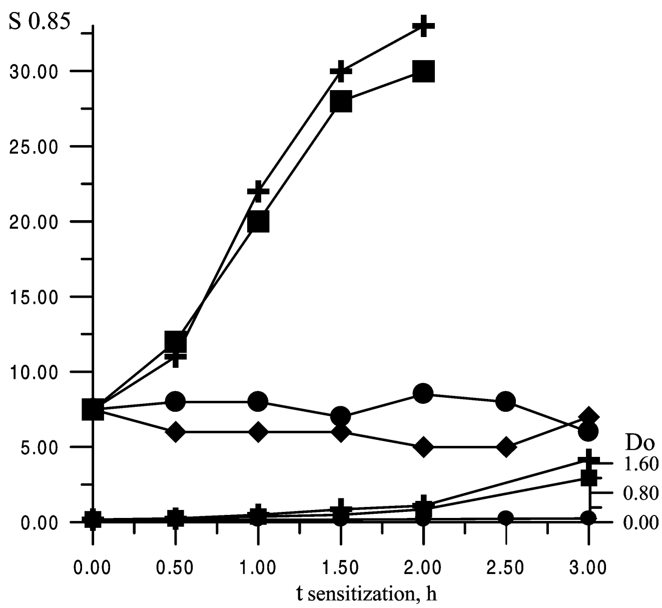

Figure.2. The change of light sensitivity and fog level from pBr value of chemical ripening AgBr (111) MC d=1 µm
● the change of light sensitivity and fog level in ripening regime 1 at pBr=1.6,
◆ the change of light sensitivity and fog level in ripening regime 2 at pBr=1.6,
■ the change of light sensitivity and fog level in ripening regime 1 at pBr=3.0,
+ the change of light sensitivity and fog level in ripening regime 2 at pBr=3.0.

Ripening conditions were not found for cubic MC (regime without the addition of photographically active admixtures). These are condition under which there would be sensitivity decrease relative to initial level.

Emulsions with T-MC obtained in the process of physical ripening of small grained emulsions with microcrystals size d=0.1 µm possess initial sensitivity somewhat higher than cubic MC (fig.3). In the process of second ripening (regime of spontaneous sensitization) sensitivity increase on these emulsions was not observed. Two-fold increment of sensitivity was observed on large T-MC, obtained by controlled double-jet crystallization.

Table 1 presents data showing that synthesis time increase of MC AgBr (111) with sizes within the limits of d=0.75-1.3 µm allows to receive in an average higher quantity $S_{0.85}$ in the regime of spontaneous sensitization.

The data obtained makes it possible to underline principle factors influencing the nature and regularities of photographic

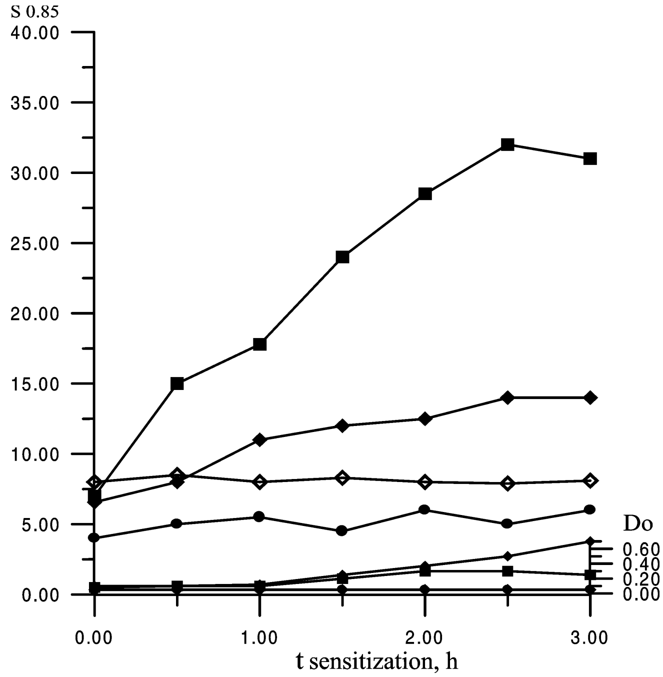

Figure3. Curves of sensitivity dependence and fog level from ripening time in regime 1 for MC AgBr (111) synthesized by two methods (CDJC and small growth emulsions ripening methods) d=1µm at spontaneous sensitization.
● the change of light sensitivity and fog level for MC AgBr (100),
◆ the change of light sensitivity and fog level for T-MC AgBr (111), synthesized by CDJC method,
◇ the change of light sensitivity and fog level for T-MC AgBr (111), synthesized by small growth emulsions ripening method,
■ the change of light sensitivity and fog level for octahedral MC AgBr (111).

sensitivity formations. Since the formation of sensitivity centers occurs without the addition of sulphury compounds one can confirm that these centers are clusters of silver (Ag_n). The formation of Ag_n particles most probably occur as a results of surface modification and MC shape change in the process of ripening under ionic equilibrium change from pBr=1.6 up to pBr=3.0-3.2. The scheme of sensitivity centers formation is supposed to include the following stages: MC solution with ratio increase r (111) / r (100),

$$AgBr \rightarrow Ag^{+}_{SOLUTION} + Br^{-}_{SOLUTION} \quad (1)$$

where r(hkl) – the distance from MC center up to its frontier in the direction (hkl).

MC growth in the direction (100) proceeds simultaneously. The formation of small phase in emulsion mass is not discovered. The latter is naturally connected with Ostwaled ripening and small phase dissolution. Further scheme of sensitivity centers formation may be written down as total combination of electron and ionic stages on the surface MC:

$$e^- + Ag^+_{SOLUTION} + AgBr \rightarrow Ag^+(AgBr) \quad (2)$$

$$e^- + Ag^+_{SOLUTION} + Ag^+(AgBr) \rightarrow Ag_2^+(AgBr)$$

$$e^- + Ag^+_{SOLUTION} + Ag_2^+(AgBr) \rightarrow ..... \rightarrow Ag_n^+(AgBr)$$

Schemes with the formation Ag_2^+(AgBr), for which greater number of electrons are necessary, are possible. Electrons (e^-), participating in the formation of sensitivity centers can be captured from the solution or crystal AgBr in the result of thermal transitions. It is noteworthy that the growth of the fog level in all investigated emulsion occurs slowly and as a rule doesn't exceed the quantity 0.1-0.2.

Sensitivity centers formation on the surface MC (111) under ripening in conditions with pBr=1.6-2.0 doesn't occur for the only mechanism resulting in the change of conditions on the surface and MC growth is Ostwald ripening. The last process for homogeneous emulsions as well as the probability of sensitivity centers formation of the type $Ag_n^+(Ag_n^0)$ seem to be improbable.

The process of latent image formation under emulsions exposition represents alternation of electron and ionic stages on the surface or in MC volume:

$$Ag_n^+(Ag_n^0) + e^- + Ag^+_i \rightarrow .... \rightarrow Ag_m,$$

where $Ag_n^+(Ag_n^0)$ – sensitivity center, Ag_m – latent image center.

If the life-time of photoelectron captured on the sensitivity center (t_1) is compared with the neutralization time of captured electron by silver ion (t_2), then sensitivity formation effectiveness in emulsions may be correlated to ionic conductivity of microcrystals (all other things being equal).

Ionic conductivity MC is known to decrease with the size growth. Under d=0.1 µm ionic conductivity of microcrystal is about two factors higher, then in macrocrystals. Therefore the

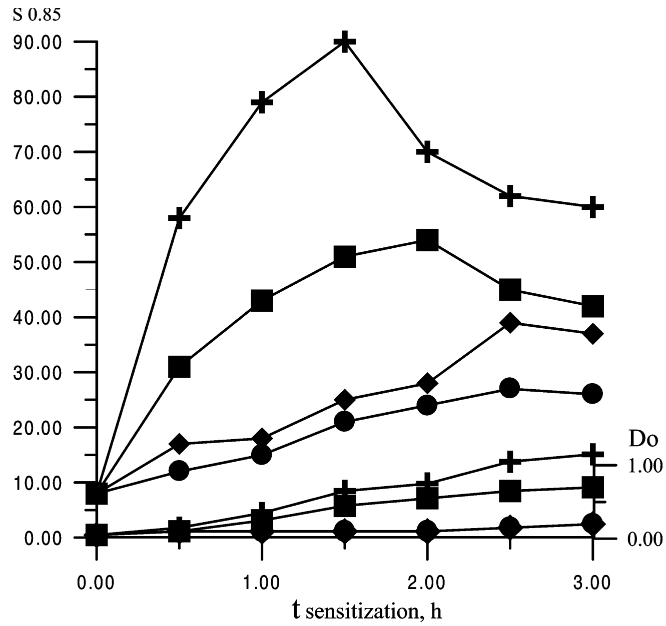

Figure 4. The change of light sensitivity and fog level in chemical ripening kinetics for MC AgBr (111) d=1.24 µm in different ripening regimes.

● *the change of light sensitivity and fog level in ripening regime 1,*
◆ *the change of light sensitivity and fog level in ripening regime 2,*
■ *the change of light sensitivity and fog level in ripening regime 4,*
+ *the change of light sensitivity and fog level in ripening regime 5.*

initial sensitivity growth MC (111) with the size increase may be connected with ionic conductivity decrease and the increase of formation probability of stability of stable centers of latent image [3].

Further conductivity decrease with the increase of sizes MC may result in the decrease of latent formation probability ($t_2 >> t_1$). This explains light sensitivity decrease (fig.2). These considerations are confirmed in comparing the results of data analysis on fig. 1, 2, 4 about the influence of introduced stabilizers on the change of sensitivity in ripening kinetics. Conductivity decrease according to the data of the work [1] may be related with the adsorption of TAI molecules. On active (low coordinated) surface spots, i.e. on defects of step crack type. Firstly, this results in surface energy decrease and diminishes the number of possible spots on the surface for sensitivity centers formation. Indeed, MC ripening in the presence of TAI is not accompanied with MC light sensitivity increase. However, the addition of TAI at the end of ripening leads to further increase of light sensitivity and the decrease of fog level. Both these processes can be understood if one suggests that TAI prevents the formation of new sensitivity centers, that it interacts with silver centers on the surface and decreases ionic conductivity. These suggestions were experimentally proved correct in the paper [1].

Table 1. Crystallization rate influence on the process of light sensitivity formation emulsions ($S_{0.85}$) in spontaneous ripening regime: S_0 - nonsensibilized emulsions sensitivity, $S_{max(1)}$ - maximum light sensitivity in ripening regime 1.

$W_{CRYSR.}$, ml/min.	d, µm	S_0	$S_{max(1)}$
V_1	1,229	21	34
$2V_1$	1.21	20	42
$2V_1$	1	11	40
$2V_1$	1	8	65
$2V_1$	0.97	9	31
$2V_1$	0.75	14	30
$4V_1$	0.83	5	14
$4V_1$	1	8	28
$4V_1$	1	5	21
$4V_1$	1.13	4	6
$4V_1$	1.25	8	27
$4V_1$	0,96	9	18

Full or partial lack of reactions 1-2 at ripening MC AgBr (100), explains the reasons of behavior difference of these MC from octahedral habit MC. Relatively lower sensitivity growth in T-MC obtained by CDJC may also be associated with higher concentration of silver interstitial ions in comparison to octahedral MC. Stabilizers adsorption on the surface of T-MC results in ionic conductivity decrease, but in a less degree than in MC AgBr (111). The absence of the effect of sensitivity rise in T-MC obtained by small grained emulsion ripening, in process second ripening may be connected with polycrystals structure MC. Thus the probability of latent image formation is lower due to excessive concentration of silver interstitial ions ($t_2 >> t_1$). Therefore the probability of stable centers formation of latent image will be low.

Growth rate is known to influence considerably crystals structure perfection. As a rule, temperature increase and the decrease of crystallization rate results in the growth of more perfect microcrystal. Polydispersed crystals having block structure grow under condensation in the conditions of low temperatures and high crystallization rate. Such microcrystals properties differ from those of perfect microcrystals. First of all it concerns ionic conductivity, which is proportional to specific surface of such MC. We have shown that the concentration of silver interstitial ions in microcrystals obtained at $W_{CRYST.} = V_1; 2V_1$ and $4V_1$ may differ by effect of two. We suppose that this is due to low effectiveness of the process of latent image centers formation.

Conclusion.

The results obtained allow us to conclude that a considerable share of sensitivity in emulsions with MC AgBr (111) is shaped without sulphur containing admixtures partisipitation. Main regularities of sensitivity growth can be explained using data on ionic conductivity change. It is shown spontaneous ripening effectiveness has a threshold character. It is maximum at sizes 0.75-1.3 μm and it decreases at further sizes growth of microcrystals. The level of spontaneous sensitization for microcrystals of equal size but synthesized at different velocities may differ by a factor of two and more.

References

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