Influence of stabilizers to an internal photosensitivity of emulsion microcrystals of a "core - shell" type

Boris A.Sechkarev, Larisa V.Sotnikova, Timothy A.Larichev,
State University of Kemerovo, Kemerovo, Russia

Introduction

Photographic systems created on the basis of "core-shell" microcrystals are successfully used in scientific and practical purposes, since advantages, which such systems have allow to vary their properties over a wide range[1,2]. However in the majority of cases "core-shell" systems are used as surface photosensitive microcrystals. Researches of an internal photosensitivity is connected to a number of problems: such as complexity of having a high electron accepting ability internal centers creation, the complexity of division of internal and surface centers at photographic processing, besides was not till now possible to receive the internal image comparable on quality with surface image. The reception of photographic systems with the internal image is perspective from the point of view of photomaterials with increased stability to an oxidation by photoholes and increased storage time creation[3]. On our opinion one of possible ways of the acceptable quality internal image reception is internal centers stabilization by photographic stabilizers.

Experimental

Object of research was "core" emulsion $AgBr_{0.96}I_{0.04}$ cubic microcrystals with an average equivalent diameter d=0.6±0.02 microns and variation coefficient C_v=15-20 %, subjected to chemical sensitization by sodium thiosulfate ($Na_2S_2O_3$ concentration - 1×10^{-3} mol/mol Ag) and by gold thiocianate (AuSCN concentration - 6×10^{-10} mol/mol Ag). The "core" emulsion after optimum chemical ripening has the following sensitometric characteristics: S_{rel} = 40; D_{max} = 3.0; D_0 = 0.06; γ= 2.5. The "core" emulsion was divided into four parts. On the first "core" emulsion portion AgBr "shell" the thickness 15 nm by a method of a controlled double jet crystallization[4] was grow. In second, third and fourth emulsion parts for chemical sensitization centers stabilization before shell grow the stabilizers was entered. This stabilizers was 1-phenil-5-mercaptotetrazol (PMT), 4-hidroxy-6-methil-1,3,3a,7-tetrazainden (TAI) and 5-methil-1,2,3-benzotriazol (BTA). The stabilizers concentration in all cases was equal 1×10^{-3} mol/mol Ag.

As is known[5-7], there are a few classes of stabilizing substances used in photographic technology and stabilization actions are distinguished by mechanisms. Basing for these work we have chosen stabilizers the most frequently used in a photo and relating to are various stabilization mechanisms. Thus "core-shell" emulsions with internal photosensitivity centers stabilized by three various types of stabilizers, and "core-shell" emulsion without internal photosensitivity centers stabilization were received. Besides was carried out an chosen stabilizers adsorption on a "core-shell" microcrystals surface in concentration 1.5×10^{3} mol/mol Ag. The photographic processing by standard methol-hidroquinone developer did not find out surface sensitivity presence on all samples of "core-shell" emulsions. For revealing the internal sensitivity the processing by UP-2 developer[8] with addition of sodium thiosulfate in concentration 4 g/l or stabilizers in concentration 6.5×10^{-3} mol/l was carried out.

Results and discussion

Stabilization of core emulsion. The dependence of the core emulsion sensitometric characteristics on stabilizer concentration was investigated. The results of this series of experiments are presented in Table 1.

Table 1. Influence of stabilizer concentration to the "core" emulsion sensitometric characteristics.

Stabilizer	Concentration, mol/mol Ag	S_{rel}	D_{max}	D_o
-	-	25	2.27	0.09
PMT	5×10^{-4}	25	2.30	0.09
	1×10^{-3}	24	2.28	0.11
	$1,5\times10^{-3}$	16	1.81	0.07
BTA	5×10^{-4}	25	2.10	0.07
	1×10^{-3}	23	1.95	0.07
	$1,5\times10^{-3}$	20	1.84	0.06
TAI	5×10^{-4}	65	2.00	0.09
	1×10^{-3}	25	2.30	0.16
	$1,5\times10^{-3}$	23	2.20	0.26

The results show, that the influence to the emulsion sensitometric characteristics is rendered by both stabilizer concentration and its chemical nature. TAI in small concentration causes increase of a photosensitivity, but thus reduces maximum optical density. The TAI large concentration do not much influence a photosensitivity and maximum optical density, however appreciably fog optical density grows. The PMT in concentration lower then 1.5×10^{-3} mol/mol Ag does not influence on the "core" emulsion sensitometric characteristics, but increase of concentration results in sharp decrease of all characteristics. For BTA smooth both fog optical density and maximum optical density reduction was received. The various stabilizers influence is connected with various adsorption ability of these substances. In further experiments the stabilizers were used in concentration, causing change of the sensitometric characteristics not more than 5 %.

Shell influence on the internal image. The AgBr shell with 15 nm thickness was growth on chemically sensitized core emulsion crystals The optimal shell thickness was determined in our early experiments[9]. The results of internal sensitivity investigation are presented on Figure 1.

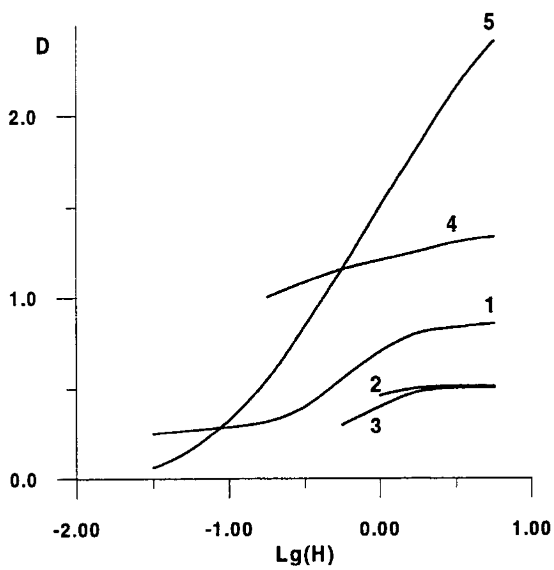

Figure 1. Internal sensitivity characteristic curves for core-shall emulsion with various stabilizers on a core:, 1 - PMT, 2 - BTA, 3 - TAI, 4 - control sample without the stabilizer,5 - core emulsion without the stabilizer.

The results show that adsorbed on a core stabilizers use does not allow to reach the internal sensitometric characteristics, close to parameters of initial core emulsion. However, the PMT use can appear more perspective for stabilization of internal centers, than the TAI.

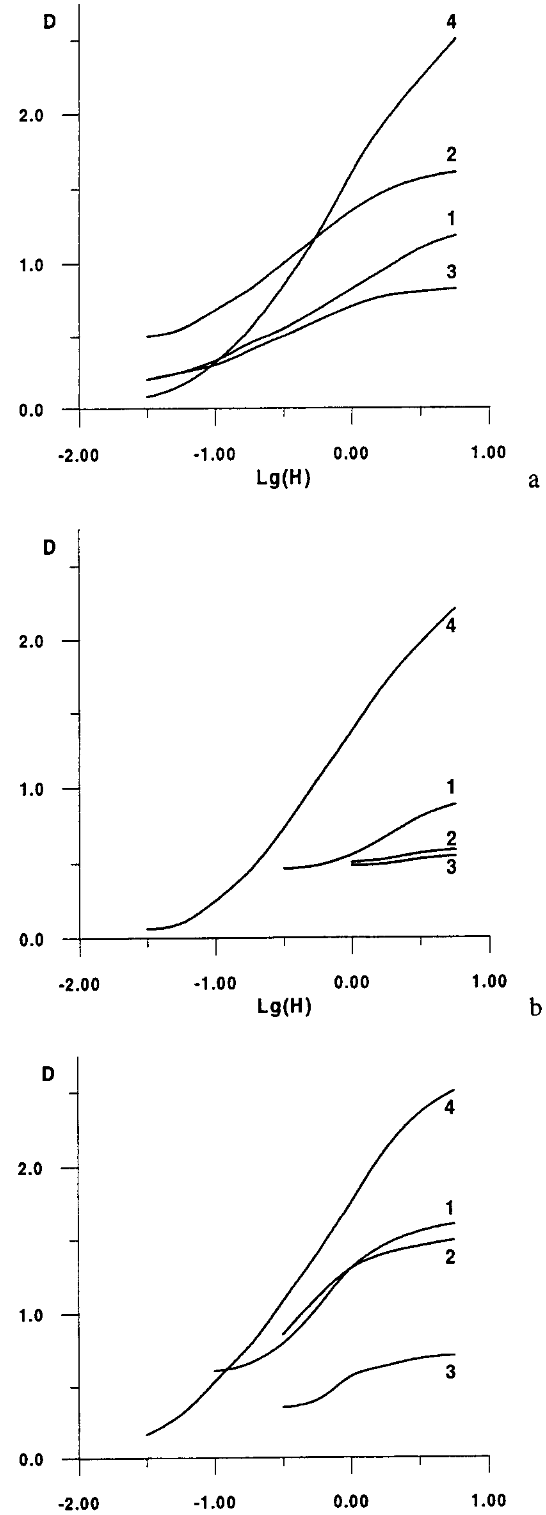

Figure 2. Internal development characteristic curves of core-shell emulsion: à) core stabilized by PMT; b) core stabilized by BTA; c) core stabilized by TAI. Curves 1 - internal developer with BTA; 2 - internal developer with TAI; 3 - internal developer without stabilizer; 4 -core surface development.

Influence of shell stabilization on internal sensitivity. The adsorbed stabilizer changes energetic conditions microcrystal surface and influences on internal photosensitivity centers formation. We investigated adsorbed stabilizers influence to the sensitometric characteristics. The results have shown rather weak influence of a stabilized shell on core sensitivity. However, it is possible to reveal the following laws: PMT adsorbed on an shell results in decreasing of maximum optical density, TAI increases a level of internal fog optical density; BTA reduces a level of an internal fog, but lowers maximum density.

Influence of stabilizers in a developing solution on internal sensitivity. The results of internal developing in many respects depend on their realization conditions. During internal development there is the effective dissolution of an shell. Therefore in a solution there is the significant Ag^+ ions excess that results in physical development and dichroic fogs occurrence. The introduction of stabilizers alloy to decrease Ag^+ ions concentration. The characteristic curves of internal development are presented on figure 2. It is necessary to note, that PMT introduction in developer completely suppress any development. This PMT action is connected with very low solubility their silver salt on a microcrystals surface. As a result there are no shell dissolution during inner development.

The BTA is usually entered in a developer to prevent fog increasing. The mechanism of its action consists in delay of a silver halide dissolution and surface development prevention. For BTA silver salt solubility is close to silver bromide solubility. Photographic treatment by developer with BTA allow to reduce internal fog optical density level. The maximum internal image optical density does not reach D_{max} of core emulsion, however, in comparison with usual internal development, appreciable increase D_{max} is observed.

The TAI use in developer allow to achieve internal D_{max} increase on samples stabilized by PMT. However, it is necessary to note, that both TAI stabilization of photosensitivity internal centers and the TAI addition in developer results in increase of a fog optical density level. Since TAI silver salt solubility is not very low it is possible to assume that in experiment conditions the formed compound are not adsorb on microcrystals surface.

Conclusion

The received experimental results have confirmed distinctions in properties of researched stabilizers and have shown an opportunity of management by development processes by stabilizers combination of various types. It is found out, that PMT is the most effective as the core stabilizer. The TAI can be perspective as the developer additive if it will be possible to find conditions of fog level reduction.

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