Complex Pd (II) Compounds as Chemical Sensitizers

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Abstract

The conditions for chemical sensitization of isometric AgBr grains in the presence of palladium ions were determined. The complex ions $[PdX_4]^{2-}$ (where X = Cl^-, Br^-, SCN^-, SO_3^{2-}) were used as a sensitizer. It was established that the process of secondary dissociation of $[PdX_4]^{2-}$ preceded the sensitization process itself. It was fond out that the electrolyte solution with the same ligand could be used for controlling the secondary dissociation process.

The chemical sensitization was shown to be most effective when using the $K_2[PdCl_4]$ complex as a sensitizer.

Introduction

Conventional methods of chemical sensitization of AgHal grains do not always provide for the required photographic characteristics. Selective localization of impurity centers on certain crystal sites is preferable when carrying out chemical sensitization. All the stages of the photoprocess can be affected by including catalytically active elements, e.g. palladium, into the composition of the latent image centers (LIC). Introduction of complex compounds, such as $[PdX_4]^{2-}$ (X = Br^-, Cl^-, NO^{2-}, SO^{3-}, SCN^-) into AgHal grains is possible both at the stage of their synthesis, and chemical sensitization.

The aim the present paper is to determine the conditions for chemical sensitization enabling the inclusion of the palladium ions in the latent image centers (LIC) structure of isometric AgBr grains and the determination photographic properties of emulsion layers including these grains.

Experiment

At the first stage a photographic emulsion containing AgBr grains {100} with the average equivalent diameter $\bar{d}$ = 0,5 mcm and coefficient of variation C_v = 10 - 15 % was prepared. Then $[PdX_4]^{2-}$ ions (from 10^{-5} up to 10^{-3} mole/mole Ag) were added into the emulsion after the basic sensitizers ($Na_2S_2O_3$ and $HAuCl_4$) during sulfur-plus-gold sensitization. The volume of the added complex solution was equal to 0,1 ml, the time of sensitization was 60 min.

Result and Discussion

The sensitometric characteristics of the resulting layers with various ligandes are submitted in Table 1.

Photographic speed increase is observed when introducing complex compounds with the concentrations - 10^{-5} - 10^{-4} mole Pd/mole Ag - for all of them except for the complex with chloride ligands.

The greatest photographic speed increase is observed when using the complex with SCN^- ligands, however, fog optical density, thereby, considerably increases (D_0 = 0,7 and 0,4 for the concentrations 10^{-4} and 10^{-5} mole Pd/mole Ag, accordingly). Probably, in this case SCN^- ions liberated from the complex as a result of its secondary dissociation act as sensitizers. Desensitization in the case of introducing the complex ion with Br^- and Cl^- ligands is most likely to be caused by the liberation of an additional amount of halide ions capable of acting as desensitizers [1]. Hence, if the processes of secondary dissociation of complex ions are excluded or limited in number, it is possible to use palladium complex compounds as chemical sensitizers.

Table 1. Influence of various ligands on the sensitometric characteristics of emulsion layers

Chemical sensitization additives		Sensitometric characteristics			
Complex	Concentration mole/mole Ag	$S_{0,2}$	$S_{0,85}$	D_{max}	D_0
—	—	2,8	11	3,5	0,04
$K_2[PdCl_4]$	10^{-3}	2,1	10	3,7	0,04
	10^{-4}	2	7	2,8	0,02
	10^{-5}	1,5	4	2,5	0,03
K_2PdBr_4	10^{-3}	1,5	9	3,5	0,03
	10^{-4}	2,3	15	3,6	0,04
	10^{-5}	3	13	3,8	0,01
$K_2[Pd(SCN)_4]$	10^{-3}	3	12	4,2	1,02
	10^{-4}	4	15	3,8	0,70
	10^{-5}	4	18	3,3	0,40
$Na_6[Pd(SO_3)_4]$	10^{-3}	1,6	9	3,39	0,01
	10^{-4}	5	23	4,46	0,01
	10^{-5}	1,3	7	3,4	0,05

The $[PdX_4]^{2-}$ complex ions are known to easily undergo secondary dissociation in water solution resulting in ion charge reduction [2]. To control the degree of secondary dissociation of complex ions is possible by adding the electrolyte containing ligand-ions into the solution. Therefore, to the complex compound solution used during chemical sensitization, the electrolyte with ligand-ions (the background electrolyte) was added. The results of the influence of the background electrolyte on sensitometric characteristics of emulsion layers are submitted in Table 2 as the values of optimum photosensitivity and maximum optical density.

For a complex compound with chloride-ligands photographic speed increase is observed at concentrations of the background electrolyte > 0,1 M. As stability of the complex to secondary dissociation is low, it can be assumed that at concentrations <0,1 M secondary dissociation does proceed. It can also be assumed that the impulse for a catalytic effect of Pd(II) ions in this compound is the process of replacement of chloride-ligands by bromide-ligands proceeding on the surface of AgHal grains which increases the activity of incorporating the Pd(II) ions into the sensitivity center (SC).

The optimum concentration of the background electrolyte is 0,01 - 0,1 M for Br^- ligands. Greater concentrations result in desensitization, probably, because of the excess of Br^- ions and their negative influence on chemical sensitization.

Table 2. Influence of the concentration of the background electrolyte on sensitometric characteristics of emulsion layers

Chemical sensitization additives		K_2PdCl_4 + KCl		K_2PdBr_4 + KBr		$K_2[Pd(SCN)_4]$ + KSCN		$Na_6[Pd(SO_3)_4]$ + Na_2SO_3	
Concentration of the complex mole/mole Ag	Concentration of background electrolyte, M	$S_{0,85}$	D_{max}	$S_{0,85}$	D_{max}	$S_{0,85}$	D_{max}	$S_{0,85}$	D_{max}
10^{-3}	-	10	3,7	9	3,5	12	4,2	6	2,7
	0,01	9	3,6	14	4,8	14	4,3	9	3,2
	0,1	12	4,0	15	4,1	10	4,5	8	3,2
	1	18	4,4	15	4,0	9	4,8	6	2,8
10^{-4}	-	7	2,8	15	3,6	15	3,8	13	3,6
	0,01	9	4,5	20	3,8	12	4,0	15	3,7
	0,1	17	4,6	18	3,6	22	5,0	14	3,5
	1	25	4,5	7	3,5	15	3,5	12	3,9
10^{-5}	-	4	2,5	13	3,8	18	3,3	7	3,4
	0,01	17	3,5	15	3,9	17	3,7	10	3,3
	0,1	12	3,4	16	4,2	15	3,7	12	3,5
	1	7	3,0	10	4,0	20	3,9	11	3,5

Based on the experimental data it can be stated that it is most expedient to use palladium complex ions with Cl^- ligands during chemical sensitization and the complex ion solution must be added in the presence of the KCl background electrolyte whose concentration > 1 M.

The compound with SCN^- ligands, when changing the concentration of the background electrolyte, reduces photographic speed due to minimum optical density increase, while some photographic speed increase is probably caused by increase in the amount of SCN^- introduced into the system, which is known as a sensitizer for grains. In this connection a number of experiments consisting in the introduction of an equivalent amount of SCN^- ions into the emulsion during sensitization have been carried out. The results of the experiments are submitted in Table 3 as optimum sensitometric characteristics.

Analysis of sensitometric characteristics of the samples allows us to state that palladium complex ions with SCN^- ligands can act as sensitizers for AgBr emulsions.

Thus, it can be assumed that CS is complicated by secondary dissociation of $[PdX_4]^{2-}$, resulting in the reduction of the charge of the complex ion. To control the degree of secondary dissociation of complex ions is possible by adding the electrolyte containing ligand ions into the solution. It is shown that it is most expedient to use the complex compound $K_2[PdCl_4]$ during CS which must be introduced in the presence of the KCl background electrolyte whose concentration > 1 M.

Table 3. Sensitometric characteristics of samples containing AgBr grains sensitized by $K_2[Pd(SCN_4)]$ with various concentrations of the background electrolyte and equivalent amount of KSCN.

Chemical sensitization additives		Sensitometric characteristics			
$K_2[Pd(SCN)_4]$, mole/ mole Ag	KSCN, mole / mole Ag	$S_{0,2}$	$S_{0,85}$	D_{max}	D_0
-	-	2,8	11	3,5	0,04
10^{-5}	-	4	18	3,3	0,03
	$5 \cdot 10^{-6}$	4	17	3,7	0,03
	$5 \cdot 10^{-5}$	3	15	3,7	0,02
	$5 \cdot 10^{-4}$	4,5	20	3,9	0,03
-	$5 \cdot 10^{-6}$	2	10	3,5	0,02
	$5 \cdot 10^{-5}$	1,5	12	2	0,02
	$5 \cdot 10^{-4}$	1,5	10	1,8	0,02

References

1. T. H. James, in The Theory of the Photographic Process, 4th ed., T. H. James, ed., Macmillan, New York (1977).

2. Lidin R.A., Andreeva L.L., Molochko V.A. The guide in inorganic chemistry. Moscow, Chemistry, pg. 320 (1987).

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Fedor V. Titov graduated from the Chemistry Faculty, Kemerovo State University in 1995 (Russia), defended the Candidate's thesis (dissertation) in 1999. Now he is Assistant Professor of the General Physics department of Kemerovo State University. The scope of scientific interests: the investigations of silver halide materials for registering the visible information; the co-author of the techniques of creating the photographic materials on the basis of silver halide grains of the heterocontact type; the author of more than 50 scientific publications.