Spectral Sensitization of Silver Halides: New Approaches

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Abstract

Efficient methods of completion of non-stabile silver atoms or latent image sub-centers to the stabile particles of latent image during exposure under the action of additional chemical energy are considered. The main idea of realization of such process lies in use of chemical intensification – *primary development* - even at the stage of exposure of photographic material. The case of point is the latensification of the latent image in the process of exposure of photographic material under the action of reducers. In this case the latensification can be aroused by either the reducers, which are present in photographic layer or the reducers, which are generated in the oxidized decomposition of the supersensitizer. Necessary condition of the effective action of reducers is their specific adsorption on the Ag_2S-centres of sensitivity.

Introduction

Silver halide is unique as the light-sensitive material. The uniqueness of microcrystals of AgHal lies first of all in the effective mechanism of concentration of photoreduced silver atoms on sole or on small number of centres by a Gerni-Mott two-stage electronic-ionic mechanism. Other reason of uniqueness of AgHal is a consequent chemical amplification of a primary light action at the stage of photographic development.

It is agreed that a minimum number of photons resulting in creation of latent image, n_{crit} = 3-4 photons, and an real number, n_{real} = 10-20 photons. The main reasons of difference of values of n_{crit} and n_{real} are the creation of several centres of the latent image on one AgHal microcrystal of as well as an instability of single silver atoms, Ag_o (pre-centres of latent image), which are oxidized before than stable particles - Ag^o_2 molecules – latent image sub-centre and, further, latent image centres will be created from them. The situation is especially complicated on spectral sensitization when catalysis of oxidation of silver atoms takes place either by dye molecule itself or by dye hole in processes of self-desensitization of dyes type I and type II [1].

As a result of consideration of a role of self-desensitization processes, in the work [2] the conclusion was made that the process of spectral sensitization of negative silver halide emulsions is determined by kinetics of secondary reactions of dyes self-desensitization rather than primary photoreactions of electron transfer from the excited dye molecule in a AgHal conduction band. The kinetic theory of spectral sensitization (SS) on the basis of redox potentials of components of photographic emulsions was developed [1, p.170]. Accumulated currently experience convincingly testifies to predominated role of chemical processes at spectral sensitization. For majority of used at the present ortho-, pan- and especially infra-red dyes (Dye) the level of the photoexcited electron is below than bottom of the AgHal conduction band [1, p.148]. Therefore a primary action of SS can be considered as a surface redox reaction of Dye* with silver ions which practically is equally probable for many dyes. Therefore the problem on efficiency of the spectral sensitization can be hold to a problem of stability of atoms and molecules of silver formed on a primary stage of the process [3].

Latensification by Reducers

It may be suggested that if there were an effective method of completion of unstable silver atoms or latent image sub-centres up to stable particles of the latent image during an exposure, it would open a perspective of significant increase of spectral sensitivity of a photographic material. The main idea of realization of such process consists in use of a chemical amplification – *development* - already at the stage of exposure of the photographic material. The case in point is latensification of the latent image during exposure. For this purpose it is necessary to create in a photographic layer a reduction environment due to introduction there of reducer (Red). The algorithm of such process should consist of the following: reducer before exposure, i.e. before formation of catalytic silver particles, does not reduce AgHal, evidently for the kinetic reasons , however, after illumination and formation of silver particles it reduces pre- and sub-centres of latent image to the stable developable latent image centres. The essence of process is illustrated by the following scheme:

$$Dye^* + AgHal \rightarrow Dye^{+\cdot} + [AgHal]^- \quad (1)$$
$$[AgHal]^- + Ag^+ \rightarrow [AgHal/Ag^o] \quad (2)$$
$$[AgHal/Ag^o] + Red \rightarrow [AgHal/Ag^o_n] + Ox \quad (3)$$

The application of reducers introduced in photographic layers is known. The case in point is first of all an ascorbic acid (AA) [4-6]. In work [7] on AgBr(I)-emulsions the action of the ascorbic acid is studied on the large number of infra-red dyes with various length of polymethine chain. In the authors opinions [7] the action of AA should promote a «survival» of small silver particles of the latent image at the expense of their enlargement in the process of "primary development". As a result, the probability of self-desensitization of I type should decrease. Really, as shown in [7], with extension of polymethine chain of thiapolycarbocyanine dyes the efficiency of AA action is increased. Thus, it is shown that ascorbic acid is an universal supersensitizer of infra-red photographic materials.

We have shown that ascorbic acid was adsorbed on Ag_2S-centres of sensitivity. Therefore, latent image latensification by the action of AA is effective, because the silver particles formed on Ag_2S-centres are subjected to the directly amplification by the ascorbic acid. Other reducers - methol, phenidone, dodecyl gallate etc., causing super-additive effect during photographic development, behave in a similar manner. Apparently their action is connected also to a specific adsorption on Ag_2S-centres of sensitivity and to the latent image latensification.

Latensification by Oxidized Form of Supersensitizers

The traditional method of a decrease of an electron - hole recombination at self-desensitization of II type consists in acceptance of the dye hole by compound oxidized easier than dye. This reduction mechanism of Gilman is widely discussed in the literature [8]. The second method of supersensitization consists in «isolation» of dye hole from centres of photoelectrons acceptance [3,9]. The third method, considered for the first time by the author [10], consists in application of supersensitizers of a new type, which, as a result of oxidation by dye holes, would undergo transformation with disintegration of an initial nuclear skeleton. In the end the other molecule would be arised with a new nuclear skeleton having reduction properties in relation to AgHal [10]. In other words, at the expense of chemical transformations of the oxidized form of supersensitizer one (or more) electron would be injected in a AgHal microcrystal, capable to amplify a latent photographic image. The scheme of process is indicated below [10]:

$$\text{Dye} + h\nu \rightarrow \text{Dye}^* \quad (4)$$
$$\text{Dye}^* + \text{AgHal} \rightarrow \text{Dye}^{+\cdot} + [\text{AgHal}]^- \quad (5)$$
$$[\text{AgHal}]^- + \text{Ag}^+ \rightarrow [\text{AgHal/Ag}^o] \quad (6)$$
$$\text{Dye}^{+\cdot} + \text{BH} \rightarrow \text{Dye} + \text{BH}^{+\cdot} \quad (7)$$
$$\text{BH}^{+\cdot} + \text{R}^- \rightarrow \text{B}^\cdot + \text{HR} \quad (8)$$
$$\text{B}^\cdot + [\text{AgHal/Ag}^o] \rightarrow \text{B}^{+\cdot} + [\text{AgHal/Ag}^o]^- \quad (9)$$
$$[\text{AgHal/Ag}^o]^- + \text{Ag}^+ \rightarrow [\text{AgHal/Ag}_2^o] \quad (10)$$
$$\text{B}^{+\cdot} + \text{medium} \rightarrow \text{Products}, \quad (11)$$

where BH is supersensitizer, R^- is base. According to this scheme supersensitizer BH is oxidized by dye hole to a cation-radical $BH^{+\cdot}$, which from acid properties interacts with the base R^-, producing a radical $B^\cdot$. The last radical can act as the reducing agent in relation to the silver halide, i.e. can inject the second electron in AgHal and amplify in this way the latent image centre.

This two-electronic scheme was realised in [11] where an of formiate anion (HCO_2^-) was used as an dye hole acceptor. The principle of oxidizing disintegration of organic compound with injection of electron in AgHal was realised experimentally in a cycle of works of Muenter et al. [12]. As dye hole acceptors X-Y, as a rule, carboxy-substituted amines are used. A reaction of disintegration of cation - radicals $X\text{-}Y^{+\cdot}$ could be a reaction of decarboxylation, deprotonation, destruction of C-C bonds etc.

Conclusion

As a matter of fact, all considered processes of supersensitization under reducers action are a like in one point: they represent reducing latensification of the latent photographic image. Therewith the latensification can be initiated both reducer present in a photographic layer (for example, ascorbic acid), and reducer formed at oxidizing decomposition of supersensitizer.

Thus, at the present the unique features of silver halide as catalytic photosensitive system are used in full measure only at the dark stage of photographic process - at the stage of development. In our opinion the use of unique catalytic properties of AgHal also at the light stage of photographic process, as a "primary development" is not less perspective. Just such strategy of spectral sensitization should bring to significant growth of a practical sensitivity of photographic materials in the near future.

References

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Biography

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The field of scientific interest includes photochemistry, scientific and applied photography, spectral sensitization of photographic materials and optical recording materials.