Photochemical Sensitivity Formation of Silver Photothermographic Media

Mikhail A. Goryaev and Vladimir S. Gerasimov
Central Design Bureau of Mechanical Engineering
St.Petersburg, Russia

Abstract

Various models of the photothermographic process in silver halide-silver carboxylate systems are considered. The technology of the water synthesis of silver halides on the surface of a silver stearate is shown to increase the photochemical sensitivity and to create the conditions for the successful realization of the sensitization by methods of the conventional photography. Features of the sulfur and gold sensitization in thermally processed compositions as well as ways of the elimination of the photographic reciprocity failure at the high light intensity by surface and volume doping of silver halides are discussed.

Introduction

Photothermographic materials (PTM) on the basis compositions of a light-sensitive silver halide and non light-sensitive organic salts of a silver are used for registration of the black-and-white intensified images[1,2] and the area of their application is constantly expanded. Thus urgent problem remains increasing sensitivity of such materials.

During formation of the image in silver PTM two main stages is possible to allocate: formation of centres of the latent image at light absorption by silver halide and amplification of these centres at thermal processing at the expense of the silver restoration from salts of fatty acids with participation of developping substances and other reagents, included in structures of thermally processed compositions.[1,2] The sensitivity of a photographic material is to a great extent determined by developping processes, but processes of the latent image formation play paramount role.

Klosterboer and Rutledge have offered the phenomenonlogical model of photothermographic process,[1] which was specified and detailed by the subsequent researchers. As far as light is absorbed by a silver halide, purely the photochemical sensitivity thermally processed compositions is determined, as well as in a conventional photogpaphy by processes of the latent image formation in light-sensitive silver salts.[2] On the basis of indirect attributes of the image formation in PTM and results of investigations of photochemical processes in model systems on compositions of the silver halide and carboxylate nanosols Zou, Sahyun and coworkers[3] had offered the photocatalytic model of the latent image formation on the silver halide - silver carboxylate interface. In this connection, conclusions about unacceptablity of the conventional silver halide photography approaches to photothermographic processes were made.[3-5]

In the present work PTM on the basis of the silver halide and carboxylate are investigated and opportunities of using classical emulsion technology methods for the regulation of photochemical processes of the latent image formation in photothermographic systems are considered in view of structure features of such materials.

Synthesis of Light-Sensitive Component

The investigations were made on sample of photographic thermally processed films, in which a silver halide was synthesized directly on the silver stearate surface.[2,6] One of manufacturing technology features of silver PTM is availability of the water insoluble chemical additives and binding in compositions, therefore the preparation of the suspension for coating is carried out in organic solvent.[1,2] At direct halidization of a silver carboxylate in organic solvent compact microparticles of a silver halide by the size up to 5 nm[6] will be formed on the salt surface.

The processes of the latent image formation in silver halide photographic materials are largely determined by semiconductor properties of light-sensitive components.[7] For high-disperse silver halide particles received at halidization of a silver stearate in organic solvent environment, it is difficultly to speak about the AgHal crystal phase, about semiconductor properties of light-sensitive components. Methods of modifying semiconductor properties of a silver halide usually assume using water soluble compounds at synthesis for doping semiconductor. With the purpose of creating conditions for the regulation of semiconductor properties technology of synthesis, allowed to receive halide on the silver carboxylate surface in the water environment, was offered.[6,8]

Silver carboxylates have the layered structure with base planes (001).[4,9] At halidization of the silver stearate in situ the particles of a silver halide will be formed at first on lateral surfaces, and then on a base plane.[9] At thermal developping PTM the transport of silver ions to centres of the latent image is executed along carboxylate base planes,[4,10] therefore AgHal microcrystals, formed on the lateral carboxylate surfaces are the most important for the photothermographic process. Silver halide formation on a stearate surface is well seen on titration curve of the silver stearate suspension by a LiBr solution.[11] Just on appearing a crystal phase embryo it is possible to make teleological synthesis of a silver halide with using conventional emulsion technology methods. Way of silver halide synthesis on the silver stearate surface was offered by the alternate introduction of $AgNO_3$ and LiBr water solutions to suspension.[6,8] The sensitivity of such compositions in comparison with the waterless synthesis is increased, in our opinion, due to increasing sizes of silver halide microcrystals. By results of electron-microscopic investigations of thermally processed compositions, the cubic microcrystals of a silver bromide by the size about 0,1 μm had been formed on the silver stearate surface at the technologies of water synthesis. A role of collective electronic processes grows, in a greater degree semiconductor properties of a solid, ensuring the autolocalization and autocatalysis of photochemical process[7] are displayed just at increasing the size of light-sensitive component particles. It should note, that the size of received microcrystals will be well agreeed radius of a influence sphere in Klosterboer-Rutledge model, the valuation of which has given size 0,055 μm.[3]

A arsenal of methods, known in emulsion technology of conventional photographic materials and which can be applied for PTM, is expanded due to the technology of the silver halide synthesis in water environment. The realization of AgBr synthesis at the presence of a ammonia, which is the growth modifier of silver halide microcrystals,[12] has also allowed to increase the sensitivity of photographic films.[8,11]

Chemical Sensitization

The most widespread receptions of increasing silver halide photographic material sensitivity is a chemical sensitization.[12] Widely used in conventional materials sulfur sensitization causes the strong fog in PTM: its optical density exceeds 1,5 at usual modes of processing.[11] At such sensitization defects will be formed with local increasing concentration of interstatial silver ions, that promotes increasing efficiency of the latent image centres formation in photographic materials.[13] In PTM the activity of sensitivity centres appearing in these conditions is so great, that at high developping temperatures (380-400 K) intensive ox-redox processes will form strong fog. One of PTM features is absence in their structure gelatin, aminogroups of which play a important role at sulfur sensitization of silver halide photographic materials.[14] Zavlin and coworkers show an opportunity of sulfur sensitization after the entering amimes to the structure of thermally processed compositions.[15,16] In the conventional emulsion technology a gold sensitization is not effective itself and it is the most frequently applied in a combination with a sulfur sensitization.[12,13] But a gold sensitization of PTM has allowed to increase sensitivity.[17]

On our opinoin, it is stipulated by defects, formed at the gold sensitization, being in the beginning hole acceptors, reduce probability of photocarriers recombination.[13] In the high-disperse silver bromide of thermally processed compositions, where a part of a surface and, hence, the role of recombination processes is great, such situation is natural. Decreasing probability of recombination increases the efficiency of the latent image centres formation and the growth of sensitivity.

Reciprocity Failure

Silver halide photographic materials have a reciprocity failure as at low, as at high light intensities. PTM on the basis of silver salts are not exception, and the strong reciprocity failure[17] are observed in samples of PTM, made on the technology of a silver halide synthesis in organic solvent: a sensitivity decreases almost on the order as at increasing exposure interval from a second up to 100 s, as at decreasing up to 10^{-2} s. In such samples of thermally processed compositions probability recombination of nonequilibrum carriers is great in silver halide particles of the small size, because the part of a surface grows in accordance with increasing AgHal dispersity. The low sensitivity level of high-resolved samples even at optimum light intensities is explained by these reasons.[18]

The technology of the silver halide synthesis on the silver stearate surface in water environment permits to increase the sizes of AgBr microcrystals and to decrease the recombination probability of photogenerated carriers. It has increased a general sensitivity level and has given a opportunity practically completely to remove a reciprocity failure within the limits of 10^{-3}-10^{2} s.[17,18] However at the exposure interval 10^{-6} s increasing sensitivity is unsufficient and the influence of a reciprocity failure remains appreciable in these photographic films.[18] At small exposure intervals a role of fast electronic processes of the latent image formation grows, and the methods of the water silver halide synthesis open a opportunity of semi-conductor properties updating for management of these processes. Besides at high intensities a role of stochastic processes of intrinsic defects formation grows in the photographic process, that it is also necessary to take into account at regulation of the reciprocity failure at the short exposure interval.[19] Effective regulators of electronic and ionic processes in silver halides are two-valent cations, in particular Cd^{2+}.[12] At the addition of cadmium ions in the silver bromide lattice influences on the sensitivity of PTM samples are weak at exposure interval 30 s, but at exposure interval 10^{-6} s a increasing sensitivity is observed.[18,20] At optimum concentration of CdBr in the halide structure about 1 mole % the sensitivity is increased in 5-7 times. The reduction of cadmium quantity reduces effect of increasing sensitivity, and the increase results in the fog growth and in the fall of the image maximum optical density.

It should note, that just at such cadmium concentration the photochemical process with participation of volumetric impurity defects begins successfully to compete to processes of stochastic intrinsic defects formation in a silver halide, nucleartion of small silver clasters, which are not effective for the latent image stable centres formation.[19]

The effective increasing PTM sensitivity at short exposure intervals is found out also at surface modification of a silver halide.[18,20] At the introduction of KCNS in compositions appreciable sensitization of PTM is observed at exposure interval 10^{-6} s.[18,20] But at large exposure intervals (30 s) the desensitization action of KCNS is observed. Such character of the sensitivity change can be stipulated by that in this case there are the new defects - effective electron traps in a subsurface. At low light intensities these centres compete to volumetric defects for capture of photogenerated electrons and in a total the number of formed stable latent image centres becomes less. At short exposure intervals the photoelectrons concentration is reasonably great for localization them as on surface, as on internal centres. Thus the created additional electronic states in a subsurface layer of a microcrystal can play a role of intermediate capture centres for more effective growth of the latent image centres at high light intensities.

It is necessary to note, that at surface modification the influence of guanidine (which increases brom-acceptor capacity of gelatinless PTM layers[21]) entered in compositions is observed. At optimum concentration of the entered additives the sensitivity of photothermographic films is increased in 7-8 times at the exposure interval 10^{-6} s.[20]

Thus, methods as volumetric, as surface silver halide modification of thermally processed compositions are effective ways of the reciprocity failure regulationy at high light intensities.

Conclusion

The considered results on sensitization PTM testify about opportunity of the conventional photography approaches to the decision of problems of increasing photochemical processes efficiency in thermally processed compositions on inorganic and organic silver salts. The conclusions of works[3-5] about application only of the photocatalytic model of the latent image formation in these systems are, on our opinion, unduly categorical. On all visibility, processes as on the silver halide - silver carboxylate interface, as in the silver halide, where the primary act of light absorption occurs, play a role at the latent image formation in silver PTM.

Consideration of alternate mechanisms and of the different features and stages of photoreactions in a solid permits essentially to expand an arsenal of methods for regulation and increasing efficiency of integrated photochemical process.

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Biography

Mikhail A. Goryaev was born in 1949. In 1972 he graduated from the Leningrad University and joined the State Optical Institute. He received the Ph.D. degree in Physics from the State Optical Institute in 1977, the D.Sc. degree in Physical Chemistry from the Kemerovo State University in 2000. Since 1982 till 1987 he was Deputy Director and Director of the State Research Institute of Photochemical Industry (Leningrad Branch). Since 1988 till 1994 he was a senior and leading research specialist of the State Optical Institute again. Since 1994 he has been a Head of Laboratory in the Central Design Bureau of Mechanical Engineering. His research interests are in the area of the solid state photochemistry, spectral sensitization, photothermographic systems, electronic imaging, physical education and history of science. He has published about 110 papers and patents in these areas. He is a member of the D. S. Rozhdestvensky Optical Society, the Society for Imaging Science and Technology and New York Academy of Sciences.