Polychromatic Images from Colloidal Silver Particles

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Abstract

The results of the study of the mechanism of formation of colloidal silver particles with purposefully regulated optical properties, from with the polychromatic photographic image can be formed on the black-and white photolayer by condensation, dispergation and combined methods, are represented. The role of impurities in these processes and their influence upon the optical properties of colloidal silver particles, which these images consist of, is discussed.

Introduction

In our previous works [1-4] it was established that under certain conditions of treatment of AgHal-photolayers it is possible to produce on them not only black-and-white image from filamentary silver or color one from dyes of various chemical nature, but also the polychromatic image (PI) with bright colors, consisting of colloidal silver particles with different size.

The report deals with two on principle different approaches allowing to obtain PI. One of them is realized by condensation methods on AgHal-photolayer with small silver content (about 1g/l), made by means of flowing of monodisperse emulsion with microcrystal (MC) size 100-125 nm on the transparent or black base. After the exposition through the negative or positive the photolayer is treated at the red light in the developing-fixing monobath (DFM). Process is completely finished within 2-3 minutes. After that the formed PI is washed by water and dried. The difference of the colloidal silver particles by their size and, correspondingly, by their optical properties, is reached due to unequal rate of their growth on the photolayer parts with various exposure and as a result containing different number of latent image centers.

Another approach is realized by dispergation methods at the expense of “chemical crushing” of filamentary silver in common black-and-white image. It is achieved at the treatment of such image in the solution, which contains simultaneously the oxidizer of the silver and the reducer of its oxidation products. Other methods of silver dispergation, which will be described later, can be used as well. In any case filamentary silver on the parts of black-and-white image with different initial optical density (D) value is transformed into colloidal silver particles with optical properties, depended on their size, shape and density of their packing in the layer.

Main Results and Discussion

The results of our investigations allow to consider, that optical properties of the colloidal silver particles in the PI formed of them also depend on the presence of various impurities on their surface. For example, the common DFM, containing sodium thiosulfate as a fixing agent, are unfit for the practical realization of condensation methods of PI producing. The inclusion of traces of sulfur compounds to the surface of growing silver particles promotes the formation not polychromatic, but monochromatic image. When sodium thiosulfate is replaced by potassium thiocyanate (in concentration up to 50 g/l) the PI of full value with wide color palette is formed, in which the blue, yellow, pink and green hues dominate. Such image consists of colloidal silver particles with spherical shape and size from 50 to 350 nm in dependence on exposure. “Clear” surface of these particles scatters strongly the incident light and PI, built of them, is the most expressive, if it is formed on the black base.

To diminish the reflectivity of colloidal silver particles and to increase the PI contrast at their formation on the transparent base (glass or film) is possible at the expense of adsorption of benzotriazole (BTA) or 1-phenyl-5-mercaptotetrazole (PMT) on the silver surface from the DFM, in which they are introduced in small amounts. In the case of PMT this effect is the most significant. The presence of this additive in DFM influences on the size of Ag-particles (they become smaller) as well as on the particle shape. When PMT is adsorbed on the particle surface, the last one becomes rough, the numerous “ hills and valleys” arise on it (Fig.1). As a result the purple, violet and blue hues appear in the image color palette. When the additive concentration increases up to 0.006 mole/l, the particle shape becomes closed to filamentary one like in common black-and-white image.

Another way to diminish the reflectivity and to increase PI contrast in transiting light is the exposition of the photolayer in the wet state and/or in the presence of halogene acceptor ($NaNO_2$, KCNS, $Na_2S_2O_3$). In this case

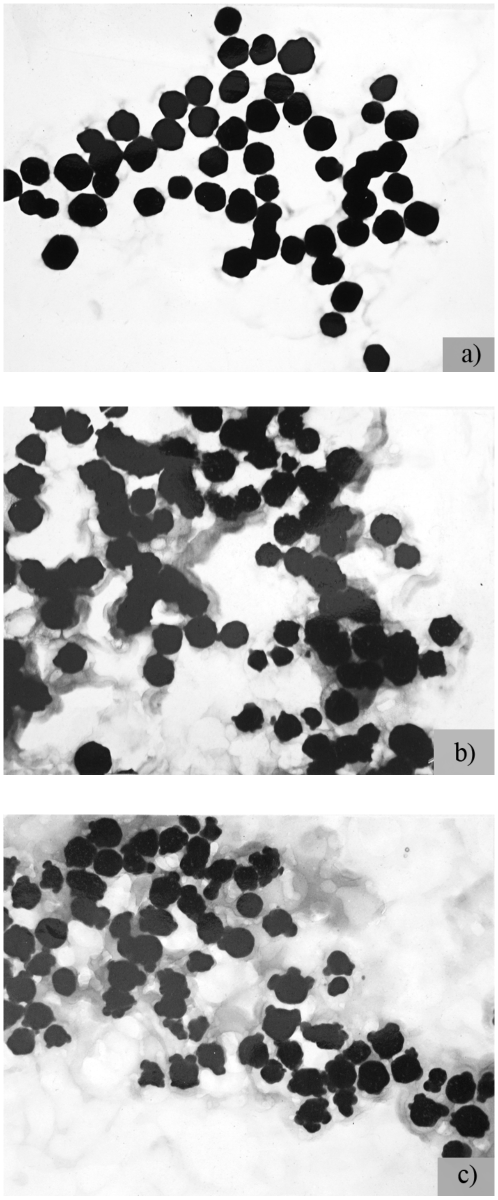

Figure 1. The evolution of the Ag-particle shape in dependence on PMT concentration in the developing-fixing solution: a) without the PMT; b,c) increasing PMT concentration

the smaller Ag-particles with size from 20 to 40 nm and not spherical, but ellipsoidal shape are formed during the exposed photolayer treatment in DFM.

For the practical realization of the PI formation processes by dispergation methods the various techniques can be applied:

1. For the destruction of filamentary silver in common black-and-white image it is possible to use the unusual by its chemical nature solution, containing the strong oxidizer of silver ($K_3[Fe(CN)_6]$) and the reducer of the oxidation products ($NaBH_4$). Interaction between these two substances is kinetically hampered in the presence of alkali. In contact with this solution all parts of black-and-white image are bleached quickly. The nature of formed products is not established. It is only established that their concentration is different on the image parts with various initial D value and during washing in water they are destroyed with the formation of ultra-fine Ag-particles with size from 2 to 20 nm. The color of PI, consisting of such particles, depends on time of the photolayer contact with the solution. At the short treatment time (30-60 s) the image acquires the brownish-yellow color. In dependence of time of further treatment (from 2-to 8 minutes) the other colors appear: the lightest places stay yellow, then red, purple, blue, green and brown fields follow. So far as in this case Ag-particles are very fine and possess very low reflectivity, PI can be produced on the transparent base (film or glass) as well as on the white opaque one (paper). Absorption spectra of differently colored image parts are shown in Fig. 2a. The spectra character changes significantly in dependence on duration of photolayer treatment in the oxidizing-reducing solution and the composition of the last one. So, while the treatment time is increasing, the absorption band is splitting into two peaks, which gradually are going away one from another (Fig. 2b). All this can be the consequence of ellipsoidal particles formation.

Let's note that the represented results were obtained using as the initial object the common black-and-white image, produced by the development in methol-hydroquinone developer and fixed in thiosulphate solution. It's interesting, that if potassium thiocyanate was used as fixing agent, the black-and-white image with decreased content of sulfuric impurities was obtained and to transform such image into polychromatic one was enough difficult. The color difference was observed only in the area of small D value. This effect is much more pronounced if the filamentary silver undergoes preliminary chemical "cleaning" from impurities of sulfur compounds by means of oxidation with bromine, followed by the reduction with methol. Under the oxidizing-reducing treatment of such silver in the solution mentioned above the PI formation was not observed at all.

2. The PI formation by the dispergation methods can be realized not only in one, but also in two separate consequent stages, including the oxidation of filamentary silver and its following reduction. The range of possible oxidizing and reducing agents is very large, and their various combinations allow to change the image color palette in wide limits. Moreover, using the certain oxidizer/reducer combinations, for example, the solution of $K_3[Fe(CN)_6]$ with addition of alkali metal halogenides as oxidizer and alkaline solutions of $NaBH_4$ or $SnCl_2$ as reducers, the monochromatic image with very high copying D (3.5-4) can be produced. It provides an effective method to intensify the black-and-white image with insufficient D on different AgHal layers [5]. The intensification coefficient can be varied from 1-1.5 to 8-10 in dependence of AgHal emulsion MC size in the photolayer.

The PI formation at the two-stage oxidizing-reducing treatment was observed with the use of various

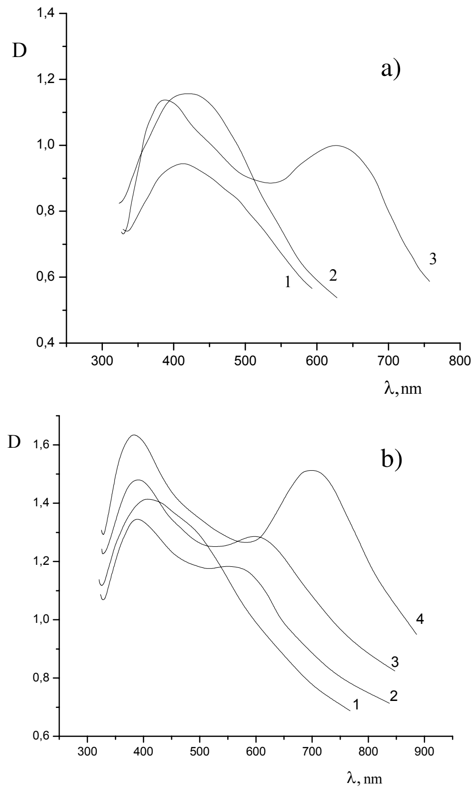

Figure 2. Absorption spectra of silver particles, formed by means of single-solution oxidizing-reducing dispergation: a) various image color (1-pink, 2-orange, 3-blue) ; b) spectra evolution with the treatment time decrease: 1)-1 min; 2)3 min; 3) 4 min; 4) 10 min.

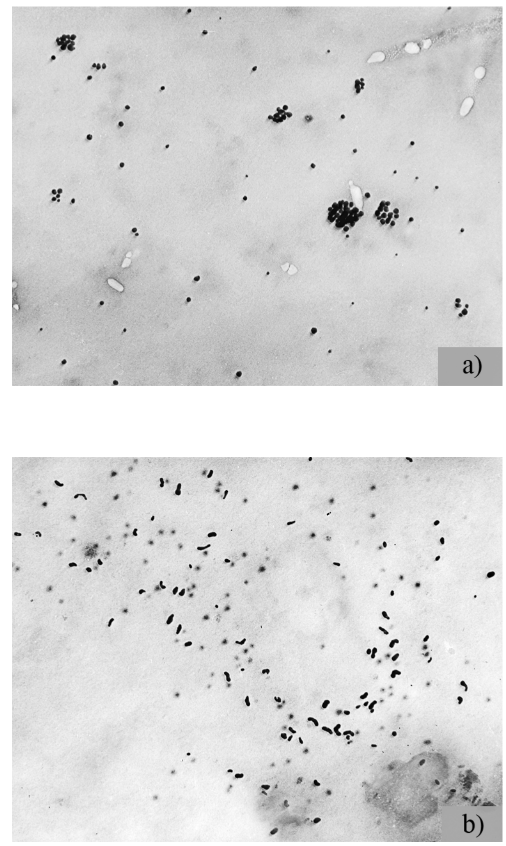

Figure 3. Silver particles, formed by means of image silver oxidation in iodine solution, followed by the reduction with pnenidone-hydroquinone super-additive couple without the PMT (a), in the presence of this additive(b)

oxidizer/reducer combinations. The most interesting results were obtained with the oxidizing solution, containing I_2 and KI, and reducing solution on the base of methol or phenidone and hydroquinone, as well as under silver oxidation in the alkaline solution of $K_3[Fe(CN)_6]$, followed by the reduction in solution, containing Fe^{2+}/Fe^{3+} redox couple. In the last case PI consists not only of colloidal silver particles, but also of ferrous compounds, colored in blue or green.

At the PI producing by means of silver oxidation in the iodine solution and its following reduction with various developing agents, such toning agent as PMT plays an essential part. Its presence in the reducing solution provides the formation of elongated ellipsoidal and rod-like particles instead of spherical ones in the absence of this additive (Fig. 3). This leads to the expansion of the PI color palette due to appearance of purple, violet and blue hues at the same time with yellow, orange and pink, observed at the PMT absence. These changes result in the absorption band splitting with the formation of two peaks instead of one (Fig. 4).

It's worth to be mentioned, that the oxidizing-reducing treatment of black-and-white image not always decreases the size of Ag-particles, forming it. In general case it is more correct to say about the transformation of the

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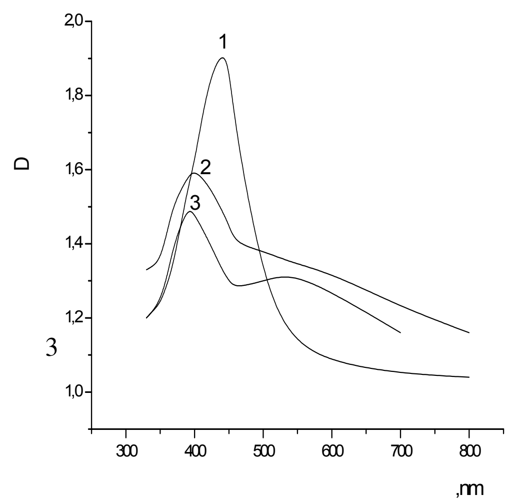

Figure 4. Absorption spectra of silver particles formed by means of image silver oxidation in iodine solution, followed by the reduction with pnenidone-hydroquinone super-additive couple without the PMT (1), in the presence of this additive(2,3)

initial filamentary structure into this one, being the totality of colloidal and sub-colloidal silver particles, which sizes vary in enough wide range. The mechanism of this transformation can be very different in dependence on the oxidizing and reducing agents nature and the treatment conditions [4]. Recently it was established by us, that the use of certain combination of oxidizer and reducer allow to obtain silver particles not only smaller, but also larger, than the initial ones. It was observed, particularly, at the oxidation of black-and-white image in the solution of $K_3[Fe(CN)_6]$ with the addition of KI, followed by the reduction with hydroxylamine. The monochromatic image of blue color, consisting of large (about 200 nm) spheroidal silver particles, was formed. But if such additives as BTA and $NaBH_4$ were introduced into the oxidizing and reducing solutions correspondingly, the violet and bright-yellow areas appeared in the image at the same time with blue ones. The violet field consists of spherical Ag-particles with mean diameter of 20 nm, the most of which are combined in closed round aggregates about 150 nm in diameter. On the yellow field the short silver filaments with diameter of 20 nm and length to 125 nm predominate.

Conclusion

The results of our investigations, very briefly discussed in this paper, allow to say that there exist the very different methods to obtain colorful PI on black-and-white AgHal-photolayers at the expense of purposeful regulation of the size and shape of colloidal silver particles as well as of introduction of impurities traces from the processing solutions into the particle structure. All this opens the new possibilities of AgHal-photomaterials application in the art photography. The obtained results also represent the interest, which is out of the framework of practical photography, because they provide the accumulation of the data about the ways and conditions of obtaining the ultra-fine silver with given particle size, shape and surface structure and characterized with various optical properties.

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Biography

Gennady Alexeevich Branitsky received his Doctor's degree in 1968 in Byelorussian State University in Minsk and took the post of professor of physical chemistry. He delivered lectures in inorganic chemistry, electron microscopy and thin film technology. Gennady A.Branitsky is the Dean of the Chemistry Department and the head of Film Systems and Phototechnologies Laboratory. Together with colleagues, he has studied the regularities of photographic image formation on metal-semiconductor and silver halide layers with diminished silver content. He devised methods for producing polychromatic images, which consists of colloidal silver particles on AgHal-photolayers and also invented new approaches to preparing catalyst-carrier systems. He has published more than 400 scientific articles including 94 patents in the field of photography, solid state and catalytic chemistry. In 1990 he was awarded by the Kosar Memorial Award for an individual significant contribution in an innovative photographic systems.