Optica Applicata, Vol. XXXII, No. 1–2, 2002

Electron microscopic analysis of the structure of the silver halide light-sensitive layers

Agnieszka Drobnik, Piotr Nowak

Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

In the paper, the results of morphology examination of silver halide light sensitive systems performed for 28 multilayer light sensitive materials, classified into three groups according to their properties, are presented. Identification of component layers, estimation of their thickness as well as the conclusions concerning both magnitude and external shapes of the sliver halide crystals contained in these layers were carried out based on computer analysis of the images of the transversal cross-section of the light-sensitive layer obtained in the electron microscope. The total thickness of the light-sensitive emulsion layer was determined using the method of intermediate (direct) measurement and the obtained results were presented in the graphic form as their relation to the nominal light sensitivity. As a result of the work carried out such characteristics of the morphology of contemporary silver halide materials were obtained which are not available in the form of experimental examination published in commercial catalogues, patents or the professional literature.

1. Introduction

The aim of the work was to perform microscopic examinations of the morphology of silver halide light-sensitive layers and to develop a method that would allow us to identify details of their structure based on computer analysis of the microscopic images of the cross-sections of the layers. In the examinations an electron scanning microscope was used enabling observation of the gelatine samples of the light sensitive layers, with magnification ranging from 2000× to 5000×.

In the experimental examinations, a group of 28 silver halide light-sensitive materials were applied which were divided into the following three classes according to their utility values:

1. Traditional negative black-and-white materials in which images are composed of silver grains.
2. Chromogene negative materials applicable to black-and-white photography in which images are created from organic dye capsules.
3. Chromogen negative materials applicable to colour photography in which three partial colour images are created from organic dye capsules.

Computer analysis of microscopic images of the cross-sections of the light -sensitive emulsion layers was aimed at identification of the nature of selected details of morphology of the light-sensitive materials used nowadays. This information, except for few cases [1] – [5], is not available in professional literature being rather diligently hidden by the competing producers of these materials, who, when patenting their own technological solutions, conceal the essential technological details influencing directly the sensitometric and structurometric usable properties of their light-sensitive materials.

The light-sensitive emulsion of negative colour materials is generally composed of several, sometimes tens of component sublayers, the total thickness of which falls within the limits of 10 – 28 μm [1], [6]. Besides the small total thickness of the light -sensitive layers, the average value and dispersion of such magnitudes as the size, crystallographic form and spatial distribution of silver halide crystals contained in a single sublayer component are of vital importance, too. Essential is also the relative distribution of the component layers in the light-sensitive multi-layer emulsion of the light sensitive materials [7], [8].

In the face of lacking any reports concerning both measuring techniques and estimation of the commercial properties of the light-sensitive layers indicated above, an attempt to elaborate our own methodology of estimation employing electron scanning microscopy and computer processing and analysis of the images obtained, was made.

2. Experimental examinations

The images of the cross-sections of the light-sensitive emulsion were observed in electron scanning microscope equipped with a detector of back-scattered electrons. The images were recorded simultaneously with the help of a digital CCD camera as well as using a traditional photographic method. The images recorded in the form of files were analysed taking advantage of the computer program algorithm elaborated by the authors. As a result of calculations, average changes in optical density of the cross-sections of the light sensitive layers determined as functions of the layer thicknesses. The value of optical density was normalized from the minimal to maximal values expressing the blackening in terms of the conventional unit within the range of 0 – 255.

For example, in Figs. **1a**, **2a**, **3a**, changes in the average value of the optical density in images of microscopic samples, chosen from three classes of the materials examined, are presented. Each time the images were recorded in three different planes of the same sample. Simultaneous presentation of the three curves and their averaging allowed us to better identify the details and to characterize more accurately the component layer morphology of the light-sensitive system under examination. The analysis of the plots enables identification of not only the light -sensitive layers but also the auxiliary layers such as protection layer, antihalo layer and filtering and intermediate layers.

The materials characterized below belong to the three distinguished classes of light sensitive materials the morphological details of which are only approximately connected with the elements of structure of the light sensitive emulsion of the other materials belonging to the same class. Traditional negative black-and-white materials in which images are created from silver grains are, in general, of single- or two-layer type. The single-layer materials contain generally polydispersive crystals of silver halide of spherical spatial form, while the two-layer materials differ in both spatial form and the size of silver halide crystals contained in particular sublayers. In this class of materials no intermediate layers between the component layers were observed, except for the protection layer.

The class of chromogen light sensitive materials in which black-and-white dye images are formed is characterized by the three-layer structure. Single layers of the light sensitive emulsion are not separated by the intermediate layers and differ (from each other) in the spatial form and the magnitude of the silver halide crystals contained in those layers. The third class consists of chromogen light-sensitive materials in which three partial dye images created from organic dye capsules are

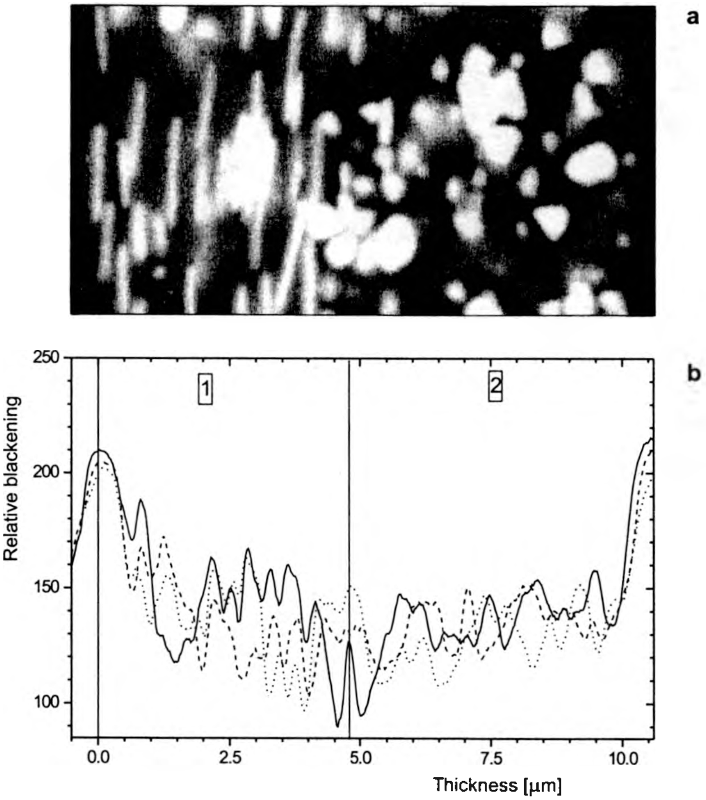

Fig. 1. Microscopic image of a cross-section of the light sensitive layer of Kodak T-max 400 negative. Magnification 5000× (**a**). Averaged profile of relative blackening in the image of the cross-section of the light sensitive layer of Kodak T-max 400. 1 — fluctuation area corresponding to surface component sublayer containing tabular crystals of AgHal, 2 — sublayer containing spherical crystals (**b**).

composed of three main layers: blue-, green- and red-sensitive ones which are separated by intermediate layers. These layers are composed of one, two or three sublayers differing in their spatial form, size and magnitude dispersion of the silver halide crystals contained in these sublayers.

Figure **1a** shows the microscopic image of the cross-section of the light -sensitive layer of a traditional black-and-white material, while in Fig. **1b** three average profiles of the optical density of this image are presented. Some distinct differences in fluctuations of the relations illustrated represent the differences in both the magnitude and the crystallographic form of the AgHal crystals contained in two well defined sublayers of this material. The differences and the division into sublayers are relatively easy to identify by analysing the image of the layer cross-section illustrated in Fig. **1a**, while simultaneous comparison of the

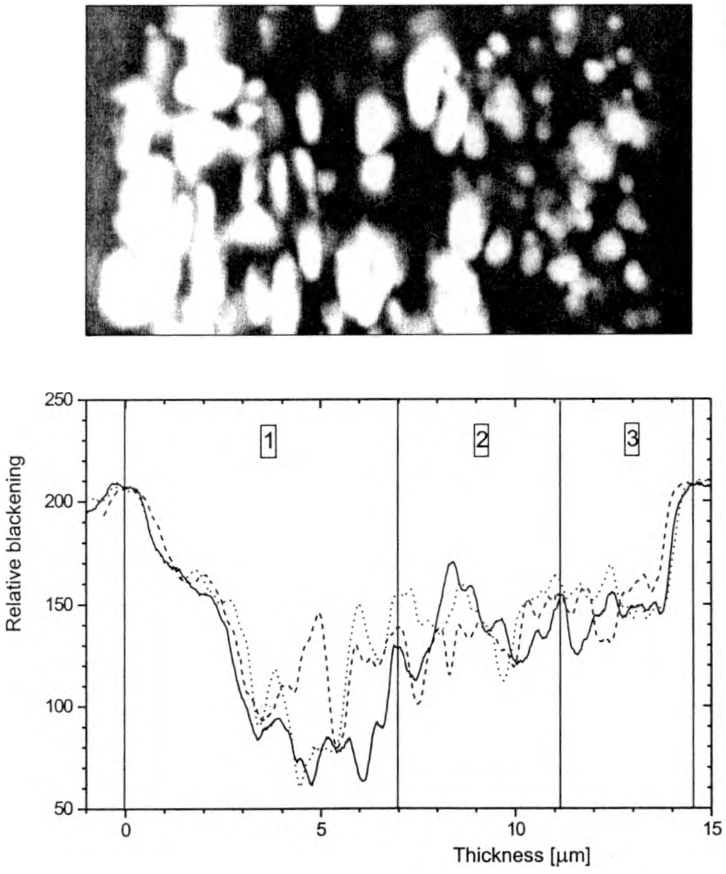

Fig. 2. Microscopic image of the cross-section of the light-sensitive layer of the Konica Monochrome VX 400 negative. Magnification 5000× (**a**). Averaged image blackening profile for light-sensitive layer cross-section of Konica Monochrome VX400. 1, 2, 3 — fluctuation areas corresponding to the layers of the light-sensitive emulsion differing from each other by the magnitude of the spherical crystals of AgHal (**b**).

results of this analysis with the shape of average optical density profile is provided in Fig. 1**b**. The surface sublayer contains silver halide tabular crystals, which is manifested by distinct fluctuations of the optical density profile (area 1), whereas the second sublayer contains spherical crystals, which corresponds to shallow fluctuations characterized by a smooth course (area 2).

Figure 2**a** is a microscopic photo of the multilayer cross-section of the black-and-white light-sensitive material which is developed in colour photographic process, while Fig. 2**b** shows three averaged profiles of this optical density. The light-sensitive emulsion of this material is composed of three basic layers being, in turn, composed of sublayers differing in magnitude and external form of the silver halide crystals.

Also, Figure 3**a** shows a microscopic photo of the cross-section of the multilayer light-sensitive material for colour photography, while Fig. 3**b** presents

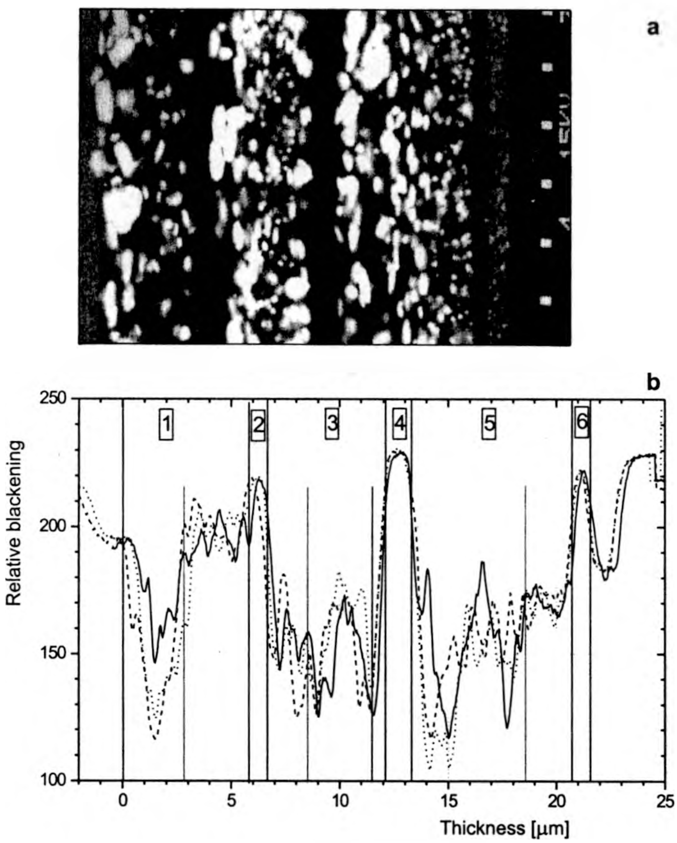

Fig. 3. Microscopic image of the cross-section of the light sensitive layer of the Fujicolour Superia 200 colour negative. Magnification 2000× (**a**). Averaged image blackening profile for light-sensitive layer cross-section of the Fujicolour Superia 200. 1, 3, 5 – fluctuation areas corresponding to main component layers: blue-, green- and red-sensitive ones. Fields 2 and 4 correspond to intermediate layers while field 6 – to the antihalo layer (**b**).

the corresponding profiles of optical density of this image. Similarly as in the previous cases the light-sensitive layer of this negative is composed of three main component layers, while each of those layers contains two or three sublayers. Particular layers differ, among each other, in the spatial form of the contained silver halide crystals, while the upper layers (looking from the protection layer side) contain tabular crystals, in general. In this material, the presence of an additional so-called fourth main layer localized at a distance of 11.6 μm, has been detected.

The computer analysis of the images of the light-sensitive emulsion of the materials under test renders it possible to determine not only partial thicknesses of the component layers but also the total thickness of the layers. Simultaneously, the thickness of the emulsion layer for the same materials was measured by the direct method using the suitable micrometer gauge. The results obtained are given in the Table.

Analysing the results presented in this Table it can be stated that the thickness of the light sensitive emulsion determined by the direct method is greater than the thickness determined from the analysis of the microscopic images. The reason for that is the evaporation of water from the gelatin layer of the light-sensitive emulsion during the preparation of a sample in vacuum and microscopic examinations that follow next. Also, an account should be taken of destructive action of the electron beam which causes a decomposition of both the binding coloid (gelatin) and the oil phase of microcapsules of the dye components as well as of the components themselves. As a result of those effects only silver halide crystals are observed in the microscopic images the relative positions of which suffer from some deformations. For some types of the materials examined small changes in thickness have been observed which can be caused by polymer binding systems showing greater

Table. Exposure index and thickness of light-sensitive layer of the silver halide materials being tested.

Trade name of light-sensitive materials	Thickness of emulsion layer [μm]	Exposure index
Agfa HDC 100	18	100/21°
Agfa HDC 200	20	200/24°
Agfa HDC 420	19	400/27°
Agfa Vista 200	18	200/24°
Agfa Vista 400	19	400/27°
Agfa Vista 800	22	800/30°
Fujicolor Superia 100	20	100/21°
Fujicolor Superia 200	22	200/24°
Fujicolor Superia 400	23	400/27°
Kodak Gold 100	21	100/21°
Kodak Gold 200	21	200/24°
Kodak Gold Ultra 400	24	400/27°
Konica VX 100	16	100/21°
Konica VX 200	17	200/24°
Konica VX 400	21	400/27°

resistivity to the conditions of microscopic examination. The deviations in the thickness measurements in light-sensitive materials may also follow from the experimental errors and the limited accuracy of both the measuring methods.

An intersting observation is the approximately proportional change in layer thickness of the emulsion of the light sensitive photographic materials which occurs jointly with the change of their nominal irradiation sensitivity. This relation was determined for the group of light-sensitive materials examined taking advantage of the results of the direct measurement of the layer thickness and the indicators of the nominal light sensitivity. The relation obtained is illustrated in Fig. 4.

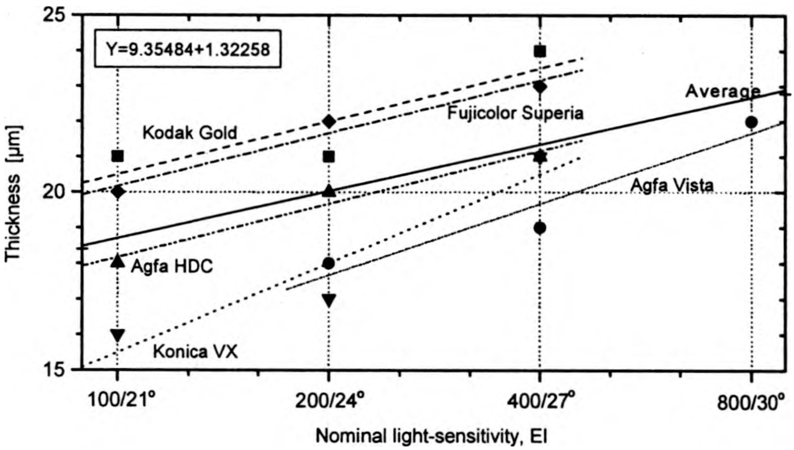

Fig. 4. Relation between the total thickness of the light sensitive emulsion layer and the nominal exposure index determined for a group of light-sensitive materials under examination.

The rate of thickness growth of the light-sensitive layers together with the growth of their irradiation sensitivity can be intepreted as an indicator of the progress made as far as technology of the silver halide light sensitive materials is concerned. From the earlier results reported in [1] and obtained on the basis of examinations of light sensitive materials produced according to the technology used a few years ago it can be stated that the indicator of progress defined in this way was about 1.95 μm/EI, whereas the value of this indicator determined on the basis of the measurements carried out was about 1.33 μm/EI, which speaks for some progress recently made in in the technology of multilayer light-sensitive materials, based on silver halide crystals.

3. Conclusions

In this work, microscopic examinations of 28 silver halide light-sensitive materials both of black-and-white and colour type were carried out and next a computer analysis of the microscopic images was made. As a result of the analysis the due plots of average values of the optical density profiles in the image determined by longitudinal scanning of the microscopic images of the cross-sections of the light-sensitive emulsion layers were provided. The characteristics of the selected properties of the silver halide light sensitive materials were obtained taking account of:

a) differentiation of the basic component layers of the particular class of light sensitive materials,

b) identification of both the sublayers of the main component layers and the presence of additional intermediate or light sensitive layers,

c) determination of the total thickness of the light sensitive layers and the thicknesses of the component layers,

d) interpretation of the images as far as the magnitude, magnitude dispersion and spatial form of the silver halide crystals contained in particular component layers of the light sensitive emulsions are concerned,

e) analysis of spatial packing of the crystals in the component layers and their mutual positions in a layer depending on their crystallographic form,

f) analysis of the thickness of the light-sensitive layers, number of component layers and spatial packing and geometriec form of the silver halide crystals as dependent on the type and applicability of the light-sensitive materials,

g) estimation of the progress in technology of silver halide light-sensitive materials.

The analysis of the component layers of the black-and-white light-sensitive materials allows us to state that the low-sensitive and medium-sensitive materials are composed of two layers while the high-sensitive materials are built of three -component layers. Also the three-layer structure is characteristic for black-and-white materials to be subjected to chromogen development. Further analysis of the microscopic images of the material cross-sections shows that the particular component layers of the two-layer and three-layer materials are built of silver halide crystals of different magnitude and different crystallographic form. Silver halide tabular crystals are contained, generally, in the upper sublayer while the lower sublayers contain spherical crystals. The smaller AgHal crystals are located in the sublayer positioned closest to the film base.

Performing a similar analysis in the case of a group of colour light-sensitive materials renders it possible to formulate the conclusions of similar character to that discussed above. The three basic layers of these materials (blue-, green- and red-sensitive ones) are composed of two- or three-component layers. The surface sublayers contain silver halide tabular crystals whereas the remaining sublayers contain, in general, spherical crystals. For some of the materials examined, the presence of the silver halide tabular crystals in all the component layers has been detected. This fact indicates that the producers of silver halide light-sensitive materials are consequently trying to lower the total thickness of the layers of light -sensitive emulsion resulting in lowering the total content of silver. This tendency is dictated by essentially better resolving power and contour acuity in photographic images obtained for thin-layer materials in which silver halide tabular crystals of high spatial concentration are applied.

The results obtained render it possible to illustrate the present state of technology of multi-layer light-sensitive materials containing silver halide crystals as light detectors. These examinations can provide a starting point for further investigations of the granulometric properties of multi-layer light-sensitive materials, especially in the correlation range of these properties with the sensitometric properties of light sensitive layers and structurometric properties of images obtained with such layers.

Acknowledgments — This work was supported by the grant No. 341992 of the Faculty of Chemistry, Wrocław University of Technology, Poland.

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Received November 19, 2001