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Model examination of application of fluorescent substance to silver halide light-sensitive layers

LESZEK LATACZ, PIOTR NOWAK

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

The results of computer simulation of the outcomes of scattering, fluorescence and absorption of actinic light inside the hypothetical light-sensitive layer containing the silver halide crystals and fluorescent substance are presented. It has been assumed that the modelled layer is exposed exclusively to the radiation of the wavelength belonging to the intrinsic sensitivity range of silver halide. The quantitative dependence of the effective light absorption by the silver halide on the fluorescent substance concentration, the layer thickness, quantum efficiency of fluorescence and the ratio of the absorption probability of a photon of wavelength belonging to the sensitized sensitivity range and the absorption probability of a photon of the wavelength from the intrinsic sensitivity range has been examined. Also, the dependence of the modulation transfer function curve on the above parameters has been studied. The results obtained indicate that under some circumstances an addition of fluorescent substance can enhance the photosensitivity of the layer and improve simultaneously the sharpness of the recorded image.

1. Introduction

The photosensitivity of the layers used for recording the optical image is connected with the light absorption within these layers. Therefore, the technology of the layer production is being more and more improved in order to increase the effective absorption leading to creation of latent image centres in the silver halide crystals (AgHal). Apart from the absorption the scattering of light occurs which follows from the heterogenic structure of the layer. The light scattering has a disadvantageous influence on the imaging accuracy of fine details and edges.

In the case of optical image recording in the range of violet and near ultraviolet the photographic emulsions are applied which are unsensitized spectrally. Their spectral sensitivity range follows from the intrinsic sensitivity of AgHal and reaches the wavelength $\lambda = 470$ nm at the most. In order to record the radiation of longer wavelength the materials containing the sensitizing dye adsorbed on the surface of the AgHal crystals are used. The dye creates some additional range of spectral sensitivity called the range of dye sensitized sensitivity.

The aim of this work is to analyze a hypothetical situation where the recording of short-wavelength radiation in the light-sensitive layer containing the sensitizing dye and the fluorescent substance is needed. It has been assumed that the fluorescent substance absorbs only short-wavelength radiation while emitting the light of

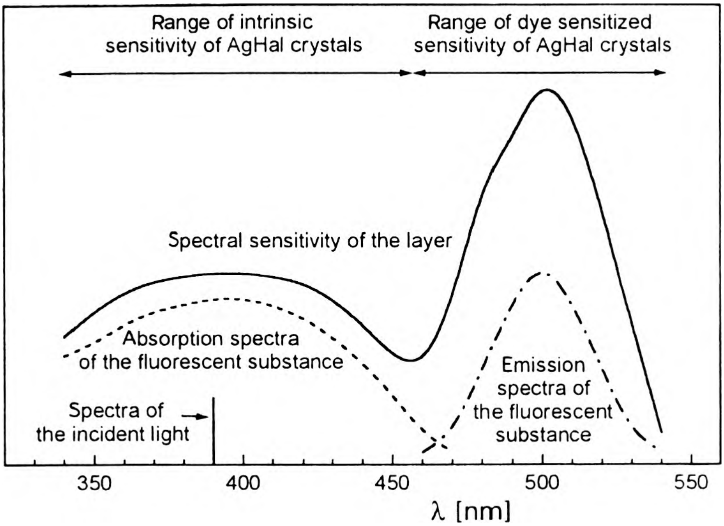

Fig. 1. Example of spectral sensitivity of the light-sensitive layer containing the effective sensitizing dye and also the absorption and emission spectra for the fluorescent substance as well as the spectrum of the recorded short-wave radiation.

possibly narrow band lying within the range of sensitized sensitivity. In Figure 1, an example of spectral sensitivity of a light-sensitive layer, containing an effective sensitizing dye as well as the absorption and emission spectra of the fluorescent substance, are shown. Also, an example of the spectrum of recorded short-wavelength radiation (monochromatic light $\lambda = 390$ nm) is given.

When the quantum efficiency of fluorescence φ amounts to 1 the number of long-wavelength radiation quanta emitted by the fluorescent substance is equal to the number of quanta of short-wavelength radiation absorbed by this substance. In such a case some enhancement of the effective light absorption can be achieved when the probability p_s of the absorption of the photon of wavelength belonging to the sensitized sensitivity range is higher than the probability p_i of radiation absorption of a photon of wavelength from the intrinsic sensitivity range. The values of p_s and p_i express the probabilities of photon absorption during a single collision with the silver halogen crystal. They are indirectly connected with the values of sensitity indicators achieved by a layer without fluorescent substance in the range of sensitized sensitivity and the range of intrinsic sensitivity of the silver halogen, respectively. The ratio p_s/p_i will be marked as P. The parameter P is of the higher value the greater the ratio of sensitized photosensitivity to the intrinsic photosensitivity of silver halide.

In the case when $\varphi < 1$, a part of photons of short-wavelength radiation suffers from ineffective absorption, *i.e.*, that failing to create the latent image centres in the AgHal crystals. Hence, the condition for increasing the effective absorption can be in an approximate way written down as an inequality

$$P\varphi > 1. \tag{1}$$

Preceding absorption the radiation can be subject to multiscattering inside the layer causing some loss of sharpness in the recorded image. Therefore, the aim of examinations carried out is to estimate the gains and losses following from the introduction of the fluorescent substance to the light-sensitive layer as far as both the effective absorption and the sharpness of the recorded image are concerned. The imaging quality can be characterized by the modulation transfer function (MTF) or by static indicators of the image sharpness. On the other hand, the values of sensitivity is connected with the value of light absorption by the silver halide crystals contained in the layer. The MTF means dependence of the magnitude defined by the ratio of the modulation of recorded optical signal M' to the modulation of the original signal M on the spatial frequencies

$$\mathrm{MTF}(f) = \frac{M'(f)}{M(f)}, \tag{2}$$

while the modulation of the sinusoidal optical signal is defined by the equation

$$M = \frac{I_{\max}-I_{\min}}{I_{\max}+I_{\min}} \tag{3}$$

where $I_{\max}$ and $I_{\min}$ denote the maximal and minimal light intensities in the signal, respectively [1]. The fine details and the edges correspond to high spatial frequencies. Hence, from the course of the MTF of a light-sensitive material it is possible to estimate its ability to image sharply the details of the picture.

2. Characteristic of the model

The models based on the Monte Carlo method used to examine the light scattering phenomena inside the photographic layers have been known for many years and their detailed descriptions as well as the examples of results obtained are given in papers [2]–[10]. A basic version of the model, which was used in the present simulation examinations is described in [8]. Below, the main assumptions accepted in our specially elaborated computer program are listed. Also, the essence of modification of the earlier simulation algorithms is explained which allows us to take account of the fluorescent substance. The results of the works connected with the model were partly presented in paper [11]. It is worth emphasizing that till now no results of modelling examination of application of fluorescent substances in the light -sensitive layers have been published in the world literature. Here are the main assumptions of the stochastic model worked out:

– All the photons penetrate the layer at one point in the direction perpendicular to the layer surface.

– Indicatrix of the radiation scattering by a single silver halogen crystal is given by the Rayleigh formula

$$I(\gamma) = \frac{(1+\cos^2\gamma)}{2} \tag{4}$$

where: I – intensity of the scattered light, γ – observation angle determined with respect to the direction of propagation of the illuminating beam.

– Photon of wavelength from the intrinsic sensitivity range of the silver halide can be subjected to absorption by the fluorescent substance only once while it is emitted in a random direction from the point in which it has been absorbed. Its new wavelength lies in the sensitized sensitivity range.

– Quantum efficiency of fluorescence $\varphi = 1$.

– Photon can suffer from multireflection (due to the multiscattering of light) while single act of absorption by a silver halide crystal ends the process of program following its path.

– Probability p_i of photon absorption of wavelength of the intrinsic sensitivity range for silver halide is 0.005.

– Internal reflections of photons from the upper layer surface are consistent with the general laws of reflection and refraction for light while the refraction index for gelatine is 1.52 and the critical angle is 41°8′.

– Lack of reflection from the lower surface of the light-sensitive layer (the existence of a perfect antihalation layer is assumed).

– Probability distribution for a photon passing a definite free path between its consecutive collisions with the silver halide crystals is defined by the exponential function, the parameter of which is the average free path of the photon l_H. In the model a constant value of $l_H = 1.0$ μm has been assumed.

– Probability distribution for a photon passing a definite path to the place of its absorption by the fluorescent substance is given by an exponential function the parameter of which is the average path of a photon l_F.

– The following magnitudes are considered to be variable in a number of simulations carried out:

i) relative concentration of the fluorescent substance in the layer C_F expressed as the ratio of the average "halide" free path of a photon to the average "fluorescent" path of the photon

$$C_F = \frac{l_H}{l_F}, \tag{5}$$

ii) parameter P,

iii) layer thickness h.

The basic version of the computer simulation algorithm [2]–[9] does not permit taking account of the presence of additional (besides the silver halide) substances absorbing the actinic light. Owing to the suitable modification of the algorithm in the earlier work [10] model examinations of the MTF and the characteristic curve for light-sensitive layers containing the dye were carried out.

When there is an additional substance absorbing actinic radiation the model must take account of a specific competition in the photon absorption existing between the silver halogen and this substance. Simplified block schemes of the algorithms of the basic stochastic model and the model taking account of the presence of the fluorescent substance in the light-sensitive layer are presented in

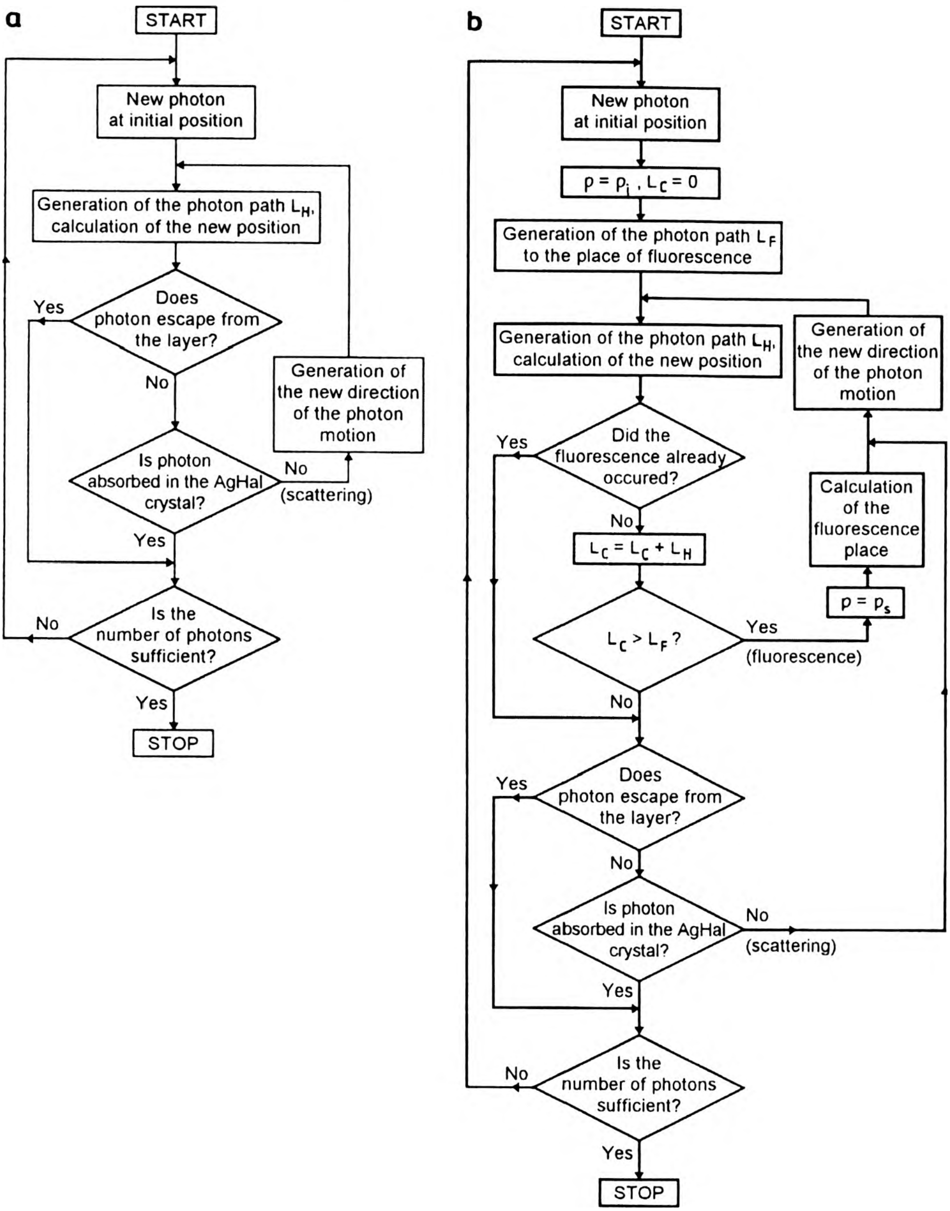

Fig. 2. Simplified block schemes of the computer simulation algorithms: a — basic model, b — model taking account of the presence of fluorescent substance in the light-sensitive layer.

Fig. 2. The modification of the simulation algorithm consists in generating for each photon a random path L_F after passing of which the photon is absorbed by the additional substance. However, the photon can suffer from multiple collisions with the AgHal crystals, and during each collision there exists a probability p_i that the photon will be absorbed by the crystal. Between the collisions the photon travels

along the random sections of the free path L_H. When the cumulative path L_C, travelled by a given photon, exceeds the length of the path L_F an absorption by the additional substance occurs. Obviously, after each collision it is necessary to check whether the photon did not escape through the upper or lower surface of the layer. The average free path l_H of the photon is inversely proportional to the extinction of the AgHal crystals suspension while the average free path l_F is inversely proportional to the extinction of the additional substance. The extinction, in turn, is proportional to the molar concentration and the molar extinction for the given wavelength of the radiation. In order not to complicate too much the model and consequently not to make the interpretation of the results too difficult by introducing so many independent variables the concentration of the fluorescent substance was expressed in a relative form by Eq. (5). When the absolute concentration of the fluorescent substance tends to zero then l_F tends to infinity and thus the relative concentration tends also to zero. Representing the concentration in terms of the quotient of magnitudes l_H and l_F is very convenient, since they are directly used during generation of the random sections of the photon free path.

It is worth to mention that there are no obstacles to take account of the nonideal fluorescence efficiency in the simulation procedure. It appeared, however, sufficent to carry out the simulation for $\varphi = 1$ in order to determine the MTF course and the value of absorption for an arbitrary value of φ. It can be achieved by calculating the weighted average of the results obtained for a given value of the parameter P and the result obtained in the case of $P = 0$. In spite of the different physical sense the case $P = 0$ is exactly equivalent to the case $\varphi = 0$ so far as the effective absorption and scattering are concerned.

3. Results

After having elaborated suitable computer program a series of simulation experiments have been carried out for different optical parameters of the hypothetical light-sensitive layer. In each of those simulation experiments the number of photons penetrating into the layer was 10^5 and the accuracy of the results obtained was sufficient for making smooth plots of the dependences examined.

In Figure 3, the curves of MTF are shown being calculated for the layers of thicknesses $h = 5$ and 15 μm without fluorescent substance and for the relative concentration of the fluorescent substance $C_F = 1.0$ and the parameter $P = 10$. In the legend to the figure, the calculated data concerning the effective absorption A are given. The course of MTF has been estimated in the range from $f = 0$ to $f = 500$ cycles per millimetre. For this purpose, the line spread function obtained as one of the results of operation of the simulation program has been subjected to a discrete Fourier transform according to Horner algorithm. In Figure 4, the dependence of effective absorption of light A by the silver halide on the relative concentration of the fluorescent substance C_F is shown for constant thickness $h = 10$ of the layer and for different values of the parameter P. In Figure 5, the cut-off frequency $f_{0.3}$ as a function of the relative concentration C_F of the fluorescent

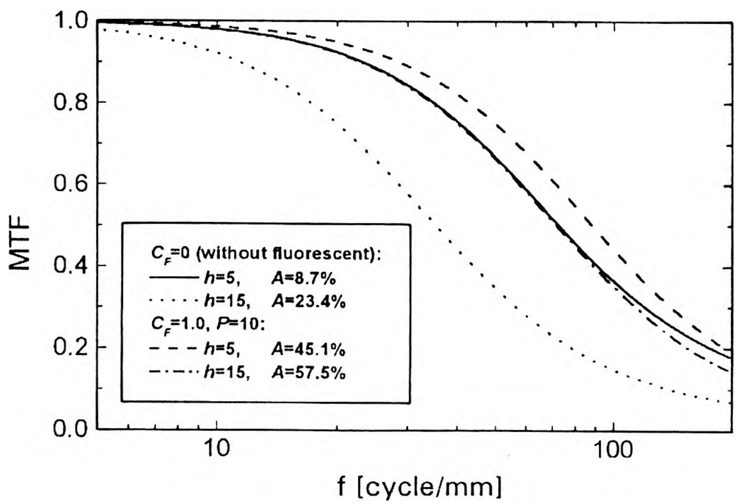

Fig. 3. The MTF curves for the layers of 5 and 15 μm in thickness, without fluorescent substance and for relative concentration of the fluorescent substance $C_F = 1.0$ and the parameter $P = 10$. In the legend the calculated values of the effective light absorption A are given.

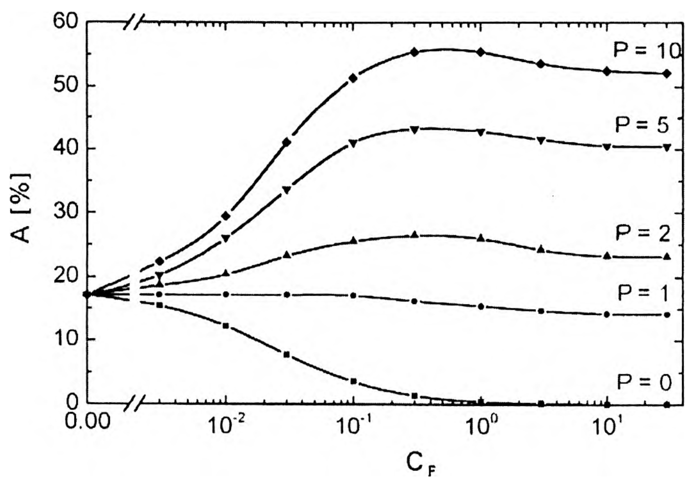

Fig. 4. Effective light absorption in silver halide as a function of the relative concentration C_F of the fluorescent substance for the layer thickness $h = 10$ μm and different values of parameter P.

substance is shown also for a constant thickness of the layer $h = 10$ μm and for various values of the parameter P. The cut-off frequency $f_{0.3}$ is understood as the spatial frequency for which the modulation transfer function reaches the value 0.3. This value is believed to be the approximate lower limit of the visual ability of perception of the recorded image details. The higher the value $f_{0.3}$, the better the quality of the detail imaging. The curve for $P = 0$ is truncated since for higher concentration of the fluorescent substance the MTF takes the values higher than 0.3 in the considered range of the spatial frequencies. In some cases, it is impossible

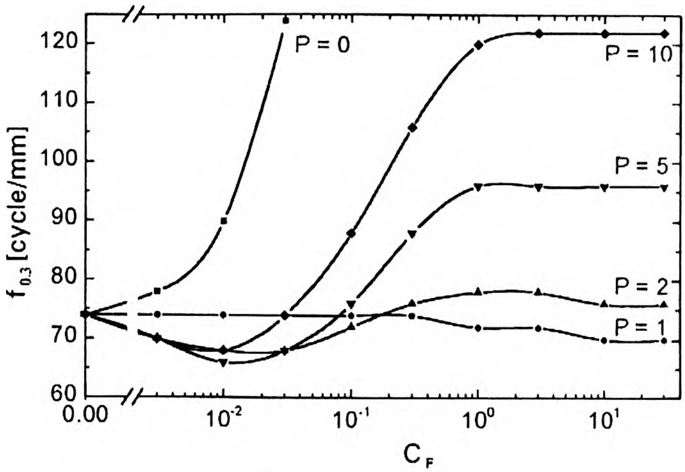

Fig. 5. Cut-off frequency $f_{0.3}$ as a function of the relative concentration C_F of the fluorescent substance for a constant thickness $h = 10$ μm and various values of the parameter P.

to determine the value $f_{0.3}$ since the MTF curve tends asymptotically to the value higher than 0.3.

The results obtained for the case $P = 0$ can be, as mentioned above, used for determining the results for quantum fluorescence efficiency $\varphi < 1$. The effective absorption can be calculated as a weighted average value obtained for a given parameter P and the value obtained for $P = 0$. The weighting coefficient for the results for a given P amounts to φ while for the results for $P = 0$ it is equal to $1-\varphi$. In an analogous way the MTF curve can be calculated for $\varphi < 1$ knowing the curves for the cases $\varphi = 1$ and $P = 0$. From the curve calculated in such a way

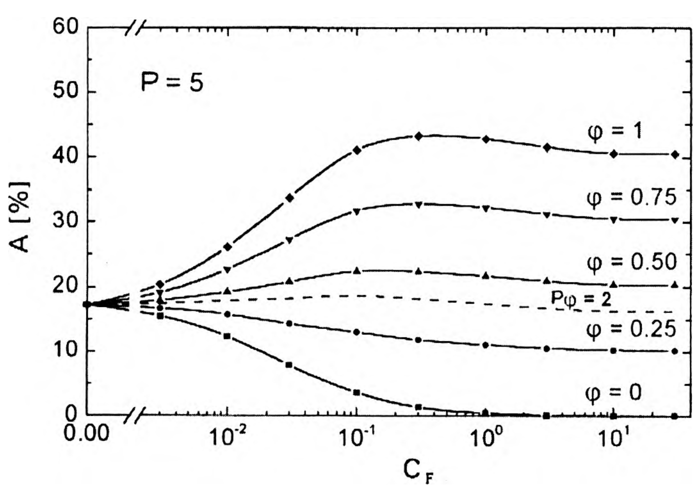

Fig. 6. Effective light absorption in the silver halogens as a function of the relative concentration of the fluorescent substance C_F for the layer thickness $h = 10$ μm, and parameter $P = 5$ for various values of quantum fluorescence efficiency φ.

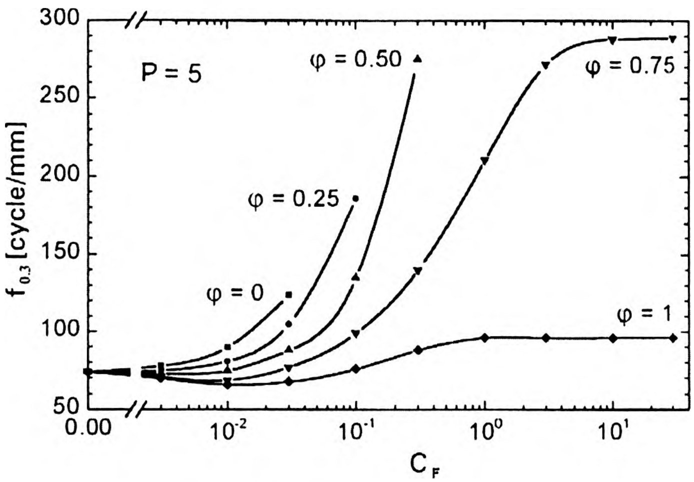

Fig. 7. Cut-off frequency $f_{0.3}$ as a function of the relative concentration C_F of the fluorescent substance for the layer thickness $h = 10$ μm and parameter $P = 5$ for various values of quantum fluorescence efficiency.

the cut-off frequency can be read out. The determination of the $f_{0.3}$ value as a weighted average value obtained for a given value of parameter P and the value obtained for $P = 0$ would lead to erroneous results. Some examples of the dependences determined in this way for a layer of thickness $h = 10$ μm at $P = 5$ are illustrated in Figs. 6 and 7. The curves for $\varphi = 0$, $\varphi = 0.25$ and $\varphi = 0.50$ in Fig. 7 are truncated since for higher concentrations of the fluorescent substances the MTF takes values higher than 0.3 in the whole range from $f = 0$ to $f = 500$ cycles per millimetre.

4. Discussion and conclusions

The results of the computer simulation showed that the consequences of adding fluorescent substance to the light-sensitive layer depend qualitatively and quantitatively on the value of parameter P. It has been found that when $P > 1$, the addition of the fluorescent substance can significantly increase the effective absorption. For low concentration of the fluorescent substance some loss of the quality of imaging occurs in the recorded photographic picture. On the other hand, high concentration of the fluorescent substance ($C_F > 0.1$) results in an increased value of the cut-off frequency. The decrease of the value $f_{0.3}$ at low concentrations of the fluorescent substance is caused by additional spread of the image due to isotropic fluorescence. For higher concentrations the photons are absorbed more and more by the fluorescent substance without being earlier scattered at the AgHal crystals and after fluorescence they are effectively absorbed in the vicinity of the penetration point on the layer. The improvement of the MTF course is the higher, the higher the value of parameter P. The effective absorption reaches its maximum value for the relative concentration of the fluorescent substance equal to 0.5, while the cut-off frequency reaches its maximum or stabilises for the concentration amounting to about 2. The drop of effective absorption for high concentrations of the fluorescent substance can be explained by the fact that the fluorescent substance absorbs the photons already after passing very small distance inside the layer. Thus, the fluorescence occurs very close to the surface and, therefore, the probability of the photon leaving the layer immediately after the fluorescence is high.

A special case, when $P = 1$, is quantitatively equivalent to application of the isotropically scattering but not light-absorbing substance in the place of the fluorescent substance. In this case both the effective absorption as well as the limiting frequency are very weakly dependent on the concentration of the scattering substance, though for high concentrations both the magnitudes suffer from some slight decrease. The decrease of the effective absorption is probably caused by increased probability of escape of the photon from the layer inside. The higher the fluorescent substrate concentration the more probable is that the photon will be absorbed by this substance without previous collisions with the AgHal crystals or after a small number of collisions. The possibility of the photon leaving the layer immediately after fluorescence without earlier collisions with the AgHal crystals diminishes the probability of the effective photon absorption.

Additionally, it has been shown that the relatively thin layers manifest significantly higher increase in the effective light absorption after adding the fluorescent substance than the thick ones. On the other hand, the thick layers show significantly stronger improvement of the imaging quality of details than the thin layers. However, independent of the layer thickness there exists a possibility of simultaneous improvement in both its sharpness and sensitivity by adding the fluorescent substance of suitable concentration and for suitable value of parameter P.

In the extreme case $P = 0$, *i.e.*, when the range of spectral sensitivity of the layer is limited only to intrinsic sensitivity range of the sliver halide the effective absorption diminishes significantly with the increase of fluorescent substance concentration. On the other hand, the course of MTF is subjected to a drastic increase which causes, in turn, a rapid increase of the limiting frequency. This case is equivalent to the zero fluorescent efficiency which occurs when applying a dye instead of fluorescent substance. A detailed analysis of this problem has been presented in paper [10].

The results obtained for the layer of thickness $h = 10$ μm at $P = 0$ were used to determine the results for quantum fluorescence efficiency $\varphi < 1$ at $P = 5$. From the course of the obtained curve (Figs. 6 and 7) it can be concluded that the addition of the fluorescent substance to the light-sensitive layer is always advantageous. For low values of φ the main advantage is that a significant improvement of the image sharpness occurs following from the restriction of the actinic light scattering occurring inside layer, through a possibility of lowering the effective light absorption should be taken into account. On the other hand, the advantage of high values of both φ and P consists in increase of the effective absorption with simultaneous improvement of the MTF course. In Figure 6, the broken line is used to mark the dependence of the effective absorption A on the relative concentration C_F for $\varphi = 0.4$, *i.e.*, for the product value $P\varphi = 2$. As can be seen, in this case the effective absorption in the examined range of concentration C_F is approximately constant. Hence the conclusion that the necessary condition for increasing the effective absorption (Eq. (1)) is not a sufficient condition. Generally, the necessary and sufficient conditions for increaseing the effective absorption can be formulated as an inequality

$$P\varphi > a \tag{6}$$

where the value of the coefficient a is a function of all the parameters characterizing the light sensitive layer. An accurate analysis of this function would require performing many additional series of simulation experiments.

Since there exists a possibility of simultaneous improvement of both the sharpness of imaging and sensitivity of the layer by adding the fluorescent substance, the presented model could find a practical application in designing the special materials for recording the optical images in the ranges of blue light and ultraviolet radiation. In the case of real fluorescent substances, however, the following variable parameters should be taken into account: quantum fluorescence efficiency less than unity, recorded radiation spectrum, spectral sensitivity distribution for the light-sensitive emulsion and the absorption and emission spectra for the fluorescent substances.

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