

# Linewidth Behavior of the ESR Signal of Dye Radicals on Spectrally Sensitized AgX Microcrystals

*T. Ceulemans, D. Schoemaker*

*University of Antwerp (U.I.A.), Department of Physics, B-2610 Antwerpen, Belgium*

*D. Vandenbroucke, R. De Keyzer*

*Agfa-Gevaert N.V., R&D Laboratories, B-2640 Mortsel, Belgium*

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## Abstract

The authors earlier introduced two models to describe the formation and decay kinetics of dye radicals in a quantitative way, measured with Electron Spin Resonance (ESR) spectroscopy.<sup>1</sup> One model is based on an equilibrium between dye molecules and dye radicals, the other on an equilibrium between dye molecules, dye radicals and doubly oxidized dye molecules. The models are able to fit and predict the experimental data. The most important new element in one of the models is the possibility of having a double oxidation of a dye molecule during intrinsic irradiation.

In the case of a system where double oxidation is observed, some dyes are found to possess a peculiar behavior of linewidth versus signal amplitude. The linewidth of the signal not only depends on the concentration of the dye radicals, but also on the relative concentration of the molecular and doubly oxidized state. This observation can be explained using the fact that there exist different mechanisms which influence the linewidth. Spin-spin interaction and charge transfer between a molecule and its cation in the vicinity are used to explain the experimental results.

## Introduction

When spectrally sensitized silver halide microcrystals are irradiated in the absorption region of the crystal (called blue irradiation), or in one of the absorption bands of the adsorbed dye molecules (called minus-blue excitation), dye radicals can be formed. These radicals originate from holes trapped at the HOMO (Highest Occupied Molecular Orbital) level of the dye and can be observed as a single narrow ESR line with a Lorentzian shape.<sup>2</sup>

When the formation of dye radicals is followed during continuous blue excitation, there is a distinct difference between the samples with AgBr and AgCl microcrystals for the dyes studied. As shown in Figure 1 the concentration of dye radicals grows to a constant value in the case of AgBr. This behavior can be described using the equation<sup>1</sup>:

$$D^+(t) = \frac{f_s I}{f_s I + b_s} \left[ 1 - \exp\{(-f_s I - b_s)t\} \right]$$

with  $D^+(t)$  the concentration of dye radicals at time  $t$ ,  $f_s$  the fraction of holes generated in the valence band (VB) of the microcrystal which become trapped by dye molecules (subindex  $s$  stands for single oxidation),  $I$  the intensity of blue irradiation expressed as number of photons absorbed per microcrystal per second,  $b_s$  the inverse time constant describing the decay of dye radicals.

For AgCl the concentration decreases after reaching a maximum during blue illumination (see Figure 1). In this case the concentration as a function of time can be described using<sup>1</sup>:

$$D^+(t) = \frac{f_s}{f_s - f_d} \left[ \exp(-f_d I t) - \exp(-f_s I t) \right]$$

with  $f_d$  the fraction of holes generated in the valence band of the microcrystals which become trapped by dye radicals (subindex  $d$  stands for double oxidation).

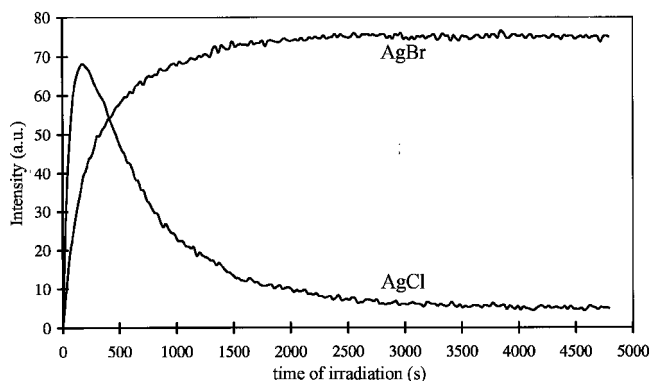


Figure 1 Formation curves of dye radicals during continuous blue excitation for spectrally sensitized AgBr and AgCl microcrystals

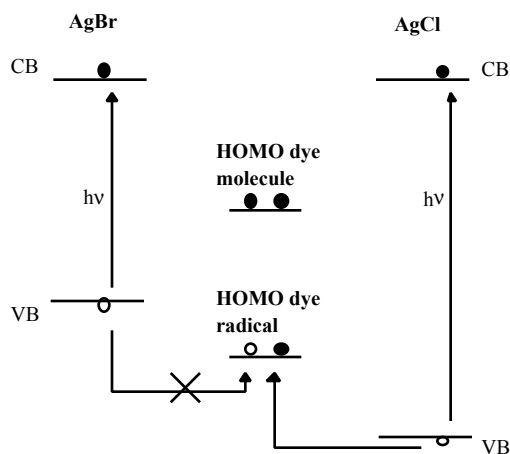


Figure 2 Dyes used as spectral sensitizers for the AgBr and AgCl microcrystals. Dye 1 is a cyanine and dye 2 is a merocyanine dye.

The reason why in the case of AgCl a second oxidation is possible for the dyes used in this study, is illustrated in Figure 2. From the literature it is known that the optical absorption of the adsorbed dye molecules shifts to shorter wavelengths when they become dye radicals.<sup>3</sup> This means that the distance between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) becomes larger. But one can also expect that the HOMO shifts down relative to the VB of AgX because there is an extra positive charge on the dye radical. It is suggested that in case of the AgBr system, the HOMO shifts below the VB of the microcrystal so that trapping of a second hole at the HOMO of the dye radical is energetically not probable. In case of AgCl where the position of the VB is energetically lower than for AgBr, the HOMO of the dye radical is still above the VB. It is possible that a second hole can be trapped by the dye which becomes a doubly oxidized molecule which is not paramagnetic and will not give an ESR signal.

The possibility that the decrease in concentration is due to dye molecules which are destroyed or desorbed from the surface when they become radicals, is excluded. When the AgCl samples are excited with a narrow band filter in the absorption region of the adsorbed dye, the concentration of radicals grows to a constant value as is observed for the AgBr system during blue excitation. Because the optical absorption of the radical is shifted over several tens of nanometers, there is no minus-blue excitation of the radical. No doubly oxidized dye molecules can be formed. An equilibrium builds up between dye molecules and radicals. If the origin of the decrease of the ESR signal during blue excitation would have been the breakdown of dye molecules when they are oxidized, this would also be observed during minus-blue excitation, which is not the case.

In this work some extra experimental observations are presented which support the idea of a doubly oxidized state of the dye molecules.

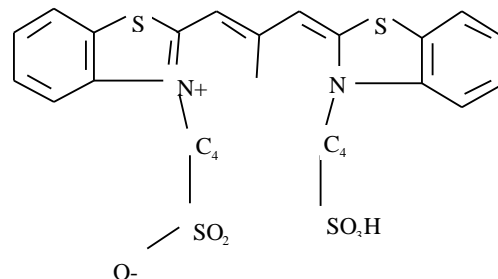
## Experimental

The ESR measurements were carried out on an X-band Bruker ESP300E electron spin resonance spectrometer. A cavity with optical windows was used to obtain uniform in situ illumination of the sample. The light source used was a PTI xenon lamp (150W) with a feedback system so that the emission intensity was constant in time. A combination of filters was used to select a spectral region of excitation.

In our experiments, it is observed that the linewidth of the ESR signal changes with the concentration of adsorbed dye radicals. One can conclude that in this case it is not correct to follow the amplitude of the signal at a fixed magnetic field value to measure the radical kinetics. Therefore, a more accurate analysis is applied to obtain information about the kinetics of the dye radicals. The ESR line is measured many times in a row with a fixed time interval and fitted to a Lorentzian. The product of the peak-to-peak amplitude and the square of the peak-to-peak linewidth is taken as a measure for the concentration of the dye radicals.

The samples used are emulsions of cubic AgBr and AgCl microcrystals with edge length of 0.4 microns prepared by the double jet precipitation method and doped with 10 ppm of  $Rh^{3+}$ -ions in the core. The microcrystals are spectrally sensitized with one of the dyes shown in Figure 3. The sensitizers used are a cyanine and a merocyanine dye. The amount of dye added is calculated to give 100 % coverage of the crystal surface. The emulsions are coated on a triacetate film base ( $4g Ag/m^2$ ).

dye 1



dye 2

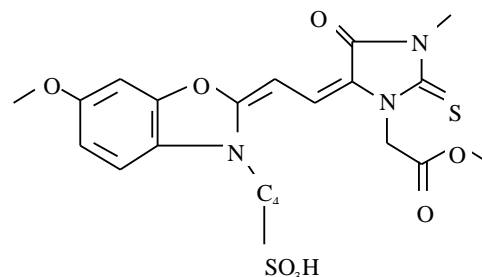


Figure 3. Dyes used as spectral sensitizers for the AgBr and AgCl microcrystals. Dye 1 is a cyanine and dye 2 is a merocyanine dye.

## Results and Discussion

Figure shows the concentration of dye radicals versus the linewidth of the ESR signal for the AgBr sample spectrally sensitized with dye 1. When the concentration becomes higher during continuous blue excitation, the width becomes smaller. During decay, after stopping the illumination, the concentration clearly decreases and follows the same linewidth behavior. For the sample with dye 2 a similar result is observed.

Figure shows that for the AgCl sample spectrally sensitized with dye 2 the linewidth becomes smaller when the concentration of radicals is growing, but there is a turn over to broader ESR lines when the irradiation continuous. There are two possible linewidths corresponding to the same radical concentration, in contrast to the AgBr sample where there is a unique relation between linewidth and amount of radicals. When excitation is stopped, the concentration hardly decreases, but the linewidth clearly becomes smaller.

These observations can be understood as follows. There are two mechanisms which can reduce the linewidth.<sup>5</sup> First there is the possibility to have a hole transfer between the molecules and their radicals when they are close together. A second contribution is exchange narrowing. Due to spin-spin interaction, the energy of a spin in the 'up' state can be transferred to a spin in the 'down' state. If this process is fast the orientation of neighboring spins is being changed rapidly through mutual spin flips, so that the local dipolar field fluctuates at a similar rate and tends to be averaged out. This leads to narrowing of the ESR line.<sup>6</sup>

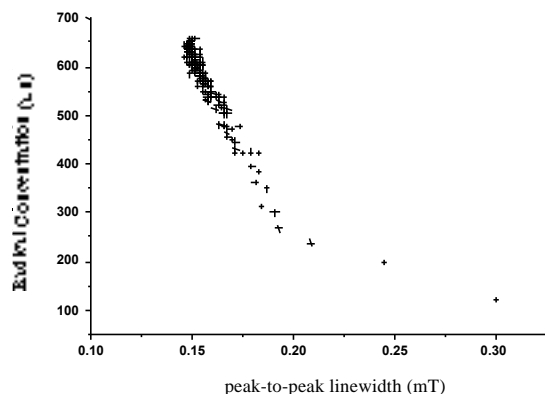


Figure 4 Relation between the concentration of dye radicals and the peak-to-peak linewidth of the ESR line for the AgBr sample with dye 1 during blue excitation.

In the case of AgBr microcrystals there is an equilibrium between dye molecules and radicals. During continuous blue excitation the equilibrium shifts towards the radical state. This increases the chance of having spin-spin interaction and makes the linewidth smaller. The charge transfer process has a high probability at the beginning when there is still a large amount of dye molecules, but decreases when they are oxidized to radicals. The contribution of this process to narrowing of the ESR

line becomes smaller. The total result is the observation of a linewidth narrowing when the concentration of dye positive holes increases.

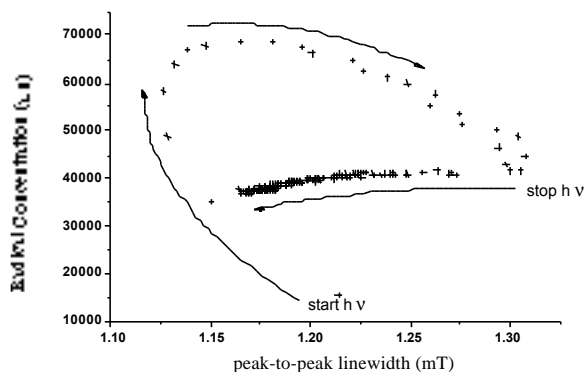


Figure 5. Relation between the concentration of dye radicals and the peak-to-peak linewidth of the ESR line for the AgCl sample with dye 2 during and after blue excitation.

For the AgCl system the situation is quite different. In that case there is an equilibrium between the molecular, radical and doubly oxidized state of the dye which shifts towards the doubly oxidized state during continuous blue excitation. In Figure the concentration of single oxidized dye molecules is growing and the width of the ESR line decreases, when blue irradiation is started. After a certain time, the linewidth begins to increase and the concentration of dye radicals goes down. There are points which describe the same amount of radicals, but have different linewidths. The spin-spin interaction is the same in both points, but the charge transfer from dye radicals to dye molecules is smaller after a longer time of excitation, because the number of dye molecules relative to the number of doubly oxidized dye molecules becomes smaller. This is a possible explanation for the larger linewidth.

One can remark that also the mobility of the holes between the radical and the doubly oxidized state can contribute to a narrowing effect. But, it seems that this contribution is less important. It is observed that the formation of the doubly oxidized state is only partially reversible. It is suggested that a number of dye molecules in this state is desorbed from the surface or made inactive in another way. The partial return from the doubly oxidized state to the molecular state, with the radical as an intermediate, restores the occupation of the molecular state. As a consequence, the contribution of the charge transfer process between dye radicals and molecules increases. This explains that the linewidth decreases again when the irradiation is stopped as shown in Figure. For the sample with dye 1 this is not observed, because there is no reversibility observed for the doubly oxidized state of the dye.

## Conclusions

The linewidth behavior is studied of the ESR signal of dye radicals formed on spectrally sensitized AgBr and AgCl

microcrystals during blue excitation. The dyes studied in this work can trap two holes from the VB of the microcrystal when they are adsorbed on AgCl. The observation of the variation in linewidth for the AgCl system supports the idea of a doubly oxidized dye molecule.

Two processes are active:

- i. a rapid spin-spin interaction
- ii. a hole transfer process between dye radicals and dye molecules

The second process can have an important influence on the photographic sensitivity. Dye positive holes which are mobile on the surface can move to the sites where latent image centers are formed. Interaction between the holes and the silver clusters will reduce the photographic response.

## References

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