

# A Qualitative Study of the Color Formation of a Color-Forming Material by Time-Resolved Specular Transmission

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## Abstract

A method for qualitative evaluation of the kinetics of color formation in a color-forming material by time-resolved specular transmission and DRS-spectroscopy is presented.

With these techniques it becomes possible to follow, as a function of time, both the silver halide-development reaction and color formation with the different couplers, incorporated in a coated material, in a dedicated chemistry.

This method makes it possible to compare the different kinetics (both silver and color) of the different layers (blue-green- and red-sensitive) in a qualitative manner, both as single layers and arranged in a complete color-forming material.

Therefore, the method can be used as an analytical tool in the development of a color-forming material to optimize, for example, the kinetics of both silver- and color-formation.

The method, together with some experimental results, will be presented.

## Introduction

In a color-forming material the final outcome of the exposure- and development-processes is the color image. The formation of this color image is, however, the sum of :

- (1) the development of the light-sensitive AgX-emulsion.
- (2) the formation of the dye by a coupling reaction of the coupler, incorporated in the emulsion-layer, with the oxidized developer, formed by the development of the silver halide-emulsion.

A simplified representation of such a color formation in a color-forming material is shown in figure 1. The reality is, however, much more complicated with e.g. competing reactions such as deamination and sulfonation of the quinone diimine (=Dev(ox)).

Furthermore, these various and complex chemical reactions take place in a coated multi-layer material passing through a developer solution, resulting in the fact that

diffusion phenomena will play a very important role in color formation. Examples are the diffusion of the developing agent into the multi-layered material, the diffusion of the quinone diimine (Dev(ox)) to the coupler, present as an aqueous dispersion in the material, diffusion of the quinone diimine to adjacent layers etc.

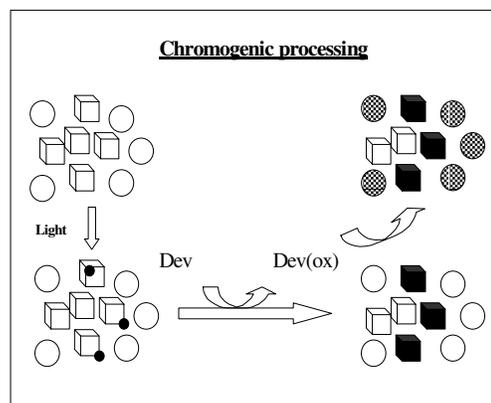


Figure 1 : chromogenic processing

In the development of a color-forming material, many material-parameters have to be investigated (ingredients; layer-thickness; hardening of the gelatin-layers etc.). After illumination and processing, the influence of the parameters investigated on the final color image is observed (color sensitivities, color densities, gradation etc.).

In order to investigate the kinetics of color formation it is, however, important not only to have an idea about the overall kinetics of color formation, but also to be able to follow the silver halide development kinetics as well and to correlate these kinetics with color formation. In addition it is very important that this study can be conducted on a coated film material in combination with commercial developers, so that the observed kinetics are as close as possible to conditions in practice. Moreover it would be

very interesting to be able to obtain such information by a relatively simple and fast technique on small-scale test-coatings.

For this reason, time-resolved spectroscopy was investigated to find out whether this technique could be of use. In this paper the method together with some experimental results are presented. An evaluation of the method is also included.

It is, however, important to emphasize that it is not the objective of this study to obtain quantitative kinetic data for color formation, nor to study the mechanism of color formation as described in various other publications (1-5).

### Method Description.

A schematic representation of the experimental set-up is shown in figure 2.

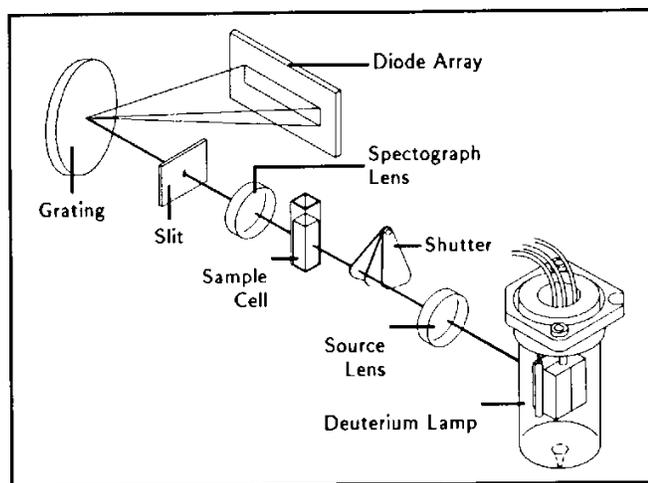


Figure 2 : schematic representation of the HP8452A spectrophotometer with labsphere.

A strip of a coated and exposed test-material is brought into the sample-holder, filled with a dedicated chemistry and kept at a particular temperature. With the HP8452A spectrophotometer an absorption spectrum (190 – 820 nm) was taken every 5 seconds during, in our case, 3 minutes.

Similar experiments were performed with a Shimadzu UV-3101PC spectrophotometer. With the latter, however, the absorption in the near infrared region can also be monitored. Unlike the HP-apparatus, however, only one wavelength at a time could be monitored.

The experimental data were collected with a PC and could be manipulated in various ways.

### Experimental Results.

In figure 3 the spectroscopic data of a blue-sensitive single layer are presented. The increasing density of the yellow dye ( $\lambda_{\max} = \pm 540$  nm), resulting from the coupling reaction of the yellow coupler with the oxidized developing agent, can be clearly seen. An increase in absorption around 800 nm can also be observed. This increase of

absorption was due to the development of silver halide. This means that by following the absorption at 540 nm and 820 nm an idea could be obtained about the kinetics of color formation on the one hand and those of the silver halide development reaction on the other. These data were obtained with consecutive spectral measurements on a single blue-sensitive coated material.

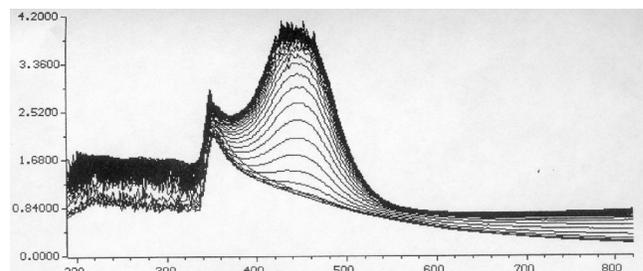


Figure 3 : spectroscopic data of a blue-sensitive single-layer

It is clear that similar results could be obtained with a red-sensitive (cyan-dye ;  $\lambda_{\max} = \pm 550$  nm) and a green-sensitive (magenta-dye ;  $\lambda_{\max} = \pm 650$  nm) single layer.

In order to be sure that by monitoring the silver-absorption at 820 nm on the HP-apparatus there was no interference due to color absorption (especially for the cyan and magenta dye-forming materials), the silver halide absorption was also monitored with the Shimadzu apparatus at 1200 nm. These data are shown in figure 4. As can be seen, both sets of data coincide fairly well.

These figures also show that a difference in the kinetics of silver halide development for different single layer materials was indeed observed, the blue- and red-sensitive materials showing the slowest silver halide development kinetics, the green sensitive material the fastest.

These figures also show minor absorption of the blue-sensitive material at 820 and 1200 nm due to the fact, that in this material, the developed emulsion crystals were large compared to those of the red- and green-sensitive materials.

As already mentioned a difference between the HP-and the Shimadzu-apparatuses is that, with the former, a complete spectrum is always taken. This means that during the measurement the sample was exposed and latent image was formed. This is of course also true for the Shimadzu apparatus, when a wavelength is monitored for which the material is sensitive. For this reason it must be emphasized that the results shown in figure 4 were the result of fully exposed materials, in which the additional illumination from the measuring device was negligible.

It is clear that with these kinds of measurements on single layers the color and silver formation during development can be followed and the influence of various parameters on both phenomena studied.

In addition to single layers, it is also possible to perform similar measurements on multi-layer materials, which are more similar to commercial products. To simplify the measurements, it is best practice to omit antihalation- and filter-dyes, although, even in the presence of these dyes,

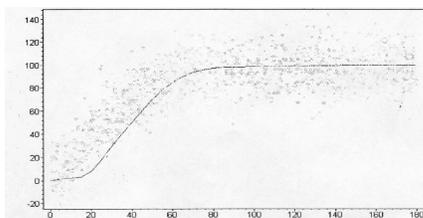
differences in the kinetics of color formation can still be observed.

With these multi-layered materials, color formation is followed, as a function of development time, by monitoring the increase in the absorption of the three dyes (440, 550 and 650 nm) formed. The silver formation kinetics (monitored at 820 or 1200 nm) are, in this case, of course, the sum of the silver formation kinetics of the three light-sensitive layers.

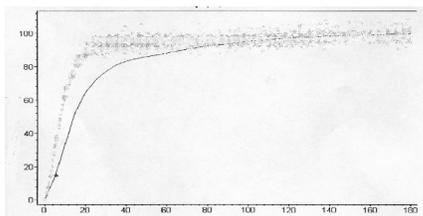
Using these kinds of measurement it is, again, clear that the influence of many parameters on both color and silver formation can be investigated by means of a simple and fast method.

By comparing, for example, the results obtained from the blue, red, and green sensitive layers coated as a single-layer with those obtained with the multi-layered material, very different kinetics are observed, proving that the diffusion of the developer into the material plays an important role in both color and silver formation. For the same reason, altering the multi-layer structure (moving a light-sensitive layer more upwards in the multi-layer structure and vice versa) also results in different kinetics.

Blue-sensitive layer



Green-sensitive layer



Red-sensitive layer

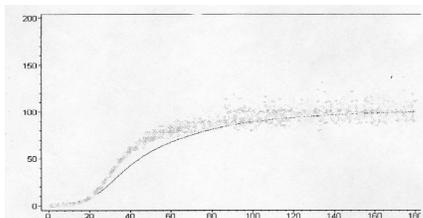


Figure 4: silver formation kinetics of single-layers

An interesting feature, which can also be studied by this method, is the so-called inter-image effect, in which the oxidized developer, formed in one light sensitive layer, diffuses to another light sensitive layer and induces in the latter undesired color formation.

## Conclusions

These preliminary results clearly show that time-resolved spectroscopy can be used as a tool to study qualitatively both color- and silver-formation in a color-forming material, both as a single layer or as multi-layers. It can also give additional information during product development research to improve further and optimize color-forming materials. Furthermore, it can help to understand the formation of the color image better.

The possibilities of this technique will be explored in greater detail.

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## Biography

Dr. Kris Viaene obtained his degree in chemistry (B.Sc. in 1984 and Ph.D. in 1989) at the University of Leuven (Belgium). His Ph.D. Research under the guidance of Prof. Dr. De Schryver involved a spectroscopic study (especially fluorescence spectroscopy) of organic detergent-like molecules adsorbed on the surface of clay particles in suspension.

In 1990, he joined the Agfa-Gevaert Research Labs in Mortsel (Belgium), where he has been involved in development and research into photographic materials for micrographic and color-forming film applications.