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Silver Dye-Bleach Color Microfilm

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Abstract Silver dye-bleach materials offer the advantages of high sharpness, simple three-solution direct-positive processing, and very good stability of the azo image dyes. Based on these features various models of microfilm with very thin layers have been developed. The light scattering effects in the imaging layers were investigated, and based on these findings the layer structure was modified in order to improve acutance. The layer and image structure, processing, and photographic properties including resolving power, color reproduction, and permanence in dark and light storage are discussed.

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Introduction

There is an increasing demand for micrographic reproductions of colored documents. These are needed for archival storage of engineering drawings, catalogues, instruction and training, geographical maps, micropublishing, and other purposes. A high sharpness and excellent stability of the dyes in dark keeping is very important for such applications. Micro-reproductions of geographical maps are also used for navigation purposes. In this case a very good light stability of the dyes is mandatory, as usually only a small and frequently the same part of a moving map is projected on a screen with a high light intensity.

Chromogenic color films based on azomethine dyes are prone to fade in the light and in the dark. Our experience with Cibachrome® products suggested that the silver dye-bleach (SDB) system might be suitable for such applications. It uses azo dyes whose very high stability has been proved in numerous tests, i.e., good results have been obtained in light-fading experiments as well as under archival type storage conditions and at elevated temperatures.[1]

The high inherent sharpness is the consequence of the presence of the azo dyes during exposure. The light scattered by the emulsion grains is strongly absorbed by the dyes, therefore sharpness is preserved. But since the dyes absorb the actinic light during exposure, the speed of such materials is low.

Direct-positive processing is easy and simple in comparison to the reversal processing of chromogenic materials, only three solutions are needed, namely developer, bleach, and fix.

First Version of SDB-Color Microfilm

There are three main factors which influence the sharpness and granularity of a silver dye-bleach microfilm:

- Size of the emulsion grains
- Diffusion properties of the azo dyes
- Layer structure

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- *Size of the emulsion grains:* During dye-bleaching, a colorless bleach halo is formed around each silver grain. The size of these bleach halos is dependent on the grain size. The granularity and sharpness, however, deteriorates due to large bleach halos. But small grains have relatively low speed. The compromise was to use a polydisperse silver bromide emulsion with 2 mol % iodide.
- *Diffusion properties of azo dyes:* The azo dyes used are of the water-soluble type.[2] They could diffuse in the monomeric form, but in the gelatin layers many molecules are aggregated in bigger particles, therefore the tendency to diffuse is considerably reduced. However, a careful selection is needed, since other properties must be fulfilled, like good color rendition, fast bleachability, and high stability. Only a few dyes are good in all respects.
- *Layer structure:* The thickness of the layers has a very marked influence on the sharpness of a color film. For a silver dye-bleach film the top layer is always yellow, the middle layer magenta, and the lowest layer cyan. This is the consequence of the spectral absorptions of the dyes (Fig. 1). The yellow layer has a high sharpness, because the blue light scattered by the emulsion grains is absorbed by the yellow dye. But its emulsion grains also scatter the green and red light. Therefore, the sharpness of the magenta image and especially of the cyan image is considerably reduced. It is obvious that the distance from top of the yellow layer to the bottom of the cyan layer is the important factor. Therefore, the thickness of the layers must be as small as possible, but the reduction of layer thicknesses has its limitations. If constant amounts of azo dyes are combined with decreasing weights of gelatin, the rheological problems of the coating solutions increase. Further-

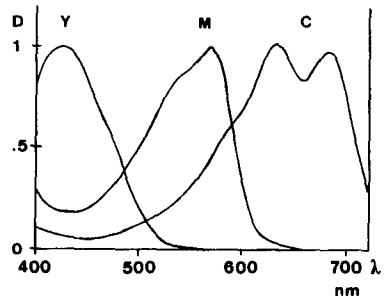

Figure 1. Spectral absorptions of the azo dyes for SDB microfilm; Y = yellow, M = magenta, C = cyan, λ = wavelength in nanometer (nm), *D* = spectral density.

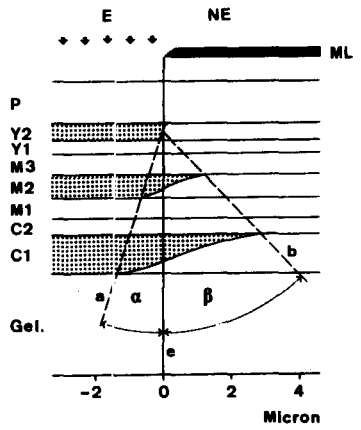

Figure 4. Edge-exposure of SDB microfilm version two, *cross-section* after silver development. Symbols like Fig. 3, layer structure like Fig. 2, *right*.

The effect of light-scattering is that a part of the exposing light is shifted from angle α to angle β.

In another experiment a film was coated which was identical to version one, but the polydisperse emulsion had been replaced by a monodisperse silverbromide emulsion containing cubic crystals with an edge-length of 0.3 microns. This emulsion was similar regarding graininess to the polydisperse emulsion of version one, but had a higher contrast. This film was slightly sharper, the angles α and β discussed above were:

α about 31°
β about 69°

The scattered light which exposed the top of the magenta and cyan layers has a low intensity and comes partly at a low angle of incidence into the colored layers. It became evident that an improvement could be attained if the silver halide grains were removed from the top of the magenta and cyan layers. Therefore, a new layer structure was chosen as shown in Fig. 2, right-hand part.

In this second version, the number of layers on the emulsion side was increased from 6 to 9, whereas the total thickness of the active layers from cyan to yellow was reduced from 5.8 to 4.4 microns. The cyan layer was subdivided in two layers (C1 and C2). The upper part, which is 1/3 of the total cyan layer thickness, contains no silver halide emulsion. The magenta layer was subdivided into 3 about equally thick layers (M1, M2, and M3), but emulsion was added only to the middle layer. Also the lower half of the yellow layer (Y1) was free from silver halide. The dyed layers which contain no silver halide are bleached by adjacency effects.[6] The dyed layers C2 and M3 without silver halide improve the sharpness. These two layers together with the silver-free layers M1 and Y1 reduce interimage bleaching effects and therefore improve the color rendition without the need for special interlayers.

The polydisperse emulsion has been replaced by a monodisperse type with cubic crystals, with edge-lengths of 0.2 microns. This emulsion has higher contrast and speed than the version one microfilm.

As a consequence of this more complex layer structure, the sharpness of the edges between exposed and nonexposed parts is improved. The edge-exposure experiment described above was repeated with results shown in Fig. 4. The angles α and β which indicate the influence of light-scattering are much reduced in version two microfilm:

α about 18°
β about 43°

This increase in sharpness of the silver image is a consequence of several factors: Thinner layer structure, no silver halide in the layers C2 and M3, smaller emulsion grains, and higher contrast. In the dye-bleach step the sharpness of the silver image is slightly reduced due to lateral bleaching and dye diffusion.

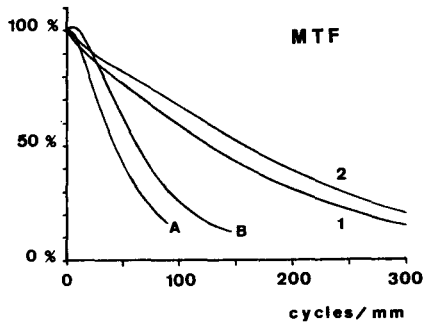

Figure 5. Comparison of modulation transfer functions: 1 = SDB microfilm version one, 2 = SDB microfilm version two, A and B = chromogenic color reversal microfilms.

TABLE III. Results Obtained with Two Versions of SDB-Microfilms in Comparison to Two Chromogenic Color Reversal Films

Criteria	SDB films		Chromogenic films	
Emulsion	Version 1 polydisp.	Version 2 monodisp.	A	B
D_{max}	2.14	2.24	2.84	2.84
D_{min}	0.06	0.07	0.07	0.12
Gamma (Dvis)	1.30	1.80	2.57	1.84
Speed, ASA (Tungsten)	0.8	2.4	5	
Resolving power (Lp/mm, 1000:1)	340	360	80	100
Modulation at 100 Lp/mm	57%	68%	12%	26%
RMS granularity (50 micron aperture, $D = 1$)	10	9	12,7	9
Acutance [$D\,\mu^{-2}$]	5×10^{-3}	14×10^{-3}	3×10^{-3}	5×10^{-3}

The results obtained with SDB microfilms version one and two in comparison to two chromogenic color reversal microfilms are given in Table III and the modulation transfer functions in Fig. 5.

It will be noted that the modulation transfer function and the acutance, especially of the version two, are considerably better than those of the chromogenic films. The improvements from version one to version two are also evident.

An image printed with a halftone screen of 6 line-pairs per mm was reduced 21 times on version two. A small part of this image was then re-enlarged in a microscope. The pattern of the halftone screen was clearly visible. A copy made of a version 2 original on version one showed good sharpness, but some loss in color rendition, especially in blues. Images of SDB microfilms can be enlarged on Cibachrome Print® and Cibachrome Copy® materials.

Permanence and Light-Fading Properties

The azo dyes used in the Cibachrome materials have been carefully selected for stability. However, the permanence of the final image is not only dependent on the chemical nature of the dyes, but is also influenced by the application method and especially by the aggregation of the molecules. Advantage has been taken of these facts and experience in the design of the SDB microfilms. The image stability of these films was tested in accelerated dark and light fading experiments.

In a first dark fading experiment carried out at 90°C and a relative humidity (RH) of 40% the change, if any, after 4 weeks was within the limits of measuring errors.

The results of further tests obtained after treatments for 4 weeks at 60% RH in the temperature range of 60 to 85°C are

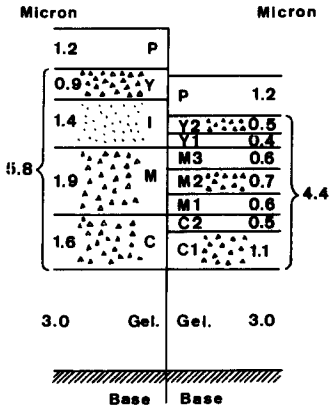

Figure 2. Layer structure of SDB microfilms, version one: left-hand, version two: right-hand. C, C1, C2 = cyan dyed layers, M, M1, M2, M3 = magenta dyed layers, Y, Y1, Y2 = yellow dyed layers. Gel. = gelatin underlayer, *I* = interlayer, *P* = protection layer. The dry thicknesses are indicated in microns.

more, the hardening and the layer adhesion are affected. The difficulties could be solved by a careful optimization of the coating technique.

The layer structure of the first version of the final product is shown in Fig. 2 (*left*). The term "active elements" in this context includes all the layers without the protection layer and gelatin underlayer. The active elements are the 4 layers cyan, magenta, interlayer, and yellow; their total thickness is 5.8 microns. Between this layer assembly and the polyester base is a gelatin layer; it is needed to improve the coating quality and layer adhesion. A protection layer is coated on top. The dyed layers contain silver halide emulsions which are spectrally sensitized to green light for magenta and to red light for cyan. The interlayer has two functions: it is a filter layer for the blue light, therefore it contains colloidal silver and a yellow azo dye, and in the bleach solution, where it is discolored, it prevents bleaching effects from the magenta to the yellow layer and vice versa. The processing sequence of SDB microfilm is given in Table I.

The developer is based on hydroquinone and phenidone. The bleach contains diluted sulfuric acid, iodide as silver ligand, a bleach catalyst, a bleach accelerator, and an oxidizing compound for the residual silver, which is a nitrobenzene sulfonic acid.[3-5] The fixing solution contains ammoniumthiosulfate. This simple 3-solution process is rather uncritical regarding time and temperature.

The process is very similar to other Cibachrome processes, the main difference being the bleach composition. It had to be adapted for the special cyan dye used in color microfilm. Processing can be carried out in various processors, in tanks or even in an amateur drum.

Most of the silver accumulates in the fixing solution from which it can be recovered by electrolytical methods.

Results Obtained with the First Version of SDB Color Microfilm (Table II)

The film has a satisfactory maximum density and a suitable contrast for the reproduction of colored documents. The speed

TABLE I. Processing Sequence at 24 and 30°C

Step	Time, min. 24°C	30°C
Developer	4	2
Water	½	⅓
Bleach	4	2
Water	½	⅓
Fix	4	2
Water	4	3
Total	17	9⅔

TABLE II. Properties of the First Version

D_{max}	2.14
D_{min}	0.06
Gamma (Dvis)	1.30
Speed (equivalent ASA)	0.8
Resolving power, contrast 1000:1	340 Lp/mm
Modulation at 100 Lp/mm	57%
RMS granularity (50 micron aperture)	10

is slow for camera work and therefore a strong illumination of the documents to be photographed is required. The reproduction of fine details is very good, and many geographical maps and similar printed matter have been successfully reproduced. The modulation transfer function of this film is presented in Fig. 5.

Second Version of SDB Color Microfilm

Further investigations of the sharpness of version one microfilm were carried out by microscopy. A test object consisting of a glass plate partly covered by a metallic layer was contact printed on the film. This test object had a very sharp border line between the transparent and opaque part. During processing, the bleaching step was omitted, so that the negative silver image would remain. A microscopic cross-section was made across the border of the exposed and the nonexposed parts. This cross-section was photographed in the swollen state. The results are shown in Fig. 3, where the layer thicknesses have been reduced to the dry state. It is obvious that the edge of the yellow layer is sharp. But in the magenta layer silver grains can be seen in the nonexposed part of the film; their number decreases with distance from the top of the layer and increasing horizontal distance from the edge. This effect is even more pronounced in the cyan layer, where the last silver grains are found 15 microns inside the edge. In a normally processed sample, these silver grains partly bleach magneta and cyan dyes with a resultant loss in edge sharpness. This effect is caused by light scattered by the emulsion grains of the yellow and magenta layers.

As the lines *a* and *b* in Fig. 3 indicate, green and red light is scattered in the yellow layer. Therefore, between the lines *e* and *a*, which include angle α, the light intensity was insufficient for a complete exposure of the magenta and cyan layers, whereas between the lines *e* and *b* (angle β), the top of both layers has been exposed by scattered light. In this experiment the angles are:

α about 36°
β about 76°

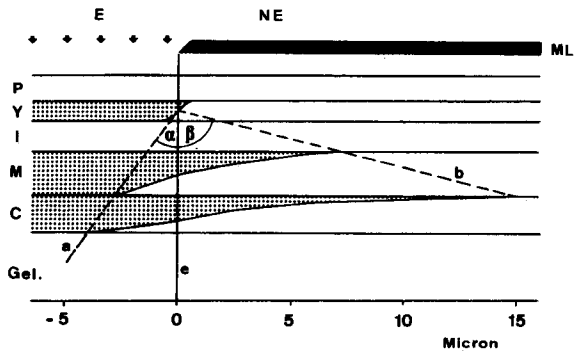

Figure 3. Edge-exposure on SDB microfilm version one, cross-section after silver development. *E* = exposed part, *NE* = nonexposed part, *ML* = metal layer (on glass plate, not shown), *e* = border line exposed/not exposed, *a* and *b* = border lines of significant light-scattering effects including angles α and β to line *e*, layer structure as Fig. 2, *left*.

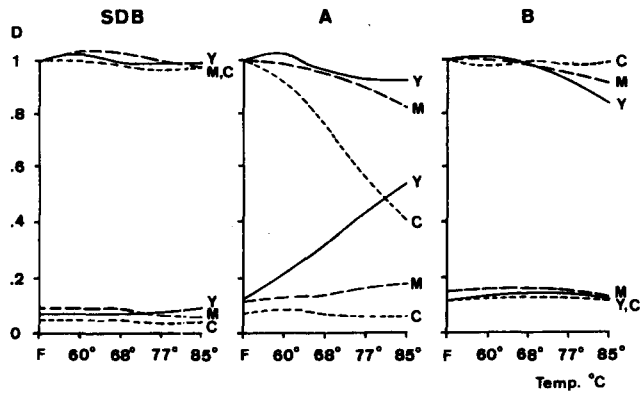

Figure 6. Dark stability test of SDB microfilms, both versions, and chromogenic color reversal films A and B at 60% RH, 4 weeks and various temperatures. *F* = fresh sample, *D* = optical density.

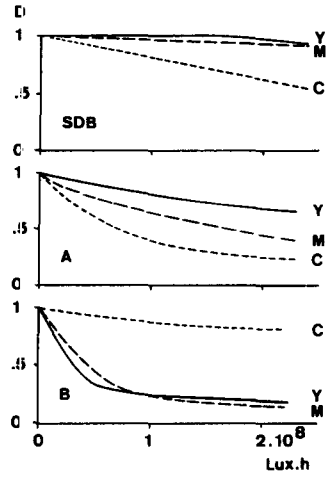

Figure 7. Tungsten light stability test of SDB microfilm, version one, and chromogenic color reversal microfilms *A* and *B*; *D* = optical density.

given in Fig. 6. It can be seen that the SDB films hardly changed, whereas the chromogenic films deteriorated badly. With film A all the dyes were affected and a very high yellow stain was formed. If this stain density would be subtracted from the $D = 1$ curve, the yellow dye curve would look similar to the cyan curve. Film B is more stable than film A, but the yellow dye decomposed significantly.

In the literature, estimates are given for the long-term stability of various chromogenic materials based on experiments at elevated temperatures. The time needed at room temperature to obtain a given degradation has been extrapolated by the classical Arrhenius equation.[7] For these tests the material is kept at a constant level of relative humidity, but at different temperatures. The data given in Fig. 6 were obtained in such an investigation. However, the Arrhenius equation is only valid if the degradation chemistry at a high temperature is the same as at the low temperature of normal storage. This has not yet been proved for SDB-materials and is questionable.

Experience with SDB materials has shown that low-humidity storage is more important than low temperature. The preferred conditions for long-time storage are 30–50% RH and

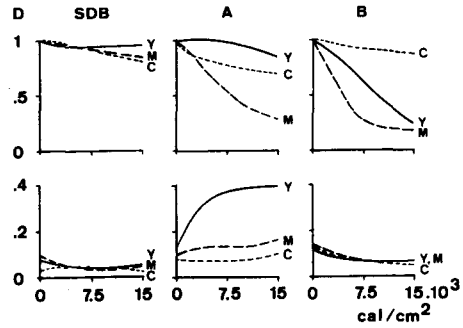

Figure 8. Xenon light stability test of SDB microfilm, version one, and chromogenic color reversal films A and B; *D* = optical density.

less than 20°C. Very good permanence during dark storage is typical for all SDB materials. The reason is that the azo dyes used in SDB products are stable against oxidation or hydrolysis under normal storage conditions.

The oldest available SDB prints were produced by B. Gaspar in 1943. They have been kept in the dark at normal room conditions, and are still in excellent condition. Further investigations regarding the long-term stability in the dark are in progress.

Tests aimed at assessing the effects of light exposure should be made under conditions which are typical for color microfilms. Therefore, the illumination system of a 16mm film projector was used, it was equipped with a 100-W quartz-iodine lamp. A heat reflection filter was included. The illumination at the surface of the sample had an intensity of 1.12×10^6 lux. After an exposure time of 180 hr corresponding to 2×10^8 lux-hours the chromogenic films had changed much more than the SDB microfilm, version one (Fig. 7).

Another light-fastness test was carried out with xenon light exposure. Again, the silver dye-bleach film was superior to the chromogenic films A and B (Fig. 8).

Conclusion

The SDB microfilms can be used for the reproduction of colored documents like geographical maps and similar originals. The important features are: excellent resolving power, in-house processing with simple and uncritical chemistry, good light stability during projection, and outstanding dark keeping quality.

Acknowledgment

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References

1. Wilhelm, Henry: *Modern Photography*, **43:** 92 (1979). Henry Wilhelm, "Relative Stability Characteristics of Common Colour Print Materials," *Photo Communique*, **3:** 8–21 (1981).
2. Yellow dyes: Pat. CH 489'038, U.S. Pat. 3'870'697 (1968). Magenta dyes: Pat. CH 398'307, U.S. Pat. 3'211'554 (1950). Cyan dyes: Pat. CH 386'247, U.S. Pat. 3'211'556 (1960).
3. Meyer, Armin: "Improvements in the Silver Dye-Bleach Process," *Photogr. Sci. Eng.*, **18:** 530–534 (1974).
4. Pat. CH 597'627, U.S. Pat. 4'138'256 (1975).
5. Pat. CH 584'914 (1973).
6. Meyer, Armin: *J. Photogr. Sci.*, **20:** 81–86 (1972).
7. Tulte, R. J.: "Image Stability in Color Photography," *J. Appl. Photogr. Eng.*, **5:** 200–207 (1979).