

The Stability and Permanence of Cibachrome® * Images

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Abstract Factors influencing the fading of Cibachrome® materials in the dark and upon exposure to light are discussed. Very long testing periods are required to study the dark fading process at temperatures up to 77°C and 60% relative humidity (RH). After 112 days at 77°C/40% RH hardly significant density changes could be observed. Above 80°C and 70% RH the absorption spectra of the Cibachrome azo dyes change noticeably within a week. This is mainly due to partial deaggregation of the azo dyes into monomers. This deaggregating process is reversible, as shown by experiments. Even at 91°C/90% RH the irreversible chemical degradation is very slow. Comparative data regarding the light fading properties are also given. They prove the excellent stability of the azo dyes toward photo-oxidation.

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1. Introduction

When we started the development of Cibachrome products in 1958, one of our basic aims was to choose a photographic system which takes advantage of highly stable dyes. Chromogenic images based on azomethine dyes were in general very unstable at that time. This was an important reason to try the silver dye-bleach process, because it is based on azo dyes. Only dyes of good stability were incorporated in the materials. Stability tests are important, as many azo dyes are quite unstable. Only very few dyes were found which are satisfactory for silver dye-bleach materials in all respects.

The good stability of azo dyes with respect to azomethine dyes may be in relation to the easier isomerization reactions of the azomethine due to the higher polarizability of the C=N double bond. The polarization of the azomethine bond may be the principal reason that it is more easily attacked by hydrolysis in the dark or by photo-oxidation.¹

Azo dyes for silver dye-bleach materials are very stable against oxidation but easily cleavable in a reductive bleach solution. The Cibachrome dyes can withstand many years of dark storage at room temperature in dry air, but are bleached in 10-25 sec in the bleach solutions of the Cibachrome processes. This bleaching occurs in two steps: First a hydrazo compound (-NH-NH-) or leucodye is formed, and in a second step this compound is irreversibly reduced to amines.

In the gelatin layers of Cibachrome materials, the azo dyes are present as aggregates consisting of many dye molecules. This improves the stability in the light and in the dark, and also the tendency to diffuse from layer to layer is reduced, as dye monomers diffuse much more rapidly than aggregates.

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2. Fading in the Dark

In the dark, heat and humidity influence the rate of degradation of a processed color image. For these tests various temperatures up to 93°C are applied. The relative humidity is kept constant for all the temperatures. ANSI has proposed 60% RH, whereas Kodak has chosen 40% for their published data sheets.² According to Dr. Charlton C. Bard from Kodak, for the case of a chromogenic yellow dye, the fading would be roughly twice as fast at 60% RH than at 40% RH, and at 15% RH the fading would be cut almost in half.³ We therefore decided to carry out tests at 40 and 60%.

They were performed in large size climatic boxes kept at constant temperature and humidity within narrow limits. Temperature and humidity were continuously recorded. Sample holders were suspended freely in the box. After a given period of incubation the samples were removed and the density changes measured densitometrically, using either a Gretag D 300 or a Macbeth RD 519 instrument. Fog is subtracted from the reported data.

First we consider the results found at a relative humidity of 40%. We found that at this humidity and at a temperature of 77°C during an incubation period of 112 days the density changes were for all three dyes and all the actual Cibachrome papers and films between ± 0.02 and 0.03; they are hardly significant. We could not find any chromogenic material up to now that was equally stable. For these comparisons we only considered the dye with the largest change in neutral patches. We compared our results with published data from Kodak² (Figs. 1 and 2).

We also compared Cibachrome II De Luxe (CPS 1K) on white-opaque polyester base to Kodak Dye Transfer Paper (Table I).

TABLE I. Dark Stability, Cibachrome, Kodak Dye-Transfer Paper

Test condition	77°C 40% RH, 112 days
Initial density	$D = 1$
Kodak dye-transfer	$\Delta D = -0.08$ (Y)
Cibachrome II De Luxe	$\Delta D = \pm 0.02$ (Y, M, C)
	$D_{\min} = \text{unchanged}$

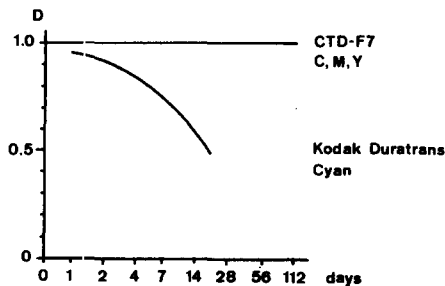


Figure 1. Dark-fading of Cibachrome Transparent Display Film (CTD-F7) and Kodak Duratrans Film at 77°C/40% RH. *D* = optical density, C = cyan, M = magenta, Y = yellow.

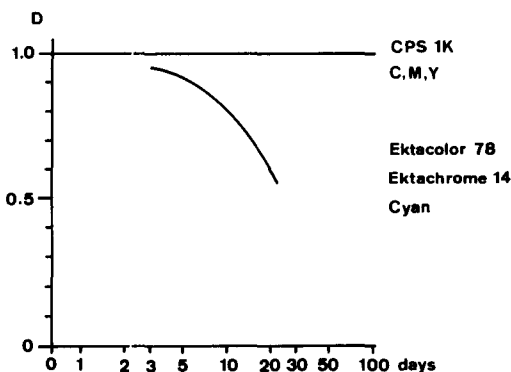


Figure 2. Dark-fading of Cibachrome II De Luxe Print (CPS 1K) and two chromogenic papers at 77°C/40% RH. *D* = optical density, C = cyan, M = magenta, Y = yellow.

According to Kodak, it is estimated that Dye Transfer Paper may show a yellow density loss from 1.0 to 0.9 in about 300 years at room temperature and 40% RH. According to Wilhelm, both materials are regarded as "most stable."⁴ A reliable estimate of the useful life of Cibachrome II De Luxe prints is not feasible now, it would probably take years until a 0.1 density loss could be observed at, e.g., 52°C and 40% RH.

Whereas no noticeable density changes were observed at 77°C, 40% RH and incubation periods up to 112 days, we have measured a significant density loss of 12% in the cyan layer of Cibachrome Transparent Display material after 224 days incubation at 85°C and 60% RH (Fig. 3). This density loss was accompanied by some increase of the minimum density measured with a blue filter. Regarding the minimum density or stain values the color with the largest change is always yellow.

There is an influence of the base. Figure 4 shows the results with two print materials, the base being the only difference:

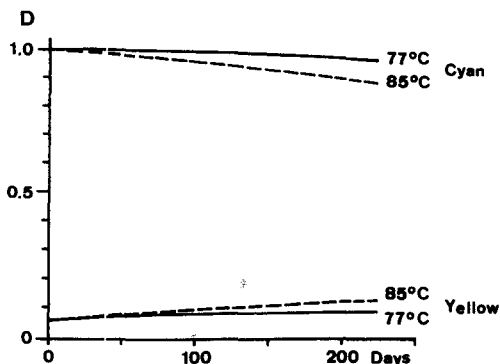


Figure 3. Dark-fading of Cibachrome Transparent Display Film (CTD-F7) at 77°C and 85°C, 60% RH. *D* = optical density.

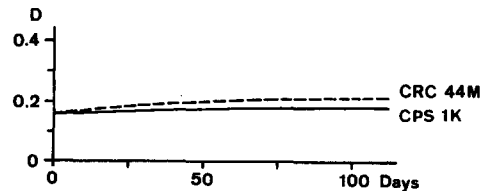


Figure 4. Dark-fading of two print materials: Cibachrome II De Luxe, glossy (CPS 1K), and Cibachrome II Paper, pearl surface (CRC 44M) at 77°C and 60% RH. *D* = optical density, D_{\min} = minimum density.

CPS 1K is Cibachrome II De Luxe, glossy
CRC 44M is Cibachrome II Paper, pearl surface

"De Luxe" is coated on white-opaque polyester base and the pearl paper is coated on resin-coated (RC) paper base. After 112 days at 77°C and 60% RH the RC paper material showed a yellow density increase of 0.06, whereas the polyester material increased only by 0.02. If a good permanence is important, the De Luxe material has a distinct advantage.

All these dark fading tests prove that Cibachrome materials are very stable. But for practical purposes some care is recommended, especially the processing must be carried out exactly according to the prescriptions. A good final wash is mandatory. Different or periodically variable conditions and pollutants may increase the degradation of the images.

In order to get a deeper insight into the mechanisms by which the azo imaging dyes are degraded in darkness, we have carried out the following experiments under carefully controlled conditions:

Samples of exposed and processed Cibachrome Transparent Display film CTD-F7 were stored at a given temperature in the atmosphere of closed glass vessels containing titrated aqueous solutions of high-purity sulfuric acid. Relative humidity, as determined from vapor-pressure curves, was maintained within $\pm 1\%$ during the whole period of our measurements (about 7 days). The temperature was maintained within $\pm 1^\circ\text{C}$ and recorded. The samples were taken out periodically and left in the laboratory atmosphere for 1 hr. Absorption spectra were then taken with a Cary 219 spectrophotometer in transmission mode and corrected for fully exposed and processed samples of the same material.

After processing and drying of the Cibachrome materials, the azo image dyes are always present in some aggregated form. These aggregates consist of several or many dye molecules. Treatment at high temperatures and humidities induces a deaggregation of the azo dyes. The assignment of the absorption maxima to dye aggregates and monomers is known from studies in aqueous solutions. In the case of the cyan dye the wavelength maxima are at 630 ± 5 nm for the dye aggregate and at 676 ± 5 and 765 ± 5 for the two monomer transitions respectively, which may be two different vibronic states. Consequently, all density variations in the cyan channel given in the next figures are read out from the spectra at these wavelengths.

CTD-F7 film was fully exposed with green and blue light and partly with red light in order to leave only the cyan dye at a density of approximately 1.0 after processing. The samples were then subjected to incubation at various temperatures and humidities (Fig. 5).

After an incubation time of 16 hr at 90% RH, the change at 40°C was small, but at 90°C a loss of about 20% of the dye aggregate density was found and the monomer density increased. After this period of time only deaggregation without chemical degradation is observed. Figure 6, as compared with Fig. 5, shows that the kinetics of deaggregation are very dependent on humidity and, less, on temperature which rather influences the thermodynamics of the dark degradation process.

Curve I of Fig. 7 shows the spectral absorption of a near gray

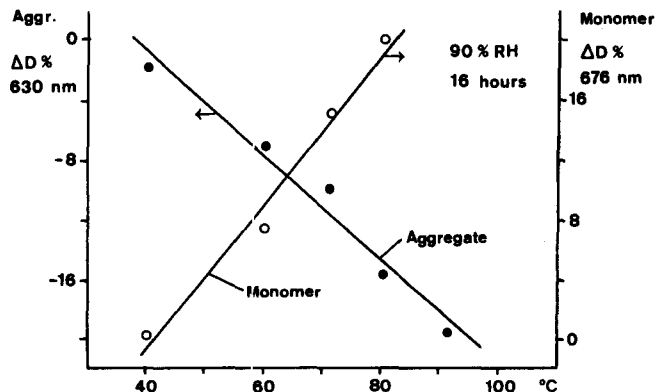


Figure 5. Dark-fading, deaggregation of cyan dye, Cibachrome Transparent Display Film (CTD-F7). Aggr. = aggregate, RH = relative humidity, $\Delta D\%$ = density difference expressed as percentage, nm = nanometer.

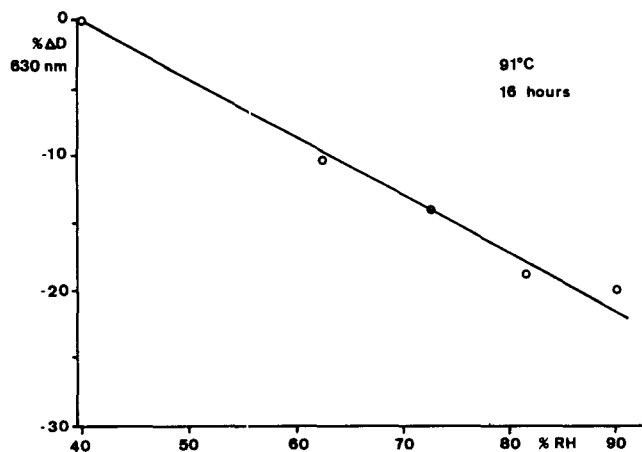


Figure 6. Dark-fading deaggregation of cyan dye, Cibachrome Transparent Display Film (CTD-F7). RH = relative humidity, $\% \Delta D$ = density difference expressed as percentage, nm = nanometer.

patch of CTD-F7 film. The dyes are mainly in the aggregated form. After an incubation of 15 hr at 80°C and 90% RH curve 2 has been measured, this shows mainly the monomer absorptions.

The dyes could be reaggregated by a treatment during 80 min in a 1/100 molar calcium chloride solution, washing and drying below 30°C. The same effect was obtained by fixing in the fixing solution of process P-3 as used for this material. The result is shown in curve 3, which closely follows curve 1. A chemical degradation, which did not occur in such a short

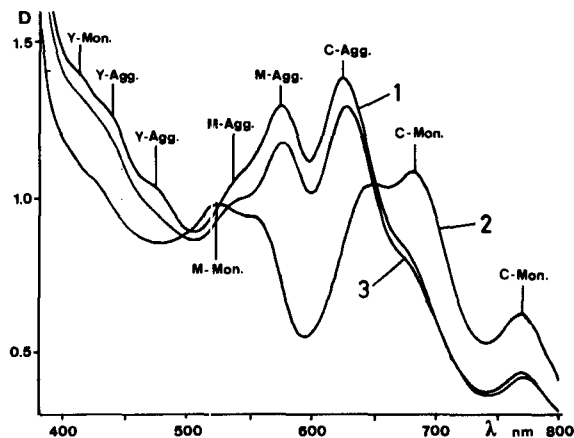


Figure 7. Curve 1: spectral absorption of near gray patch of Cibachrome Transparent Display Film (CTD-F7). Curve 2: after incubation, 15 hr at 80°C, 90% RH. Curve 3: film of curve 2 after reaggregation. λ = wavelength, nm = nanometer, D = optical density, Mon. = monomer, Agg. = aggregate, Y = yellow, M = magenta, C = cyan.

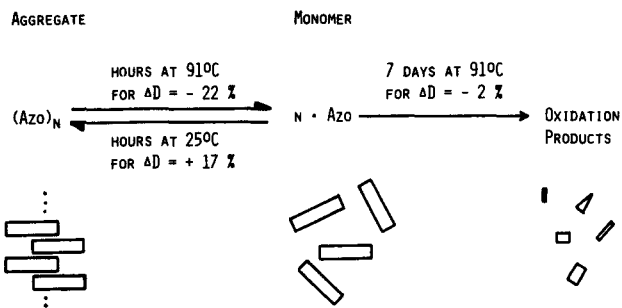


Figure 8. Dark-fading of cyan color of Cibachrome Transparent Display Film (CTD-F7) at high temperature and high relative humidity. There is a temperature dependent equilibrium between the aggregated dye $(Azo)_N$ and its monomer $N \cdot Azo$, the chemical degradation at 91°C/90% RH is slow. ΔD = optical density difference.

time, may be measured at the isosbestic points, where curves 1 and 2 cross.

By comparing the deaggregation of the 3 image dyes versus humidity at 91°C we observed that the cyan dye is the easiest to deaggregate followed by the magenta dyestuff and the yellow dyestuff. This deaggregation results in brownish images, which can be brought back to the initial state by fixing. The degree of reaggregation is limited, however, by diffusion of the dyes which becomes noticeable in the deaggregated state of the dyes.

At a high humidity, there is a temperature-dependent equilibrium between aggregate and monomer. Even at high temperature and high humidity the irreversible oxidation is very slow (Fig. 8).

Hence, Cibachrome materials having been altered at conditions of high humidities and high temperatures can be partly regenerated by a treatment in 1/100 molar calcium chloride solution or simply by fixing during 10 min in FX-3 and washing in tap water.

3. Light Fading

The mechanism and rate of the light-fading of azo dyes are strongly dependent on the substrate and state of dispersion of these dyes. High humidity and high temperature enhance light fading. If proteins like wool or gelatin as substrates are used, a photoreduction of the azo dyes has been observed.⁵ It is probable that these substrates take part chemically in the light-fading reaction. Under conditions of very high humidity and exposure to high illumination levels, as typical for tropical countries, the azo groups of the Cibachrome dyes are probably degraded by a photo-oxidation. Earlier investigations on the light stability of Cibachrome Transparent Display film have been published in 1974.⁶

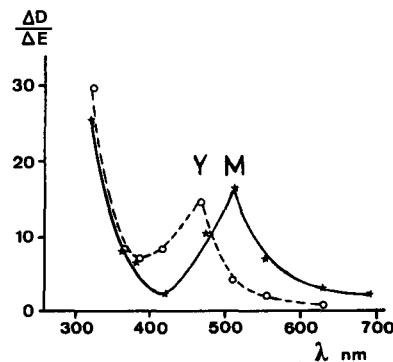


Figure 9. Light-fading, Cibachrome Transparent Display Film, spectral influence of the light source. λ = wavelength of the incident light, nm = nanometer, ΔD = optical density difference, ΔE = light energy for $\Delta \lambda$. $\Delta D/\Delta E$ is an arbitrary unit for the spectral light fading rate. Y = yellow, M = magenta.

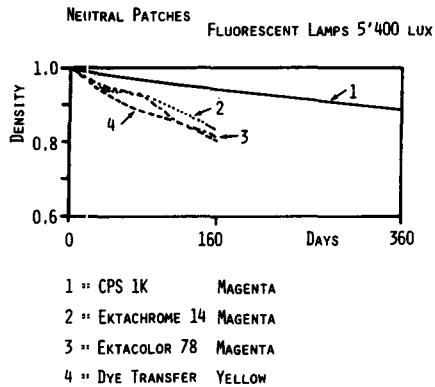


Figure 10. Light-fading, neutral patches, fluorescent lamps, comparison of 3 Kodak color print materials and Cibachrome II De Luxe Print (CPS 1K).

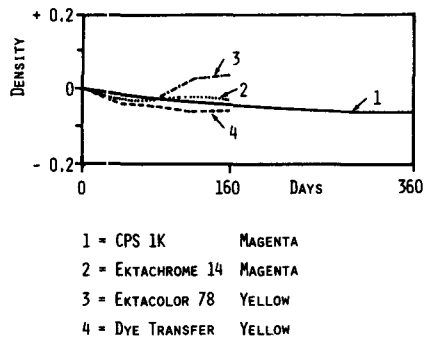


Figure 11. Light-fading, minimum densities, fluorescent lamps, comparison of 3 Kodak color print materials and Cibachrome II De Luxe Print (CPS 1K).

Figure 9 partly reproduces a figure of the above mentioned paper.⁶ It shows the wavelength-dependence of the light fading reaction for the yellow and magenta dyes. In this figure $\Delta D/\Delta E$ is an arbitrary unit for the spectral light fading rate. ΔD is the density loss obtained if the light energy ΔE is absorbed. ΔE is the light energy of the light source emitted between the two closely spaced wavelengths λ_1 and λ_2 . The cyan dye has been omitted, as at that time another cyan dye was used. The near UV and the visible light are important for light fading. In the visible spectrum a peak of the fading effect is observed close to the absorption maximum of the dye under investigation. Also a reciprocity law failure of the light fading effect was discovered when the light intensity was varied.

The data on light fading of a number of color photographic materials have been published by Kodak.² The samples were exposed to fluorescent light with an intensity of 5'400 lux at the plane of the test objects up to 160 days. The temperature and RH values are not published. We applied the same method for our tests, but with an intensity of 10'800 lux. By calculation, we transformed our results to Kodak's intensity

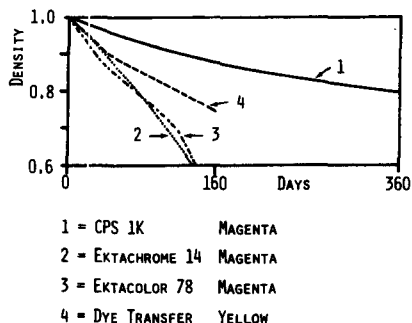


Figure 12. Light-fading, color patches, fluorescent lamps, comparison of 3 Kodak color print materials and Cibachrome II De Luxe Print (CPS 1K).

TABLE II. Light Keeping, Neutral Patches (Optical Density = 1) (Fluorescent Lamps, 5'400 Lux)

Materials	ΔD , most changing dye	
	160 days	360 days
Chrom.		
pap. neg. (78)	-0.18 M	—
Reversal (2203)	-0.13 Y	—
Reversal (14)	-0.17 M	—
Cibachrome		
Print CPS 1K	-0.06 M	-0.11 M
Print CRC 44M	-0.05 M	-0.11 Y
Transp. CTD-F7	-0.06 Y	-0.09 Y

TABLE III. Light Keeping, Minimum Densities (Fluorescent Lamps 5'400 Lux)

Materials	ΔD , most changing dye	
	160 days	360 days
Chrom.		
pap. neg. (78)	+0.04 Y	—
Reversal (2203)	+0.04 Y	—
Reversal (14)	-0.02 M	—
Cibachrome		
Print CPS 1K	-0.04 M	-0.06 M, Y
Print CRC 44M	-0.07 Y	-0.08 Y
Transp. CTD-F7	-0.01 C	-0.04 C, M

TABLE IV. Light Keeping, Color Patches (Optical Density = 1) (Fluorescent Lamps, 5'400 Lux)

Materials	ΔD , most changing dye	
	160 days	360 days
Chrom.		
pap. neg. (78)	-0.49 M	—
Reversal (2203)	-0.34 M	—
Reversal (14)	-0.48 M	—
Cibachrome		
Print CPS 1K	-0.12 M	-0.21 M
Print CRC 44M	-0.10 M	-0.21 M
Transp. CTD F7	-0.09 M	-0.18 M

level of 5'400 lux, disregarding a relatively small reciprocity law failure. The duration of exposure corresponded to 360 days at Kodak's intensity level. In our case the temperature of the samples was 40°C and the relative humidity 35%. The results are listed in Tables II to IV and Figs. 10–12. Only the dyes with the largest change are considered.

After 160 days the density loss of the dye showing the largest change with Cibachrome was one third of the loss in chromogenic papers. After 360 days of exposure the density loss was about 75% of the one found with chromogenic papers in only 160 days. A similar result was obtained in comparison to Kodak Dye Transfer paper. When only transparent films are considered, the gap between Cibachrome Transparent Display film and several chromogenic films is even wider.

Regarding the minimum densities, the Cibachrome materials show generally a slight loss in 160 days. There is a slowly increasing tendency when the test is prolonged to 360 days. Widely used chromogenic papers show first a loss in yellow density. Then this density increases to about +0.04 after 160 days, and when the test is prolonged, this increase continues and a yellow stain becomes quite noticeable. This is one of the typical differences in behavior as compared with Cibachrome.

In the color patches the dye which changed most was always magenta. For Cibachrome materials the density loss was about twice as high when compared to the neutral patches. The chromogenic materials already changed drastically after 160 days of exposure. Their density loss was about 2.7 times higher than in neutral patches and about 4 times higher than with Cibachrome materials.

All these tests prove that the Cibachrome materials, especially those coated on polyester base, are relatively stable toward exposure to light. However, some precaution is recommended: In reality, the images may suffer from a number of factors which are not included in the laboratory tests. The light source may contain more UV, its intensity is unpredictable, and the temperature and relative humidity may be higher. Also pollutants, and even microorganisms may reduce the permanence of the images.

The worst case is probably a glass box illuminated by daylight in a humid place. In such cases very high temperatures will occur. The effect is a more rapid bleaching of the dyes, and also some shrinking and brittleness of the gelatin layers have been observed. Post-processing treatments of Cibachrome images: Lacquering did hardly improve the light stability. A significant effect was found if the prints are laminated with a foil of a low permeability for water, like polypropylene. In this case an improvement of the light stability by about a factor of 3 was found. A polyester foil was nearly as good, but with cellulose acetate and PVC only small effects were found. If chromogenic images were laminated with these foils, the improvement was in all cases quite small.

4. Base Materials

The high permanence of the Cibachrome dyes is only useful if the base materials are at least as stable as the dyes. All transparent Cibachrome products are coated on polyester film bases. Cibachrome II De Luxe print and Cibachrome II Amateur are available on a white-opaque polyester base also called "voided polyester." The stability of processed photographic films coated on polyester base has been investigated by Adelstein and McCrea from Eastman Kodak.⁷ Their conclusion is: "The physical properties of polyester-base films are predicted to be satisfactory for several thousand years." Therefore, we believe that the base should be stable enough for all practical purposes. For a number of applications a mat surface and cheaper materials are preferred. Therefore, the Cibachrome Print products and Cibachrome Copy papers are also

available on resin-coated paper base. It is well known that such a paper base is less stable than polyester, and therefore it is recommended to use the polyester film base materials if a very good permanence of the photographic images is important for a specific application.

5. Conclusion

Our dark keeping tests with Cibachrome materials did not allow prediction of a time period for a given density loss at room temperature and 40 or 60% RH. Very much longer test periods than 224 days would be needed. The permanence was far better than with any chromogenic material we could compare until now. Also in the fluorescent light keeping tests (40°C, 35% RH) the Cibachrome products showed distinct advantages over all the color photographic materials of which the fading data are published. ▲

6. Acknowledgments

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