Modelling Light Fading of Hard Copy Media

*R.E. Jacobson and A.E. Saunders**
Imaging Technology Research Group, University of Westminster
Watford Road, Harrow, Middlesex, United Kingdom
**Visiting Researcher, Exchequer Printing pty*

Abstract

Conventional chromogenic photographic papers have evolved over a period of at least fifty years and much research has been carried out to improve their light stability. One of the earliest technologies for obtaining photographic quality output from digital data was by the thermal dye diffusion process. Original versions of this medium had very poor light stability when compared with chromogenic media and this limitation was also found in ink jet printing systems. Whilst much effort has been given to providing more light-stable hard copy output from digital media, little work has been published on modelling their light fading characteristics. This paper is concerned with the provision of a simple model for the light-fading kinetics of a layer consisting of a molecular dispersion of dye in a transparent binder. It is assumed that the product of fading is non-absorbing and that reflection is ideal. The results obtained using this model are compared with those obtained experimentally for a selection colorants and substrates. The model provides effective quantum yields for light fading as a means of bench marking and predictions of the fade curves of density plotted against time. Modifications to the proposed model are discussed which have become necessary due to deviations between predicted and measured fading curves and better agreement obtained. These modifications predict that enhanced stability to light can be obtained by assuming that the image microstructure is composed of lines or hard-edged dots and gaps whilst increased fade rates occur if the microstructure is of uneven or noisy density.

Introduction

In recent years a great deal of attention has been given to the provision of colorants for application in hard copy output with increased stability to ambient lighting conditions. Modern conventional chromogenic photographic papers have evolved over a period of at least fifty years and much research has been carried out to improve their light stability.[1] It is only very recently that a standard has been proposed for measuring the image stability of imaging materials[2] and this only applies to photographic colour films and paper prints. One of the earliest technologies for obtaining photographic quality output from digital data was the thermal dye diffusion process (D2T2).[3,4] Original versions of these media had very poor light stability when compared with chromogenic media.[1] In 1994 high quality colour output was first provided for the desktop environment in the form of ink jet printing with the introduction of the first Epson Stylus Color 720 dpi printer.[5] Improvements in the light stability is a current concern of those providing hardware and consumables for hard copy output from digital data. Practical comparative light fade data for many ink jet inks and papers under controlled conditions are being provided by Wilhelm Imaging Research Inc.[5]

Earlier work in these laboratories investigated the rates of fading of chromogenic and D2T2 media.[1] It showed that the kinetics of light fading was very complex and did not conform to any simple relationship. The results obtained for these materials indicated different light fastness characteristic curves which were thought to be characteristic of colorants with more heterogeneous sizes that changed with density.[1] Also the differing curve shapes found for the fading of chromogenic and D2T2 media required further investigation. The concave exponential shape for fading (see Figure 1) of chromogenic media may, by analogy to other studies,[6] be caused by fading associated with dyes in molecular dispersions or aggregates, whilst the convex shape of the fading shown under some conditions for D2T2 media[1] may be due to an increased fading rate with time due to continuous breakdown of dye particles.[7] However, little work has been published on modelling light fading of layers of colorants and how these differing curve shapes could be accounted for.

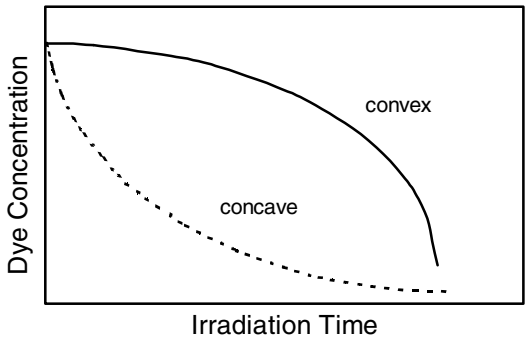

Figure 1. Two types of fade characteristics.[6]

In order to investigate fading more thoroughly a more fundamental approach involving first principle modelling of the fading process was adopted in more recent work carried out in these laboratories.[8]

This work provided models for light fading that could explain the differing shapes of the fading curves shown in Figure 1 when applied to investigations of the fading of single colorants in a variety of media (chromogenic, D2T2, ink-jet and bubble jet). Furthermore this modeling process was shown to provide a simple means for estimating effective quantum yields as a fundamental means of benchmarking the light stability of colorants. This modelling approach is now being extended and applied to fading of colorants when coexisting with other colorants in fading from neutral densities which is the more usual way of investigating light fading[2,9] and is compared with the fading of single colorants.[8]

Basic Light Fading Model

In order to shed more light on the complex kinetics of fading, it was decided to apply a fading model[8] which was originally developed by Saunders.[10] The fading model is derived completely elsewhere[8] and is based on the following assumptions:

- the colorant is uniformly distributed (homogeneous)
- the colorant is molecularly dispersed and hence non-scattering
- incident radiation is uniform over the surface layer
- internal reflections are absent at surfaces of the layer
- the number of photons absorbed is proportional to the number incident
- there is no inner filter effect: any products of photochemical degradation of the colorant are transparent and any binders or components of receptor layers are transparent.

Using these assumptions applied to a slab of colorant of defined depth, photon flux of irradiation and initial colorant concentration as functions of depth and time, the equations, given below, were derived[8] for modelling the change in density with time of irradiation and the quantum yield for fading:

$$quantum\ yield, \phi = \frac{1}{\varepsilon F t \log_{10} e} \log_{10}\left[\frac{10^{D_0} - 1}{10^{D_t} - 1}\right] \quad (1)$$

where, D_0 = density at zero time of irradiation, ε = the molar extinction coefficient, F = the irradiation flux, t = time, D_t = density at time t. Assuming that the molar extinction coefficient is known, then it is possible to determine the quantum yield for fading from very easily measured experimental parameters at known fading times, i.e., from the original density, D_0, the density, D_t at time, t, and the irradiance, F.

$$normalized\ density = \frac{\log_{10}\left[1 + (10^{D_0} - 1)\right] e^{-\varepsilon \phi F t}}{D_0} \quad (2)$$

Thus if the molar extinction coefficient, ε, the quantum yield, ϕ, and the irradiation used for fading, F, are known it is possible to determine the density at varying times, t, from the original density of the un-irradiated material, D_0. The quantum yield may be obtained from the previous equation.

Experimental Procedure

Results previously obtained[1] from the fading of neutral, cyan magenta and yellow colour patches for the chromogenic and D2T2 media were used for evaluating the fading model. Additional results were obtained from colour patches similarly prepared for ink jet and bubble jet media. Samples were irradiated in an Heraeus SUNTEST CPS Accelerated Exposure Unit, fitted with a UV absorbing filter, at an irradiance of 604 Wm^{-2} (135600 lux) for the periods of time indicated. ISO Status A densitometry was used for measuring dye densities at the time intervals indicated. For chromogenic media, the densities were corrected for stain by subtraction of the corresponding primary density for a irradiated area of zero initial density.

Results and Discussion

Quantum Yields

Quantum yields were determined as before[1] from equation 1, using a value of 5.45×10^4 l mol-1 cm^{-1} for the molar extinction coefficient. This is a mid-range value of published values for typical image dyes[11] This assumed value if incorrect will only have an effect on the absolute value for the quantum yield and it may be more appropriate to call those determined in this work 'effective quantum yields'. Results obtained for effective quantum yields at mid primary density of 1.0 are given in Table 1.

Table 1. Effective Quantum Yields For All Media At A Mid Primary Density Of 1. All values x 10^{-7} and ± 0.25

Colorant	CG	D2T2	IJ	BJ
Cyan	1.5	4.9	0.2	2.4
Cyan (N)	1.1	5.2	1.0	1.7
Magenta	1.7	4.9	5.0	12.1
Magenta (N)	1.0	3.9	2.0	6.3
Yellow	2.8	4.6	1.0	3.5
Yellow (N)	1.5	3.7	1.2	2.4

CG=Chromogenic (Kodak RA-4), D2T2=thermal dye diffusion (Kodak ColorEase), IJ= Epson Stylus Color II ink jet printer and Photo Quality paper, BJ=Canon BJC-250 Bubble jet printer and HR-101 high-resolution paper. (N) = colorant in combination with others as a neutral.

Table 1 indicates that in most cases the effective quantum yields were lower for the colorants in the presence of others as neutrals. Also it is apparent from the data that for the single colorant with the highest effective quantum yield for each of the media is in the sequence:

Bubble Jet (magenta) >> D2T2 (cyan) ~ Ink Jet (magenta) > chromogenic (yellow).

This implies that the life expectancy to fading by light is in the reverse order. This sequence is the same for the media when the dyes are in combination as neutrals. The absolute values of the quantum yields compare reasonably with published values[7] of around 1.1×10^{-4} to 1.3×10^{-6}. The order of magnitude decrease between those of Table 1 and values reported for disperse dyes in nylon and polyester[7] may be due to the spectral sensitivity for fading. For example the irradiance used in equation 1 was based on the assumption that the radiation inducing fading was effective throughout the spectral range. If, however, fading is spectrally selective than the energy involved should be calculated after cascading with the spectral sensitivity for the fading of each individual colorant. This would reduce the value of F in equation 1 which would raise the value obtained for the effective quantum yield. Additional factors might be due to the assumed value for the molar extinction coefficient, or to the assumptions of the model which may not entirely reflect the real situation under which dyes fade in actual media. The model does, however, provide a measure of effective quantum yield of image forming colorants which is a fundamental parameter by which their light fastnesses may be measured and compared. The provision of these single numbers, however, does not indicate if there is a precise fit between the model and the fading characteristics of various colorants which are best determined from equation 2.

Rates of Fading of Colorants

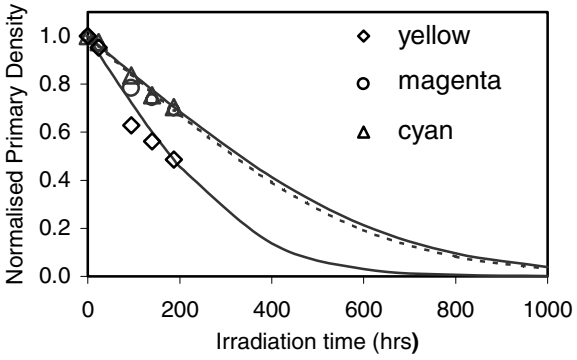

Figure 2. Predicted (curves) and measured values (points) for light fading of colorants of the chromogenic material for initial densities of a neutral of around 1.

Figure 2 shows a typical result for a good fit between measured and densities predicted by the model from equation 2 for the chromogenic medium. The correlation coefficients are given in Table 2 for the single colorants and for those in combination as neutrals for differing initial densities of fade for the chromogenic and the thermal dye diffusion media.

Table 2. Correlation Coefficients Between Measured And Predicted Densities For The Light Fading Of The Chromogenic And Thermal Dye Diffusion Media

Colorant	Chromogenic Medium		D2T2	
	Initial Primary Density	Correlation Coefficient	Initial Primary Density	Correlation Coefficient
Cyan alone	1.52	0.9919	1.41	0.8924
	1.45	0.9974	1.26	0.9319
	1.13	0.9976	1.06	0.9641
	0.60	0.9989	0.82	0.9709
Magenta alone	2.14	0.9957	2.03	0.9903
	1.89	0.9962	1.60	0.9928
	1.45	0.9949	1.35	0.9928
	0.88	0.9951	0.89	0.9998
Yellow alone	1.77	0.9963	1.70	0.9923
	1.64	0.9965	1.23	0.9881
	1.35	0.9985	0.82	0.9925
	0.84	0.9986	0.59	0.9908
Cyan neutral	1.56	0.8981	1.42	0.9246
	1.52	0.9646	1.06	0.9272
	1.22	0.9958	0.83	0.9137
	0.66	0.9933	0.59	0.9639
Magenta neutral	2.71	0.9256	2.02	0.9573
	2.26	0.9691	1.12	0.9091
	1.20	0.9833	0.82	0.9079
	0.55	0.9933	0.57	0.9359
Yellow neutral	1.91	0.9825	1.72	0.9202
	1.78	0.9731	1.06	0.9241
	1.05	0.9822	0.76	0.9095
	0.46	0.9736	0.56	0.9542

The high correlation coefficients obtained between the measured values and those predicted by the model can be seen in Table 2 which also indicates the validity of the model for the chromogenic medium. At the 5 % level the critical value[12] for the correlation coefficient for the four values compared is 0.9500. The first value of 1.00 has been ignored on which the data sets were normalized. The correlation coefficients that were obtained for the dyes in combination as neutrals in the chromogenic medium, also shown in Table 2, although good are slightly lower than those when the dyes are in isolation. This is to be expected for two main reasons. Firstly, the model is not expected to apply to more than one colorant, especially when their individual rates of fading are different. Secondly, primary densities have been used as a selective measure of fading of the individual dyes and this may not be a truly selective measure, being influenced by the changing secondary densities of the other dyes. This good agreement between predicted and measured values is perhaps surprising in view of the assumptions on which the model is based, particularly

that the model was devised for the simpler case of transmission media and not for the refection media actually used. However, linearity between reflection and transmission densities has been shown to apply to photographic print media.[13] The corresponding fade curves for the chromogenic medium showed that the higher the initial density the slower is the rate of fading. Similar results were obtained for the fading of the dyes when they were in combination as neutrals but with a decrease in their rates of fading.

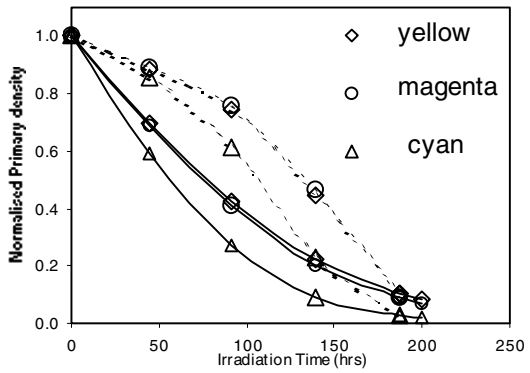

Figure 3. Predicted (full curves) and measured values (points and dashed curves) for light fading of colorants of the thermal dye diffusion material for initial densities of a neutral of approximately 1.

It is immediately apparent from Figure 3 that the model is less applicable to the D2T2 medium which is shown by the convex shape of the fade curve. This is further shown by the poor correlation coefficients of Table 2 in comparison with those for the chromogenic medium. Critical values[12] for the correlation coefficients of 0.9500 were only exceeded for the magenta and yellow colorants alone. In most other cases correlations were poor. Generally as the initial density decreases the correlation coefficients improve and exceed the critical value. These results suggest that different mechanisms may be involved in the fading, that the colorant morphology or distribution is different for different media and that this may depend on the initial density levels, or that the model is wrong.

For the ink-jet media investigated concave fade curves were found. An example is shown in Figure 4. Whilst the bubble jet medium gave results that were a good fit to the basic model with all correlation coefficients in excess of the critical values. For the ink jet medium the critical value of 0.9969 at the 5% level[12] for the correlation coefficients between measured and predicted densities was not exceeded for any of the conditions investigated (see Table 3). The above results pose a problem for modelling if there is a change in the required model depending upon the medium and conditions. However, preliminary modifications to the existing model[8] indicated that changes in curve shape may be modelled by changing the assumptions concerning the basic structure of the colorant. For example, if the structure of the image colorant is such that it comprises areas of low density and areas of density greater than one, as may be the case in digital output which might involve a distribution of dots or lines, it can be shown that the curve shape is convex. If however, the overall colour patch is noisy or blotchy then the curve is the more usual concave shape. This image morphology will vary with the nature and type of the components of the printing system, such as the dot size, amount of colorant deposited, the substrate and the nature of dithering etc.

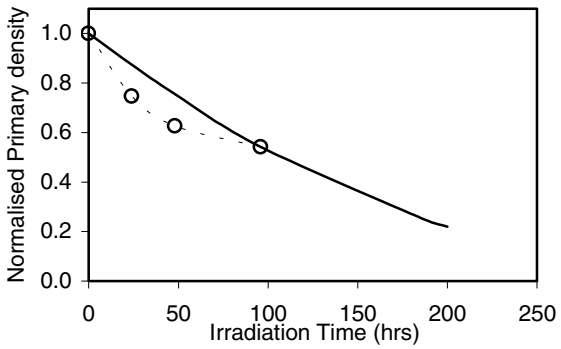

Figure 4. Predicted (full curve) and measured values (points and dashed curves) for light fading of the magenta colorant of the ink jet medium from an initial neutral of density of 0.83.

Table 3. Correlation Coefficients Between Measured and Predicted Densities For The Light Fading of the Ink Jet Media

Colorant	Initial Primary Density	Correlation coefficient
Cyan alone	0.96	0.9233
	0.81	0.8312
	0.73	0.9628
Magenta alone	1.05	0.9424
	0.85	0.9375
	0.74	0.9236
Yellow alone	0.76	0.9688
	0.60	0.9868
	0.50	0.9910
Cyan/neutral	1.10	0.9901
	0.76	0.9512
	0.69	0.9759
Magenta/neutral	1.42	0.9928
	0.83	0.9297
	0.66	0.9293
Yellow/neutral	1.23	0.9721
	0.70	0.9410
	0.62	0.9727

Modified Fade Models

Two modified models have been investigated so far.[8] These were termed the *stepped* and *noise* models respectively and are summarized below. The full derivations of these models and the basic model are given elsewhere.[8]

Stepped Model

In addition to the assumptions listed earlier for the basic fade model it was assumed that the sample has stepped densities of values D_1 and D_2 (where $D_1 < D_2$) with no intermediate values within an area of measured density D_0. This is modelled as a one step summation of all the microdensities in which, α, is the fraction of the sample having density D_1 and the remainder $(1 - \alpha)$ has a density of D_2 . These additional considerations led to the derivation of the following equation:

$$\text{normalised density} = \frac{-\log\left[\dfrac{\alpha}{1+(10^{D_1}-1)e^{-\varepsilon\phi Ft}} + \dfrac{1-\alpha}{1+(10^{D_2}-1)e^{-\varepsilon\phi Ft}}\right]}{D_0} \quad (3)$$

An example for the results obtained from this model for the neutral fade of the magenta colorant for the thermal dye diffusion material is given in Figure 5.

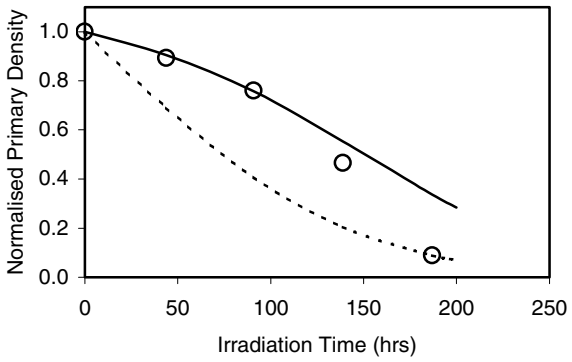

Figure 5. Magenta colorant fade curves for thermal dye diffusion medium from a neutral density of 1.12. Dashed line: basic model, full curve prediction from stepped model with $D_1 = 0.05$, $D_2 = 1.9$. *The points represent experimentally determined values.*

Using this modified stepped model the correlation coefficients between measured and predicted values was increased from 0.9091 to 0.9929.

Noise Model

This model makes the additional assumptions, to those listed earlier for the basic fade model, that the sample has uneven density of values between D_1 and D_2. The densitometer acts as a band-pass filter that can be modelled as a wedge shaped density from D_1 to D_2.

This led to the following model and steeper concave curves than predicted by the basic model:

$$\text{normalised density} = \frac{\log\left[1-e^{-\varepsilon\phi Ft}\right] - \log\left[1 - \dfrac{\log\left[\dfrac{1+(10^{D_2}-1)e^{-\varepsilon\phi Ft}}{1+(10^{D_1}-1)e^{-\varepsilon\phi Ft}}\right]}{(D_2-D_1)}\right]}{D_0} \quad (4)$$

Where D_0 is give by[8]:

$$D_0 = \log_{10}\left[\frac{D_2 - D_1}{\log e\left(10^{D_1} - 10^{D_2}\right)}\right] \quad (5)$$

Applying this model to the fade data for the ink jet media improved the correlation coefficients. For example, the correlation coefficients between the measured and the predicted values for the fading data of the magenta colorant from a neutral of density 0.83 increased from 0.9297 to 0.9914 with values of D_1 and D_2 of 0.81 and 0.86 respectively (see Figure 6).

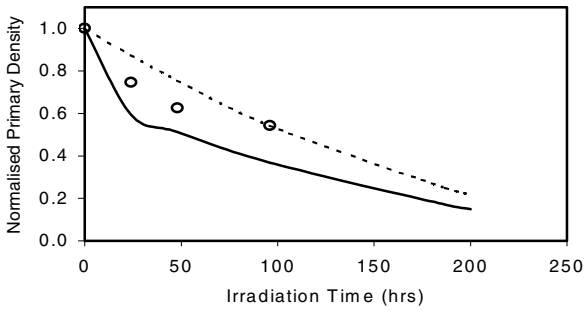

Figure 6. Magenta colorant fade curves for ink jet medium from a neutral density of 0.83. Dashed line: basic model, full curve: prediction from the noise model with $D_1 = 0.0.81$, $D_2 = 0.86$. *The points represent experimentally determined values.*

However, although high, these correlation coefficients do not exceed the critical value and for the neutral fade data did not exceed their critical values for a several combinations of the two densities, D_1 and D_2 . This model although providing steeper concave curves did not fit the data precisely.

Conclusions

The basic fade model gave excellent fits for fading of the chromogenic and bubble jet media. Generally correlations between predicted and measured results less for fading from neutral densities than from the single colorants in isolation. The 'stepped' model gave a better fit for the fading of the magenta colorant of the thermal dye diffusion material than predicted by the original model, whilst the 'noise' model gave a better fit for the magenta colorant of the ink jet medium.

Whilst these models have provided good correlations with experimental data it should be emphasized that this may be a fortuitous consequence of the equations and density values used rather than a fundamental validation of the models themselves. Further work is being carried out on physical investigations of the colorant structure and uniformity of a range of media and printing devices. Furthermore the models are being extended to account for more complex considerations of layers in actual materials, rather than using the simple assumptions of this model. Examples include considerations of surface reflections and scatter.[14,15] In addition the application of analytical densitometry[16] for measurement may be more precise especially when measuring the fading from colorants in combination as neutrals.

This modelling approach generally works well and provides good agreement between predicted and measured values and provides a simple means for 'benchmarking ' in the form of effective quantum yields that could be used for comparing colorants. It could be used for predicting fading from small number of measurements over a short time span. Revised models can accommodate deviations from the original model but this requires further confirmation and investigation. More information is needed on structure, morphology and coverage of colorants.

Acknowledgements

Grateful thanks are expressed to: Bryan Tong for the Chromogenic and D2T2 fade data, Ken Maclennan-Brown for the Ink Jet fade Data, and Aaron Kidd.for the Bubblejet fade data. All are former undergraduate students in Photographic and Electronic Imaging Sciences at the University of Westminster.

References

1. Jacobson, R. E., Attridge, G. G., McDermott, D., Mitchell, C. & Tong, B. Light Stability of Colour Hardcopy Materials. *J. Photogr. Sci.* **44**, 27-30 (1996).
2. ISO. Imaging Materials - Processed photographic colour films and paper prints-Methods for measuring image stability. ISO TC 42/SC N4584 (03/11/2000).
3. Hann, R. C. & Beck, N. C. Dye Diffusion Thermal Transfer (D2T2) Color Printing. *J. Imaging Technology* **16**, 238-241 (1990).
4. Komerska, J. F. *Chapter 11, Thermal Imaging Materials* (ed. Diamond, A. S.) Marcel Decker, New York, 1991.
5. Wilhelm, H. Wilhelm Imaging Research Inc., www.wilhelm-research.com: wir_permanence_06_20_00.pdf, Grinnell, Iowa 50112, USA, 2000.
6. Allen, N. S. Photofading and light stability of dyed and pigmented polymers. *Polymer Degradation and Stability* **44**, 357-374 (1994).
7. Giles, C. H. & Forrester, S. D. in *Photochemistry of Dyed and Pigmented Polymers* (ed. Allen, N. S.) Applied Science, London, UK., 1980, pg. 51-91.
8. Jacobson, R. E. & Saunders, A. E. On the Light Fading of Colorants in Hard Copy Media, Paper Presented at RPS Symposium, DF 2000, University of Westminster, Harrow, September 11-13, 2000. Paper Submitted for publication to *Imaging Science Journal* (December, 2000).
9. Hubbell, D. C., McKinney, R. G. & West, L. Methods for Testing Image Stability of Colour Photographic Products. *Photogr. Sci., and Engng* **11**, 295-305 (1967).
10. Saunders, A. E., private communication (1995).
11. Egerton, P., Goddard, J., Hawkins, G. & Wear, T. Analytical studies of light fading of colour image dyes:effect of dye aggegation and coloured fade products. *RPS Conference Proceedings: Colour imaging systems*, 128-136 (1986).
12. Siegel, A. F. *Statistics and Data Analysis, An Introduction,* John Wiley and Sons, New York, USA, 1988, pg 430.
13. Attridge, G. G., Jacobson, R. E., Newman, P. & Roychoudhury, J. Observations Concerning Inter-Image Effects in a Colour Printing Paper. *J. Photogr. Sci.* **31**, 197-206 (1983).
14. Williams, F. C. & Clapper, F. R. Multiple Internal Reflections in Photographic Color Prints. *J. Opt. Soc. America* **43**, 595-599 (1953).
15. Emmel, P. & Hersh, R. D. A unified Approach for Color Prediction of Halftoned Prints. *J. Imaging Science* **44**, 351-359 (2000).
16. Evans, R. E., Hanson, W. T., & Brewer, W. L., *Principles of Color Photography*, John Wiley and Sons, New York, USA, 1953, pg 441.

Biography

Ralph Jacobson has BSc, MSc and PhD degrees of the University of London. He is currently Professor of Imaging Science, in the School of Communication and Creative Industries at the University of Westminster where he has been teaching and carrying out research on various aspects of Imaging Science for more than 25 years. He is Director of the University's Imaging Technology Research Group and the author of more than 70 papers.