The Relation between Light Fastness of Colorants and their Particle Size

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Published evidence relating the rate of fading of a colorant to its physical state in the substrate, and to the photochemical layer effect, is discussed, and a new theoretical model of light fading is proposed. In this the rate of oxygen diffusion from the atmosphere is considered, first in traversing the polymeric substrate, and then in entering an embedded colorant particle, under illumination. Expressions are derived which show that the rate of fading should vary with $1/a^2$ *(a = radius of particle), for large particles. As the particles become smaller, the rate tends towards a* $1/a$ *dependence, and eventually, with very small particles, it is independent of their size. Recently reported rates of fading of pigments of measured particle size gave results in agreement with the present treatment; the smallest particles thus considered are of the same order of magnitude as those of high light fastness direct dyes in cellulose, as observed by electron microscopy. Thus the model may be applicable to at least some water-soluble dyes as well as pigments.*

Introduction

The light fastness of pigments tends to fall when their particle size decreases provided that no interfering factors operate. This is a commonly accepted fact in industry, but little quantitative investigation upon it has been reported. Qualitative tests have been made in confirmation [1], and one recent quantitative investigation is described below. The effect is clearly due to the greater specific surface of colorant exposed to light and air as the particles become smaller.

These principles apply to dyes as well as to pigments, although experimental demonstration is less direct in most cases, because of the difficulty in determining the particle size. However, by using electron microscopy on cellulose film dyed with a range of direct dyes, Weissbein and Coven [2] demonstrated that the dyes with the smallest particle sizes have the poorest light fastness. Bean and Rowe, using optical microscopy, found a similar qualitative relation with insoluble azo dyes in cellulose [3]. However, there is a large amount of indirect evidence bearing on this aspect of light fastness [4, 5, 6].

Relation between Light Fastness of Colorants and their Concentration in the Substrate

The variation of light fastness of colorants with their concentration in the substrate is partly a function of their particle size (the variation of particle size with change in concentration [4, 5, 6]). The diagram in Figure 1 illustrates how the change in specific surface of the colorant particles with concentration depends on the mode of their growth. In any system where particles are formed from a liquid phase they appear in a random range of sizes; (indeed very special means are required to form particles of *uniform* size). Moreover, their average size increases with concentration. Clearly, system A in Figure 1 will be met only in dyed systems which are molecularly dispersed, and it is likely to occur with pigments dispersed in a medium.

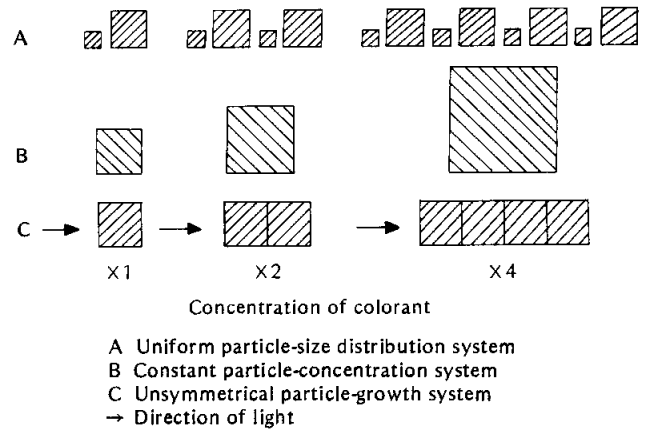

Figure 1 – Idealized systems of growth of colorant particles with increase in total concentration in the substrate, in the ratios 1:2:4 [5]

The tendency of light fastness to increase with colorant concentration in a medium has long been known, but the first quantitative study of the effect seems to have been made by Barker, Hirst and Lambert [7]; their explanation was that a given amount of light must decompose a given amount of dye, and the amount decomposed forms a smaller proportion of the initial weight as concentration rises. However, this may be an over-simplified statement of the situation. Several authors later suggested [8, 9] equations relating dye concentration to fading (see reference 6 for a summary). Work in this laboratory [4, 5, 10, 11] showed that there is a linear relation between fastness grade (BSI scale) or the log of time to fade to a given extent and the log of initial colorant concentration, which extends over a very wide concentration range (in some cases over fifty-fold). Slopes of these curves vary over a wide range of values, from near zero to about 4. These plots were termed CF or CFG (characteristic fastness or characteristic fastness grade) curves, as appropriate. A number of tests illustrated the relation between light fastness and change of

colorant particle size distribution with concentration [1, 5]*. The relation between light fastness and particle size was shown to extend to even the few disperse dyes which exhibit anomalous behaviour, i.e. light fastness decreasing with increasing dye concentration in the substrate. These showed a similar anomaly in the sp. gr. of the dyed material fell with increasing dye concentration, even though the sp. gr. of the pure dye is higher than that of the substrate. The effect is clearly due to formation of voids by dye particles blocking intermolecular spaces [13]. Thus, in all coloured systems, there appears to be a relation between the particle size of colorant and its light fastness, so that a theoretical treatment of the effect such as that given below is widely applicable.

The Photochemical 'Layer' or 'Filter' Effect, and the Influence of the State of the Colorant

This effect is a result of the attenuation of illumination through successive layers of absorbing molecules. Calvert and Pitts [14] state that in practice the 'local' rate of fading, i.e. that nearest the illumination, is similar to the average rate for the whole depth of the system if less than 50% of incident light is absorbed, i.e. if the absorbance is <0.3. This would mean that dyeings of low or moderate depth would not show the effect. A test was made with a pack of four cellulose films, each identical and dyed [12] with C.I. Direct Blue 1 with an absorbance at λ_{max} (640 nm) (ca 0.5% depth of dyeing). At the blue end of the spectrum, where most fading is likely to occur, the absorbance of each film was about 0.07. The rate of fading for the first two films, outward from the lamp, was almost identical, but a slight reduction became apparent at the third film and more so at the fourth. Thus the filter effect was beginning to be evident at absorbance values of not less than between 0.15 and 0.7, depending upon the wavelength that has the most actinic effect on this dye. This agrees with the statement of Calvert and Pitts [14]. Thus the rate of fading for films of absorbances greater than approximately 0.7 would decrease as dye concentration increases, even if the dye were monomolecularly dispersed. Actual measurements, however, on cellulosic films dyed with this dye (Figures 14 and 16, reference 5) show that the decrease is evident (i.e. the CF curve has a positive slope) even below the concentration of the individual films mentioned above. Moreover, the rate of fading for a given dye concentration increases with the degree of order in the cellulose (Figures 14, 15, 23 and 24, reference 5), thus indicating that the physical state of the dye in the substrate also influences fading.

Blair and Boyd [15] showed that the filter or layer effect operates with films of nylon dyed with model disperse dyes, and with films of cellulose dyed with direct dyes of low light fastness, in a significant paper.

Thus it seems that both the layer effect and the specific surface of the absorbed dye, discussed above, operate in determining the light fastness of many colorants, particularly those present in the substrate in very finely dispersed form, and at low depths of colour. From first principles, however, the specific surface of the colorant becomes increasingly important in the determination of light fastness as the particle size increases. This can be appreciated by considering the ideal systems illustrated in Figure 1. As more dye is introduced into the substrate, some of it will be located *alongside* that already there, rather than *above* it; thus as light passes through, new absorbing particles of dye will be located in 'parallel' with some of the original ones, rather than in 'series' with them, to use an analogy from electrical circuitry. With these new entrants, the colorant specific surface, rather than the layer effect, will be most important.

It is evident that the particle size of the colorant is an important factor in probably most systems, and an examination of the exact relation likely to be found between particle size and rate of fading should give results of wide application. A mathematical model to relate the fading rate of a colorant particle to its radius, when fading occurs by the combined action of light and oxygen, has therefore been developed.

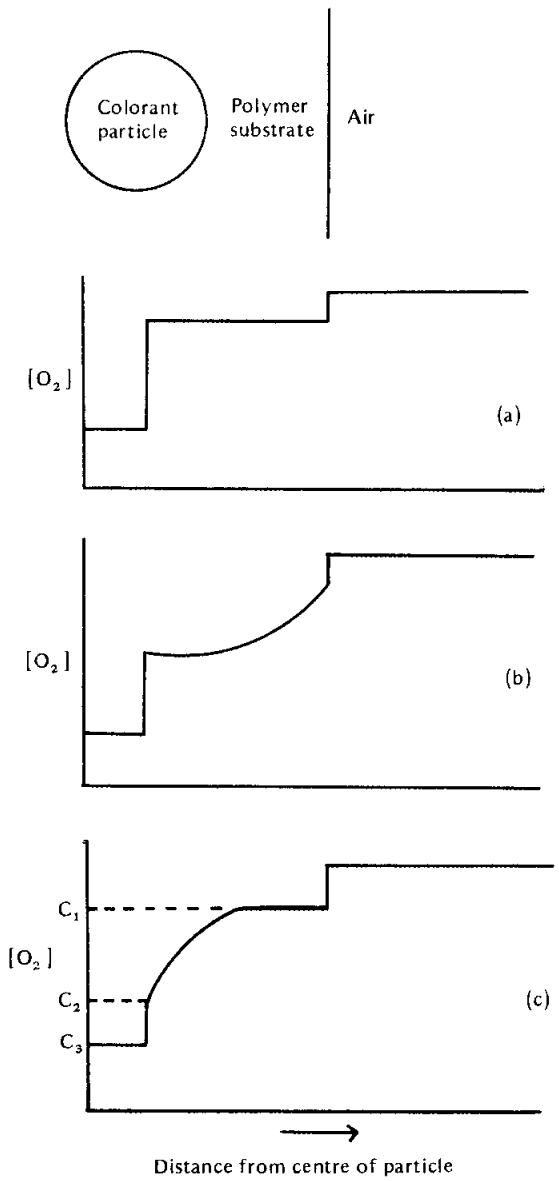

Figure 2 – The concentration gradient of oxygen between the external atmosphere and a polymer substrate containing dye or pigment particles

*The shape of the rate-of-fading curve is a better indication of the presence or absence of discrete particles of colorant, rather than molecularly-dispersed dye or small molecular aggregates. This was demonstrated by a number of experiments [12].

Theoretical Discussion

TRANSPORT OF OXYGEN

Consider the system shown in Figure 2, which represents a particle of colorant embedded deeply in a matrix of a solid polymer substrate, and in presence of oxygen, which has the concentration levels shown, varying with distance from the outer surface of the polymer in the manner illustrated. Figure 2a shows the situation in absence of diffusion control, but Figures 2b and 2c show the situation where diffusion in the substrate is the rate-controlling factor for fading. The rate-controlling effect of oxygen diffusion in the substrate has been demonstrated experimentally [13]. The steps involved in the diffusion and fading are as follows:

(i) O_2 (gas) $\overset{k_1}{\rightarrow}$ O_2 (in substrate) (= C_1, say)

(ii) O_2 (in substrate) $\overset{k_2}{\rightarrow}$ O_2 (in colorant particle) (= C_3, say)

(iii) $D^0 + h\nu \overset{k_3}{\rightarrow} D^*$

(iv) $D^* \overset{k_4}{\rightarrow} D^0$ (= C_D, say)

(v) D^* + O_2 (in colorant) $\overset{k_5}{\rightarrow}$ products.

D^0 and D^* are the ground state and excited state of the colorant molecule, respectively.

Consider the situation where diffusion from the substrate into the particle is the slowest step. On the assumption that the diffusion rate of oxygen in the colorant particle is high, or that the particle is very small, it then follows from simple thermodynamics that

$$KC_3 = C_2 \tag{1}$$

where K is a constant and C_2 is the concentration of oxygen in the substrate adjacent to the particle/substrate boundary (this ignores any possible skin effects, but will be used as a simplifying assumption).

The mass of oxygen, Q_t, passing into the particle in time t is given by the expression

$$Q_t = 4\pi Dt\frac{ab}{b-a}(C_1 - C_2) \tag{2}$$

(ref. 14) where D is the diffusion constant, and b and a the radii of the substrate and the particle, respectively, assuming both to be spherical. If, as in this case, $b \gg a$, then the expression reduces to

$$Q_t = 4\pi aDt(C_1 - C_2) \tag{3}$$

and the mass transported in unit time, into all particles per unit volume of material is given by

$$\frac{dQ}{dt} = \frac{4\pi aD(C_1 - C_2)C_D}{\rho 4/3\,\pi a^3} = \frac{3D(C_1 - kC_3)C_D}{\rho a^2} \tag{4}$$

where ρ is the sp. gr. of the colorant. Now Eqn 3 gives the rate of formation of active species:

$$\frac{d(D^*)}{dt} = I_{\text{absorbed}} = I_0 - I_T \tag{5}$$

where I_0 and I_T are the intensities of illumination before and after absorption, and Eqn 4 gives the rate of deactivation:

$$-\frac{d(D^*)}{dt} = k_4\,(D^*) \tag{6}$$

and Eqn 5 gives the rate of fading:

$$\frac{d(\text{products})}{dt} = k_5\,C_3\,(D^*) \tag{7}$$

It follows from Eqn 4 and 7 that under steady-state conditions:

$$\frac{d(C_3)}{dt} = \frac{3D(C_1 - kC_3)C_D}{\rho a^2} - k_5C_3(D^*) = 0 \tag{8}$$

and

$$\frac{d(D^*)}{dt} = (I_0 - I_T) - k_4(D^*) - k_5C_3(D^*) = 0 \tag{9}$$

The practical effect of the situation revealed by Eqn 9 can then be discussed for two limiting cases, as follows:

(I) Large Sizes of Colorant Particles

If a is large (but still much smaller than radius of the substrate and the intensity of radiation reasonably high, C_3 is small, so that from Eqn 7 and 8,

$$\frac{d(\text{products})}{dt} = k_5C_3(D^*) = \frac{3DC_1C_D}{\rho a^2} \tag{10}$$

both the rate of formation of products and the rate of fading is proportional to $1/a^2$.

Therefore, if the particle size distribution of the colorant moves in favour of the larger particles with rise in colorant concentration, as almost always appears to be the case, the stability of coloured substrates to light will rise with colorant concentration (with relatively large particle sizes). Furthermore, if the particle size distribution remains constant over a range of concentrations, as it may do in certain special cases, then the stability to light is constant; both these conclusions have been demonstrated experimentally [8, 16].

(II) Small Sizes of Colorant Particles

If the particles are composed of only single molecules or associated groups of small numbers of molecules, then a will be very small, $C_1 \rightarrow C_2$, C_3 is independent of a and thus, from Eqn 7 and 9

$$\frac{d(\text{products})}{dt} = \frac{k_5C_3(I_0 - I_T)}{k_4 + k_5C_3} \tag{11}$$

Now $\frac{k_5 C_3}{k_4 + k_5 C_3}$ is a constant and equals ϕ, the quantum yield,

so that $\frac{\text{d(products)}}{\text{d}t} = \phi (I_0 - I_T)$,

and in time t the number of molecules, Δn, of colorant decomposed per unit area of substrate is given by

$$\Delta n = (I_0 - I_T)t\phi \quad (12)$$

$$= I_0\phi t(1 - I_T/I_0) \quad (13)$$

$$= I_0\phi t(1 - 10^{-A}) \quad (14)$$

$$= I_0\phi t(1 - 10^{-C_D\epsilon^1}) \quad (15)$$

and this situation results in the layer or filter effect becoming noticeable in the change of rate of fading with colorant concentration.

In practice it appears that situation II, and consequently the layer effect, is encountered with dyes in the molecular state or as small particles, examples being direct dyes of low light fastness, and disperse dyes in hydrophobic substrates, particularly polyester fibres, and then only with depths of dyeing giving absorbances at λ_{max} of above about 0.3.

Thus it is clear that as D, and thus C_D, increases, the term in parentheses (Eqn 15) increases up to a limiting value of unity. Moreover, ϵ varies with wavelength and is at a maximum at the peak of the absorption band of the colorant. It follows from these two considerations that the slope of the plot of log t_F against log D, i.e. the CF curve, will increase with colorant concentration and will also vary with the wavelength of illumination, being highest with illumination giving greatest absorption and quantum efficiency of fading. Thus in fading under normal technical conditions, where multiwavelength irradiation is used, the slope will clearly be lower than the last-mentioned value.

(III) Intermediate Sizes of Colorant Particle

For an expression covering intermediate sizes of colorant particle, in which range many real systems would be expected to lie, Eqn 8 and 9 must be solved for (D*) and C_3, to give an expression for $k_5 C_3$(D*) independent of these terms. This solution proves to be complex and has not been included here.

On a less rigorous basis however it can be seen that as the particle size decreases from that corresponding to System I to System II, the dependence of rate of fading on particle radius moves from a factor of $1/a^2$ to a condition of independence. This can be expressed as a progression from $1/a^2$ to a^2/a^2, and therefore at some intermediate stage the factor will be a/a^2, i.e. $1/a$. A number of actual substrate/colorant systems, which show a $1/a$ dependence, would therefore be expected.

Experimental Test of the Relations

As far as the authors are aware the only recorded investigation which gave data suitable for testing the above relations between particle size and light fastness of colorants, is a recent one by Hafner [15]. This author took three pigments, each in two ranges of particle size, which were determined by electron microscopy, and followed their rates of fading in various paint binders (at equal pigment concentrations). The binders themselves influenced the light fastness to some extent, but in a given binder each pigment gave consistently better light-fastness ratings in the larger particle size variety. For two of the pigments the particle size ranges are quoted, and therefore direct comparisons can be made between size and fastness. The rate-of-fading curves tend to be irregular in shape in the early stages (a feature of many rate-of-fading curves [5]), but their slopes can be compared readily over the later portions, which are regular (Figures 3 and 4). The results can be summarized as follows:

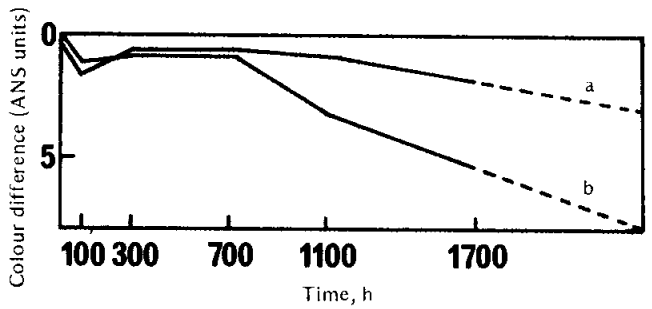

Figure 3 – Light fading (Atlas Weather-Ometer) of C.I. Pigment Orange 36 in air-drying alkyd medium [17]
(a) Large particles; (b) Small particles

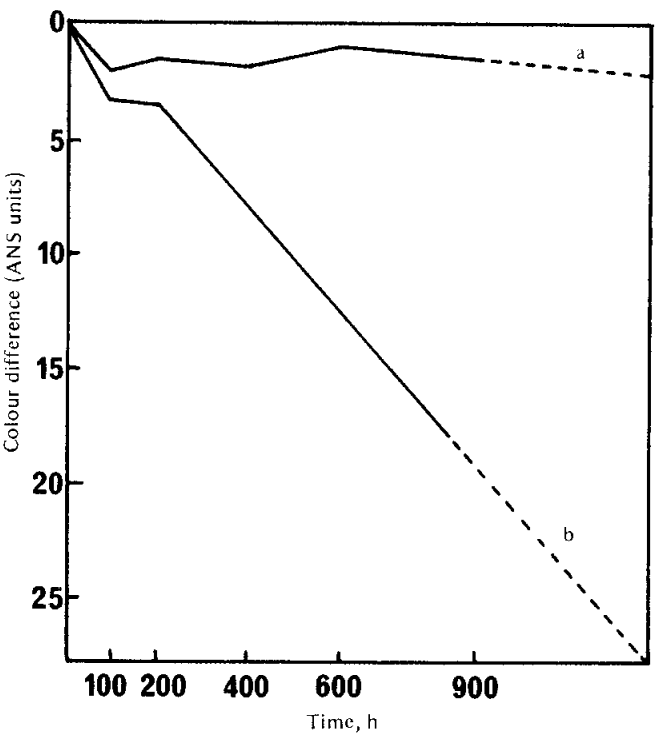

Figure 4 – Light fading (Atlas Weather-Ometer) of C.I. Pigment Yellow 83 in air-drying alkyd medium
(a) Large particles; (b) Small particles

Larger Particles

The pigment for which both size ranges were relatively large – C.I. Pigment Orange 36 – had particle sizes between 0.2 and 0.4 μm, and between 0.4 and 0.6 μm, respectively. Their rates of fading were (in air-drying alkyd) in the ratio 2.3:1, respectively. The ratio of the squares of the two mean particle

dimensions is 1:2.8, which agrees with the predicted reciprocal value from Eqn 10 above. An exact correspondence would not be expected, because the particles, as seen in the electron micrographs, are prismatic and not spherical as in the present theoretical treatment.

Smaller Particles

The second pigment for which the necessary data are given by Hafner is C.I. Pigment Yellow 83. Its particle sizes were in the ranges from 0.05–0.09 μm and 0.3–0.6 μm, respectively. Their rates of fading were (in air-drying alkyd) in the ratio 12:1. The ratio of the squares of the mean dimensions is 41.3, but that of their linear dimensions is 6.43:1. Thus the rates of fading lie between a dependence on $1/a^2$ and $1/a$, as predicted above for intermediate sizes of particle.

WATER-SOLUBLE DYES

Particle sizes, referred to as intermediate, are of the same order of magnitude as those of direct dyes of high light fastness in cellulose [2], and therefore the above treatment should be applicable to at least some types of water-soluble dye.

References

1. Giles, Baxter and Rahman, Text. Research J., **31** (1961) 831.
2. Weissbein and Coven, ibid., **30** (1960) 58, 62.
3. Bean and Rowe, J.S.D.C., **45** (1929) 67.
4. Giles and Eaton, ibid., **73** (1957) 127.
5. Baxter, Giles, McKee and Macaulay, ibid., **71** (1955) 218.
6. Giles and McKay, Text. Research J., **33** (1963) 127.
7. Barker, Hirst and Lambert, J.S.D.C., **43** (1927) 263, 264.
8. Sommer, Angew. Chem., **44** (1931) 61; Mitt. deut. Materialprüfungsanstalt, Sonderheft No. 24 (1934) 11; through Chem. Abs., **28** (1934) 5243.
9. Cunliffe and Lambert, J.S.D.C., **48** (1932) 59.
10. Desai and Giles, ibid., **67** (1951) 376.
11. Eaton, Gordon and Giles, ibid., **68** (1952) 394.
12. Giles, Johari and Shah, Text. Research J., **38** (1968) 1048.
13. Giles, Yabe and Shah, ibid., **38** (1968) 467.
14. Calvert and Pitts, 'Photochemistry' (London: Wiley, 1966) p.640.
15. Blair and Boyd, J.S.D.C., **91** (1975) 112; Idem, ibid., **92** (1976) 14.
16. Giles, Shah, Johari and Sinclair, ibid., **88** (1972) 59.
17. Crank,'The Mathematics of Diffusion' (Oxford: Clarendon Press, 1956) Chapter VI.
18. Hafner, J. Paint Tech.,**47** (1975) 64.