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Penetration of Radiation into Old Paint Films

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Introduction

The surface is of supreme importance in paintings. Where this surface film, the paint, is organic or partly so, as is the case with all easel paintings, it will be subject to deterioration by photo-oxidation. Therefore an absolutely basic requirement in the close study of painting deterioration is an understanding of the penetration of ultraviolet (UV) and visible radiation into the paint [1]. This penetration is a function of the absorption and scattering of light by the paint medium and pigment particles. The appropriate theoretical analysis has come to be known as Kubelka – Munk (K – M) analysis, after the two researchers who laid its foundation [2].

In the field of conservation K – M analysis has already been used fruitfully by van Asperen de Boer to determine the wavelength for optimum penetration of infrared radiation in the study of under-drawings on paintings, and by Johnson and Feller to discuss certain optical effects in paint films, including chalking [3,4]. However here we are interested in a more general and fundamental matter: if a paint film changes colour under the action of light, this change will be greatest at the surface, affecting subsequent penetration and therefore subsequent deterioration. Interesting phenomena such as the formation of a dark brown layer over unchanged copper ‘resinate’ green sometimes result.

The purpose of this article is to propose a basis by which such phenomena can be understood quantitatively and, very tentatively at this stage, to tie this in with actual measurements on old paint.

In summary, a method is described for calculating the intensity of UV and visible radiation within a paint film whose composition varies with depth and changes in time.

Photo-oxidation in the paint layer

A paint film, even indoors, deteriorates and is ultimately destroyed by photo-oxidation. That is to say the paint medium and certain of the pigments are slowly attacked by the oxygen in the air, and the energy for this attack arrives in the form of visible and ultraviolet radiation. If there is a shortage either of oxygen or of radiation then deterioration is reduced. In the total absence of one or the other, then the destruction, if not completely prevented, is reduced to a tiny fraction of its normal rate.

In a previous paper [5] the possibility of the lower layers of a paint film being starved of oxygen, and therefore deteriorating more slowly than the surface, was examined. It was concluded that, for these very

slow processes, oxygen always has plenty of time to diffuse into all parts of the paint. Neither is there any possibility of applying any kind of known varnish over the paint in order to reduce significantly the supply of oxygen. Of course the whole painting could be sealed within a case without oxygen, but such an elaboration of technology interferes with looking at paintings and is costly and difficult to maintain. We are also uncertain whether all the pigments in a painting would benefit from this treatment, since certain unusual colours change through reduction rather than oxidation.

By contrast radiation can be prevented access to a paint with the greatest of ease. The apparently absurd extreme of keeping a painting in the dark does this, of course, and can form part of the conservation regime: when a painting is not being looked at it need not be lit. But we can do more. During normal exhibition the UV radiation can be eliminated by placing filters over light sources [6]. For the relatively stable materials of oil paintings this will almost certainly more than halve the rate of deterioration.

The purpose of this article, however, is not so much to suggest ways of reducing radiation damage as to examine how radiation penetrates or fails to penetrate a paint. To further our study of deterioration we need to get this on a quantitative basis.

For a non-diffusing film of uniform composition the problem is elementary. But old paint films are both diffusing and non-uniform in depth. Furthermore this non-uniformity changes with time under the action of radiation, since the change is always more rapid at the surface. The mathematical treatment becomes a bit more complicated. An extreme case is the copper ‘resinate’ green pigment which turns brown. In many cases two layers have formed: a brown upper layer which is so opaque that it protects a lower layer of unchanged green [7].

The passage of radiation through a paint

A parallel beam of radiation passing through a clear absorbing film such as a piece of coloured glass gets progressively reduced in strength so that it leaves the glass weaker. Let us look at this beam at a depth x within the film. Its intensity at this point is I . As it penetrates further by a very small distance δx the absorption of the film causes a reduction in intensity of $-\delta I$. This reduction is proportional both to the intensity I and to the thickness of the thin layer δx :

$$-\delta I = k I \delta x \quad (i)$$

where k , the constant of proportionality, is known as the absorption coefficient.

Mathematically this is equivalent by integration to the standard expression for the absorption of a parallel or collimated beam of radiation:

$$I = I_0 \exp(-kx) \quad (\text{ii})$$

where I_0 is the intensity of the radiation on entry into the film, and 'exp' stands for exponential.

Unfortunately in studying paint we cannot use this well-known expression for three reasons. Firstly, paint not only absorbs radiation but scatters it; secondly, we do not usually look at paintings under a parallel beam of radiation but in conditions where it arrives from many directions; and thirdly, we look at the radiation reflected not the radiation transmitted.

To take account of scatter we have to include, not only the *absorption coefficient*, K (capital K since this absorption coefficient for diffuse conditions takes a different value from the k for a parallel beam in Equation (ii) above), but a *scattering coefficient*, S .

If we could work with a parallel beam which is both absorbed and scattered, we could still use Equation (ii), but in the expanded form:

$$I = I_0 \exp(-Kx - Sx)$$

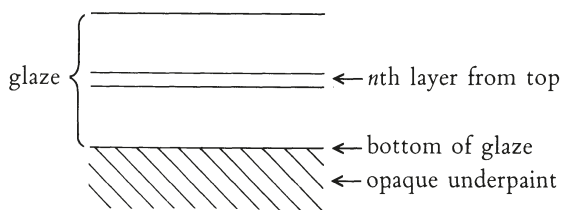
Our situation in a paint film is, however, more complicated, and at first glance might look hopeless. Radiation is coming from all directions. It enters the paint and is partly absorbed, partly scattered by each pigment particle it encounters. If we could select and follow a very narrow pencil of the radiation we would find that it underwent many such absorptions and reflections, changing direction and becoming weaker each time, and perhaps finally emerging from the paint having undergone a net change in direction

Kubelka – Munk analysis

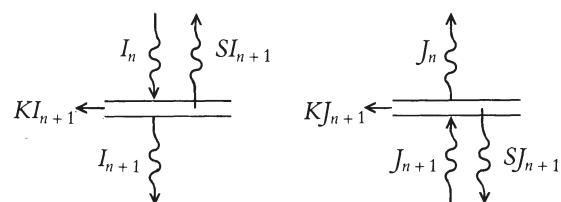
We go back to first principles: we expand on Equation (i). To reduce the complexity of a flow or 'flux' of radiation proceeding in all directions through the paint Kubelka and Munk proposed an elegant simplification. The mark of its success is that it is now to be found in all the textbooks of colour science and is still the subject of discussion and improvement. It is particularly appropriate for our purpose, since the analysis as here developed gives a measure of the total radiant flux in the film at any depth, and this is precisely what we need in photochemistry.

Kubelka and Munk divided the flux into just two components: that proceeding in a net downward direction, designated I , and that proceeding upwards, designated J .

Normally a paint is considered to be opaque. In fact the major use of K – M analysis in industry has been for formulating paints with maximum covering power at minimum cost. But the general case is a paint which is not fully opaque, in other words a glaze. This glaze is applied on top of another paint (or ground) presumed opaque.



We suppose this glaze to be composed of a large number of very thin layers, numbering down from the top, and we look at what is happening to the radiant fluxes in a single layer somewhere in the middle, number n . This n th layer is diagrammed twice below, for the downward flux I and for the upward flux J .



We form the equations from these diagrams by working upwards (for a reason which will be apparent later). Looking at the left-hand diagram for I , the diffuse downward flux entering layer n , I_n , has got to supply the continuing downward flux leaving the layer, I_{n+1} , and also fractions absorbed, KI_{n+1} , and back-scattered, SI_{n+1} . But since a fraction SJ_{n+1} from the right-hand diagram becomes downward flux this must be subtracted:

$$I_n = I_{n+1} + (K + S)I_{n+1} - SJ_{n+1} \quad (\text{iii})$$

Analysing the right-hand diagram in the same way:

$$J_n = J_{n+1} - (K + S)J_{n+1} + SI_{n+1} \quad (\text{iv})$$

These equations refer to every layer. When the downward flux I reaches the base of the glaze, a portion of it, $R_g I$, is reflected back upwards to become part of J , where R_g is the fraction reflected from the ground or underpaint.

This is the basis of K – M analysis. If we had a uniform colorant layer to deal with, we could now forget about theory and choose from among the considerable list of formulae derived from these basic equations which are to be found in the standard textbooks of colour science [8 – 10]. Unhappily, though the glaze can be assumed to start life uniform in depth, photochemistry soon brings this state of affairs to an end. We therefore pursue the alternative of using Equations (iii) and (iv) just as they stand as the basis for a computer algorithm.

The algorithm

An algorithm is a set of steps taken in order to carry out a long sequence of calculations. Here the set of steps is in the form of a program which causes a computer to repeat cycles of operations as many times as is desired. In effect we are instructing the computer to simulate, firstly, the penetration of radiation into the glaze and, secondly, its destructive effect on that glaze. The instructions cover the following sequence of events.

Diffuse radiation is sent down through the glaze, being absorbed and scattered in the process according to Equations (iii) and (iv). That radiation which penetrates as far as the paint under the glaze is diffusely reflected by it back up through the film, and more absorption and scattering occurs. Finally some fraction of the incident radiation leaves the top of the film as diffusely reflected radiation. The total radiant flux in each case of 100 layers is calculated in this way.

Now we imagine that this total radiant flux acts over a period of time sufficiently short to cause a small photochemical change in the glaze, the amount of change at each of the 100 levels being proportional to the radiant flux at that level. The product formed by this chemical change will in general have new absorption and scattering coefficients (for example, copper 'resinate' turns from translucent green to opaque brown). Very soon the result is that each of the 100 layers, having its own proportion of reactant (the original glaze) and product, will have its own absorption and scattering coefficients, K_n and S_n .

To continue with our algorithm, we have sent the radiation through the glaze, and we have allowed it to act on the glaze so as to change it slightly. We then repeat this cycle, sending the radiation once again through this slightly changed glaze to find a new flux distribution, causing this to act on the glaze, finding thereby a new product distribution, and repeating the whole process many times over.

The equation relating the total radiant flux at any level to the amount of deterioration it causes may be varied as required. The simplest and most plausible assumption is that the amount of product formed is proportional both to the total radiant flux and to the concentration of reactant:

$$\delta P_n = C(I_n + J_n)(1 - P_n) \delta t \quad (\text{v})$$

In a short period of time δt a small amount of product δP_n is formed in layer n , where P_n is the concentration of product already formed, and therefore $(1 - P_n)$ is the concentration of reactant remaining, original concentration being set at unity. C is the reaction constant.

Lastly K and S , wherever they appear in Equations (iii) and (iv), must be amended to K_n and S_n as the product builds up, K_n and S_n changing slightly after each complete cycle of operations, according to:

$$K_n = (1 - P_n)K_1 + P_nK_2 \quad (\text{vi})$$

and

$$S_n = (1 - P_n)S_1 + P_nS_2 \quad (\text{vii})$$

where K_1 and S_1 refer to reactant (for example, green copper 'resinate') and K_2 and S_2 to product (brown). K_n and S_n are the mixed absorption and scattering coefficient in layer n .

Now for any particular paint or glaze both absorption and scattering depend on wavelength, hence the colour. Photochemical deterioration also depends on wavelength. Thus all the above equations are to be applied, not to white light, but to radiation of a specified wavelength or, less rigorously, to a waveband, so long as one can be reasonably sure that

absorption and scattering coefficients, and in addition the photochemical reaction constant, hold approximately constant values through the waveband.

The algorithm can be developed as required. We are primarily interested in the distribution of flux and product with depth (Figs. 4–6). Radiation being always strongest at the surface, fading or colour change will always start at the top and work down. Sometimes, as with the copper 'resinate' glaze which is the particular subject of this article, quite a sharp division forms between unchanged reactant beneath and product on top. We would like to be able to simulate this with our algorithm. On the other hand, as a lake pigment fades it becomes more transparent and a sharp division between faded and unfaded appears less likely, since the paint becomes more transparent.

But even in the apparently simple case of the fading lake, if the fading were to depend on UV radiation and if the paint were to be strongly UV-absorbent, then it is possible that a protective layer might form here too. This emphasizes the importance of carrying out the calculation at different wavebands. What might seem transparent to us may be quite opaque to UV radiation.

Some further details of the algorithm used, designated program KM8, are given in the section headed 'Further technical details: computing'.

Penetration of radiation into an old painting

The K – M parameters, K (absorption) and S (scattering), are not easy to measure. Indeed debate continues on how to measure S [11]. The difficulty arises from the peculiar conditions required by the theory: the paint must be both illuminated and viewed diffusely. It is clear that this must be so, since light within a paint is diffuse and the theory deals wholly with diffuse fluxes, light scattered more or less evenly in all directions. Diffuse illumination is not unrealistic, being near enough for our purpose to the actual illumination of pictures in a gallery. But how can we view diffusely? The eye cannot collect light from all directions at once. We normally view pictures from directly in front of them. It must suffice to say at this stage (but see p.30) that it is not difficult to relate approximately the diffuse upward flux at the top of the paint, J as calculated from K – M analysis, to the amount of light leaving the paint as reflected light and entering the eye or a measuring instrument.

In the present case, where measurements were to be made on an old and valuable painting, the decision was made not to attempt the direct measurement of K and S , but to choose instead two parameters which could be measured conveniently. These were the top-surface reflection on the painting, and the absorption in a transparent cross-section from the same area.

From reflection measurements, J at the top of the glaze could be derived, and from the absorption of collimated light in a cross-section a figure for the penetration of diffuse radiation, I , through to the bottom of the glaze layer could be obtained.

With some trial-and-error work on a short

Table 1 Measurements at position marked on Fig.1, Piazza, No.1152.

	Wavelength								
	375	400	450	500	550	600	650	700	750 nm
Trans.% of the brown glaze in a 10-micron-thick cross-section	33.5	26.5	22	28	40	49.5	56	60	65
Measured reflection R% from Fig.2	0.85	0.85	0.80	1.0	1.4	2.1	3.1	4.8	6.8

Table 2 Trans.% of a green glaze under brown in a 10-micron transparent cross-section taken from a contemporary portrait of Elizabeth I.

	Wavelength								
	375	400	450	500	550	600	650	700	750 nm
Trans.%	43.6	45	53	71.5	77.5	72.5	61.7	59.7	65.25

Table 3 Measured reflection of a laboratory-prepared sample of copper 'resinate' green glaze over a light ground. For this rather speculative estimate only round numbers are given.

	Wavelength								
	375	400	450	500	550	600	650	700	750 nm
Measured refl.R%	5	5	10	25	30	15	5	5	7.5

computer program, values for K and S to fit these two derived parameters could be found. The full simulation program could then be run to predict how deterioration would proceed in such a film.

Measurements on a copper 'resinate' glaze

Even the tiny sample required for a cross-section cannot lightly be taken from an important part of a valuable painting. Therefore a detail near the edge of a relatively minor work, Piazza No.1152 (Fig.1) was chosen. The copper 'resinate' glaze in this detail was dark brown and painted over a light blue sky. It looked almost opaque. The hope that there would be some green remaining underneath was not, however, realized.

The necessary two parameters over a range of wavelengths were assembled as follows:

1. A reflectance curve was taken of the area in question by Mrs Bullock with the Wright – Wassall spectrophotometer (Fig.2) [12], and an estimate was made of the reflectance of the sky underpaint.
2. A sample was taken from the centre of this area and cut to a transparent cross-section of thickness approximately 10 microns by Dr Roy.
3. A transmittance spectrum for collimated light was taken on this sample, using the Leitz MPV microscope with photomultiplier, as described in [13].
4. In the absence of green copper 'resinate' in the cross-section an estimate of what its parameters would have been was obtained from experience with three previous measurements of green copper 'resinate' under brown.
5. Because of its fugitive nature we can say that, although some copper 'resinate' remains in the green

**Figure 1** No.1152. Ascribed to Martino Piazza, *S. John the Baptist in the Desert*. Measurements were made at the point marked by the arrow (top left).

Table 4 Conversion of measurements on Piazza, No.1152 and associated material.

	Wavelength								
	375	400	450	500	550	600	650	700	750 nm
Brown glaze:									
Trans.% from Table 1	33.5	26.5	22	28	40	49.5	56	60	65
Absorbance k	1.09	1.33	1.51	1.27	0.92	0.70	0.58	0.51	0.43
$5k$	5.45	6.65	7.55	6.35	4.60	3.50	2.90	2.55	2.15
I_{100}	0.43	0.13	0.05	0.17	1.0	3.0	5.5	7.8	11.6
Refl.% from Table 1	0.85	0.85	0.80	1.0	1.4	2.1	3.1	4.8	6.8
J_0	1.8	1.8	1.7	2.1	2.9	4.3	6.3	9.6	13.3
Green glaze (est.):									
Trans.% from Table 2	43.6	45	53	71.5	77.5	72.5	61.7	59.7	65.25
Absorbance k	0.83	0.80	0.63	0.34	0.25	0.32	0.48	0.52	0.43
$5k$	4.15	4.0	3.15	1.7	1.25	1.6	2.4	2.6	2.15
I_{100}	1.6	1.8	4.3	18.3	28.7	20.2	9.1	7.4	11.6
Refl.% from Table 3	5	5	10	25	30	15	5	5	7.5
J_0	10	10	20	40	50	25	10	10	15

Table 5 K and K/S corresponding to the measured parameters I_{100} and J_0

Wavelength		I_{100}	J_0	K	K/S
375 nm	Green	1.6	10	0.0345	4
	Brown	0.43	1.8	0.054	26
400 nm	Green	1.8	10	0.0335	4
	Brown	0.13	1.8	0.0665	27
450 nm	Green	4.3	20	0.0212	1.5
	Brown	0.05	1.7	0.0759	28
500 nm	Green	18.3	40	0.0073	0.45
	Brown	0.17	2.1	0.063	22
550 nm	Green	28.7	50	0.0039	0.24
	Brown	1.0	2.9	0.044	16

(Refl. of sky under glaze approx. 40%)

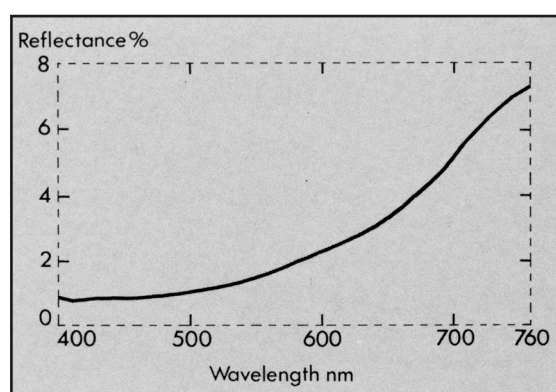
state on the surface of some old paintings, this green will certainly have changed to some extent. Therefore reflection measurements were made on samples of copper 'resinate' prepared in the laboratory.

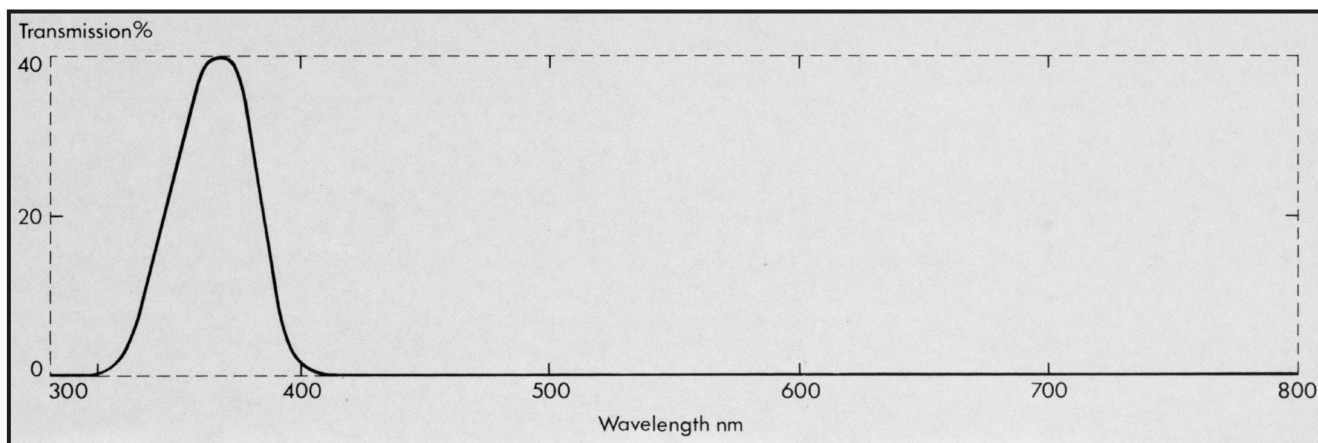
Penetration of diffuse radiation through the glaze, I_{100}

To convert from transmittance readings for collimated light through a 10-micron cross-section (Tables 1 and 2) to penetration of diffuse radiation through a 25-micron glaze (the thickness of the brown glaze on the Piazza), the effective path-length of the beam must be adjusted in two respects.

First, transmittance, T , is converted to absorbance, k , by the standard relation, $k = -\ln(T)$. (Natural logarithms, \ln , are used throughout.) k is then multiplied by $2\frac{1}{2}$ to increase the path length from 10 to 25 microns.

Second, since the path length for scattered radiation is longer than that for a collimated beam, the path length must be further increased. The factor here is 2 [11]. Thus the 10-micron path length must be multiplied by $2\frac{1}{2} \times 2 = 5$.

**Figure 2** Reflection curve at the point marked on Fig.1.



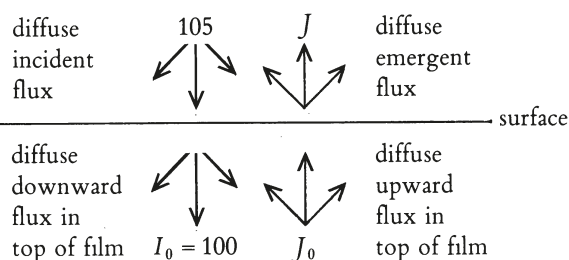
Finally we reconvert to glaze transmittance: $T = \exp(-5k)$ (Table 4). This is the figure we need for the diffuse radiation penetrating through to the bottom of the glaze. It is I_{100} , or I for the 100th layer in the computer print-outs (Figs.4–6).

Diffuse upward flux at the top of the glaze, J_0

Here we have to consider the reflections at the top surface of the glaze (plus varnish), both of radiation striking the film from outside the painting and of radiation within the glaze trying to get out. The flux figures at the top of the glaze, I_0 and J_0 refer to the flux at the top but just within the glaze.

Consider a beam striking the surface normally. Assuming a refractive index, N , of 1.54 for the top surface (for example, dammar or mastic varnish), the Fresnel equation gives a value for the radiation which never enters the glaze because it is reflected back from the surface of $((N-1)/(N+1))^2 = 4\frac{1}{2}\%$.

In the Wright instrument the beam strikes the painting normally and the diffuse radiation reflected at 45° is measured. Our K–M analysis assumes that we collect the whole of the diffuse reflection, but a comparison between measurements made under the Wright conditions and measurement of the whole of the diffuse reflection shows that the correction of $4\frac{1}{2}\%$ will apply quite well to our analysis. Thus, since the analysis starts with a downward flux within the top of the glaze of 100, the flux incident on the surface must be given the value $100/(100-4\frac{1}{2}\%)$, say 105.



A large part of the diffuse radiation which has worked its way back to the surface, and which is designated J_0 , or J for level 0 in the computer print-out, cannot get out, but is reflected back by partial or total internal reflection. There is some uncertainty in the literature as to the value to be put on this. The best we

Figure 3 (Above) The UV window for measurement at 375 nm.

KM8. TOTAL FLUX IN GLAZE.

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No.1152. Piazza.

Wavelength 550nm.

	Original			Final			
	I	J	Flux	I	J	Flux	Final Prod. Distr
0	100.000	49.754	149.754	99.999	3.756	103.756	.9999
5	94.174	46.745	140.919	79.654	3.351	83.005	.9986
10	88.679	43.899	132.579	63.533	3.068	66.602	.9922
L 15	83.495	41.208	124.703	50.806	2.858	53.664	.9778
20	78.604	38.661	117.265	40.786	2.685	43.471	.9538
25	73.989	36.249	110.238	32.908	2.528	35.436	.9208
e 30	69.633	33.965	103.598	26.710	2.378	29.089	.8806
35	65.521	31.799	97.320	21.822	2.232	24.055	.8353
40	61.639	29.745	91.384	17.954	2.091	20.045	.7872
v 45	57.973	27.795	85.768	14.876	1.955	16.831	.7382
50	54.511	25.942	80.453	12.414	1.826	14.241	.6896
55	51.239	24.180	75.420	10.432	1.707	12.139	.6426
e 60	48.148	22.503	70.651	8.826	1.599	10.425	.5976
65	45.225	20.905	66.130	7.516	1.502	9.019	.5553
70	42.460	19.379	61.840	6.442	1.417	7.859	.5157
1 75	39.845	17.922	57.767	5.555	1.344	6.899	.4790
80	37.369	16.527	53.896	4.819	1.282	6.102	.4451
85	35.024	15.189	50.214	4.204	1.233	5.438	.4140
90	32.802	13.905	46.707	3.689	1.196	4.886	.3855
95	30.695	12.669	43.364	3.256	1.170	4.427	.3595
100	28.695	11.478	40.173	2.890	1.156	4.047	.3359

Reactant 0.00390 S 0.01625 K/S 0.2400
 Product 0.04400 0.00275 16.0000
 Refl. of lower layer(R) = 40 %
 Rate const. = .00005 per unit time.
 NOTE. Photodegr. prop. to I. Print-out when layer 5 prod.].999

Proportion of product -

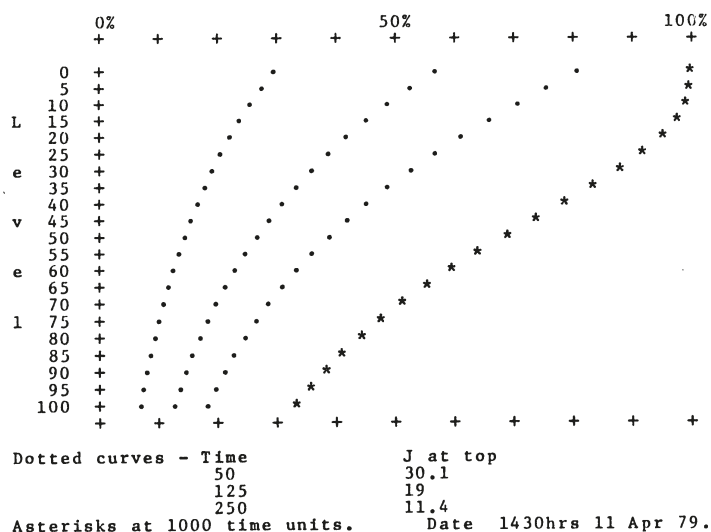


Figure 4 Print-out at 550 nm. After the numbering of every 5th level, the first three columns give, from top to bottom of the new glaze, downward flux (I), upward flux (J), and their sum, the total flux. The second three columns repeat this information for the glaze at the time given in the print-out, 1000 time units. The last column gives proportion of product in each 5th layer at this time. For the product graph, the vertical scale represents depth in the glaze, and the horizontal scale proportion of product formed at various levels from 0 to 100%. The final state curve is marked with asterisks, and various previous states selected by the program are shown dotted.

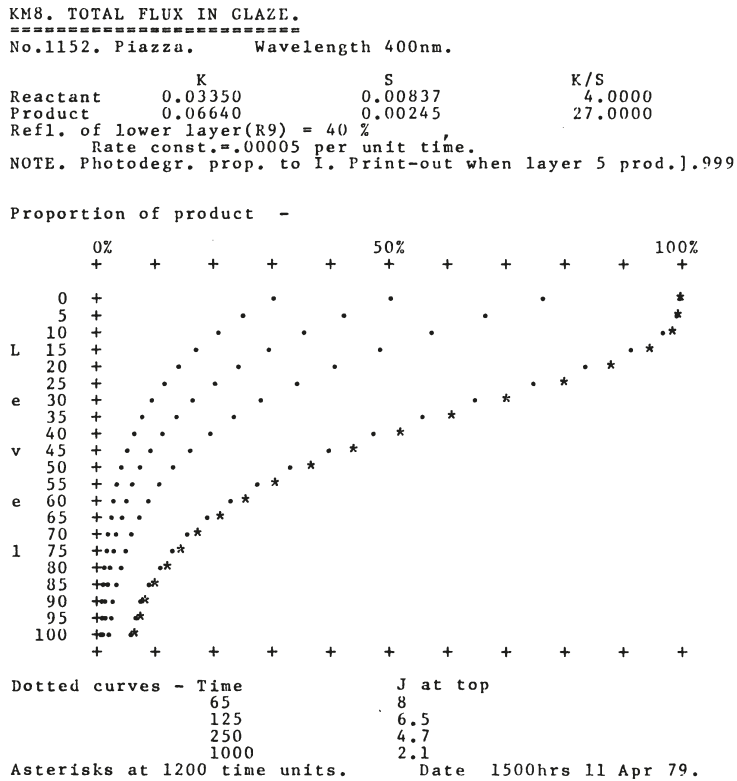


Figure 5
Product curve for 400 nm.

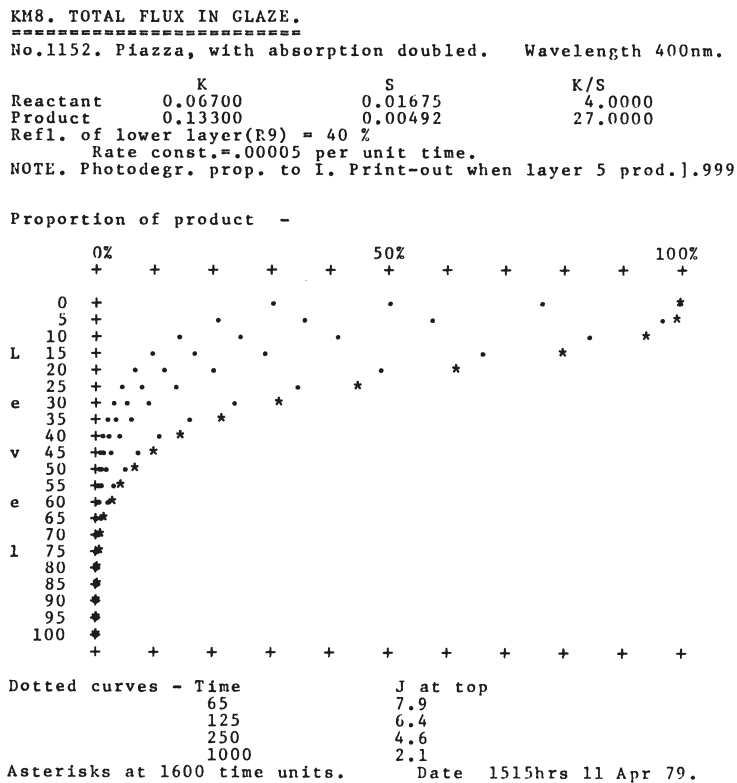


Figure 6
Product curve at 400 nm obtained by doubling K and S for both reactant and product. Thus this represents a glaze of the same composition as in Fig.4 but of double the thickness.

can do is to insert an average value of 0.5 for a coefficient in a correction due to Saunderson [14], which has been slightly modified for our purpose:

$$J_0 = \frac{J}{1-0.5(1-J)}$$

The reflection we have actually measured, $R = J/105$, and therefore:

$$J_0 = \frac{1.05R}{1-0.5(1-1.05R)} = \frac{R}{0.476 + 0.5R}$$

(Note that in applying this formula, J_0 and R are entered as fractions not percentages.)

As can be seen in Table 4, J_0 takes about double the value of R .

We have now to find a fit by trial-and-error, using a subsidiary program, between the values for I_{100} and J_0 derived from measurement and the Kubelka - Munk values we need, K and S . There is no need to go right through Table 4 because we can safely assume that photo-oxidation will be negligible at wavelengths longer than 550 nm. Results of this search are summarized in Table 5.

Further technical details: experimental

Details in this and the next section are for the record, and can be passed over for a discussion of results (p.32).

For transparent cross-sections samples were mounted in a cold-setting polyester resin with plasticizer and cut on a glass-knife microtome set to a nominal thickness of 8 microns.

For measuring light transmission through the cross-section under the microscope, wavelengths were selected at 50 nm intervals by placing narrow-band interference filters in the light beam (half-widths about 7 nm).

The photomultiplier mounted on the microscope had a useful response between 300 nm and 900 nm. To select an area of the cross-section for measurement, the cross-section was imaged at an adjustable rectangular aperture. An image of this aperture superimposed on the cross-section could be obtained, and photographed if necessary, at a subsidiary viewing position [13].

To obtain the transmittance at any wavelength, the sample was moved laterally on the stage to expose clear background through glass slide etc. to the rectangular aperture, and the photomultiplier output was adjusted to give 100 divisions deflection from the dark-current point on a mirror galvanometer. The sample was then returned to the measurement position, and the galvo deflection recorded. Note that interface reflections are the same for sample and reference, giving true transmittance values. Each reading in Tables 1 and 2 is the mean of three, agreement being usually within $\pm 1\%$ of the deflection.

For the UV reading peaking at 375 nm special arrangements were made to exclude infrared radiation. The beam from a UV lamp was passed through a

Figure 7

Selections from the programme KM8, showing input lines and equations (iii) to (vii).

Capacity required, including data arrays, 13K bytes.

For each level:

$I()$ = downward diffuse flux

$J()$ = upward diffuse flux

$K()$ = K — M absorption coeff.

$S()$ = K — M scattering coeff.

$P()$ = proportion of product formed.

$T1$ = the current time interval between calculations.

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30 PRINT "KM8. TOTAL FLUX IN GLAZE."
70 REM
250 INPUT "REACT.ABS.(K1) & ABS./SCAT.RATIO(K1/S1)", K1, R1
260 S1=K1/R1
270 INPUT "PROD.ABS.(K2) & ABS./SCAT.RATIO(K2/S2)", K2, R2
280 S2=K2/R2
290 INPUT "REFL.% OF LOWER LAYER, R9", R9

370 J(101)=R9/100
380 I(101)=1
390 FOR N=100 TO 1 STEP -1
400 I(N)=I(N+1)*(1+K(N)+S(N))-S(N)*J(N+1)
410 J(N)=J(N+1)*(1-K(N)-S(N))+S(N)*I(N+1)
420 NEXT N
430 REM Z IS NORMALIZING FACTOR.
440 Z=100/I(1)
450 FOR N=1 TO 101
460 I(N)=Z*I(N)
470 J(N)=Z*J(N)
480 NEXT N

830 FOR N=1 TO 101
840 P(N)=P0(N)+.00005*(I(N)+J(N))*(1-P0(N))*T1
850 K(N)=(1-P(N))*K1+P(N)*K2
860 S(N)=(1-P(N))*S1+P(N)*S2
870 NEXT N

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Wood's glass filter and an infrared-absorbing filter, thus selecting a UV window with maximum transmission at 375 nm and a half-width of 30 nm (Fig.3). For the dark current, a UV-absorbing filter (VE Perspex) was placed in the beam, completely occluding the UV window.

Reflection readings on the Piazza were taken following the routine procedure described in [12].

The fresh copper 'resinate' glaze of Table 3 was prepared in 1977 from 6 g basic copper acetate and 36 g abietic acid in 40 ml turpentine, heated for 1½ hours. It was painted out over various grounds.

Further technical details: computing

Selections from the program developed, KM8 in Basic, corresponding to Equations (iii) to (vii) are shown in Fig.7. It may seem perverse to number from the top downwards, which is natural, but then to work upwards. However in order to be able to start the program we have to insert the original values for I and J . I at the top of the film can be given the value 100, but what is J to be? We could run an additional search program to find this automatically, but this would be extremely time-consuming. There is no need to. The relation between I and J is fixed at one position in the glaze: at the bottom. Here J_{100} must always be $R_g I_{100}$, where R_g is the reflectance of the lower, opaque layer. In Basic this is written: $J(101)=R9*I(101)$, where $R9=R_g$. For operational reasons levels 0 to 100 are labelled 1 to 101 in the program. At the start of the program I_{100} is given the value 1, so that $J_{100}=R_g$. Having in this way obtained values by working upwards for I_0 and J_0 we normalize all values to $I_0=100$.

That 100 layers is sufficient to produce an accurate record of K — M flux distribution can be checked by comparing the upward flux at the top of the film, J_0 , with reflectance as calculated from the standard K — M formula:

$J_0 =$

$$\frac{(R_g - R_\infty)/R_\infty - R_\infty(R_g - 1/R_\infty)\exp(SX(1/R_\infty - R_\infty))}{R_g - R_\infty - (R_g - 1/R_\infty)\exp(SX(1/R_\infty - R_\infty))}$$

where $R_\infty = 1 + K/S - (K^2/S^2 + 2K/S)^{1/2}$ and is the

reflectance of an infinitely thick film with absorption K and scattering S . X is the thickness of the film.

In all cases there is agreement to 0.2% of the value, or better. Since J_0 is the last value to be computed, the flux in all layers can be relied on.

For simulation of the photo-oxidation (Equation (v)), only the simplest case has been used in the print-outs, but the equation can be modified very easily. For example some runs were made with rate of photo-oxidation proportional to the square of the flux.

To bring all computer runs to the same point of comparison, these were all terminated on the criterion: end program and print-out when layer 5 product > 0.999.

The time units on the print-outs mean nothing in real time until we can relate our arbitrary rate constant, chosen purely for convenience as 0.00005 per unit time, to real rates of degradation. For this no experimental details are yet available.

Our computer is not a fast one, a run taking about a quarter of an hour. Since the general pattern of flux change is set up early in the life of the glaze, it was arranged that the increment of time between successive calculations was steadily increased on an approximately log scale, starting at 0.25 time units and building up to a limit of 150.

The program was devised for maximum generality. Thus the units used for K and S are 'per 100th layer', a dimensionless figure. To convert K and S to real values, say 'per micron', for any desired thickness, the thickness of the glaze must be specified. Here it is 25 microns. Thus $100/25 = 4$ layers represent 1 micron, and K or S per 100th layer must each be multiplied by 4 to give K or S per micron.

Discussion of results

The first objective of these calculations is to be able to predict how the intensity of radiation (the total flux) varies with depth in an old film. To the extent that K — M theory can be relied on, this objective can be considered achieved (Figs.4–6). It is a basis for future photochemical studies on old paint.

The particular objective of the experimental test was to find out whether this numerical method would

predict a clear distinction between an upper brown layer in copper 'resinate' glazes and a lower green. We must recall that in the actual sample chosen no green remained (Figs.4 – 6).

If we examine the 'Proportion of product' graph for photo-oxidation at 550 nm (Fig.4), there is obviously no clear distinction between two layers at any time in the life of the film. Deterioration proceeds throughout the film, though naturally faster at the top. This implies that, if light at 550 nm were responsible for the oxidation as here, no two layers would form.

But the product graph for the most strongly absorbed wavelength, 400 nm (Fig.5) is less easy to interpret. Green has been changed more or less completely to brown product down to about a quarter of the depth, and green remains more or less unchanged in the lowest quarter, though it is not entirely protected from change. But the region in between is indefinite.

However suppose that the glaze had been twice as thick (50 microns) or, which amounts to roughly the same thing, that a stronger copper 'resinate' had been used with twice the absorption but the same K/S ratio. We then get Fig.6. This has a pronounced interlayer at about level 25 (at 1600 time units), and the lower half of the glaze is almost completely protected from change, and will consequently remain green. Thus in this particular example, where the glaze on the Piazza did not in practice prove quite thick enough to form a protective layer, theory and practice agree well.

The program is very flexible, so that any kind of paint deterioration can be studied by simulation, whether darkening, fading, change in transparency, surface ablation, chalking, etc. It is also possible to examine the effects of different kinds of photochemical reaction mechanism, simply by altering Equation (v). For example some runs were made with the rate of reaction proportional to the square of the light intensity. Such 'two-photon' reactions are a possibility in old paint films. They would have the effect of sharpening the boundary between reactant and product.

The input parameters that must be known, estimated or inserted by trial-and-error are the K – M coefficients, K and S for both reactant and product, making four, together with the fifth, reflection at the lower layer of paint if the layer we are investigating is not opaque. However this very flexibility makes it difficult to generalize from the results or to detect patterns of behaviour. Further study may reveal such patterns.

With the increasingly widespread use of computers, this numerical method based on the Kubelka – Munk equations could be combined with further measurements on actual old paintings as an aid to elucidating photochemical processes. As an example, figures for a very different type of paint to copper 'resinate', such as an opaque high-scattering layer made with fugitive red lake in lead white, might prove interesting.

To summarize on this and the last paper, 'Oxygen Starvation in Paint and Other Films' [5], it should

now be apparent that, whereas the lower levels of an old paint film cannot very easily be made inaccessible to oxygen, they are quite frequently almost totally protected from radiation and therefore from photo-oxidation. However, if, instead of studying the effects of oxygen and radiation separately, as in these two papers, it were thought advantageous to combine them in one simulation, there would be no difficulty in devising a program of this wide generality.

Notes and references

1. The term *radiation* is here used to cover that part of the electromagnetic spectrum emitted by light sources used in museums, both natural and artificial. It comprises ultraviolet (UV) radiation of wavelength 300 nm to 400 nm (1 nm = 1 millionth of a millimetre), visible light from 400 nm to 760 nm, and infrared radiation from 760 nm. We need not be concerned with the background of high-energy radiation, which is negligible.
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