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# Oxygen Starvation in Paint and Other Films

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Paint films both 'dry' (solidify) and deteriorate through combination with the oxygen in the air. This oxygen must diffuse into the depths of the film from the surface. If, during drying, the lower layers are starved of oxygen then their drying will be retarded. This is particularly evident in a fast-drying oil such as tung oil. The surface receives plenty of oxygen, and through combination with it forms a lightly cross-linked skin. But the lower layers are still liquid through lack of oxygen. The surface film will then soak up the lower-layer liquid just as it would do with other organic liquids. This will make it expand and wrinkle.

But a much more serious concern to the conservator is that the oxygen, having dried the film, proceeds, though very much more slowly, to destroy it. During this slow oxidation are the lower layers starved of oxygen, or could we induce starvation and hence reduce deterioration? It has often been suggested that the chemist ought to develop a varnish which could completely protect the valuable object beneath it, whether an oil painting, a mural or a Chinese bronze. Could a suitably chosen varnish at least enhance permanence?

This question can be divided into two parts. Radiation, whether ultraviolet or visible, is necessary as energy for the oxidation. Thus both oxygen and radiation must penetrate to the lower part of the film, and we can consider their penetration separately. This article concerns oxygen, but it may as well be said that the more difficult as well as the more rewarding study is the penetration of UV and visible radiation into a pigmented film. This will be described in a later article.

Oxygen starvation at any level beneath the surface of a film is conditioned by two factors: (A) the rate at which oxygen is used up at that level, and (B) the rate at which fresh oxygen can be supplied from the air by diffusion through the film. Conditions for starvation are a fast rate of oxidation and a slow rate of diffusion.

## (A) Rate of oxidation

The rate of oxidation is affected by a number of factors, each of which may gain dominance as the drying and subsequent deterioration of the film proceeds. At all stages, radiation, whether UV or visible, will be important. In order to put this variable aside for the present, we need only assume that it is always kept constant.

During the later stages of oxidation, as will be seen, there is such a plentiful supply of oxygen that small variations in this supply will not affect the rate. For

example, at a late stage of fading, when there is only a small amount of the fading pigment left, the rate will depend almost entirely on the quantity remaining.

But since our concern is to find out whether conditions of starvation exist or not at some stage we are assuming *per se* that the rate does depend on the oxygen concentration in the film. In such situations kinetic studies show that we are justified in assuming that the rate of oxidation depends directly on the oxygen concentration, to a first approximation (1-3).

The appropriate mathematical expression is the differential equation:

$$-\frac{dC}{dt} = KC \quad (i)$$

where

$C$  = oxygen concentration in the film,

$\frac{dC}{dt}$  = its rate of increase,

and

$K$  = the rate constant.

For example, if the oxygen concentration falls by a small amount, say 0.001% in 10 secs, then:

$$-\frac{dC}{dt} = \frac{0.001 \times C}{100 \times 10} \quad \text{and} \quad K = 10^{-6} \text{ sec}^{-1}$$

$K$  does not depend on the units in which we measure  $C$ , since it is a ratio. In unit time (1 sec)  $K = -dC/C$ . But of course it is important to measure oxygen uptake by the film,  $-dC$ , in the same units as oxygen solubility in the film,  $C$ .

All chemical reactions proceed faster at higher temperatures, and so  $K$  is very temperature-dependent.

## (B) Rate of diffusion

The rate of diffusion of oxygen is characterized by a relation known as Fick's Law, which we can expect to be obeyed in this case. Fick's Law states that, if we mount a film so that there is more oxygen (or other diffusant) on one side of it than on the other, the amount of oxygen diffusing through the film to the side of lower concentration is proportional to the area of the film, the time, and the concentration gradient of oxygen across the film. The concentration gradient is the difference in concentration between the two sides divided by the thickness of the film. The constant of proportionality is  $D$ , the Diffusion Constant. In this statement we are assuming, though we need not if we use a differential expression, that the concentration gradient remains constant:

$$Q = DA t(C_1 - C_2)/h \quad (ii)$$

where

$Q$  = quantity of oxygen passing through the film of area  $A$  in time  $t$ ,

$D$  = the Diffusion Constant,

and

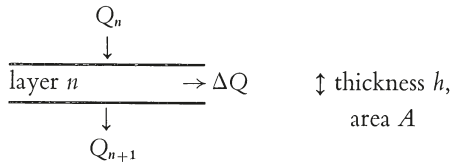
$C_1$  and  $C_2$  are the concentrations on either side of a film of thickness  $h$ , so that  $(C_1 - C_2)/h$  is the concentration gradient.

**Relating oxygen consumption to  $K$  and  $D$**

At least two solutions to this problem have been published (see the Theoretical Section on p.68), but before the author was aware of these he had developed a simple numerical method for use with a computer. Since this expresses the relation rather simply, without the use of second-order differential equations, it is described here in outline.

Let us imagine a paint film which, for the sake of simplicity, is on an oxygen-impermeable ground. The concentration of oxygen just within but at the surface of the film is equal to its solubility in the film, and remains unchanged. But as we proceed down into the film, the concentration of oxygen will decrease since it is being used up in photo-oxidation. Perhaps this will be a negligible decrease, perhaps not. It is our object to find this out.

We first imagine the film split up into a large number of extremely thin layers so that the difference between one layer and the next will be very small. We now examine how the oxygen situation changes as we go from one layer to the next:



The diagram shows any one of the layers, number  $n$ , and indicates that in time  $t$  a quantity of oxygen  $Q_n$  enters the layer, a small quantity  $\Delta Q$  gets used up by photo-oxidation in the layer, and a quantity  $Q_{n+1}$  passes on to the next,  $(n+1)$ th layer.

Thus  $\Delta Q = Q_n - Q_{n+1}$ .

For small changes  $\Delta C$  in concentration and  $\Delta t$  in time, Equation (i) can be put in the form:

$$-\frac{\Delta C}{\Delta t} = KC$$

where

$$-\Delta C = \Delta Q / (\text{volume of layer}) = \frac{Q_n - Q_{n+1}}{Ah}$$

so that, for the rate equation, we can now write:

$$Q_n - Q_{n+1} = KC_n Ah \Delta t \tag{iii}$$

For diffusion through two successive layers,  $n$  and  $n+1$ , Equation (ii) gives us:

$$Q_n = DA \Delta t (C_{n-1} - C_n) / h$$

or, for simplicity,

$$Q_n = DA \Delta t \cdot \Delta C_n / h$$

and

$$Q_{n+1} = DA \Delta t \cdot \Delta C_{n+1} / h$$

whence the difference between them,

$$Q_n - Q_{n+1} = \frac{DA \Delta t}{h} (\Delta C_n - \Delta C_{n+1}) \tag{iv}$$

Equating (iii) and (iv):

$$\frac{\Delta C_n - \Delta C_{n+1}}{C_n} = \frac{Kh^2}{D}$$

This expression can be shown to be equivalent to:

$$C_n = C_{n-1} (1 - \sqrt{Kh^2/D}) \tag{v}$$

for, if this is so (putting  $G = Kh^2/D$ ),

$$C_n = C_{n-1} (1 - \sqrt{G})$$

$$\Delta C_n = C_n - C_{n-1} = C_n \sqrt{G}$$

$$\Delta C_{n+1} = C_{n+1} \sqrt{G} = C_n (1 - \sqrt{G}) \sqrt{G}$$

therefore

$$\Delta C_n - \Delta C_{n+1} = C_n \sqrt{G} - C_n (1 - \sqrt{G}) \sqrt{G} = C_n G$$

and

$$\frac{\Delta C_n - \Delta C_{n+1}}{C_n} = G = \frac{Kh^2}{D}$$

Now Equation (v) is one which we can use directly in an algorithm which instructs a computer to simulate the passage of oxygen down through the film. Having entered values for  $K$ ,  $h$  and  $D$ , Equation (v) is used by the computer to work out the oxygen concentration in one layer from the concentration in the layer above, from the top of the film to the bottom. The result is a measure of the fall in concentration with depth, which can be summarized in the curve of Fig.1. From this curve we can deduce the approximate relation:

$$S = 3\sqrt{D/K}$$

where  $S$  is the 'starvation depth' (depth where the oxygen concentration falls to about 1/10th of its surface value).

If  $D$  and  $K$  are in cm, sec units,  $S$  will be in cm.

That  $S$  should depend on the ratio of  $D$  and  $K$  is not surprising. We have already noted that for starvation (small  $S$ ),  $D$  must be small and  $K$  large.

Those familiar with the method of dimensions will see that with  $D$  measured in  $\text{cm}^2 \text{sec}^{-1}$  and  $K$  in  $\text{sec}^{-1}$ , the square root of their ratio has the unit of length.

**Conclusions**

There is a fuller discussion of the derivation of the formula  $S = 3\sqrt{D/K}$  in the Theoretical Section below, and of its verification in the Practical Section following. Finally, in the section 'Starvation depth in old oil films' the possibility of oxygen starvation is examined and rejected for a normal stable mature oil or tempera paint. Neither does it seem practical to reduce oxidation of the paint medium to a worthwhile extent by applying a varnish chosen for its low permeability to oxygen, such as polyvinyl alcohol. However there does remain the possibility that very unstable films could be aided in this way.

The question of whether the above arguments apply to the pollutant gases, such as sulphur dioxide, nitrogen dioxide or ozone, must remain open. These larger molecules are likely to have lower diffusion

constants, but the figures are not available in the literature. In the absence of these figures one tends to assume that, here also, we are not likely to encounter starvation.

Finally, as was mentioned at the beginning of this article, 'radiation starvation' in the lower layers of a paint is an entirely different matter. Fortunately for our works of art, it is quite usual. But this is another topic which will be dealt with elsewhere.

## Theoretical

Since the rate of oxidation of polymers is of considerable practical interest in their fabrication and use, there have been theoretical attempts to relate thickness of sample to diffusion-limitation of oxygen. Not surprisingly these have been mainly concerned with thermal oxidation at temperatures high enough for the rate of oxidation to become measurable in the laboratory.

Earlier attempts were too specific to be of general value (4), but two useful conclusions, one a very generalized equation (5), and one quite close to our particular needs (3) will be briefly described. They agree closely, both with each other and with the computer algorithm described earlier in this paper.

Both  $K$ , reaction rate constant, and  $D$ , diffusion constant, are temperature-sensitive, but their values at any temperature can be calculated from the Arrhenius equation, provided that the appropriate Arrhenius factors and activation energies are known. To a first approximation, in the temperature range we are considering, the solubility of oxygen in polymer films does not vary greatly with temperature.

[1] French and Rosborough (3) noted that, in the heat-aging of a carboxyl-terminated polybutadiene, oxidation darkened the colour of the resin so that the boundary between oxidized and unoxidized resin could be clearly seen and measured in cross-section. This is the boundary between starvation and no starvation. They deduced the relation:

$$x = (C_0 \pi D / 2KC)^{1/2} [1 - (C/C_0)]^{3/2}$$

where

$C_0$  = the concentration of oxygen in the surface,  
and

$C$  = the concentration of oxygen at depth  $x$ .

Putting  $C/C_0 = 0.1$  (i.e. 10%) at  $x = S$

$$S = 3.4 \sqrt{(D/K)}$$

[2] Wilson's equation (5) allows for the calculation of the build-up of oxygen in the first stages of oxidation:

$$\frac{C_0}{C} = \frac{\sinh x (K/D)^{1/2} + \sinh (h-x)(K/D)^{1/2}}{\sinh h(K/D)^{1/2}} + \sum_{n=1,3,5}^{\infty} \frac{4C_0 K \sin(n\pi x/h)}{(Dn^3\pi^3/h^2) - n\pi k} \cdot \exp[-Kt - Dn^2\pi^2 t/h^2]$$

For large  $t$  (i.e. when the oxygen concentration has settled down to a steady state), this can be simplified to:

$$C/C_0 = \frac{E_1 - E_2}{E_3 - E_4} [1 - \frac{1}{2}(E_3 + E_4)] + \frac{1}{2}(E_1 + E_2)$$

where

$$E_1 = e^{xy} \quad E_2 = e^{-xy}$$

$$E_3 = e^{hy} \quad E_4 = e^{-hy}$$

and

$$\gamma = \sqrt{(K/D)}$$

Rather than manipulate this equation to make it explicit in  $x$  it is quicker to run a program giving  $C/C_0$  throughout the film for various values of  $h$ ,  $K$  and  $D$ . The results fit, with French and Rosborough and the author's algorithm, on the curve of Fig. 1.

In using the theoretical result from this curve,  $S = 3 \sqrt{(D/K)}$  its very approximate nature should be borne in mind. Even allowing for perfect Fick-type diffusion, it takes no account of

the factors other than oxygen concentration which might influence the rate of oxidation, in particular the accumulation and diffusing-away of oxidation products. Nevertheless, as the results of the Practical Section show, it is accurate enough for our purposes.

## Practical

All published results with the relevant data known to the author appear in Table 1.

If the data available make it more appropriate, another form of the equation for starvation depth may be used, replacing the diffusion constant,  $D$  by the permeability constant,  $P$ .

Let

$R$  = experimental rate of oxygen consumption in  $\text{ml}_{\text{STP}} \cdot \text{g}^{-1} \cdot \text{sec}^{-1}$

$U$  = solubility of oxygen in the film in  $\text{ml}_{\text{STP}} \cdot \text{g}^{-1}$  per  $\text{cm} \cdot \text{Hg}$

$p$  = oxygen pressure in  $\text{cm} \cdot \text{Hg}$

$P$  = the permeability constant in  $\text{cm}^2 \cdot \text{sec}^{-1}$  per  $\text{cm} \cdot \text{Hg}$

Then

$$K = \frac{R}{U \cdot p} \text{ and } D = \frac{P}{U}$$

(The relation between  $D$ ,  $P$  and  $U$ , though commonly used in diffusion studies, may not be intuitively obvious (e.g. see (9) pp.45-6).)

Hence an alternative form for starvation depth is:

$$S = 3 \sqrt{(Pp/R)}$$

This is the form used in Tables 1 and 3.

The variation of  $P$  with temperature can be calculated from the Arrhenius equation, as with  $D$ . In fact, activation energies for  $P$  are not on the whole available, and I have assumed them to be approximately similar to those for  $D$  (see, for example (10)). Activation energies for both  $P$  and  $D$  are not only close to each other, but do not vary greatly from polymer to polymer.

Figures for  $P$  are from (11), and for activation energy (of diffusion) from (12). Bearing in mind not only the causes of inaccuracy mentioned at the end of the Theoretical Section, but the latitude we must give to the permeability data, the agreement between theory and practice can be said to be reasonable enough for our purpose.

## Starvation depth in old oil films

In this section we must make some rather crude estimates, since neither the permeability nor the oxidation rate of old oil films have been measured. It will help first of all to tabulate starvation depth against rate of oxidation.

Using the formula

$$S = 3 \sqrt{(Pp/R)}$$

and putting

$t$  = time in secs for 1% oxidation by weight

and

$$p = 15 \text{ cm} \cdot \text{Hg}$$

then

$$R = \frac{0.01 \times 22400}{32t} \text{ ml} \cdot \text{g}^{-1} \cdot \text{sec}^{-1}$$

giving

$$S = \text{about } 4.5 \sqrt{(Pt)}$$

Table 2 gives the permeability coefficients for a number of common polymers. Most of these are bracketed within the range  $(0.3 \text{ to } 30) \times 10^{-10}$ , and an old oil film is much more likely to be at the high end of this range. Table 3 can then be constructed:

No paint film could last for centuries with a rate of oxidation of 1% per month or faster. Therefore oxygen starvation would appear not to operate in stable mature oil or tempera paint.

Does the possibility remain of coating a painting with a highly impervious varnish to reduce the rate of oxidation?

**Table 1**

No.	Polymer	Temp (°C) <i>T</i>	Oxygen pressure (cm Hg) <i>p</i>	Experimental rate of oxygen consumption in ref.	Rate in ml <sub>STP</sub> g <sup>-1</sup> sec <sup>-1</sup> <i>R</i>	Assumed values			Starvation depth, <i>S</i>		Ref.
						Activation energy for permeability (kcal mole <sup>-1</sup> )	Permeability at 25°	Permeability at <i>T</i> °	Experimental	From $S = 3 \sqrt{\left(\frac{Pp}{R}\right)}$	
1	High-density polyethylene	157°	65	6 × 10 <sup>-4</sup> g g <sup>-1</sup> min <sup>-1</sup>	7 × 10 <sup>-3</sup>	9	0.7 to 1.1 × 10 <sup>-10</sup>	7.2 to 11.3 × 10 <sup>-9</sup>	100–200 μ	245–305 μ	(6) Fig. 5
2	Polypropylene	130°	76	8 × 10 <sup>-4</sup> g g <sup>-1</sup> min <sup>-1</sup>	9.3 × 10 <sup>-3</sup>	9	0.4 to 2.3 × 10 <sup>-10</sup>	2.0 to 11.7 × 10 <sup>-9</sup>	100–200 μ	120–290 μ	(6) Fig. 5
3	Polypropylene	150°	76(?)	1.8 ml <sub>STP</sub> g <sup>-1</sup> min <sup>-1</sup>	0.03	9	0.4 to 2.3 × 10 <sup>-10</sup>	2.7 to 15.4 × 10 <sup>-9</sup>	5 mil (125 μ)	90–210 μ	(2) Fig. 2
4	Docos-1-ene under gamma radiation	25°	atmos. = 15	av. of four = 11.47 μmoles g <sup>-1</sup> hr <sup>-1</sup>	3.7 × 10 <sup>-4</sup>	9	10 <sup>-10</sup>	10 <sup>-10</sup>	greater than 30 μ	60 μ	(7)
5	Polybutadiene	50°	76	0.714 ml <sub>STP</sub> g <sup>-1</sup> hr <sup>-1</sup>	2.0 × 10 <sup>-4</sup>	7	19 × 10 <sup>-10</sup>	4.75 × 10 <sup>-9</sup>	greater than 0.7 mm	1.25 mm	(8) Fig. 10
6	Neoprene gum	100°	atmos.	15 ml <sub>STP</sub> g <sup>-1</sup> in 400 hrs	1.04 × 10 <sup>-5</sup>	9.5	3.9 × 10 <sup>-10</sup>	9.5 × 10 <sup>-9</sup>	greater than 1.15 mm	3.5 mm	(4) Fig. 16

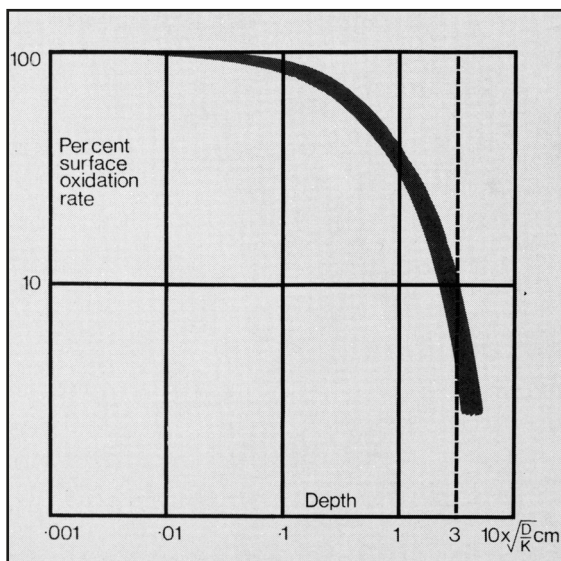
**Table 3**

Time for 1% oxidation	1 minute	1 hour	1 day	1 month	1 year	100 years
Starvation depth, <i>S</i>	2–20 μ	15–150 μ	70–700 μ	0.4–4mm	1.5–15mm	1.5–15cm

**Table 2** Permeabilities of some common polymers in cm<sup>2</sup> sec<sup>-1</sup> (cmHg)<sup>-1</sup>. Multiply all figures by 10<sup>-10</sup>. (cmHg<sup>-1</sup> indicates that the figures are for a pressure difference of 1cm of mercury.) (11).

Polymer	<i>P</i> × 10 <sup>10</sup>
Natural rubber	20–24
Polybutadiene	19
Neoprene	3.9
Polycarbonate	2–3.9
Low-density polyethylene	2.1
Butyl rubber	1.3
Teflon	1.3
Polyvinyl acetate	1.2
Polypropylene	0.4–2.3
Polystyrene	0.6–1.7
High-density polyethylene	0.7–1.1
Cellulose acetate	0.4–0.8
Polymethyl methacrylate	0.1
Polyethylene terephthalate (Mylar)	0.03–0.05
Nylon 6,66	0.03
Polyvinylidene chloride	0.0006–0.008
(Polyvinyl alcohol at normal RH estimated similar to polyvinylidene chloride)	

**Figure 1.** Generalized curve for oxidation versus depth (log scales). The width of this curve covers the small variations between the formulae of Wilson (*s*), French and Rosborough (3) and the author. If we take starvation depth *S* as the depth in cm for 10% of the surface oxidation rate, then  $S \approx 3 \sqrt{(D/K)}$  from this curve. Whether the film is free or on an impermeable ground makes only a small difference to *S*.



In the short term oxygen starvation induced in this way can be demonstrated by preparing a copper resinate glaze in oil, allowing it to dry, then coating it with a thin varnish of polyvinyl alcohol. Exposure to UV radiation will then cause the oil medium to reduce the green copper resinate to a colourless cuprous form. If the polyvinyl alcohol is now stripped off, the cupric green colour will return within minutes. But in the long term the parameters are very different.

Since we are already likely to have an oxidation rate of considerably better than 1% per month, we might suppose a reasonable benefit would amount to 1% in 10 years:  $t = 3 \times 10^8$  secs. A varnish film of  $50 \mu$  ( $50 \times 10^{-4}$  cm), though thick, might be acceptable.

$$\text{Then } P = \frac{S^2}{(4.5)^2 t} = 4 \times 10^{-15}$$

The best oxygen barriers among the thermoplastics are polyvinyl alcohol and polyvinylidene chloride, at about  $10^{-13}$ , so that our objective is beyond range, though there remains the possibility of aiding a very unstable film.

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