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## The effect of relative humidity and pigment type on paint films<sup>☆</sup>

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### Abstract

The Courtauld Institute of Art in London has initiated a project to determine the moisture content of ten differently pigmented paint films [1]. This was carried out by exposing the paint films to varying conditions of relative humidity and weighing the paint films at selected time intervals until they reached equilibrium moisture content. The rationale for this is to provide paintings' conservators with data on the moisture response of paint films. Moisture is used in conservation treatment to remove surface deformations on paintings [2, 3]. A measure of the time to reach equilibrium moisture content and the quantity absorbed in terms of weight uptake for different pigment types is of importance. Diffusion coefficients for moisture sorption of these paint films have also been calculated for different relative humidity values and pigment type. The aim of this paper is to use thermogravimetry (TGA) to continuously monitor the increase in mass with moisture uptake as a function of time for a given temperature and relative humidity.

The paint films were provided by the Courtauld Institute of Art. They had been prepared in 1991 from mixtures of prussian blue and basic lead carbonate oil-based tube paints in different proportions. The paint films were conditioned at 20°C and at 30%, 60%, 75% and 85% RH. The electrical properties of the same paint films were then studied by low frequency dielectric spectroscopy (LFDS) over the frequency range  $10^{-4}$  to  $10^5$  Hz. LFDS was selected because it is non-destructive and it gives additional information on the structure and behaviour of multicomponent complex systems.

One of the measured parameters, the critical frequency, was found to increase with increasing values of relative humidity and moisture content. It was shown that values for both the capacitance and conductance increased with increases in relative humidity. The dielectric

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responses indicated that adsorbed water layers formed on the interior surfaces of one of the components of the paint films. The observed effect was much greater in the prussian blue than in the basic lead carbonate paint films and so it can be deduced that the adsorbed water layers are in fact formed on the surfaces of the pigment grains. This was further substantiated by direct temperature-resolved pyrolysis mass spectrometry (DTMS) where it has been shown that there is a reduction in the long chain fatty acids (e.g. stearic, palmitic) in the hydrated samples. A model is presented to describe the “charge hopping” process which occurs in the adsorbed water layers and which gives rise to the low frequency dispersion.

*Keywords:* Direct temperature-resolved pyrolysis MS (DTMS); Low frequency dielectric spectroscopy; Moisture content; Paint films; Pigments; Relative humidity; TCA

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## 1. Introduction

The mixtures of pigments basic lead carbonate and prussian blue were used since there is currently interest in the fading and colour change of prussian blue [4]. When the invention of prussian blue was announced in 1710, the pigment was described as durable in both oil and watercolour and unchanged by atmospheric conditions. However, the reputation of prussian blue as a durable pigment was not maintained throughout the century, and it appeared as though an admixture of the pigment with a large quantity of white had some influence on its stability. Prussian blue is commonly used in mixtures with basic lead carbonate in pigmented areas of skies. Recent studies have reported examples of faded prussian blue in 18th century oil paintings, Canaletto's ‘Stonemason's Yard’ (NG 127) and ‘Venice: The Upper Reaches of the Grand Canal with San Simeone Piccolo’ (NG 163) [4], paintings which are considered to be great masterpieces of Canaletto's early maturity and which are part of the National Gallery's collection in London. In view of this, paint films containing mixtures of prussian blue and basic lead carbonate (flake white) paints were prepared to evaluate their behaviour in respect of moisture. The pigment volume concentrations of these paints have been determined by thermogravimetry and the glass transition and softening temperatures will be reported in another paper in this volume.

## 2. Experimental

### 2.1. Samples

Samples were cast from prussian blue (PB) and basic lead carbonate (flake white, FW) tubes of artists' oil colour paints (Winsor and Newton, London) and their mixtures in different proportions (PF1, PF2 and PF3). The paint films were prepared in January 1991 by A. Phenix of the Courtauld Institute of Art. Fig. 1 shows the tube paints together with the range in colour intensity.

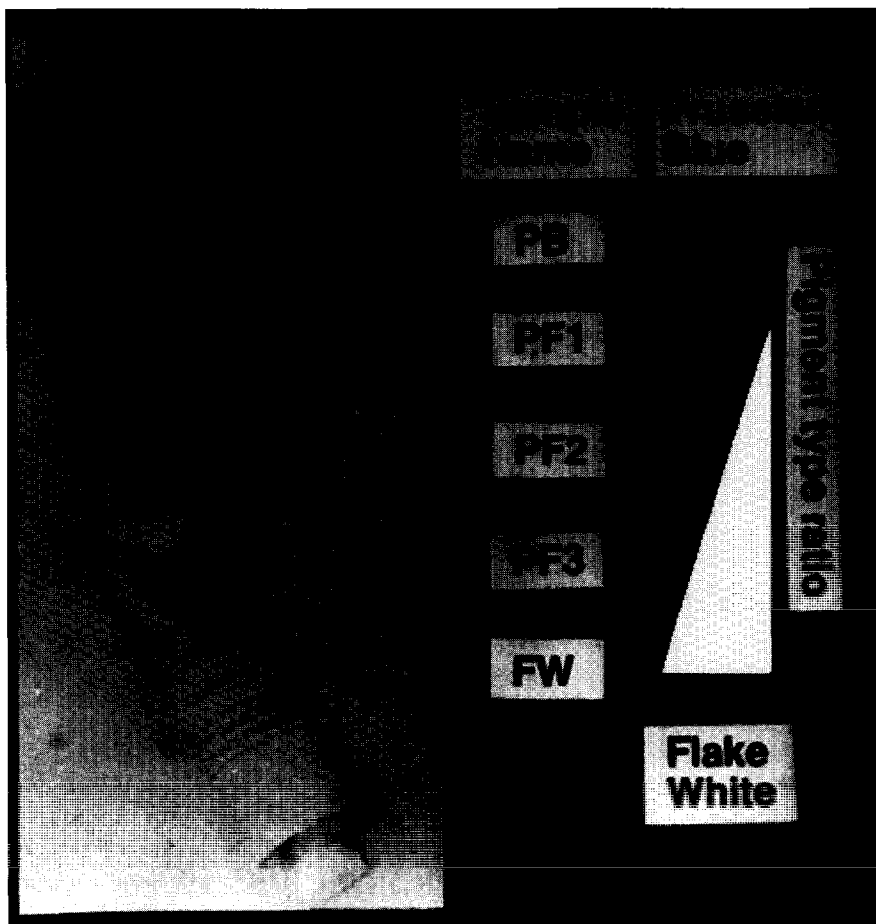


Fig. 1. Photograph of artists' tube paints and paint films.

## 2.2. Thermogravimetry

In order to study the process of moisture uptake the weight of the sample was recorded by a Shimadzu TGA-50 thermogravimetric analyser (TGA) as a function of time. The prepared paint films were of a thickness of  $100\ \mu\text{m}$ . They were cut into square pieces of  $5 \times 5\ \text{mm}^2$  and loaded vertically into a platinum crucible. This was suspended in a platinum stirrup attached to a quartz hook. The sample was heated at a constant rate of  $10^\circ\text{C}\ \text{min}^{-1}$  up to  $110^\circ\text{C}$  under a stream of dry nitrogen and kept for 30 min to remove the physically adsorbed moisture. The sample was then subjected to a conditioned atmosphere, which was generated as described below, and the weight of the

sample under test was recorded every five minutes. The measurement system was automated by use of an IBM 486 computer.

A sulphuric acid solution (30% by weight) was placed into a flask. A conditioned atmosphere was generated by using a peristaltic pump to bubble air into the sulphuric acid solution. The air (at about 75% RH) was then cycled through the sample chamber of the TGA and the enclosed system of the flask at a rate of  $100\text{ cm}^3\text{ min}^{-1}$ . The temperature of the sulphuric acid solution was controlled by a water bath set to laboratory temperatures. The TGA was also maintained at this temperature. A purge gas of nitrogen at a flow rate of  $60\text{ cm}^3\text{ min}^{-1}$  was allowed to flow through the balance mechanism both during and after measurement. The experimental system was allowed to equilibrate overnight before measurements were started on the sample. Sorption isotherms of the five paint film samples were studied at 78% RH (as measured by an RH sensor at the end of the experiment).

The measurements were performed for sufficiently long periods to allow samples to reach their equilibrium moisture content. Initially all isotherms appeared to follow Fick's law and so diffusion coefficients were calculated using the equation derived from Fick's law [5]. Assumptions were made that the moisture sorption was diffusion-controlled with a constant value for the diffusion coefficient and that the sample was not swollen by water during the humidification process.

### 2.3. *Low frequency dielectric spectroscopy (LFDS)*

This technique measures the electrical properties of a material when subjected to an alternating field and has been described elsewhere [6]. The technique is non-destructive and gives additional information on the structure and behaviour of multicomponent complex systems. The test samples (free unsupported films) were conditioned in a desiccator to the appropriate RH which was monitored by a hygrometer. The length of time was such that it allowed the sample to reach equilibrium moisture content. This could be verified in the case of the sample tested at about 75/78% RH where the information was provided by thermogravimetry. Each sample was clamped between a pair of brass shim electrodes and then between two pieces of a PTFE block to form a sample cell. The sample cell was then placed in a modified desiccator conditioned to four RH values (30%, 60%, 75% and 85%) before and during measurement. The desiccator was kept in the environmental chamber to maintain the required temperature.

The samples were measured using a dielectric spectrometer (Dielectric Instrumentation Ltd., Herts, UK). A voltage of 1 V r.m.s. was applied and the returning signal analysed over a frequency range of  $10^5$  to  $10^{-4}$  Hz at a temperature of 20°C. A Solartron frequency response analyser (FRA, Solartron, London, UK) was used in conjunction with a measuring box (Chelsea Interface, Chelsea Dielectric Group, London, UK) to generate a signal. The signal was passed through the sample and subsequently analysed by the FRA to enable calculation of capacitance ( $C$ ) and the loss ( $G/\omega$ ), where  $G$  and  $\omega$  refer to the conductance of the system and the angular frequency, respectively.

### 3. Results

#### 3.1. Calculation of diffusion coefficients from previous studies

Initially calculations were carried out using the data previously collected on the naturally aged paint films at the Courtauld Institute of Art [1]. These paint films have been aged for a longer period of time (ca. 12 years) than the ones used in this study (ca. 3 years) and they are thicker (250  $\mu\text{m}$  compared to 100  $\mu\text{m}$ ). The values of the diffusion coefficients are give for flake white and prussian blue in Table 1. The values of the coefficients were calculated from the time required for the samples to reach half of their equilibrium moisture content ( $t_{1/2}$ ) during the moisture uptake process. With increasing pigment volume concentration such as in the case of the flake white (low medium content) there is an increase in the value for the diffusion coefficients. Though the trend with increasing values of relative humidity does not show a simple linear increase, there are some indications that values do increase (e.g. prussian blue from 52% and  $1.36 \times 10^{-9}$  to 90% and to  $2.91 \times 10^{-9}$ ). This may be due to the measuring procedure involved and that the weight uptake was recorded at various intervals or it may be that the relationship with increasing relative humidity due to the pigmentation is more complex.

#### 3.2. Thermogravimetry

Sorption isotherms of the five paint film samples studied at 78% RH (as measured by an RH sensor at the end of the experiment) and laboratory temperatures are shown in Fig. 2. The diffusion coefficients which were calculated in the same manner are shown in Table 2. The order of magnitude is similar to that observed previously for paint films and there is once again some variation with differences in pigmentation and relative humidity values.

Table 1  
The values of the diffusion coefficients for flake white and prussian blue

Relative humidity/%	Diffusion coefficient/( $\text{cm}^2 \text{s}^{-1}$ )	
	Prussian Blue	Flake White
< 4–17	$1.29 \times 10^{-9}$	$6.21 \times 10^{-9}$
17–32	$1.72 \times 10^{-9}$	$4.31 \times 10^{-9}$
32–52	$1.36 \times 10^{-9}$	$3.97 \times 10^{-9}$
52–72	$1.25 \times 10^{-9}$	$4.31 \times 10^{-9}$
72–82	$1.36 \times 10^{-9}$	$2.76 \times 10^{-9}$
82–90	$2.91 \times 10^{-9}$	$2.46 \times 10^{-9}$
90–94	$1.29 \times 10^{-9}$	$5.54 \times 10^{-9}$
94–100	–	$7.45 \times 10^{-10}$

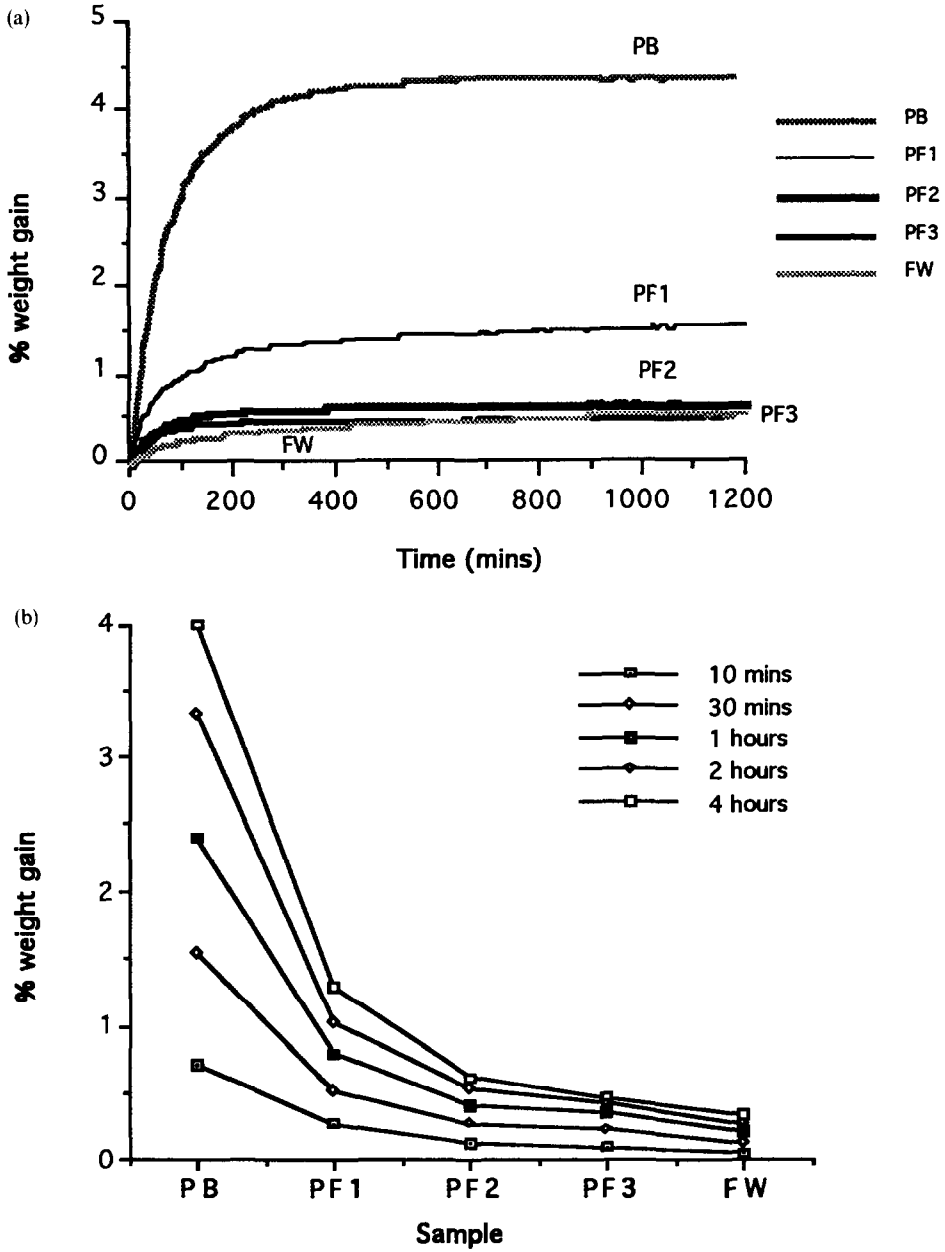


Fig. 2. (a) Sorption isotherms of unsupported paint films at 78% RH and laboratory temperature; (b) percentage weight gain of unsupported paint films at 78% RH and laboratory temperature.

Table 2

The values of the diffusion coefficients at 78% RH and laboratory temperature

Sample	Thickness/mm	Diffusion coefficient/( $\text{cm}^2 \text{s}^{-1}$ )
PB	0.117	$2.1 \times 10^{-9}$
PF1	0.128	$2.2 \times 10^{-9}$
PF2	0.132	$3.2 \times 10^{-9}$
PF3	0.118	$3.0 \times 10^{-9}$
FW	0.139	$1.2 \times 10^{-9}$

### 3.3. Low frequency dielectric spectroscopy

The spectral form of the complete dielectric response remains unaltered with variation of humidity (Fig. 3). The frequency,  $\omega_c$ , at which the real ( $C$ ) and imaginary ( $G/\omega$ ) components of the response are numerically equal shifts through several orders of magnitude. It is called the critical frequency ( $\omega_c$ ) and it describes the rate of the charge transport processes occurring in the system. Fig. 4 shows the variation of  $\omega_c$  with moisture content, calculated from the thermogravimetry data at 1200 min (Fig. 2a) for the range of pigmented films at equilibrium moisture content at RH 78%. This frequency could be used as a parameter to indicate the water content of the system.

Results show there are two separate regions of frequency-dependence. These are known to characterise two different physical mechanisms, of which the low frequency one may be regarded as being primarily associated with the process of “charge hopping” in the material, giving values of the exponent in the typical range  $0.6 < p < 0.8$ , while the high frequency process is more closely linked with properties related to dipole relaxation [7]. It is further known that the presence of low frequency dispersion response (LFD) can be associated with water present as an adsorbate [8]. In polymers, for example, it is known that water diffuses into the materials relatively easily and adsorption may occur at the interface between the crystalline and amorphous regions. It is therefore probable that the observation of LFD in all the hydrated samples is a consequence of the formation of adsorbed water layers on the interior surfaces of one of the components [8].

Fig. 5 shows variation of critical frequency with pigment type so that values are highest for the unmixed pigment films (prussian blue and flake white) for both 30% and 60% RH. Values decrease for mixtures and for flake white treated with ammonia. It is clear that  $\omega_c$  (critical frequency) is also influenced by the manner in which moisture sorption is affected by pigment type and medium content. Since the observed effect is much greater in the prussian blue than in the basic lead carbonate paint films, it can be deduced that the adsorbed water layers are, in fact, formed on the surfaces of the pigment grains. This is further substantiated by direct temperature resolved pyrolysis mass spectrometry (DTMS) discussed below. Values of the diffusion coefficients of these paint films at the different relative humidities have also been calculated for different RH and pigment type (Table 2).

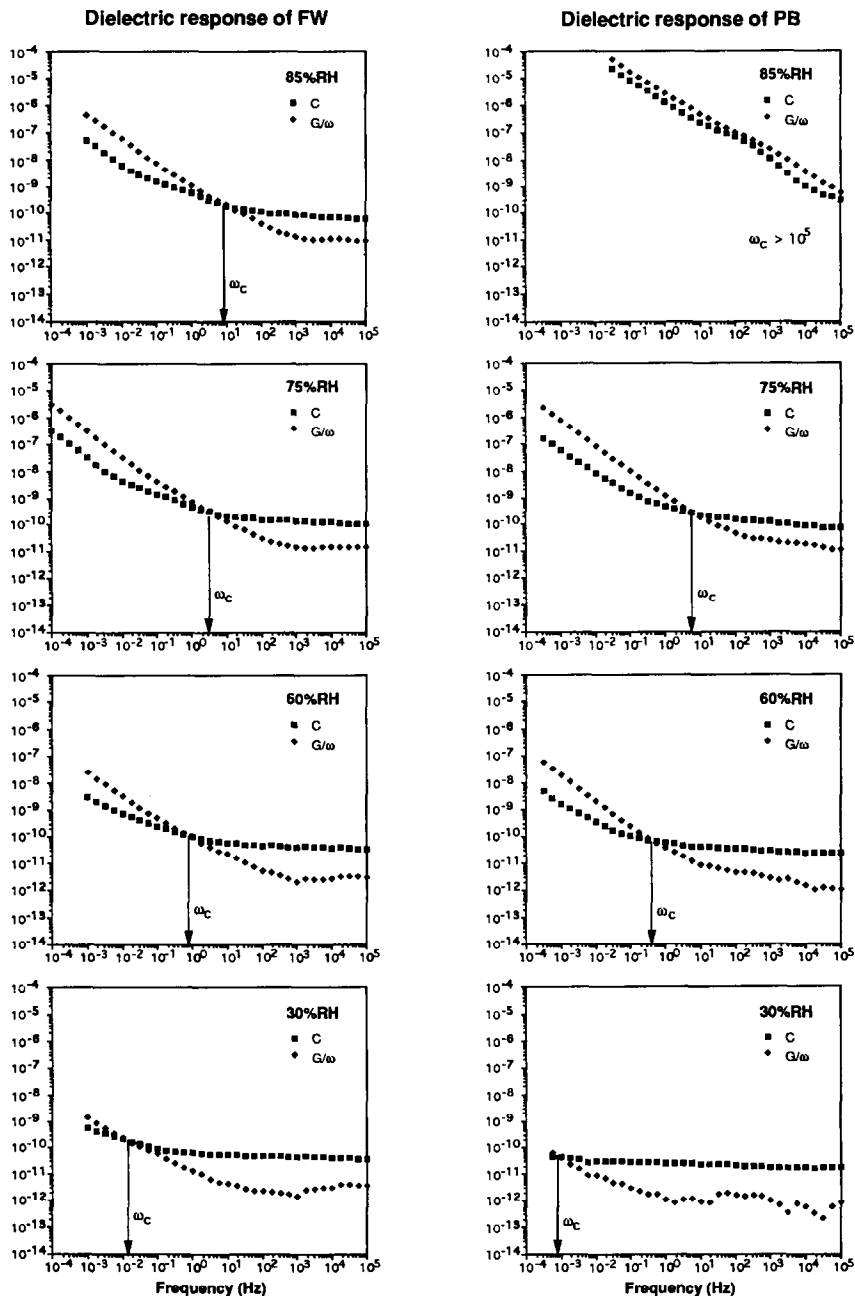


Fig. 3. Dielectric reponses of prussian blue and flake white paint films at different RH values.



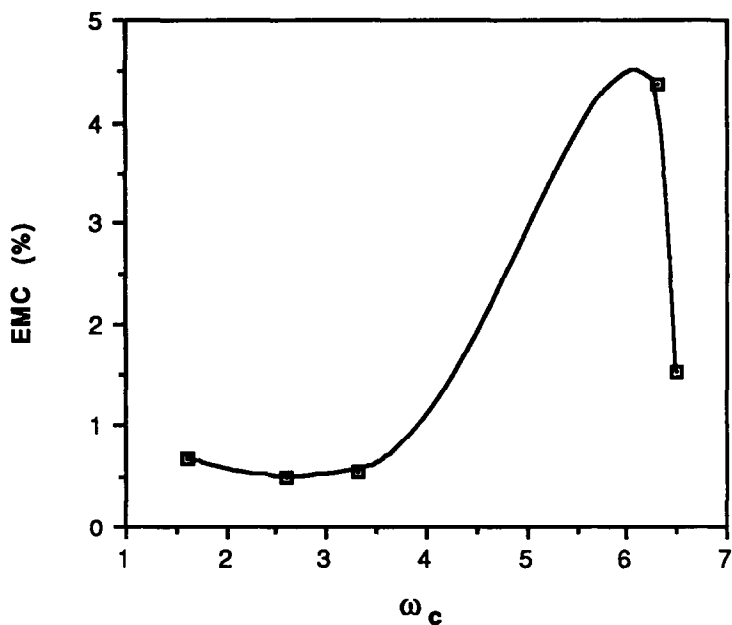


Fig. 4. Plot of equilibrium moisture content (EMC) against critical frequency ( $\omega_c$ ).

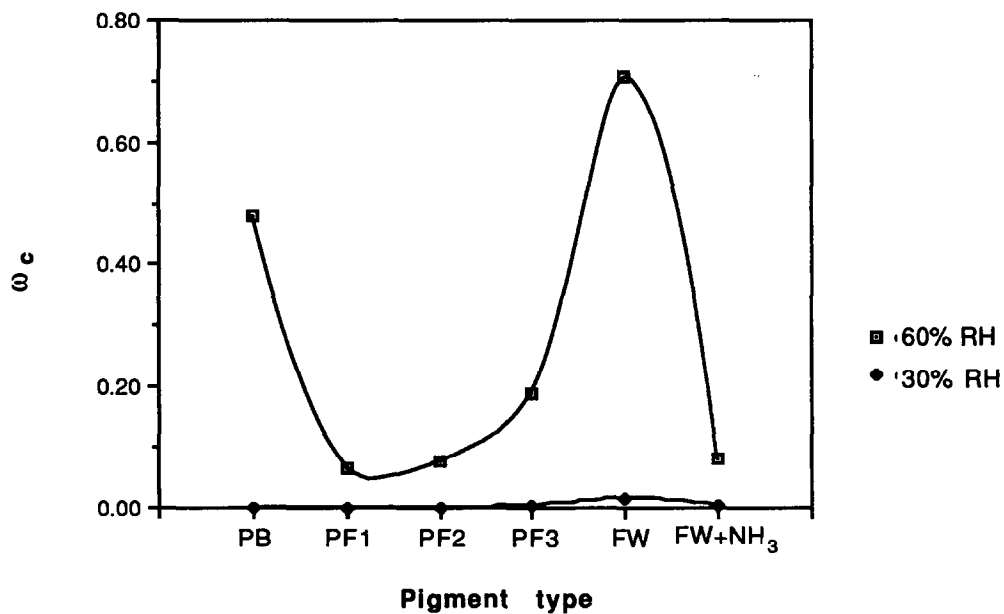
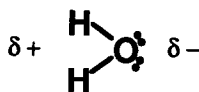
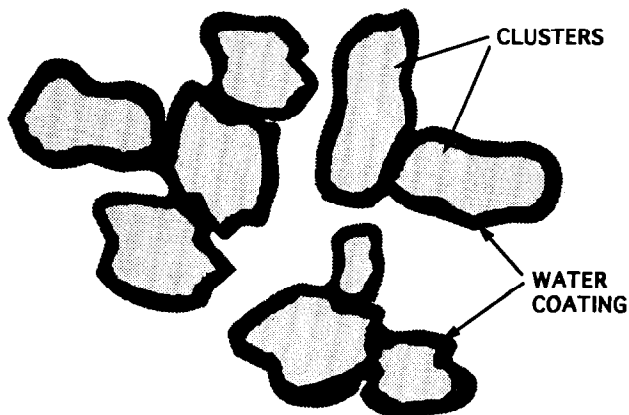


Fig. 5. Plots of critical frequency with pigment type at 30% and 60% RH.

Another parameter, exponent  $p$ , increases with RH, demonstrating that water molecules activate charge transfer i.e. “charge hopping”. The model which is presented attempts to explain the phenomena in terms of polarisation of clusters by a succession of proton transfers within the system. The structure of the water molecule provides a path for charge transport by continually forming and breaking hydrogen bonds with neighbouring molecules. This mechanism is demonstrated in Fig. 6. The rise in humidity leads to an expansion of the cluster and rapid increase in the number of routes available for relaxation. Hence the values for the capacitance and conductance of the system are increased. The prussian blue shows small variation in diffusion coefficient. This may, perhaps, be because water molecules are forming immobilised clusters. The flake white shows a larger variation in the diffusion coefficient with RH (comparable

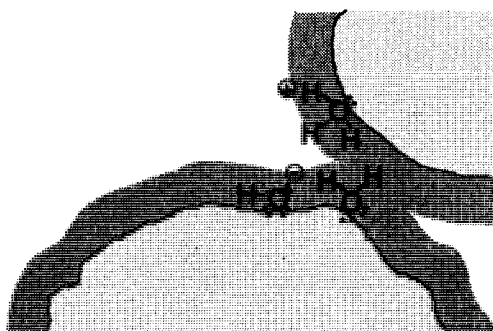
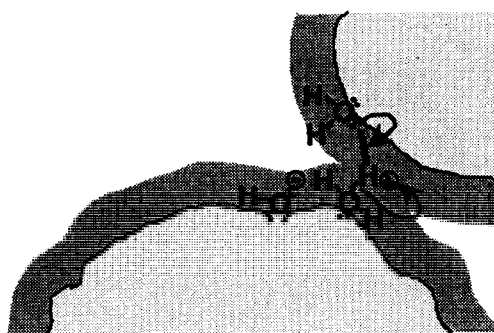
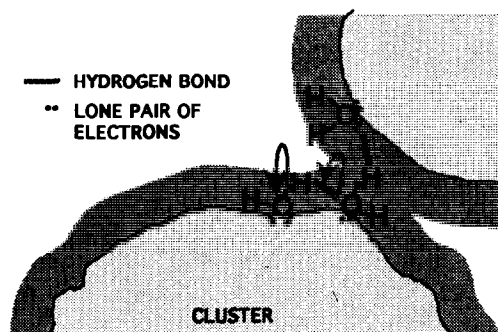


(a)



(b)

Fig. 6. (a) The structure of a water molecule; (b) the adsorbed water layers on the surfaces of pigment grains; and (c) the “charge hopping” mechanism.

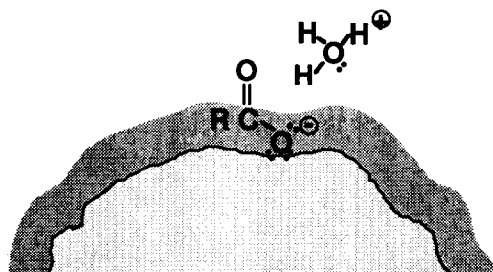
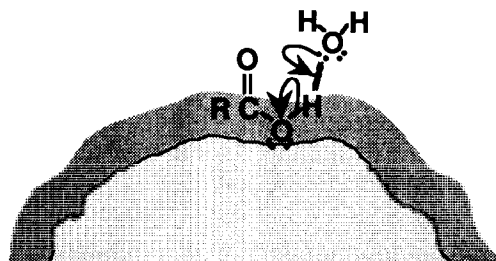


(c)

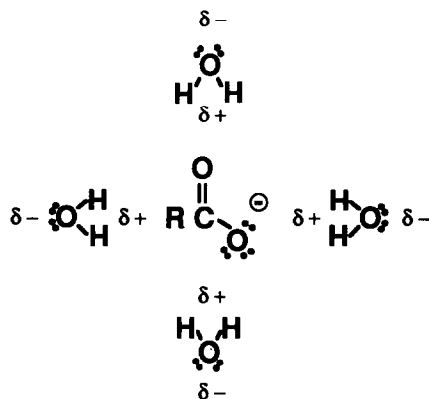
Fig. 6. (Continued)

with the effect at lower RH in prussian blue). Indications are that the values are of a similar order of magnitude to those quoted in the literature [9].

These changes indicate what is happening at the surfaces of pigment grains. It is known that fatty acids are adsorbed on the surfaces of the pigment grains [10]. These



(a)



(b)

Fig. 7. (a) "Charge hopping" onto fatty acid; (b) hydrolysis of fatty acids by the highly polar water molecules.

acids can be readily hydrolysed by the highly polar water molecules as shown in Fig. 7. This process may also liberate sites for further adsorption of water molecules on the cluster surfaces. As a result, the capacitance and conductance of the system are increased while the content of the fatty acids in the system is reduced. Preliminary

measurements using direct temperature resolved pyrolysis mass spectrometry have indicated that a reduction in fatty acid content ( $C_{16}$  and  $C_{18}$ ) does occur [11] which implies that the excess water molecules are possibly affecting the adsorbed layers of long chain fatty acids.

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