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Some characteristics of pigments that affect the kinetics of fading of prints made from water-based liquid ink formulations

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Abstract

A series of inks has been formulated that, when printed, give different fading profiles on exposure to Xenon Arc light. Such prints were designed to form the basis of a replacement for the ISO Blue Wool Scale, which is defined by BS EN ISO 105:B02. The effect of the crystal form of the titanium dioxide that was employed in the inks was investigated. It was shown that the anatase crystal form of titanium dioxide has a greater influence, than the rutile crystal form of titanium dioxide, on accelerating the fading of prints made from such inks. There is an optimum amount of titanium dioxide that should be added to such formulations, to protect the print from fading on exposure to xenon arc light. This situation was observed for both the rutile crystal form of titanium dioxide and the anatase crystal form of titanium dioxide. The effect of the particle size, of Pigment Blue 61, on fading was also evaluated. It has been shown that for a given mass of the blue pigment in a water-based ink, the lightfastness of subsequent prints increased for inks containing Pigment Blue 61 samples that contained smaller particle sized species.

1. Introduction

In recent times, a need has arisen for an alternative system of light fastness evaluation to replace the Blue Wool Scale that has, for so long, been the accepted standard for light fastness. To this end, a series of printed standards has been developed using gravure printing as a means of print formation and water-based inks as the ink media. This paper is concerned with the fading characteristics of such prints.

Liquid inks are used in gravure printing processes and in flexographic printing processes. Generally, such inks can contain between 30 and 70% by weight, of solvent. The solvent is an important, although temporary component of the ink system. Generally, liquid inks cure by evaporation of solvent from the ink or by UV curing. A variety of solvents have been used: the choice of solvent(s) depends on the polymeric film former and on the nature of the required drying profile.

One type of film former that can be used for water-based printing inks is based on sulphopolyester technology. Sulphopolyesters are formed via a polycondensation reaction between 5-(sodiosulpho) isophthalic acid, diethylene glycol and 1,4-cyclohexanedimethanol resulting in a linear polyester [1,2]. It is the pendant sulphonate groups that give the polymer its hydrophilic properties,

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and water dispersibility [3]. A film former of this type was used in the current study.

Water-based liquid inks, containing C.I. Pigment Blue 61 (Fig. 1) and titanium dioxide, were examined as a series of inks to give prints that would fade in a controlled manner on exposure to xenon arc light. This paper concerns scrutiny of the factors that influence the kinetics of fading of prints made from low viscosity ink systems.

Alkali Blue pigments have a triphenylmethane structure. Because of the non-uniform reaction process, the commercially available grades contain a mixture of reaction products that is dependent on the conditions employed in the reaction. The degree of sulphonation achieved will also be condition specific [4]. As the degree of sulphonation increases, so does the solubility of the pigment in water, to the point when the pigment is converted into a dye.

Colorants with a triphenylmethane structure generally have poor fastness to light [5]. Triphenylmethane dyes are used for standards one, two and three of the Blue Wool Scale [6], illustrating the typical values for lightfastness of this class of colorant.

C.I. Pigment White 6 (titanium dioxide) acts as an opacifying agent as well as providing changes to the behaviour of the ink system, in terms of the photoactivity of the system [7].

2. Materials and methods

Factors that affect the fading characteristics of selected inks were established, with respect to the pigments that are present within the formulation. To this end, all of the inks were printed onto carton board and exposed to xenon arc light using a Xenotest Alpha LM, for fastness testing using a defined test methodology[6]. After exposure to xenon arc light, colour measurement of the printed specimens was carried out using a Datacolor Spectraflash SF 500 spectrophotometer.

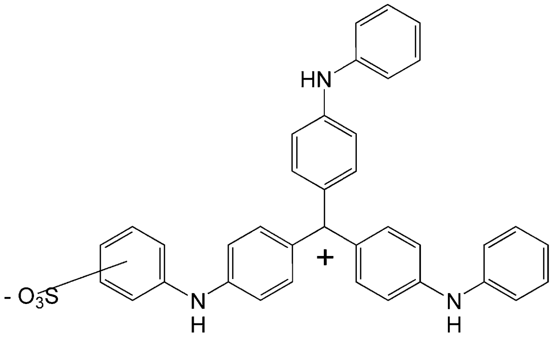

Fig. 1. Molecular structure of C.I. Pigment Blue 61[5].

With the liquid ink systems in mind, two factors were examined in detail. These were, the effect of the titanium dioxide crystal form (i.e. rutile or anatase polymorphic forms) and the influence of the concentration of titanium dioxide, on the fading rate of a series of water based inks and the effect of the Pigment Blue 61 particle size on the fading behaviour of a series of water-based inks.

C.I. Pigment Blue 61 was supplied as Reflex Blue R54, by Clariant UK Ltd, Horsforth, Leeds, UK as a dry powder. C.I. Pigment Blue 61 may also be supplied (by Clariant UK Ltd) as a flushed paste, Flexo Blue RX. Flushed pastes are water-based dispersions of pre-milled pigments, which often contain a dispersion aid. Flexo Blue RX has the composition: Pigment Blue 61 (40.50%), ethane-1,2-diol (10.00%) and water (49.50%).

Flushed pastes are suitable for incorporation into water-based inks and surface coatings. The rutile crystal form of Pigment White 6 used in the current study was Tioxide R-HD2, supplied by Tioxide Europe Ltd, Billingham, UK. This pigment is produced by the Chloride process. The composition of the pigment is 94.2% titanium dioxide, 3.36% aluminium oxide, with trace amounts of silicon dioxide, zirconium dioxide and carbon. The pigment is suitable for incorporation into water-based systems. The specific gravity of the pigment is 4.1 g cm^{-3}.

The anatase crystal form of Pigment White 6 used in the current study was Tioxide A-HR, supplied by Tioxide Europe Ltd, Billingham, UK. The pigment is produced by the Sulphate process. The composition of the pigment is 98.65% titanium dioxide, with trace amounts of aluminium oxide, silicon dioxide, zirconium dioxide and carbon. The specific gravity of the pigment is 3.2 g cm^{-3}. The pigment is suitable for incorporation into water-based systems.

The film former used was Eastek 1100, supplied by Eastman Chemical (UK) Ltd, Hemel Hempstead, UK. It was supplied as 32.58% (w/w) solids dispersion in water and is completely free from volatile organic compounds. The dispersion has a flow time of 40 s using a Zahn No. 2 Flow Cup.

A poly(ethylene) wax was also added to each of the inks. This was Hordamer PE-03, supplied by Clariant UK Ltd.

The carton board used was Iggesund IGD Carton Excel, supplied by Iggesund, Cumbria, UK. Carton Excel is coated with a poly(ethylene) latex dispersion on the top surface (15 g m^{-2}) and a poly(ethylene) coating on the reverse (277 g m^{-2}).

Ball milling was employed in the formulation of liquid inks. Five hundred grams of zirconium spheres (10 mm diameter) were added to the milling vessel. The vessel was a cylindrical, 500 cm^3 ceramic mill pot with ceramic lid. Placing a rubber gasket between the lid and the vessel and clamping the two together sealed the pot. The spheres filled approximately one third of the volume. The total mill charge was approximately 50% of the total volume. The milling vessel was horizontally rotated at a specified speed for a defined period of time. This technique is denoted as Dispersion Method 1.

The mixer that was selected to form ink dispersions was a Silverson L2/R mixer, manufactured by Silverson Machines Ltd, Chesham, UK. The mixer was fitted with a 5/8″ micro mixing assembly, which consisted of a rotor, surrounded by a stator that had a 16 mm outside diameter and was fitted with a general purpose disintegrating head. The mixing vessel was selected to ensure that it was filled to 50% volume, and that the stator was sufficiently immersed in the liquid. In each case, the formulation was agitated at full velocity (6000 rpm) for 5 min. The initial quality of the dispersion was assessed visually. This method is denoted as Dispersion Method 2.

In the third method, the formulation was agitated by hand. This method was employed for very small volumes, when Dispersion Methods 1 and 2 could not be employed. This method is denoted as Dispersion Method 3.

Prints were produced as a drawdown using a number 2 K-Bar coater, supplied by RK Print Coat Instruments Ltd, Hertfordshire, UK. A number 2 K-Bar coater gives a wet film thickness of approximately 12 μm. A piece of Carton Excel board, measuring approximately 150 × 100 mm was placed on a standard drawdown pad, approximately 1 cm^3 of ink was applied using a disposable pipette, and drawdowns were made. Several prints were made in each case to provide consistency of proofing.

The first method of particle size analysis involved the use of a N4 Multisizer, manufactured by Beckman Coulter (UK) Ltd, High Wycombe, UK. The N4 Multisizer measures the particle size by laser diffraction. The laser is scattered by the particles that are suspended in the continuous medium. The refractive index and the density of the continuous medium are known. The deflections caused by the particles in the continuous medium are collected, and translated into particle size values. This method can be used to measure sub micron particle sizes. This technique is denoted as Particle Size Method 1.

The second particle sizing technique used was a Coulter Counter. This counting mode involves an electrical sensing zone method that gives values for the particle sizes and particle volumes in a conductive liquid medium. This technique is denoted as Particle Size Method 2, being used to measure particles that have an average diameter that is greater than 1 μm.

Colour measurements of the prints were carried out using a Datacolor Spectraflash SF 500 colour measurement unit. The conditions were specified as follows:

- 10° observer
- D65 (standard daylight) illuminant
- ultra violet light included
- specular light included (SPIN)
- two pulses for each reading
- three readings for each specimen
- 5 mm aperture

The data obtained from the Datacolor unit were presented in a variety of ways, depending on the information that was required. The data were presented as a series of reflectance values in graphical form when colour strength development studies of the pigment were being conducted. This approach illustrated the heightening and sharpening of the main absorbance peak, indicating that the colour was getting stronger and brighter. The L^*, a^* and b^* tristimulus values were tabulated for the data that represented a change in colour. From these values, the colour difference, dE^*, was calculated using CIE $L^*a^*b^*$ (1976). For each sample, the dE^* value was calculated using averages from measurements taken from the exposed portions of the sample, and from the unexposed portions of the sample.

During the lightfastness test, the specimens were placed in the holders with half of each of the specimens covered. The samples were then exposed in a Xenotest unit, using standard test conditions [6], for a period of 2 h, removed from the Xenotest and measured using the Datacolor Spectraflash. Once colour measurement was complete, the samples were returned to the Xenotest unit, and fading continued for a further 2 h. This procedure was repeated until the samples had been exposed for 20 h.

2.1. Methods—formulation

2.1.1. Effect of titanium dioxide on fading rate of a series of water-based inks

A series of inks was formulated to examine the effect that the amount of TiO_2 has on the fading properties of the prints, via the effect on the extent of fading for inks containing either rutile TiO_2 or anatase TiO_2. The inks were assembled by adding all of the components to a 200 cm^3 glass jar, and dispersing them using Dispersion Method 2, for a period of 2 min. The inks are denoted as inks 1–8. The formulations are specified in Table 1.

Table 1
A series of ink formulations, used for assessing the effect of TiO_2 on fading kinetics

Ink	Anatase TiO_2	Rutile TiO_2	Eastek 1100	Flexo Blue RX	Hordamer PE03	Water
1	0	5.00	61.39	4.94	2.00	26.67
2	0	10.00	61.39	4.94	2.00	21.67
3	0	20.00	61.39	4.94	2.00	11.67
4	5.00	0	61.39	4.94	2.00	26.67
5	10.00	0	61.39	4.94	2.00	21.67
6	20.00	0	61.39	4.94	2.00	11.67
7	2.00	0	61.39	4.94	2.00	29.67
8	0	2.00	61.39	4.94	2.00	29.67

The two variables in the ink formulations were the amount of TiO_2 pigment and the amount of water. The TiO_2 pigment level was chosen to replicate the amount of the pigment that may be added to ink formulations to achieve an acceptable print. Both crystal forms were used separately to assess the effect that the two different crystal forms had on the fading rates of the prints. The amount of water added to the inks was varied to make up the volume. Prints were made using each of the inks. The prints were allowed to dry. They were then cut into squares measuring 45 × 45 mm and were mounted on white cards, to fit the sample holders of the Xenotest Alpha LM. The lightfastness test was carried out on the specimens.

2.1.2. Effect of pigment particle size on the fading behaviour of inks containing Pigment Blue 61

The particle size of a pigment is known to affect the lightfastness of the pigment [8]. Thus, the larger the particle size, the greater is the lightfastness. This is because the surface area to volume ratio decreases as the particle size increases. Only the surfaces of a pigment particle can be directly affected by incident light.

A series of inks was formulated in an examination of the effect of particle size on the lightfastness of selected gravure ink formulations. A pigment dispersion was formulated, and is denoted as dispersion PB61A. Sufficient of each of the components was added to the ceramic mill pot to make 100 g of dispersion. The dispersion was milled using Dispersion Method 1. The components of the dispersion were:

Dispersion PB61A	%
Pigment Blue 61 (powder form)	10.00
Eastek 1100	20.00
Deionised water	70.00

Samples were removed from the milling regime at time intervals of 1, 2, 4 and 24 h. Particle size analysis was carried out on each of the samples using

Particle Size Methods 1 and 2. The samples were also used to make up inks containing titanium dioxide and the dispersion PB61A, collected at the specified time intervals. Evaluation of the kinetics of fading was conducted.

A white ink was formulated, and is denoted as Ink 9. The components of Ink 9 were dispersed using Dispersion Method 2, resulting in 80 g of ink.

Ink 9	%
Eastek 1100	71.74
TiO2 A-HR	12.50
Hordamer PE03	1.88
Deionised water	13.89

Several compositions containing 2 cm^3 of dispersion PB61A and 8 cm^3 of the white ink were assembled. Four inks were made by adding the dispersion to the white ink. The two components were mixed using Dispersion Method 3. Prints were made for each of the inks. These prints were prepared for lightfastness testing.

To ascertain if the crystal structure of the titanium dioxide affected the lightfastness of the subsequent inks, the experiment was then repeated, replacing the anatase crystal form of titanium dioxide (A-HR) with a rutile crystal form (R-HD2).

3. Results

3.1. *Effect of titanium dioxide on the fading rate of a series of water-based inks*

It was assumed that Pigment Blue 61 would be the more vulnerable species in prints because the film former was considered to be more stable to light than the pigment. Thus, in fading, the colorant is preferentially degraded relative to the film former.

Although oxidation of the anatase titanium dioxide pigment is reversible, oxidation of the surrounding system is not. Photocatalytic degradation may also be observed for rutile titanium dioxide, but to a lesser extent due to the more compact crystal structure and the presence of fewer deformed ions. The energy difference between the valance and conductivity bands of the pigments is 3.05 eV for rutile and 3.29 eV for anatase [9]. It was thought that the inclusion of anatase titanium dioxide might increase the rate of fading of the blue pigment, and to a greater extent than that given by the rutile titanium dioxide.

For each of the pair of inks, the rate of fading of prints from the ink was followed. The CIE $L^*a^*b^*$ dE value was calculated from the colour measurement data and plotted against exposure time. The results are presented graphically, in Figs. 2–5.

In each case, the presence of the anatase grade of TiO_2 caused prints from the ink to fade more quickly than prints from the ink containing the rutile grade of TiO_2. Figs. 2–5 show this trend.

The colorant, in this case Pigment Blue 61, is the most vulnerable species in the ink. Possible, irreversible degradation routes for Pigment Blue 61 are illustrated in Fig. 6.

The effect of pigment loading on fading was evaluated. In general, increasing the loading of TiO_2 reduces the rate of fading. A possible reason for this occurrence is thought to be due to a "shielding" effect of the titanium dioxide. A higher proportion of titanium dioxide could increase the scattering of the incident light. This would prevent the penetration of the light, and would, therefore, be unable to induce reduction of the titanium ions. If the reduction of titanium ions does not occur, then the breakdown of Pigment Blue 61 via an oxidative mechanism would not be catalysed. In such an event there would be a reduction of fading.

Another reason for the observed fading rates may be that titanium dioxide may protect Pigment Blue 61 from direct breakdown by the incident light. It is known that for systems that contain species that are subject to photochemical breakdown, addition of titanium dioxide can reduce the rate of degradation, by absorbing a proportion of the incident radiation [11].

Initial observations of the rate of fading suggested that the relationship between the exposure time and fading behaviour was linear. However, on further analysis, it was found that the data

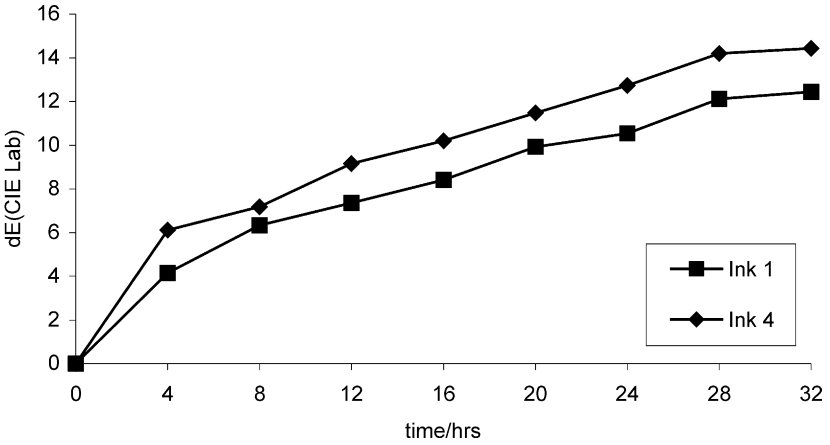

Fig. 2. dE (CIE $L^*a^*b^*$) vs. exposure time for prints from Ink 1 and prints from Ink 4. Ink 1 contains 5% (w/w) rutile TiO_2 and Ink 4 contains 5% (w/w) anatase TiO_2.

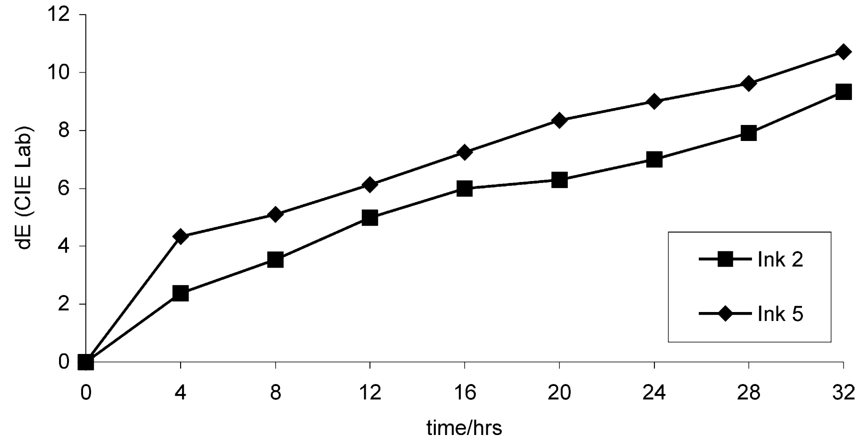

Fig. 3. dE (CIE $L^*a^*b^*$) vs. exposure time for prints from Ink 2 and prints from Ink 5. Ink 2 contains 10% (w/w) rutile TiO_2 and Ink 5 contains 10% (w/w) anatase TiO_2.

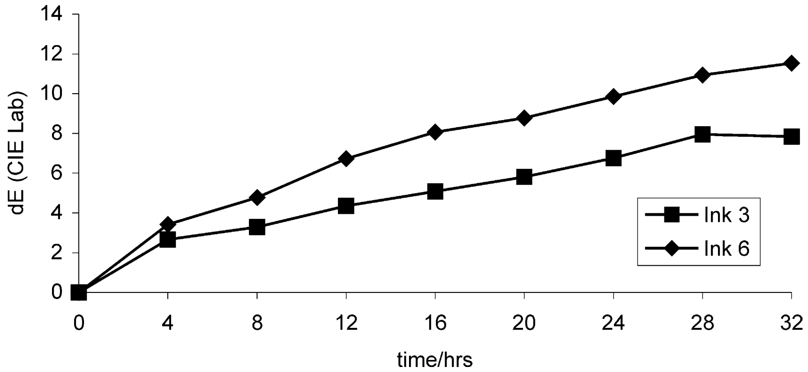

Fig. 4. dE (CIE $L^*a^*b^*$) vs. exposure time for prints from Ink 3 and prints from Ink 6. Ink 3 contains 20% (w/w) rutile TiO_2 and Ink 6 contains 20% (w/w) anatase TiO_2.

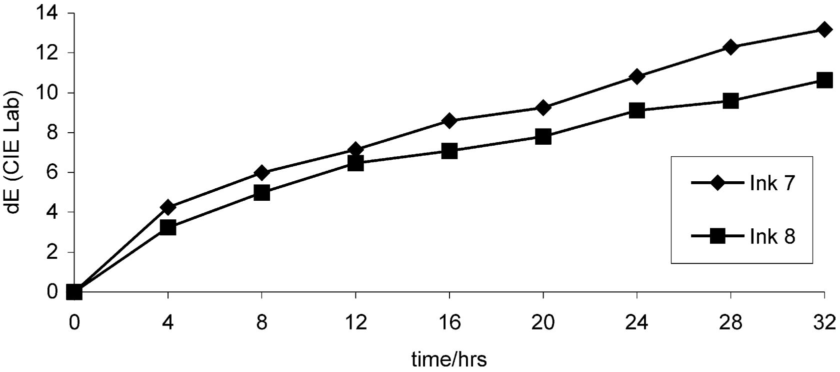

Fig. 5. d*E* (CIE $L^*a^*b^*$) vs. exposure time for prints from Ink 7 and prints from Ink 8. Ink 7 contains 2% (w/w) anatase TiO_2 and Ink 8 contains 2% (w/w) rutile TiO_2.

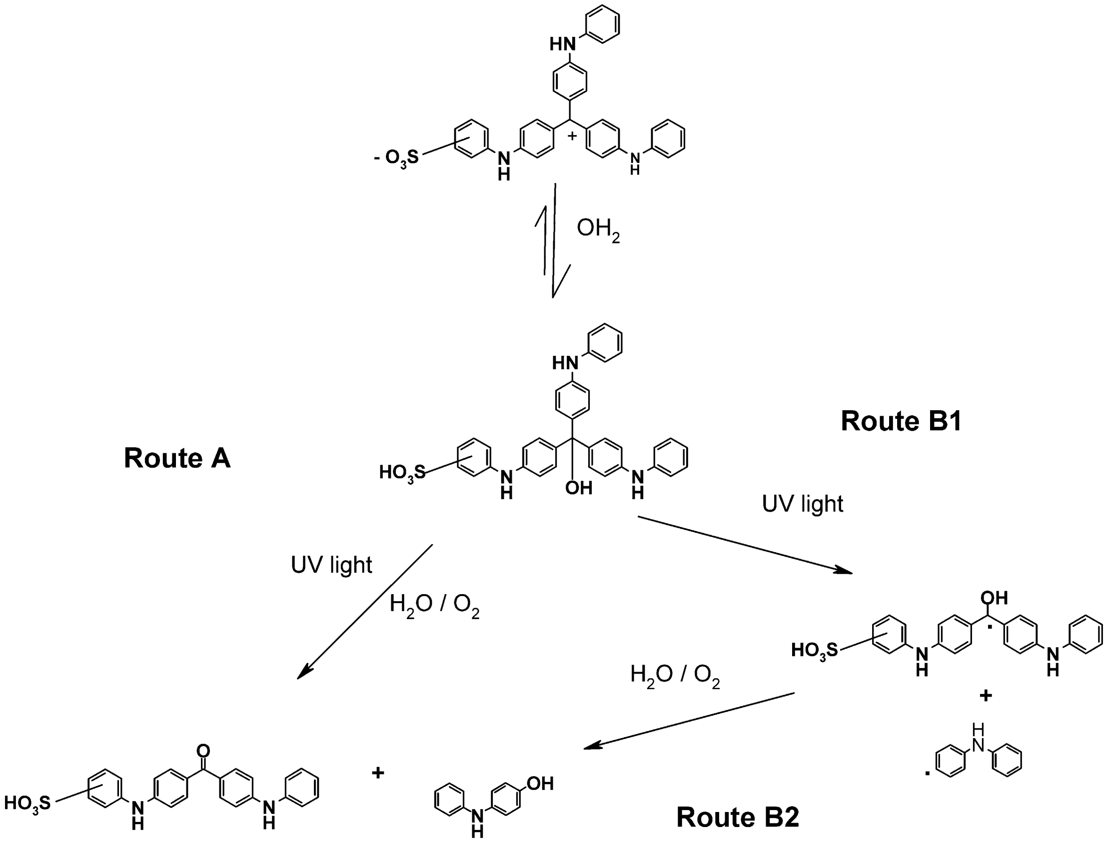

Fig. 6. Proposed degradation routes for Pigment Blue 61 [10].

followed a logarithmic pattern more closely. The data suggest that the fading of the printed ink is a first order reaction with respect to one of the reactants in the system, Pigment Blue 61. The reaction can be considered to be the breakdown of the Pigment Blue 61. As the "reaction" proceeds, the amount of Pigment Blue 61 remaining decreases and the rate of reaction slows down. There are several possible explanations for the observed fading behaviour of the prints.

Singlet oxygen that is involved in the degradation process would affect the smaller Pigment Blue 61 particles first [12]. Any degradation of Pigment Blue 61 within the binder matrix might require migration of the oxygen or singlet oxygen into the polymer matrix before further degradation could occur. The time dependency of migration could lead to a non-linear rate of fading initially, because pigment below the surface would not be degraded until the oxygen or singlet oxygen had migrated through the polymer matrix. For larger particles, the time dependency of migration of the oxygen into the particles could be greater than the time dependency of migration of the agents into the polymer matrix. This would lead to the observed effect of a reduction in the fading rate of the prints.

The second possible explanation for the first order fading rate is that one of the newly formed colourless breakdown products (Fig. 6) may stabilise the system by interaction with oxygen or singlet oxygen. The colourless product may quench any singlet oxygen formed, if singlet oxygen is involved with the reaction. It is a reasonable conclusion that singlet oxygen could be involved with the breakdown mechanism. If ground state oxygen was involved in the degradation process, then Pigment Blue 61 could break down in the absence of light. However, light is necessary to cause the breakdown of the colorant; the prints were stable when stored in the dark. Oxygen can migrate into compositions containing organic molecules [13]. Oxygen could migrate into the polymer matrix used in the formulation of the prints in the current study. Singlet oxygen can be caused by the excitation of ground state oxygen by visible and ultra violet light. In a vacuum, singlet oxygen can have a lifetime of one hour. However in the presence of other molecules, collisions occur, causing transfer of energy from the singlet oxygen in the form of reactions. In either situation, it is known that Pigment Blue 61, like most triphenylmethane structures, is relatively susceptible to breakdown [9]. It is therefore possible that singlet oxygen is involved in the breakdown of the colorant in the current study.

A third possible explanation for the observed nature of fading, and therefore rate of reaction is that an intermediate breakdown product may be formed (Path B1–B2, Fig. 6). This intermediate breakdown product may then react with further singlet oxygen, introducing competition in the system for the singlet oxygen. As the primary breakdown product and the secondary breakdown products would both be colourless, the observed effect would be an initial rapid breakdown of colour, as only the coloured pigment molecules would be affected. By examining the proposed mechanisms for degradation, it can be seen that Route B involves two degradation stages, breakdown of the carbinol base to form a secondary alcohol and a secondary amine, followed by oxidation of the alcohol to form a benzophenone. This degradation route would support the observed rate of reaction, as competition for singlet oxygen could exist between the carbinol base (Path B1) and the secondary alcohol (Path B2), as the reaction proceeded.

A fourth possible explanation is related to the physical properties of the print. As the amount of Pigment Blue 61 in the surface decreases, due to breakdown, the relative amount of titanium dioxide in the system would increase. The increasing proportion of titanium dioxide could lead to increased scattering of incident light. If the incident light is scattered rather than absorbed, degradation will not occur. This situation is illustrated in Figs. 7 and 8. The light must be absorbed for the breakdown of the colorant to occur. Evidence for this mechanism can be seen from the relative fading rates of inks 1, 2 and 3. The fading rates decrease with increasing titanium dioxide content. This supports the concept that a higher titanium dioxide content increases the degree of scattering and thus protects the Pigment Blue 61 from degradation.

Analysis of the reflectance values for each of the prints also yielded similar results to analysis of the dE (CIE $L^*a^*b^*$) values. In each case, the $\lambda_{\max}$ value was 440 nm. The reflectance value at this wavelength was tabulated after each exposure time, for each of the inks. The reflectance value at 440 nm, before fading, was also recorded. The reflectance value at the $\lambda_{\max}$ value for the print is directly related to the amount of the Pigment Blue

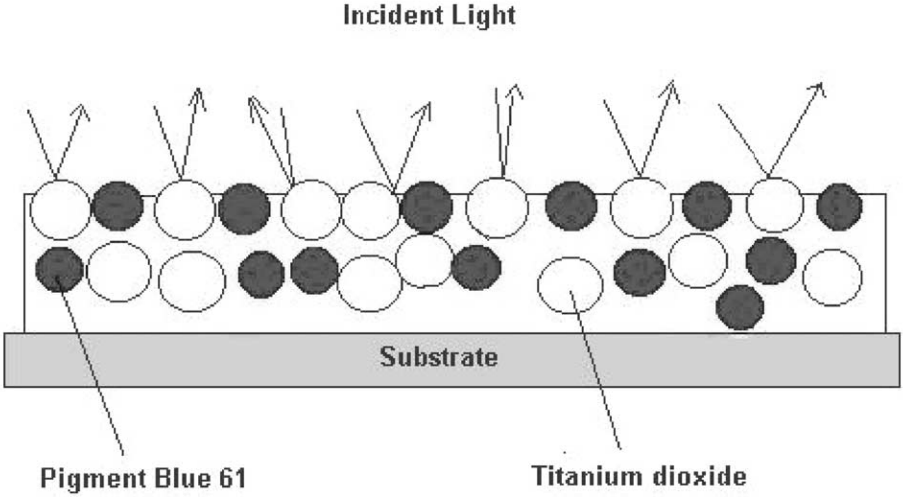

Fig. 7. Schematic diagram of ink pigmented with titanium dioxide and Pigment Blue 61 before breakdown of Pigment Blue 61.

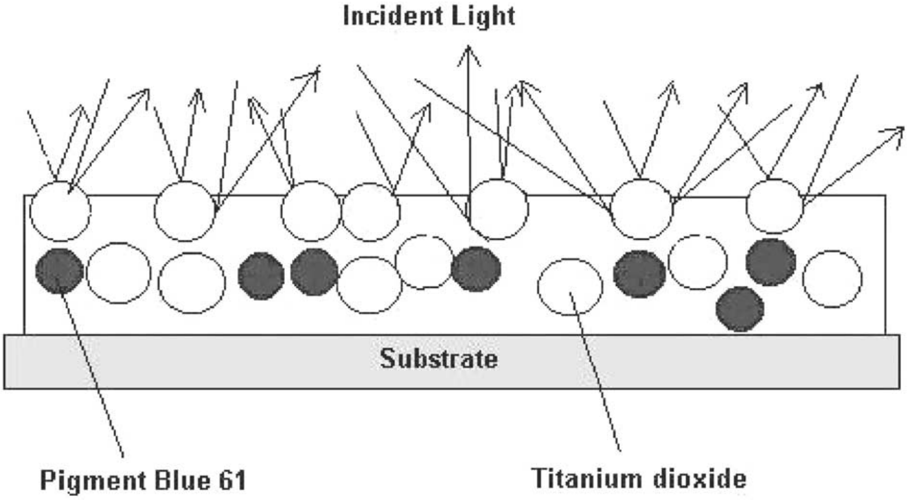

Fig. 8. Schematic diagram of printed ink pigmented with titanium dioxide and Pigment Blue 61 after breakdown of Pigment Blue 61 at the surface. The opportunities for scattering of incident light by titanium dioxide are greatly increased.

61 present in the print at any given time. The reflectance value at 440 nm was plotted against exposure time for each of the printed inks. The logarithmic 'best fit' curve was calculated for each of the data. The regression of the logarithmic fit of the data was also recorded. The results are presented in Table 2.

In every case, the ink containing anatase titanium dioxide faded more quickly than the corresponding ink containing rutile titanium dioxide. For both series of inks, the fading rate was at a maximum when the amount of titanium dioxide was at 5% (w/w) of the liquid ink. This supports the concept that above a certain ratio of Pigment Blue 61:titanium dioxide, the titanium dioxide swamps the blue pigment and reflects light from the sample and protects the blue pigment.

Table 2
The percentage (w/w) of anatase titanium dioxide and of rutile titanium dioxide, Pigment Blue 61 solids and Eastek 1100 solids present in the dried film of each of the inks (the logarithmic equation of 'best fit' and the regression of the logarithmic fit of reflectance at 440 nm versus exposure time for each of the inks, numbered 1–8 are also shown)

Specimen	% Eastek 1100	% Pigment Blue 61	% Anatase titanium dioxide	% Rutile titanium dioxide	Reflectance value (440 nm) logarithmic equation of 'best fit'	Regression of logarithmic fit
Ink 48	83.4	8.3	0	8.3	$y = -4.31\ \mathrm{Ln}(x) + 44.5$	0.96
Ink 41	74.1	7.4	0	18.5	$y = -4.80\ \mathrm{Ln}(x) + 41.9$	0.97
Ink 42	62.5	6.3	0	31.2	$y = -3.88\ \mathrm{Ln}(x) + 41.4$	0.98
Ink 43	47.6	4.8	0	47.6	$y = -3.41\ \mathrm{Ln}(x) + 42.8$	0.98
Ink 47	83.4	8.3	8.3	0	$y = -4.55\ \mathrm{Ln}(x) + 49.7$	0.99
Ink 44	74.1	7.4	18.5	0	$y = -5.34\ \mathrm{Ln}(x) + 46.9$	0.97
Ink 45	62.5	6.3	31.2	0	$y = -4.42\ \mathrm{Ln}(x) + 40.5$	0.96
Ink 46	47.6	4.8	47.6	0	$y = -3.71\ \mathrm{Ln}(x) + 41.8$	0.95

3.2. Effect of pigment particle size on the fading behaviour of inks containing Pigment Blue 61

After milling the pigment dispersion for a specified time period, a sample of the dispersion was removed from the milling regime. The particle size distribution for the pigment was measured. The average particle size diameter for the pigment, after the specified milling time, is given in Table 3.

The colour strength for each of the inks, formulated after each of the time intervals is shown graphically in Fig. 9. The reflectance curve for each of the inks is illustrated. The reflectance curves illustrate that the pigment was becoming more intense as the milling time was increased, indicated by a narrowing of the reflectance curve. This observation is indicative of a reduction in particle size, and a narrowing of the particle size distribution. This finding corresponds to the measured particle size values, and to the observed particle size distributions.

Table 3
Milling time for the Pigment Blue 61 dispersion, PB61A, and the respective particle sizes, measured using Particle Size Method 1 and Particle Size Method 2, after the defined time intervals

Milling time (h)	Median particle size (nm) (Method 1)	Median particle size (nm) (Method 2)
1	795	4548
2	365	4548
4	263	4309
24	215	3351
Flexo Blue RX[a]	165	3112

[a] The average particle size for the commercial preparation Flexo Blue RX is also shown.

The fading rate behaviour each of the prints is shown graphically in Fig. 10.

The results indicate that as the milling time was increased and, hence, the particle size was reduced, the lightfastness of the pigment was improved. This is contrary to previous studies [14] that showed that a reduction in particle size leads to poorer lightfastness. There are a number of possible explanations for this observed effect. The pigment is represented by mass. As the particle size of the pigment is reduced, there are more discrete particles per unit mass. Each particle imparts colour. Therefore, the more particles that there are, the more intense would be the colour. If the colour was more intense, a greater degree of exposure to light would be needed to provide an observed colour change. A greater number of particles would need to undergo a change from being coloured to being colourless, to have a noticeable effect.

Another explanation for the observed change in colour is that the titanium dioxide may be assisting the fading process. The inks containing Pigment Blue 61, that have a smaller particle size, will contain more blue particles. Therefore, the number of titanium dioxide particles per blue particle in the inks that have the smaller particle size will be less. It follows that the photocatalytic effect of the titanium dioxide will be less, per Pigment Blue

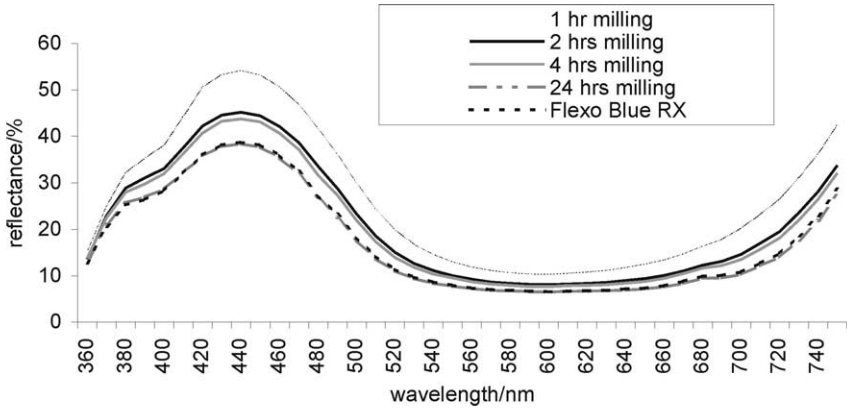

Fig. 9. Reflectance curves for a series of inks. The inks were formulated using Pigment Blue 61 that had been milled for various time periods.

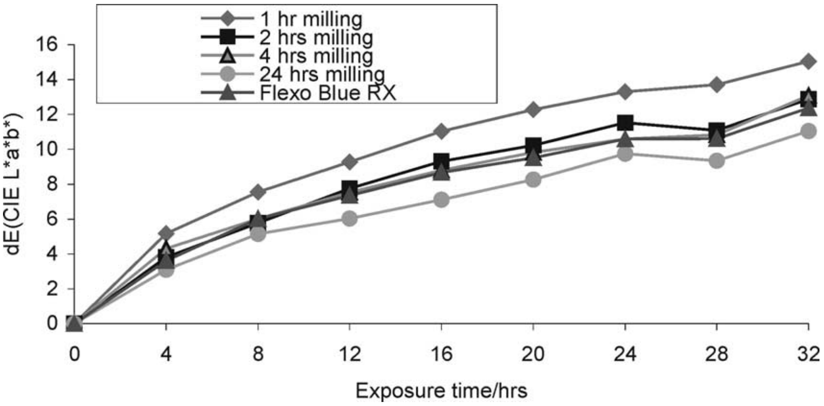

Fig. 10. d*E* (CIE *L*a*b**) vs. exposure time for prints from a series of inks. The inks were formulated using Pigment Blue 61 that had been milled for various time periods, anatase titanium dioxide and Eastek 1100.

61 particle, as there are more of the blue particles. If there is a smaller effect from the titanium dioxide particles, the observed fading of the print will be less severe.

The experiment was repeated, using a similar procedure. The difference was that the anatase grade of titanium dioxide was replaced with a rutile grade, TiO_2 R-HD2. This was done to see if the anatase grade of titanium dioxide would cause a modification to the expected result, for the similar series of inks. The same Pigment Blue 61 dispersions, collected after the specified milling time periods, were used as in the previous series of inks. This was done to ensure that the only factor that had changed was the crystal form of the titanium dioxide.

The fading characteristics of the prints, assembled from the series of inks are shown in Fig. 11. Fig. 11 shows that similar trends to those observed using the anatase crystal form of titanium dioxide in the ink formulation were observed, with the exception of the fading rates of the inks with pigment milled for 1 and 2 h being reversed. The prints made from inks containing the Pigment Blue 61 dispersion with the larger particle size faded more quickly. This would appear to support the concept that it is the number of particles present that determines the light stability of the print, and not the actual particle size of the pigment. The differences in the degree of fading for the various particle sizes are much less pronounced. This would suggest that the anatase titanium dioxide is

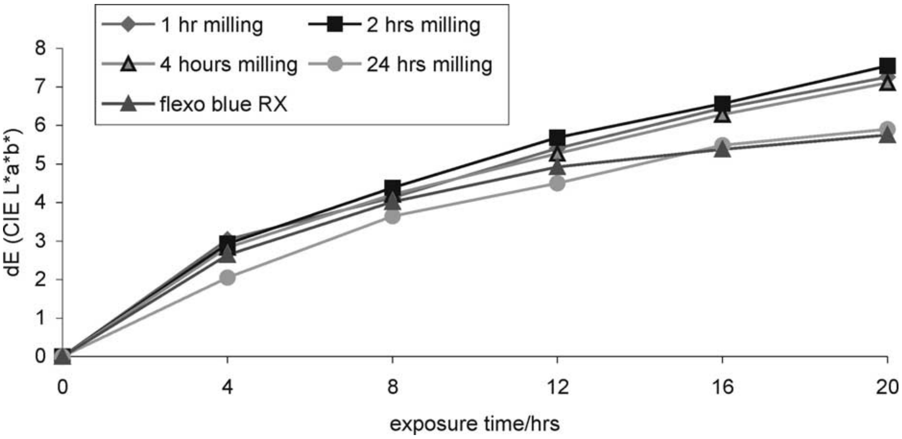

Fig. 11. d*E* (CIE *L*a*b**) vs. exposure time for prints from a series of inks. The inks were formulated using Pigment Blue 61 that had been milled for various time periods, rutile titanium dioxide and Eastek 1100.

having an influence on the lightfastness properties of the formulation containing the blue pigment. This observation supports the findings outlined in the previous section.

For the inks based on anatase titanium dioxide, and the inks based on rutile titanium dioxide, the fading profile of Pigment Blue 61 followed a logarithmic curve. This evidence supports the findings of the previous section.

4. Conclusions

The effects of the two different crystal forms of titanium dioxide on the fading profiles of prints from inks containing Pigment Blue 61 have been established. The anatase crystal form catalyses the rate of fading more than the rutile crystal form catalyses the rate of fading. Increasing the amount of titanium dioxide present in the ink formulation may reduce the observed fading rate of prints from such inks, by increasing scatter of the incident light.

The effect of the particle size of Pigment Blue 61 on fading behaviour has been successfully evaluated. Prints of inks containing blue pigment of a smaller particle size give better lightfastness than the prints of inks containing the same amount of blue pigment of a larger particle size. This effect is thought to arise because the number of blue pigment particles in the ink is reduced when the particle size is larger. As the number of blue pigment particles in the ink is reduced, the subsequent inks have a lower lightfastness. It is essential that, in formulating inks for light fastness evaluation, the milling regime is carefully controlled, because any changes to the particle size of the pigment will affect the overall light fastness of the end product.

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