JOURNAL OF
Materials
CHEMISTRY

Reversibly thermochromic systems based on pH-sensitive spirolactone-derived functional dyes

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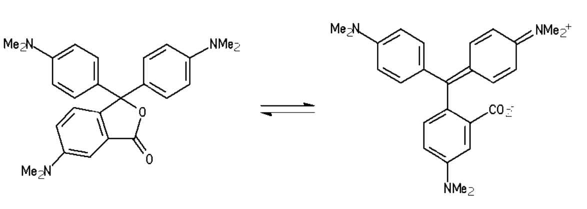
Received 30th July 1998, Accepted 9th October 1998

Composites formulated from pH-sensitive colour formers mixed with fatty acid co-solvents and acidic developers have been prepared and their thermochromic properties investigated. Possible explanations for the thermochromic effect have been considered and evidence is presented in support of a mechanism based on phase changes occurring within the compositions during heating and cooling.

Introduction

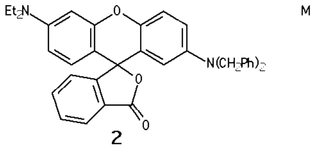
Colour formers that are pH-sensitive have been utilised commercially in the production of thermographic recording materials for around thirty years. The main outlet for such technology is facsimile paper in which the colour formers are designed to change irreversibly from colourless to coloured states on the application of heat.[1,2] However, thermochromic systems are known which utilise colour formers in order to produce thermally-triggered reversible switching between coloured and colourless states.[3] In addition to a pH-sensitive colorant, these systems also contain a readily fusible solid co-solvent and a colour developer. The co-solvent is a relatively low-melting hydrophobic compound that acts as a medium in which the colour former and developer can interact; the material typically has a long chain aliphatic character and may be a fatty acid, amide or alcohol. Provided that the mixture is formulated correctly, a striking colour change from coloured to colourless occurs upon heating the composition above its melting point, the original colour returning when the material solidifies through cooling. Reversibly thermochromic systems based on acidic developers and spirolactone colour formers are typical of the formulations encountered in the literature: an example of the latter component is Crystal Violet lactone (**1**), which in its lactone form, **1a**, is colourless, but on ring-opening (Scheme 1) converts to the intense blue species **1b**. The ring-opening may be induced by the addition of a proton or through an increase in the polarity or hydrogen-bonding ability of the host environment. The reaction is fully reversible.



1a 1b

Scheme 1

Despite the many patent applications concerning thermochromic materials based on co-solvent/developer/colour former compositions, little has been published that addresses the mechanism of the thermochromic effect.[3–5] This paper describes the behaviour of thermochromic compositions formulated with fatty acids, spirolactone colour formers (**1**–**4**) and phenolic developers. From the observed influence of molecular structure of the developer on thermochromism, and also the significance of fractional composition on the efficacy of thermochromism, a mechanism for the process has been proposed.



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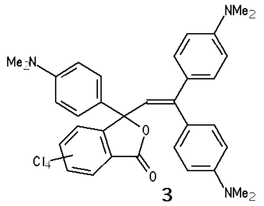

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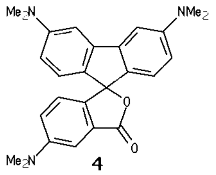

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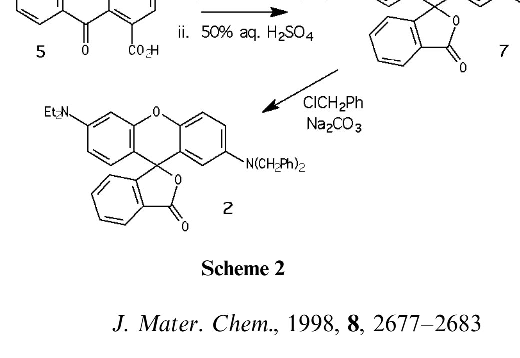
Results and discussion

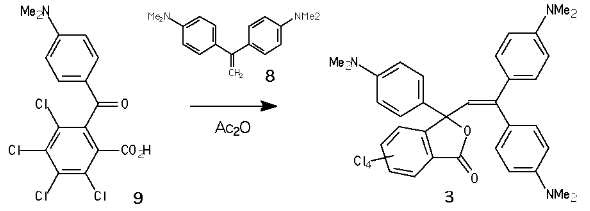
Synthesis and properties of the colour formers

The colour formers employed in this investigation are typical of the classes of colorant used industrially: diarylphthalide (**1**), fluoran (**2**), vinylphthalide (**3**) and fluorene (**4**). Crystal Violet lactone, **1**, is readily available commercially. The fluoran **2** was prepared by condensation of the benzoylbenzoic acid **5** with 4-acetylaminophenol (**6a**) followed by hydrolysis to give fluoran **7**, the primary amino group of which was then dibenzylated (Scheme 2).[6]



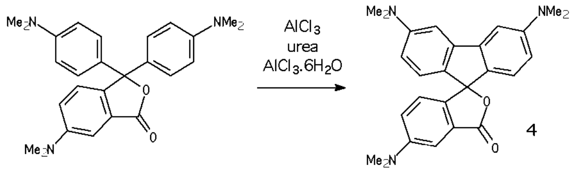
Scheme 2

The phthalide **3** was synthesised by condensing Michler's ethylene (**8**) with the tetrachloro-substituted benzoylbenzoic acid **9** (Scheme 3).[7]



Scheme 3

While **4** has been obtained from an aminospirolactone by diazotisation and intramolecular coupling[8] or treatment with sodium sulfite in concentrated sulfuric acid followed by addition of copper powder,[9] a method involving an intramolecular Friedel–Crafts reaction[10] was chosen owing to the availability of the starting material, **1** (Scheme 4).



Scheme 4

Each colour former showed strong infrared absorption in the 1750–1760 cm^{-1} range characteristic of phthalides.[11] In its solid form, **3** displayed photochromism in that the initially green crystals turned darker and more yellow in sunlight, returning to their original colour in the dark.

The lactones, when examined by thin layer chromatography, rapidly became coloured on contact with alumina or silica, as was expected with such polar media: **2**, **3** and **4** gave dark green, turquoise and pale green spots, respectively. The colour of the spots paralleled the absorption maxima of the derivatives in acetic acid solution (Table 1).

Preparation and properties of the compositions

Thermochromic compositions were prepared from each colour former **1**–**4** in the following manner: stearic acid, Bisphenol A and colour former in the ratio 50 : 2 : 1 were mixed and heated above the melting point of the fatty acid to produce weakly coloured or colourless solutions, which were then rapidly cooled by the addition of cold water causing simultaneous solidification and coloration of the wax. The reflectance minima of the dried, powdered compositions accorded well with the absorption maxima of the corresponding colour former in acetic acid.

Each composition exhibited reversible thermochromism. At the onset of melting of the composition, colour loss started to occur and within a few degrees above the melting point, the majority of the colour had been lost. Depending on the fractional composition and colour former, the difference in temperature between the onset of colour loss and complete loss of colour varied from only a few degrees to over 40 °C (Table 2). At 75 °C, the melts of the 50 : 2 : 1 (stearic acid : Bisphenol A : dye) samples based on **2** and **3** were almost colourless, although it was observed that after melting of the compositions, some coloured solid remained, which dissolved at higher temperatures to complete the colour loss. Reducing the proportions of co-solvent to developer and colour former from 50 : 2 : 1 to 50 : 1 : 1 and 25 : 1 : 1 made little difference to the initial colour intensity, but raised the temperature at which complete colour loss occurred (Table 2). However, in all cases, the onset temperature coincided with the start of melting of the composition, which was little different from that of stearic acid itself (mp 67–69 °C).

Table 1 Absorption maxima of the colour formers in acetic acid (99%)

Colour former	λ_{max}/nm
2	609, 464, 437
3	706
4	915, 836, 621

Compositions were prepared from the colour formers and Bisphenol A using fatty acids other than stearic acid. Onset of colour loss was again observed to be related to the melting point of the co-solvent. For example, 50 : 2 : 1 (fatty acid : Bisphenol A : **1**) compositions prepared using lauric acid, myristic acid and palmitic acid as the co-solvent component exhibited colour loss onset temperatures of 45 °C, 52 °C and 62 °C, respectively, which correspond well with the melting points of the co-solvents (42–46 °C, 51–53 °C and 61–63 °C respectively).[12] For a given co-solvent, varying the mixture ratio of the components had little effect on the point at which the composition started to melt or change colour and the switching temperature was determined solely by the temperature at which each formulation began to melt.

The colour change was found in all cases to be fully reversible: no colour loss was noted on repeated heating and cooling of the samples. For example, when the composition (50 : 2 : 1) based on **2** was subjected to thirty cycles of heating to 90–100 °C and allowing to cool below 40 °C, no significant differences in reflectance minima were noted.

Mechanism of the thermochromic effect

While the mechanism of irreversible thermochromism of spirolactone-based thermographic materials that change from a colourless to a permanently coloured state on heating is well understood,[13] little is known about the mode of operation of the reversible coloured-to-colourless compositions described above, despite the volume of patent material which has appeared and the widespread use of such compositions (in microencapsulated form) in textile and novelty goods.

Theories involving steric considerations[3] or phase separation[3–5] have been put forward in an attempt to explain why these compositions have only slight colour, if any, when molten, and yet are intensely coloured in the solid state. One theory proposes that steric factors determine the generation and loss of colour, whereas another explains the phenomenon in terms of temperature-driven phase changes within the composition. However, direct experimental evidence supporting either mechanism is surprisingly lacking. It is useful first to summarise the two mechanisms and then describe our own observations which strongly support the second mechanism.

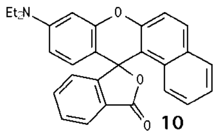
Sterically-induced mechanism of thermochromism. In this premise, it is argued that the existence of the coloured species (*e.g.* **1b**, Scheme 1) is more favourable sterically in the solid matrix of the composition compared to that for the colourless form (*e.g.* **1a**). Whereas the more restricted environment of the solid composition favours the coloured, relatively planar ring-opened structure over the tetrahedral colourless spirolactone structure, in the molten composition, the smaller steric requirement of the coloured species is less important and conversion to the lactone (and thus colour loss) can take place more readily. The argument is based on the supposition that steric factors regulate the position of the ring-opening equilibrium: cooling and solidification of the composition, which when molten contains the colour former predominantly in the colourless form, moves the equilibrium towards the coloured form since the planar geometry of the latter structure is more favourable in the solid.

However, X-ray diffraction data and molecular modelling

Table 2 Temperatures of melting, colour loss onset and completion for compositions of stearic acid/Bisphenol A/colour former

Colour former	Mixture ratio	Melting point/°C	Onset of colour loss/°C	End point of colour loss/°C
2	50:1:1	67–68.5	67	72
2	50:2:1	67–69	67	*ca.* 83
2	25:1:1	67–68.5	67	90
3	50:2:1	67–69	67	*ca.* 110

cast doubt on this theory. While X-ray crystallography has confirmed the non-planar nature of the spirolactone colour formers, like fluorans,[14] the ring-opened coloured species have also been found to be non-planar. Thus: (1) the aromatic rings of Crystal Violet Lactone cation (**1b**) complexed with metal iodides have a propeller-like orientation;[15] (2) the cation from benzofluoran **10** complexed with metal iodides has a near-planar xanthene component, although the carboxy-substituted ring is almost perpendicular to it;[16] (3) the ring-opened hydrochloride salt of the anilinofluoran **11** was found to have a structure in which the pendant phenyl ring is at right angles to, and the anilino substituent twisted out of plane of, the xanthene structure.[17]



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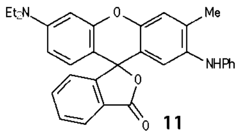

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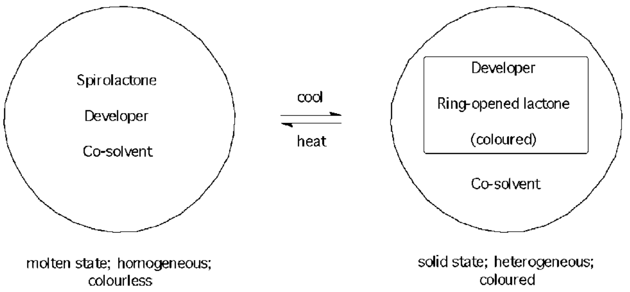
Molecular modelling reproduced the non-planar features of the structures in the first two examples listed above. Other ring-opened species were predicted to be significantly non-planar, for example, the structure of **3**, in which none of the aromatic rings were co-planar because of the crowded nature of the molecule.

From the X-ray studies and molecular modelling, it is clear that the coloured species are not planar and do not possess significantly smaller steric requirements over the corresponding colourless lactone forms. Thus a mechanism based on sterically-driven thermochromism seems unlikely.

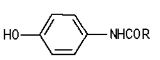
Phase separation mechanism of thermochromism. A more attractive theory for the mechanism of the thermochromic effect assumes that phase separation plays a major role. Thus little or no colour generation occurs in the molten composition because the colour former and acidic developer are dissolved in the co-solvent; the average environment experienced by the chromogenic compound is therefore relatively non-polar, which encourages lactonisation, so that the equilibrium is well over to the ring-closed, colourless spirolactone side. On cooling, the solubilities of the colour former and developer fall, so that eventually a proportion of these two components separates from the bulk monodisperse solution phase on solidification. The developer precipitates, bringing colour former with it (or *vice versa*). In this phase, the colour former experiences a more polar environment and intimate contact with the developer, resulting in ring-opening and generation of colour. On heating, the two phases merge and the colour former returns to its colourless spirolactone form. A simplified diagrammatic representation of the phase changes is shown in Scheme 5.



Scheme 5

This explanation of the mechanism has many implications. In addition to having the correct balance of acidity of the developer and basicity of the colour former, a balance must also be struck between the solubilities and solvating powers of the components in the composition. The theory suggests that the developer must be soluble enough to dissolve in the molten fatty acid, but not so soluble that it does not precipitate when the composition solidifies. Also, if too much co-solvent is present in the system, the solutes will not precipitate to a sufficiently high degree for satisfactory colour development. Conversely, too little co-solvent will prevent complete dissolution on melting and inhibit colour loss. The consequence of a system lacking any co-solvent, or the use of one that does not melt in the temperature range of interest, would be that the colour change would be more gradual and less complete. There will be no sudden removal of material into solution and consequent rapid colour loss.

The effectiveness of a developer can therefore be anticipated to depend not only on its acidity, but also on its solubility in the co-solvent. In order to verify this suggestion and to test the validity of the phase separation theory, a series of *N*-acylaminophenols **6** ($R = CH_3$ to C_7H_{15}, $C_{17}H_{35}$) of varying hydrophobicity, and thus solubility, has been synthesised. Each member has been used as a developer in stearic acid-based compositions in conjunction with a variety of colour formers, and the effect of developer structure on thermochromism measured.



6a, R = Me; **6b**, R = Et;
6c, R = n-Pr; **6d**, R = n-Bu
6e, R = n-C_5H_{11}; **6f**, R = n-C_6H_{13};
6g, R = n-C_7H_{15}; **6h**, R = n-$C_{17}H_{35}$

The consequences of using different ratios of components have also been examined. In addition to giving rise to a dilution effect, a high ratio of co-solvent to developer and colour former should, in terms of the phase separation theory, inhibit precipitation of the solutes, leading to a low degree of colour development, whereas too little co-solvent should prevent complete dissolution on melting and restrict colour loss. To examine these effects, a series of compositions of differing mixture ratios based on stearic acid and incorporating the developers **6** were prepared.

All the developers **6a–h** caused colour development, but to varying degrees depending not only on the colour former used, but also on the structure of the developer, the ratio of the components and the age of the composition (see following Sections).

Effect of developer structure. The colour intensity of each composition in the solid state was determined by measuring the reflectance of the powdered material at the λ_{max} of the colour former. The results are summarised in Fig. 1–3. All showed a similar pattern of colour development. Thus developers with short alkyl chains (**6a**, **6b**) conferred relatively pale colours; inserting one or two methylene fragments into the

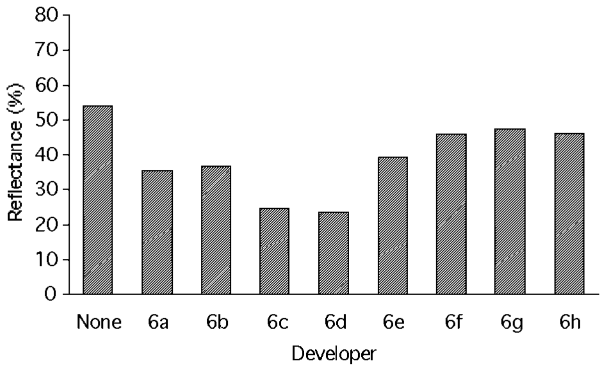


Fig. 1 Reflectance of powdered 50 : 1 : 1 stearic acid–**6**–**1** compositions at 610 nm.

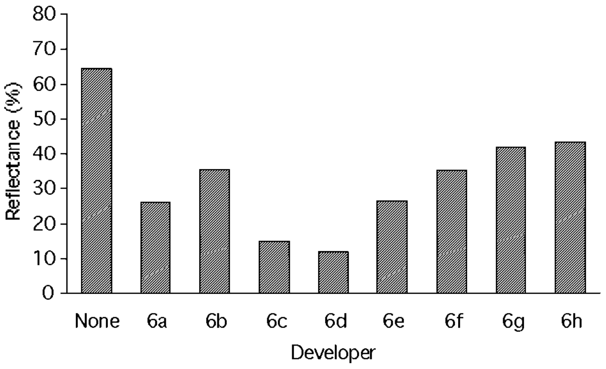


Fig. 2 Reflectance of powdered 25 : 1 : 1 stearic acid–**6**–**2** compositions at 605 nm.

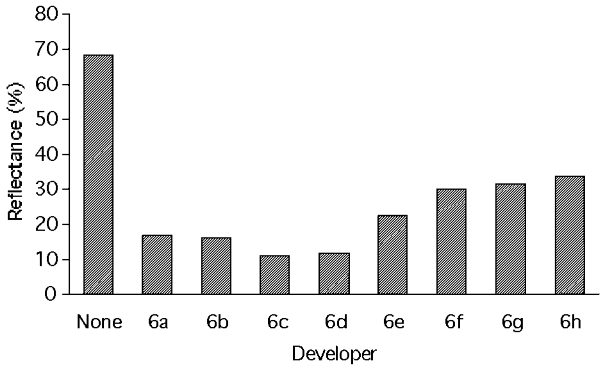


Fig. 3 Reflectance of powdered 50 : 2 : 1 stearic acid–**6**–**3** compositions at 720 nm.

chain of the latter to give **6c**–**d** caused deepening of the colour of the compositions, but further lengthening of the alkyl residue decreased the colour intensity.

In the case of the 50 : 1 : 1 stearic acid : developer : **1** compositions, addition of **6a** or **6b** brought a reduction in minimum reflectance of around 20% compared to the formulation lacking developer (Fig. 1); use of the propyl and butyl analogues led to a further lowering of the minimum, while the colour yield with **6e** was close to the level obtained with **6a** and **6b**.

The developers with the longest chains produced the highest reflectances (weakest colours), the formulation containing **6g** having a reflectance approaching that corresponding to the residual colour of **1** in stearic acid alone, *i.e.* a composition with no developer at all.

A similar pattern was shown by the series based on **2** (Fig. 2). Colour development was generally greater than in the previous series; even the long chain developers produced significantly lower reflectances than the mixture containing the colour former alone. The developers were particularly effective in conjunction with **3** (Fig. 3); reflectance values of compositions containing **6c** or **6d** approached those achieved with Bisphenol A. While colour development decreased with the employment of developers of longer chain length, the colour yields were significantly greater than without any developer. Both the visible and near infrared absorption of compositions formulated with **4** exhibited a strong dependence on the structure of the developer (Fig. 4).

All these findings conform to the predictions of the phase separation theory. The developers with short alkyl chains (**6a**, **6b**) are polar and not very soluble in the co-solvent (stearic acid), so that they conferred only pale colours when the compositions solidified on cooling, because much of the developer did not dissolve in the melt during composition preparation. On the other hand, the developers with long alkyl chains (**6f**–**h**) were found to be very soluble in the molten compositions, but gave only weakly coloured waxes, presumably because their high solubility inhibited phase separation on cooling. The developers possessing alkyl chains of intermediate length (**6c**, **6d**) seemed to have the required balance of satisfactory solubility in the molten stearic acid and poor solubility in the cold wax, so that in these cases, the highest amount of phase separated material was produced and colour development was greatest.

Effect of fractional composition on thermochromism. The influence of the mixture ratio on the colour strengths of solid stearic acid : **6a**–**g** : **1** compositions of ratio 25 : 1:1, 50 : 1:1 and 100 : 1:1 is depicted in Fig. 5. Increasing the ratio of co-solvent to developer and colour former generally lowered colour strength of the solids as anticipated. In addition to diluting the colour, the increased proportion of co-solvent reduces colour development by inhibiting precipitation of the components on solidification of the molten composition. Consequently, while the pattern of colour strength in relation to developer chain length as described above for the 50 : 1 : 1 series (see Section above) was generally reproduced in the 25 : 1 : 1 and 100 : 1 : 1 formulations, the average colour strength

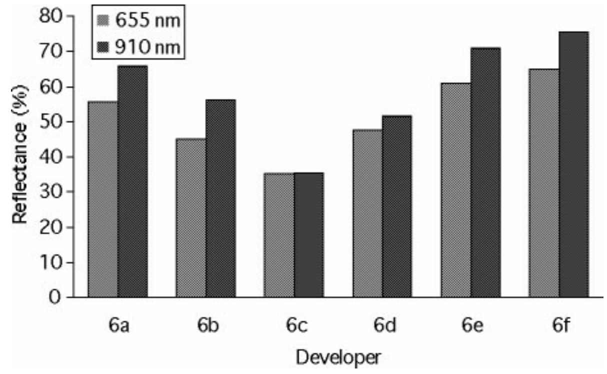


Fig. 4 Reflectance of powdered 50 : 2 : 1 stearic acid–**6**–**4** compositions at 655 nm and 910 nm.

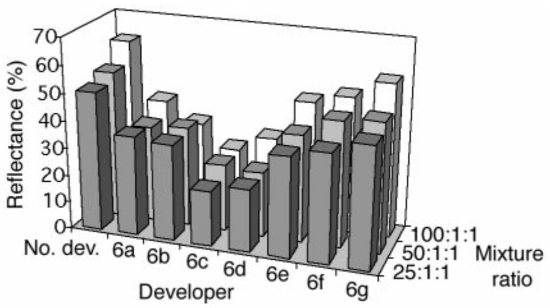


Fig. 5 Reflectance of powdered 25 : 1 : 1, 50 : 1 : 1 and 100 : 1 : 1 stearic acid–**6**–**1** compositions at 610 nm.

of the former series was stronger than that of the 50 : 1 : 1 compositions, whereas the average minimum reflectance of the latter series was higher. Wax constituting a 100 : 1 : 1 mixture of stearic acid : **6g** : **1** was almost as pale as the corresponding material lacking developer, suggesting that the acylaminophenol in the former composition had little tendency to separate from the stearic acid phase and/or form a separate phase with **1**.

The compositions containing **6b** did not conform to the typical pattern: colour yield slightly increased on raising the proportion of co-solvent from 50 : 1 : 1 to 100 : 1 : 1, presumably because more developer can go into solution and consequently separate with colour former on cooling.

Effect of ageing on the solid composites. Whereas all the coloured solid compositions containing Bisphenol A remained intensely coloured over long periods of time, the compositions formulated with the 4-acylaminophenols tended to lose their initial colour on standing with varying degrees of rapidity (Fig. 6–8). The series of 25 : 1 : 1 and 100 : 1 : 1 stearic acid : **6** : **1** compositions exhibited a similar pattern of colour loss to that displayed by the analogous range of 50 : 1 : 1 formulations shown in Fig. 6.

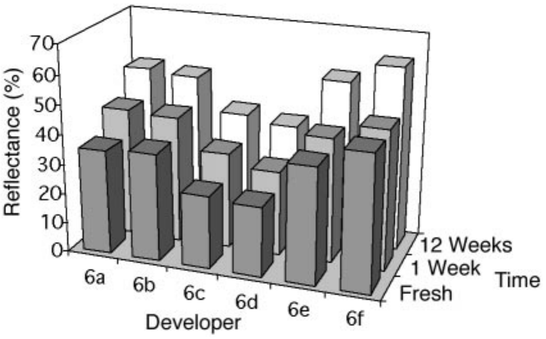


Fig. 6 Time dependence of reflectance of powdered 50 : 1 : 1 stearic acid–**6**–**1** compositions at 610 nm.

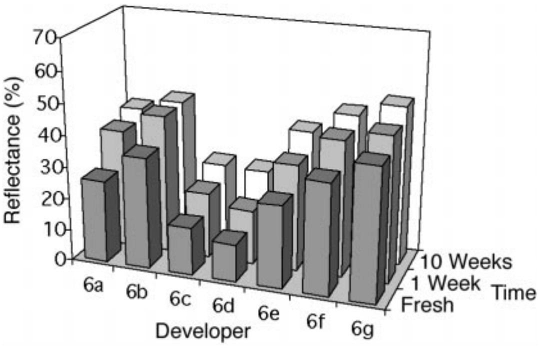


Fig. 7 Time dependence of reflectance of powdered 25 : 1 : 1 stearic acid–**6**–**2** compositions at 605 nm.

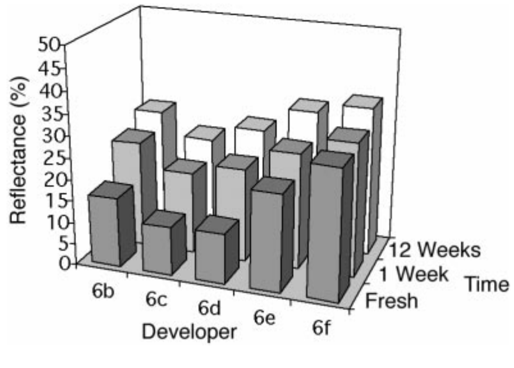


Fig. 8 Time dependence of reflectance of powdered 50 : 2 : 1 stearic acid–**6**–**3** compositions at 720 nm.

Week-old compositions were generally more weakly coloured than freshly prepared material. In certain cases, the colour change occurred sufficiently rapidly to be perceptible to the naked eye; for example, molten 25 : 1 : 1 and 50 : 1 : 1 stearic acid : **6g** : **1** compositions gave dark blue waxes when first quenched, which, over a few seconds, faded to pale blue. The corresponding 50 : 2 : 1 composition based on **3** lost colour over the course of a few minutes, while changes in the colours of 25 : 1 : 1 stearic acid : **6f**–**g** : **1** and 50 : 2 : 1 stearic acid : **6f**–**g** : **1** formulations were noticeable after a few hours.

The phenomenon can be explained in terms of phase separation: rapid cooling of the molten mixture brings about brief colour development through the initial co-separation of developer and colour former; secondary separation then takes place, whereupon colour former crystallises out of the developer (or *vice versa*) so that colour is lost as the former is no longer intimately associated with the latter. When the incompatibility between colour former and developer is particularly great, separation occurs rapidly enough for the colour of the wax to fade perceptibly over the course of several seconds or minutes. Thus not only is the solubility of the developer in the co-solvent an important factor, but the solubility of the colour former in the developer (or association between them) is of major relevance.

Experimental

Thin layer chromatography was performed using alumina plates (DC Alufolien Aluminiumoxid 150 F_{254} neutral type T, Merck). Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Thermal, FTIR and elemental analyses were performed on a DuPont 2000 differential scanning calorimeter, using a Perkin-Elmer 1740 spectrophotometer and in the Department of Chemistry of the University of Leeds, respectively. Reflectance measurements were obtained by means of a Perkin-Elmer Lambda 9 UV/visible/NIR spectrophotometer.

Preparation of the colour formers and developers

Fluoran colour former 2. 4-Acetylaminophenol **6a** (4.98 g, 33 mmol) and 2-(4-*N*,*N*-diethylamino-2-hydroxybenzoyl)benzoic acid **5** (8.91 g, 28 mmol) were added portionwise to stirred sulfuric acid (98%, 15 ml) over 20 min so that the temperature remained under 45 °C. The mixture was heated and stirred at 55 °C for 22 h, water (15 ml) added, maintaining the temperature below 85 °C, and then heated with stirring for 3 h at 90–95 °C. The intense red solution was cooled to room temperature and poured into a solution of sodium hydroxide (18 g) in water (130 ml) at such a rate that the temperature did not exceed 80 °C; aqueous ammonia (32%, *ca.* 8 ml) was added to make the pH of the purple suspension weakly alkaline. The solid was collected, washed with very dilute aqueous ammonia and dried to give crude 2′-amino-6′-*N*,*N*-diethylaminofluoran **7**.

Crude **7** (8.00 g, 21 mmol) was added to sodium carbonate (5.71 g, 54 mmol), benzyl chloride (98.5%, 6.75 ml, 58 mmol) and water (20 ml), before heating to 90 °C overnight to give a dark green mixture. This was cooled to room temperature, the aqueous phase decanted off and the residual dark green tarry product washed several times with water. Stirring with ethanol (20 ml) at 65 °C for 30 min furnished a green suspension which was cooled to room temperature and filtered. The collected solid was washed with a little ethanol (5 ml, twice) and then butanone (5 ml) to give crude **2** as a pale green powder (10.04 g, 86% crude yield). A portion (1.00 g) of this material was recrystallised twice (ethanol–DMF, 15 : 1) affording analytically pure, pale beige crystals (0.58 g, mp

172.5–174 °C). Microanalysis found C, 80.5; H, 6.1; N, 5.0% ($C_{38}H_{34}O_3N_2$ requires C, 80.5; H, 6.0; N, 4.9%). DSC and TLC (alumina, 9 : 1 toluene–ethyl acetate) indicated purity, showing a sharp endotherm at 172.3 °C and a single dark green spot respectively. FTIR (KBr)/cm^{-1}: 1752 (lactone C=O).

Vinylphthalide colour former 3. Magnesium (98%, 4.2 g, 0.17 mol) and diethyl ether (20 ml) were stirred under nitrogen as iodomethane (99%, 25.0 g, 0.17 mol) was added dropwise over 20 min at such a rate as to maintain a continuous exotherm and gentle refluxing. The mixture was gently refluxed for 25 min by which time almost all of the magnesium had dissolved. The reaction mixture was protected from light and a solution of Michler's ketone (98%, 9.0 g, 33 mmol) in toluene (280 ml) at room temperature was run in. The mixture was stirred under nitrogen in the absence of light at ambient temperature for 22 h, before cautiously quenching with water (200 ml) to give a light blue emulsion, which was stirred for 15 min. A solution of ammonium chloride (30 g) and acetic acid (99%, 15 ml) in water (150 ml) was added and the whole stirred for 3.5 h. The aqueous phase was washed twice with toluene (50 ml) and the extracts combined with the organic phase, from which the solvent was removed by rotary evaporation after drying overnight with magnesium sulfate. The pale blue-green residue (8.59 g, 98% crude yield, mp 116–120 °C) was recrystallised in ethanol, furnishing Michler's ethylene (**8**) as a pale blue lustrous solid (7.15 g, mp 121–123 °C, lit.,[18] 121–122 °C).

A mixture of **8** (1.33 g, 5.0 mmol), 2-(4-*N*,*N*-dimethylaminobenzoyl)-3,4,5,6-tetrachlorobenzoic acid **9**[19] (2.04 g, 5.0 mmol) and acetic anhydride (7.5 ml) was stirred and heated to reflux for 20 min. The dark green mixture was allowed to cool and poured into a mixture of toluene (50 ml), ice (50 ml) and aqueous ammonia (32%, 10 ml). The emulsion was destroyed by addition of a little dichloromethane; the organic phase was collected and the aqueous phase extracted with more dichloromethane. The combined extracts were washed several times with water, dried (magnesium sulfate) and rotary evaporated to dryness, giving a dark yellow-brown solid (2.94 g, 90% crude yield, mp 220–222 °C). Recrystallisation (methoxyethanol, methoxyethanol–DMF 12 : 1 twice) furnished **3** as green needle-like crystals (1.03 g, mp 227.5–229 °C), which darken in sunlight, but return to their original colour in the dark. Microanalysis found C, 61.9; H, 4.8; N, 6.1; Cl, 20.8% ($C_{34}H_{31}N_3O_2Cl_4$ requires C, 62.3; H, 4.8; N, 6.4; Cl, 21.6%). DSC indicated reasonable purity, showing a single endotherm at 226.6 °C. TLC (alumina, 9 : 1 toluene–ethyl acetate) revealed one blue-green spot. FTIR (KBr)/cm^{-1}: 1758 (lactone C=O).

Fluorene colour former 4. Aluminium chloride (96%, 50.0 g, 0.36 mol), urea (7.5 g, 0.12 mol) and aluminium chloride hexahydrate (99%, 0.75 g, 3.1 mmol) were stirred and heated to 125 °C. Crystal Violet Lactone (**1**) (97%, 5.2 g, 12 mmol) was added and the mixture stirred at 135–140 °C for 4 h. Heating was continued for another 18 h by which time the reaction mixture had become a solid mass. The reaction was quenched by gradual addition of water (400 ml) to give a blue-green suspension, which was treated with hydrogen peroxide (30%, 1.2 ml) and stirred for 1.5 h. The suspension was extracted several times with dichloromethane; the combined extracts were washed and dried over magnesium sulfate. Removal of the drying agent and solvent furnished a dull green solid (4.43 g, 89% crude yield). Three recrystallisations (toluene/charcoal) gave **4** as buff crystals (1.20 g, mp 225–227.5 °C). Repeated recrystallisation of 0.40 g of this material from toluene and ethanol afforded analytically-pure pale cream crystals (0.07 g, mp 237–242 °C, lit.,[8] 244–246 °C, lit.,[10] 240–245 °C). Microanalysis found C, 75.3; H, 6.7; N, 10.15% ($C_{26}H_{27}N_3O_2$ requires C, 75.52; H, 6.58; N, 10.16%). DSC indicated reasonable purity, analysis revealing a small endotherm at 248.4 °C and a sharp, major endotherm at 261.7 °C, with decomposition occurring at around 316 °C. TLC (alumina, 9 : 1 toluene–ethyl acetate) revealed a single green spot of R_f 0.57. FTIR (KBr)/cm^{-1}: 1752 (lactone C=O).

Developers 6a–h. Apart from the readily available **6a**, the developers **6** were synthesised from 4-aminophenol by the methods of Fierz-David and Kuster.[20] The 4-propionyl analogue **6b** was obtained using propionic anhydride, whereas the longer alkyl chain derivatives ($R = C_3H_7$ to C_7H_{15}) were synthesised from the corresponding acid chlorides, while the stearoyl derivative **6h** was prepared by condensation with stearic acid.

Preparation of the compositions

Formulations of 50 : 1 : 1 stearic acid (2.00 g), developer **6** (Table 3) and **1** (0.040 g) were prepared by heating the mixture to 100–105 °C and stirring until dissolution was complete, or until no more dissolution occurred, and quenching with the addition of *ca.* 20 ml of cold water. The solidified wax was filtered off, allowed to air-dry overnight and powdered.

Series of compositions of ratio 25 : 1 : 1 and 100 : 1 : 1 were also prepared in a similar manner. Formulations containing **2** (25 : 1 : 1), **3** (50 : 2 : 1) and **4** (50 : 2 : 1) were made by the same procedure, except that the mixtures were heated to 95–100 °C, 105–110 °C and 100–105 °C, respectively. The ratios strictly only apply to compositions containing **6a**; the amounts of developer listed in Table 3 are equimolar so that, within a particular series of compositions, each member of the range consists of a fixed molar ratio of developer to colour former and co-solvent.

The procedure for measuring the reflectance of the powdered formulations involved packing the material into a glass-fronted cylindrical cell comprising two close-fitting components. The composition was compressed in the cell by insertion of the cylinder and the reflectance measured (scan speed 240 nm min^{-1}); the powder was displaced and re-compressed before taking a second measurement. The technique was found to yield consistent results.

Molecular modelling

The 'Hyperchem' software package (Release 3 For Windows, Autodesk Inc.) was used in an attempt to visualise the geometry of the ring-opened colour former molecules. The procedure involved optimising the geometry by using molecular mechanical methods, conducting the iterative energy-minimising routines to the desired energy gradient (0.01 kcal Å^{-1} mol^{-1}) with the Polak–Ribiere algorithm. The MM+ force field was used as it was deemed the most appropriate for relatively small molecules like the colour formers. For the sake of simplicity, the colour formers were assumed to ring open to give a free carboxylic acid group, *i.e.* the nature of the developer and the type of association was not considered in the modelling.

Table 3 Masses of developers **6** used in 50 : 1 : 1 compositions

Developer	Mass/g	Developer	Mass/g
6a	0.0400 ± 0.0004	**6e**	0.0549 ± 0.0005
6b	0.0438 ± 0.0004	**6f**	0.0586 ± 0.0005
6c	0.0475 ± 0.0004	**6g**	0.0623 ± 0.0005
6d	0.0512 ± 0.0005	**6h**	0.0995 ± 0.0005

Conclusions

Thermochromic systems have been prepared which deliver sharp reversible changes from coloured to colourless states when heated above their melting points. A mechanism for the phenomenon based on steric considerations was rejected on the basis of X-ray crystallographic data and molecular modelling predictions. An explanation in terms of phase changes was investigated by preparing compositions from developers of differing hydrophobicity. The findings lent weight to such a theory, although more direct evidence of the existence of the proposed phases and phase changes is necessary for confirmation of its validity.

Several influences on colour yield were identified; for example, developer structure had a significant effect. The developers with short alkyl chains were polar and not very soluble in the co-solvent, so that they conferred only pale colours when the compositions solidified on cooling, whereas the developers with long alkyl chains were found to be very soluble in the molten compositions, but gave only weakly coloured waxes, presumably because their high solubility inhibited phase separation on cooling. The developers possessing alkyl chains of intermediate length seemed to have the required balance of satisfactory solubility in the molten stearic acid and poor solubility in the cold wax, so that in these cases, the highest amount of phase separated material was produced on solidification and colour development was greatest. As anticipated, colour strengths were observed to be dependent on mixture ratio: increasing the ratio of co-solvent to developer and colour former generally lowered colour yields. However, in certain cases, an increase in the proportion of co-solvent relative to developer improved colour development as more of the latter could be dissolved and consequently separate with colour former on cooling. While formulations containing Bisphenol A have not been observed to change colour over time, compositions prepared from the *N*-acylaminophenol developers were found to fade to different extents with varying degrees of rapidity from over the course of seconds to weeks. The phenomenon may arise through phase separation of the colour former and developer from each other after the initial separation of the developer together with the colour former on cooling.

If, as suggested by the above findings, the explanation of the thermochromism lies in phase separation, there are a number of conclusions that can be drawn concerning the design and optimisation of compositions based on co-solvent/developer/colour former combinations. The developer must possess just enough solubility in the molten co-solvent to cause complete dissolution and yet have sufficiently poor solubility in the cooled composition to maximise phase separation. In addition to the colour former having satisfactory solubility in the co-solvent and the correct basicity for colour changes of high contrast, the colorant must be compatible with the developer, otherwise phase separation between these two components will occur after the initial separation from the co-solvent, resulting in loss of colour after solidification of the composition.

Phase separation can also explain the thermochromism of a two-component system based on **1** and β-estradiol that gives a change from colourless to coloured on melting,[4] which is the reverse of that observed for the three-component composites discussed above. Presumably the β-estradiol assumes the roles of both developer and co-solvent as not only does it have a phenolic residue, typical of the first component, but it also has a hydrophobic alkyl skeleton, characteristic of the second. In the molten composite, the colorant is ring-opened and thus coloured, because it is dissolved in, and can interact with, the β-estradiol, whereas on solidification, the colorant separates from the bulk phase, ring-closes and the formulation loses its colour.

Within the framework of the proposed mechanism, it would appear that another approach to produce coloured-to-colourless formulations comprising only two components is possible: in these, a colorant of a design which combines the functions of both colour former and developer, for example a spirolactone bearing phenolic residues, is formulated with a co-solvent. Provided the colorant is readily soluble in the melt, separates from the bulk phase on solidification and has the correct balance of basicity and acidity, the composition will be reversibly thermochromic: in the molten composition, lactonisation will be favoured, while cooling will lead to separation of a colorant phase in which intermolecular interaction between the lactone and phenolic elements can occur causing ring-opening and colour generation.

Acknowledgement

The authors wish to thank the Defence Clothing and Textiles Agency (Colchester, UK) for the funding and support of this work.

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Paper 8/05994B