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A General-Purpose Colourimetric Air pressure Indicator

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Abstract

A general-purpose air pressure *colourimetric* indicator is described based on a sensitive CO₂ indicator, which responds to the change in partial pressure of CO₂ in air. The indicator uses the pH indicator dye thymol blue (TB) and is green in ambient air (at 1 atm), bright blue under high vacuum (< 0.01 atm) and bright yellow at high air pressures (> 10 atm). The TB indicator is cast from an ink and its change in colour monitored mainly using digital photography coupled with colour analysis and quantitatively related to air pressure. The response of the TB indicator is initially probed using different Ar/CO₂ gas mixtures at 1 atm pressure and then used to monitor: (i) sub-ambient air pressures, P , over the range 0.1-1 atm and (ii) super ambient air pressures over the range 1-14 atm. Colour analysis of all the photographic images taken in the two studies reveals a consistent data set that is readily related quantitatively to P , with a typical 50% colour change at 1.02 ± 0.03 atm of air, *i.e.* or $(4.2 \pm 0.1) \times 10^{-4}$ atm of CO₂. The 90% response and recovery times of the indicator to sudden changes in pressure are fast, < 1.7 min. Two possible applications of the TB indicator, in vacuum packaging and as a pressure sensitive paint in aerodynamics are demonstrated. This is the first example of a general-purpose air pressure colorimetric indicator and in particular one that can be used to monitor super-ambient air pressures up to ca. 10 atm.

Keywords: colour indicator; air pressure, vacuum-packaging; aerodynamics

1. Introduction

Optical sensing based on colour or fluorescence is a growing area and a number of such sensors are now established as commercial products [1-4]. Possibly the most notable type of commercial optical sensor developed to-date is the O₂-sensitive indicator, commercial manifestations of which include the: OxyDot® (Oxysense) [5], RedEye® FOXY (OceanOptics) [6] and OpTech® (Mocon) [1, 7]. These indicators are mainly used for monitoring the level of O₂ in packaging, especially of food and drink, and in the environment (air or water) [1]. However, as commercial luminescent 'dot' indicators are relatively expensive, typically \$4 – \$30 each [1], as is the associated excited-state lifetime measuring equipment used to interrogate the indicators, the use of oxygen indicators in food packaging is largely limited to packaging research [8, 9].

Vacuum packaging (VP) is often used in wholesale and retail food packaging of fresh and processed meat and fish, cheese, chocolate, sweets and many different dried goods, such as rice, and can extend the shelf-life of foods by days, although more often weeks and, in some cases, months [10]. VP is also used for pharmaceutical and medical products, electronic components, coins and collectables [11]. Although there have been some reports [8, 9] of using O₂ indicators to monitor air pressure in VP, their relative high cost has prevented widespread use. As a consequence, there remains no quick, simple, inexpensive method for measuring the air pressure inside vacuum-packed packages, and so no routine way to assess package integrity after VP.

In the last 40 years the same luminescence technology associated with O₂ sensing in packaging has been used by the aeronautical and automobile industries to monitor super- and sub-ambient air pressures on plane and car surfaces in wind tunnel experiments in order to help visualise air flow and optimise the aerodynamics [12, 13]. The indicator is usually applied to the surface as a paint film, and so the technology is often referred to as pressure sensitive paints, PSPs [14]. Although commercial PSPs are available [15], once again the equipment needed to help visualise the flow is costly and so their use is usually limited as a research tool in well-funded research laboratories and test facilities [16].

Given the expense and limitations of the *luminescence*-based approach referenced above for monitoring air pressure using an optical sensor, in food packaging and aerodynamic

studies for example, there is a clear need for a general-purpose, simple, inexpensive *colourimetric* indicator for monitoring air pressure, as such an indicator could be readily assessed qualitatively by eye or quantitatively using digital photography.

One way such an indicator might be created is by using a colourimetric indicator to monitor the very low level of CO₂ that is in air, ca. 4.11×10^{-4} atm (*i.e.* 0.0411 %) [10], since any increase or decrease in ambient air pressure would be reflected by a proportionate increase or decrease in the partial pressure of CO₂. Recently this group reported a vacuum air pressure purple to colourless colourimetric indicator based on this principle which has a halfway colour changing point of 0.033 atm of air (at 17 °C), and so is colourless at 1 atm [17]. This indicator, and the more general-purpose air pressure indicator described here are based on inks that contain an ion-pair of a pH indicating dye anion, D⁻, with a lipophilic quaternary ammonium cation, Q⁺, so that the ion-pair's formula is: D⁻Q⁺xH₂O [18, 19]. The phase transfer nature of the ion-pair, D⁻Q⁺xH₂O, renders it readily soluble in a solvent-based ink which, when allowed to dry, yields a coloured, plastic film that responds to CO₂ due to the following equilibrium reaction:

Colour **A** Colour **B**

where, D⁻Q⁺xH₂O and HCO₃⁻(x-1)H₂O.DH are the usually very differently coloured deprotonated (D⁻) and protonated (HD) forms of the pH-indicating dye, D. It follows from the above reaction equation that

$$R = [HD] / [D^{-}] = \alpha \times \%CO_2 \quad (2)$$

where *R* is a measure of the degree of transformation of the dye from the deprotonated to protonated form due to the presence of CO₂, [HD] and [D⁻] are the concentrations of Q⁺HCO₃⁻.HD.(x-1)H₂O and Q⁺D⁻.xH₂O, respectively, and α is a proportionality constant (units: %⁻¹), which provides a measure of the sensitivity of the CO₂ optical sensor under test. The halfway colour changing point for such indicators occurs at a %CO₂ = 1/ α %. It can be shown that the value of α is related both to the *pK_a* of the dye and the base concentration, with the sensitivity of the CO₂ indicator largely defined by the former, but then amenable to fine tuning by varying the latter. Thus, when constructing a low, *i.e.* 1-5 % CO₂-responding ion-pair indicator, this and other groups have used pH-indicator dyes with relatively high *pK_a*

values, such as *meta*-cresol purple (MCP; $pK_a = 8.28$) or Cresol Red (CR; $pK_a = 7.95$) [20-25]. In contrast, dyes with lower pK_a values, e.g. Phenol Red (PR; $pK_a = 7.52$), have been used [20, 23] to make >10% CO₂-responding indicators.

In our recent paper reporting on a colourimetric vacuum air pressure indicator, the dye *ortho*-cresolphthalein, OCP, $pK_a = 9.32$, was used and the resulting indicator was so sensitive it changed colour at air pressures much less than 1 atm, i.e. sub-ambient air pressures [17]. In order to make a more general-purpose air pressure indicator, i.e. one that can be used to monitor both sub- and super-ambient air pressures, it follows that a less sensitive CO₂ indicator is required. Thus, in this work, we use Thymol Blue (TB), which is bright blue coloured in its deprotonated (D⁻) anionic form and bright yellow in its protonated (*i.e.* DH) form and has a pK_a of 8.90 [26], to construct and characterise the first reported example of a general-purpose air pressure *colourimetric* indicator.

2. Experimental

Materials

Unless otherwise stated, all chemicals and solvents were purchased from Sigma Aldrich in the highest purity available. All gases used were purchased from BOC at the highest purity.

Preparation of the Thymol Blue (TB) ink

The CO₂-sensitive thymol blue (TB) ink was prepared as follows: 0.04 g of TB, 2 g methanol, 1 ml of 1 M tetrabutylammonium hydroxide (TBAH) in methanol, 0.5 ml tributyl phosphate (TBP) and 5 g of a 10 wt% ethyl cellulose (EC) solution in 80:20 (v/v) toluene:ethanol, were mixed together in a 30 ml beaker and stirred for 2 hours using a magnetic flea. The ink was then cast onto a 50 µm PET film using a K-bar 3 coater to draw down a ca. 24 µm wet film which dried within a few minutes in air to form an ink film with a thickness of ca. 6 µm.

Methods

All UV-vis absorbance measurements were made using an Agilent Technologies CARY 60 UV-Vis spectrophotometer. In this work the TB indicator was placed in a gas cell, the details of which are described elsewhere [27], and purged with different Ar/CO₂ mixtures, produced using a gas blender, *vide infra*. All digital photographs were taken using a Cannon 600D digital camera and HiraLite 14 W full spectrum Daylight lamp (colour temperature (CT): 5000

K) as the illumination source; for good colour reproduction all photography needs to be carried out in a well white light lit environment. Before each photographic session the Custom White Balance (CWB) feature of the camera was activated on the camera using a white card, so that the camera locked into the colour temperature of the white light lamp from the light reflected from the card [28]. This process helps ensure that the indicator colour recorded in the digital images was true and independent of the white light source. Thus, not surprisingly, using the CWB feature of the camera, other photographic work carried on the same indicator, but using different light white light sources, namely: cool white and warm white light fluorescent strips (with CTs of 4100 K and 2700 K, respectively [29]), revealed no significant differences in the recorded digital photographic images of the TB indicator, nor in the calculated subsequent values of the key RGB-based parameter R' , *vide infra*.

All digital images were processed for their red, green and blue colour space values (*i.e.* RGB values) using the freely available photo-processing software, *Image J* [30]. Different gases with different levels of CO₂ were generated using a gas blender (two tube gas proportioner, Cole-Parmer, UK) and their exact %CO₂ level confirmed using a Legend O₂/CO₂ gas analyser (Anéolia, France). Unless stated otherwise, all work was carried out at 18 °C.

In the studies of the TB indicator carried out under reduced atmospheric air pressure, the indicator was placed inside a vacuum chamber with a glass lid (model: DP1.5, Applied Vacuum Engineering, UK), connected to a vacuum pump (model: LC.4, DVP vacuum technology, Italy). This system allowed the simultaneous monitoring of: (i) the ambient vacuum pressure, measured using a digital vacuum manometer (model: LEO record, Keller AG, Switzerland), placed inside the chamber, and (ii) the colour of the indicator, using digital photography.

In the studies of the TB indicator carried out at above atmospheric air pressure, the indicator was placed inside a stainless-steel reactor with a toughened soda lime glass window, which had a 47 atm maximum working pressure (type P flow indicator, Visilume Ltd., UK). This system was used to record, through digital photography, the change in colour of the TB indicator as a function of air pressure inside the pressurised steel reactor.

3. Result and Discussion

3.1 Initial experiments at 1 atm using different %CO₂

In order to establish the veracity of reaction (1) and Eq. (2), the TB indicator (a TB ink film on 50 μm PET) was placed in gas cell [27] and exposed to a range of different CO₂ levels, varying from 0 - 100% CO₂, and the colour changes produced in the indicator were recorded both photographically and spectrophotometrically. The results of this work are illustrated in Fig. 1 and reveal that, in the absence of CO₂ the TB indicator is bright blue and, as the level of %CO₂ is increased, the indicator changes colour, eventually ending up bright yellow at 100% CO₂.

Fig. 1. (a) Digital photographs of the TB indicator in a gas cell as a function of the %CO₂ in the gas stream and (b) simultaneous recording of the UV-vis absorption spectrum of the indicator (from top to bottom) as the %CO₂ is increased from 0 to 100%. The insert diagram is a plot of R vs %CO₂, where the values of R were calculated using Eq. (3) and the absorbance data in the main diagram for $\lambda(\text{max}) \text{ D}^-/\text{TB}^-$, 630 nm.

The absorbance, A , at the $\lambda_{\max}$ of D^- , *i.e.* 630 nm, of the TB dye in the air pressure indicator film, is a measure of the concentration of $[D^-]$ and can be used, *via* Eq. (2), to calculate a value for, R , which is related directly to %CO₂, since:

$$R = (A_0 - A)/(A - A_\infty) = [HD]/[D^-] = \alpha \cdot \%CO_2 \quad (3)$$

where, A_0 is the value of absorbance due to the pH-indicating dye at $\lambda_{\max}(D^-)$ when %CO₂ = 0 (*i.e.* when all the dye is in its deprotonated form) and A_∞ is the absorbance of the film when all of D is in its protonated (colourless) form, *i.e.* as HD , *i.e.* when %CO₂ = ∞ ; the latter absorbance is assumed here to be that measured when the %CO₂ = 100% and the film is bright yellow coloured. As predicted by Eq. (3), and illustrated in Fig. 1(b), a plot of R vs %CO₂ yields a good straight line and helps to confirm that the key process is readily described by reaction (1), where $D = TB$. More importantly, the value of the gradient of the line of best fit to the data in the insert plot in Fig. 1(b), *i.e.* α , is ca. $25.6 \pm 0.7 \%CO_2^{-1}$, so that $1/\alpha$ (the halfway colour changing point of the indicator) is $0.039 \pm 0.001 \%CO_2$.

The latter level of CO₂ is about the same as that in air (411 ppm [17]), and so, if air pressure was used to change the colour of the TB indicator, its halfway colour changing point occurs at ca. 1 atm air, which is 30 times greater than that of the OCP vacuum air pressure indicator (0.033 atm of air) reported earlier [17]. As a result, the TB indicator is much less sensitive to CO₂/air pressure than the OCP vacuum air pressure indicator and so more appropriate for a general-purpose air pressure indicator.

One of the novel and highly desirable features of the TB general-purpose air pressure indicator is that it possesses a halfway colour changing point that is ca. 0.0411%, i.e. ca. 1 atm of air pressure.

Thus, for the TB indicator, if the ambient air pressure is gradually reduced below 1 atm, so that the partial pressure of CO₂ is, in turn, reduced below 4.11×10^{-4} atm, the TB indicator will turn increasingly blue from its original (intermediate) green colour (in air at 1 atm). Similarly, if the ambient air pressure is gradually increased above 1 atm, so that the partial pressure of CO₂ is, in turn, increased above 4.11×10^{-4} atm, the TB indicator will turn increasingly yellow. As we shall see, it follows that the TB indicator, with a $1/\alpha$ value of $0.039 \pm 0.001 \%CO_2$, can be used as an air pressure indicator for pressures ranging from well below 1 atm (down to ca. 0.1 atm) to those well above it (up to ca. 10 atm), *i.e.* it is well suited as a general-purpose air pressure indicator.

Finally, a similar experiment as outlined in Fig. 1, conducted at 18 °C, was also carried out at 5.5, 10 and 34 °C and the results, plotted in the same form as that in the insert diagram in Fig. 1(b), were used to derive a series of values for α as a function of temperature. Since α' is an equilibrium constant, it is expected, from the van't Hoff equation, that a plot of $\ln(\alpha)$ vs $1/T$ will yield a straight line with a gradient = $-\Delta H/R$, where ΔH is the enthalpy change associated with reaction (1), with TB as the pH indicating dye. In fulfilment of this prediction, a plot of $\ln(\alpha)$ vs $1/T$, yielded a good straight line, with a value for the gradient that allowed a value for ΔH of $41 \pm 4 \text{ kJ mol}^{-1}$ to be calculated, which is similar to those reported for other CO₂-sensitive colourimetric indicators (*i.e.* 32-77 kJ mol⁻¹) [18].

3.2 Digital and spectrophotometric analysis

Recent work has shown that, for simple colour-changing systems such as here, digital photography coupled with colour analysis, using red, green and blue colour space values (*i.e.* RGB), can be used to generate apparent absorbance values, A' , which are directly proportional to their real absorbance value, A , counterparts [31-33]. Apparent absorbance values are calculated using either the red, green or blue component values (ranging from 0-255) of the digital image of the indicator, *i.e.* $RGB(red)$, $RGB(green)$ and $RGB(blue)$, depending what colour the dye absorbs most strongly. In the case of the TB indicator, the $RGB(red)$ component varies most significantly with the variation in partial pressure of CO₂, and so at any %CO₂ its value, derived from a typical digital image illustrated in Fig. 1(a), is used to calculate an associated apparent absorbance value, A' , for the vacuum indicator, using the expression:

$$A' = \{\log 255 / RGB(red)\} \quad (4)$$

It follows also that Eq. (3) can be rewritten, in terms of apparent absorbance values, as follows, *i.e.*

$$R' = (A'_0 - A') / (A' - A'_{\infty}) = \alpha \cdot \%CO_2 \quad (5)$$

Thus, for every digital image of the TB indicator, such as illustrated in figure 1(a), at a known %CO₂, a value R' can be calculated.

In section 3.1 Eq. (3) was validated using the *spectral data* shown in Fig. 1, as illustrated by the straight line plot of R vs %CO₂ in the insert plot in Fig. 1(b). Here, Eq. (4) was similarly validated using the $RGB(red)$ data extracted from the digital images illustrated in Fig. 1(a) to

construct a plot of R' vs $\%CO_2$, which also yielded a good straight line with almost the same gradient as that reported above from real absorbance measurements, *i.e.* $24.2 \pm 0.8 \%CO_2^{-1}$ (*i.e.* $1/\alpha = 0.041 \%CO_2 \equiv 1.0 \text{ atm of air}$) compared to $25.6 \pm 0.7 \%CO_2^{-1}$ (*i.e.* $1/\alpha = 0.039 \%CO_2 \equiv 0.95 \text{ atm of air}$).

The above findings show that the TB indicator can be used to monitor $\%CO_2$ levels similar to those found in ambient air, *i.e.* 0.0411% , or $4.11 \times 10^{-4} \text{ atm}$, and that the monitoring can be carried out using either UV-vis spectrophotometry, or the much less expensive technique of digital photography coupled with digital image colour analysis. In addition to low cost, the latter method is much easier to apply than UV-vis spectroscopy and ideal for measuring $\%CO_2$ levels in packaging for example, via an appropriate colour indicator, especially using the digital camera in a mobile phone and an appropriate RGB measuring colour App, of which there are many [28]. As a consequence, digital photography coupled with digital image colour analysis was used in all subsequent work on the TB indicator.

As the TB indicator responds to the partial pressure of CO_2 in the ambient atmosphere, if this parameter is varied by varying air pressure, P , as in VP and in aerodynamic studies, it follows that Eq. (5) can be rewritten as:

$$R' = (A'_{00} - A') / (A' - A'_{\infty}) = \alpha' \cdot P \quad (6)$$

The initial work described above and Eq. (6) suggests that, through digital photography, coupled with colour analysis, the TB indicator can be used to monitor sub- and super-ambient air pressures quantitatively as well as qualitatively and these features are explored below.

3.3 TB indicator under sub-ambient air pressures

The colour change in the TB indicator was monitored as a function of sub-ambient air pressure by placing it in a vacuum chamber with a glass lid and photographing its responses at different air pressures. Some of the results of this work are illustrated in Fig. 2(a) and show that at 1 atm air pressure the TB indicator is green coloured but, with ever-increasing vacuum, it turns increasingly blue. The photographs of the indicator in 100% CO_2 (far right hand side) and that under high vacuum (or Ar atmosphere) conditions (far left hand side), where the indicator is in its fully protonated (bright yellow) and fully deprotonated (bright blue) forms, respectively, are also illustrated in Fig. 2. Each and every one of the digital

photographs taken as a function of sub-ambient air pressure, including those in figure 2(a), were used to extract an $RGB(red)$ value for each associated air pressure, P . Each $RGB(red)$ value was then used to calculate an apparent absorbance value, *via* Eq. (4), which in turn was used to calculate a value of R' , using Eq. (6). As predicted by the latter equation, and illustrated in Fig. 2(b), a plot of R' vs P yielded a good straight line with a gradient, $\alpha' = 1.14 \pm 0.02 \text{ atm}^{-1}$ (i.e. $1/\alpha' = 0.88 \text{ atm}$ of air).

Fig. 2. (a) Photographs of the TB indicator under different reduced air pressures. The far right image was recorded under 100% CO₂, as it represents the colour of the indicator when all the dye is in its protonated form. Similarly, the far left image was recorded under high vacuum ($< 0.01 \text{ atm}$), as it represents the colour of the indicator when all the dye is in its deprotonated form. All the digital photographs, taken of the indicator as a function of P , were then used to construct the plot of R' vs P illustrated in (b).

In an additional set of experiments, the indicator was photographed as a function time as it was exposed to a cycle of high vacuum ($P < 0.01 \text{ atm}$) whereupon A' increases, followed by no vacuum, i.e. $P = 1 \text{ atm}$, whereupon A' decreases. The results of this work, plotted in a form of an A' vs time oscillating profile, are illustrated in Fig. 3, from which values for the 90% response (to applied vacuum) and recovery (release of vacuum) times of 1.1 and 1.6

min, respectively, were calculated. Note: the indicator's response (to vacuum) time, although fast (1.1 min), is also not too dissimilar to the time it actually takes to evacuate the chamber which holds the TB indicator, which suggests that the actual response time of the indicator may be much less.

Fig. 3. Measured variation in apparent absorbance of the TB indicator when exposed to a continuous cycle of: ambient (1 atm), i.e. low A' , followed by reduced (<0.01 atm), i.e. high A' , air pressure.

3.4 TB indicator under super-ambient air pressures

The colour change in the TB indicator was also monitored as a function of super-ambient air pressure by placing it in a stainless-steel reactor with toughened glass window and photographing it as a function of increasing air pressure, delivered in a regulated manner using a cylinder of air. Some of the results of this work are illustrated in Fig. 4(a) and show that as the air pressure is increased from 1 atm to 14 atm of air pressure it turns from an initial green colour to an increasingly bright yellow.

Fig. 4. (a) Photographs of the TB indicator under different super ambient air pressures. The far right image was recorded under 100% CO₂, as it represents the colour of the indicator when all the dye is in its protonated form. Similarly, the far left image was recorded under high vacuum (< 0.01 atm), as it represents the colour of the indicator when all the dye is in its deprotonated form. All the digital photographs taken of the indicator as a function of P were then used to construct the plot of R' vs P illustrated in (b).

As before, the digital photographs were used to extract an $RGB(red)$ value for each associated air pressure, P and then derive, *via* Eq. (4) and (6), a value of R' . Once again, as predicted by the latter equation and illustrated in Fig. 4(b), a plot of the data in the form of R' vs P yielded a good straight line with a gradient $\alpha' = 0.98 \pm 0.03 \text{ atm}^{-1}$ (i.e. $1/\alpha' = 1.02 \text{ atm}$ of air). Other work showed that when the TB indicators was exposed to a cycle of high air pressure (ca. 10 atm) followed by 1 atm air pressure, it yielded an A' vs time oscillating profile, similar to that illustrated in Fig. 3, from which 90% response (to applied high pressure) and recovery (release of high pressure) times of 0.2 and 1.4 min, respectively were calculated.

3.5 TB indicator as a general-purpose air pressure indicator

The overall response of the TB indicator to air pressure is best represented by combining the data in the sub- and super-ambient plots, illustrated in Fig. 2(b) and 4(b), and plotting the data set in the form of $\log(R')$ vs $\log(P)$, the results of which are shown in Fig. 5. The good fit of the data to a straight line with a gradient of unity is as expected from Eq. (6). According to the latter, the intercept of the line of best fit to the data ($= 0.0078 \pm 0.014$) should be equal to $\log(\alpha')$, from which a value of $0.98 \pm 0.03 \text{ atm}^{-1}$ can be calculated for α' . The reciprocal of α' is the air pressure at which the TB indicator is 50% between its protonated and deprotonated form, *i.e.* the value of P where $R' = 1$. The value of $0.98 \pm 0.03 \text{ atm}^{-1}$ for α' , obtained from the data in Fig. 5, reveals a value for $1/\alpha' = 1.02 \pm 0.03 \text{ atm}$ of air, or $0.042 \pm 0.001 \text{ \%CO}_2$ for the TB indicator, which compares very favourably to the value of $1/\alpha = 0.039 \pm 0.001 \text{ \%CO}_2$, derived from the spectroscopic data illustrated in Fig. 1, where the TB indicator was exposed to different levels of CO_2 in Ar at 1 atm. Thus, in all this work the TB indicator acts as a consistent low- CO_2 pressure indicator, regardless of how this low level of CO_2 is generated, *i.e.* by using Ar/ CO_2 mixtures or by using sub- and super-ambient air pressures.

Fig. 5. Plot of $\log(R')$ vs $\log(\text{air pressure}, P)$ for the TB indicator using the data illustrated in Fig. 2 and 4. The line of best fit yields a gradient of 1.02 ± 0.02 and an intercept, $-\log(\alpha') = 0.0078 \pm 0.014$, *i.e.* $1/\alpha' = 1.02 \text{ atm}$ of air.

3.6 The TB indicator in action

As indicated earlier, one possible application of a colourimetric air pressure indicator is as a *qualitative* indicator of packaging integrity in vacuum packaging. In order to illustrate this, a TB indicator was vacuum packed alongside a coin and photographed before and after opening the VP. The results of this work, illustrated in Fig. 6(a), show, as expected, that the TB indicator is bright blue coloured when vacuum packed, but green when the package seal is broken and air allowed in. Other work showed that the TB indicator was stable, and unchanged in terms of sensitivity, when stored for months under VP and subsequently tested.

Also, as noted earlier, another potential application of a colourimetric air pressure indicator is as a PSP and as a simple illustration of this feature a model car was painted with the TB indicator ink and then exposed to a stream of compressed air, and the colour changes recorded using digital photography. The results of this work are illustrated in Fig. 6(b) and show that when exposed to a high velocity stream of air the TB indicator paint turns from its original green to yellow at the highest pressure point.

Fig. 6. Photographs of: (a) the TB indicator vacuum packaged before (top image) and after (bottom image) opening and (b) a model car partially coated with the TB ink before and after exposure to a high pressure (6 atm) stream of air.

Although it might be argued that in its present form the TB indicator doesn't have the resolution for a PSP, the above images show that it is capable of highlighting air flow patterns and it does represent the first example of a potential colourimetric PSP.

In both cases illustrated in Fig. 6, *i.e.* whether used as a vacuum indicator or high air pressure indicator, the colour change exhibited by the indicator is reversible, as expected given the colour change is based on reaction (1).

3.7 Comparison of the TB general-purpose air pressure and OCP vacuum pressure indicators

As noted earlier, in a recent previous paper [17] this group reported a vacuum air pressure indicator, which works on the same principles as the TB indicator described here, but utilises the pH-indicating dye OCP, with a $pK_a = 9.32$ and a colour change: purple to colourless, rather than TB ($pK_a = 8.90$; colour change: blue to yellow). Due to the difference in pK_a of the two dye, the OCP indicator is much (>30 times) more sensitive towards CO_2 , and so 30 times more sensitive towards air pressure, than the TB indicator. The strikingly different air pressure sensitivities of these two indicators is well illustrated by a plot, shown below in Fig. 7, of the fractional absorbance (*i.e.* colour) change, A^* (where $A^* = (A' - A_{\infty}') / (A_0' - A_{\infty}')$) exhibited by each indicator as a function of $\log(P)$, where P is air pressure (in atm). The associated colour changes exhibited by the two indicators as a function of P are also illustrated in Fig. 7 in the form of two colour strips. The broken vertical lines in Fig. 7 highlight the halfway colour change and associated pressure ($= 1/\alpha'$) for each indicator ($1/\alpha' = 0.033$ atm and 1.01 atm for the OCP and TB indicators, respectively). The two colour strips illustrated in Fig. 7 underline a basic feature of the OCP vacuum indicator, namely that it is so very sensitive (towards CO_2) that it can only be used to monitor vacuum air pressures (*i.e.* < 1 atm, with $1/\alpha' = 0.033$ atm) and therefore is particularly appropriate for use in vacuum packaging, given most vacuum packages are evacuated down to ca. 0.04 atm [10]. In marked contrast, from the data illustrated in Fig. 7, it is clear that the TB indicator is a more general-purpose air pressure indicator, one that is able to monitor both sub-ambient (down to ca. 0.1 atm) and super-ambient (up to ca. 10 atm) air pressures, and likely to find use in a wider range of applications, such as in packaging and air flow monitoring.

Fig. 7. Plot of the calculated (solid line) and observed (data points) variation in the fractional absorbance (i.e. colour) change, A^* (where $A^* = (A' - A_\infty)/(A_o' - A_\infty)$) of the OCP (red line and points) and TB (black line and points) indicators as a function of $\log(P)$, where P is the air pressure in atm. The colour changes exhibited by the two indicators are illustrated by the colour strips and the broken vertical lines identify the respective pressures ($= 1/\alpha'$) at which each indicator is halfway through its overall colour change.

The data in Fig. 7 shows that the sensitivity of this new type of air pressure indicator can be altered significantly by simply choosing a pH-indicating dye that has a different pK_a . However, as noted earlier, it should also be possible to fine tune the sensitivity of such indicators by changing the amount of base, TBAH in this work, used in their formulation. In a simple demonstration of this feature the usual 1 ml of TBAH, used to formulate the TB indicator (producing an indicator with $1/\alpha' = 1.01$ atm) was changed to 0.5 and 2 ml to produce two new air pressure indicators with $1/\alpha'$ values of 1.14 atm and 0.72 atm respectively, i.e. indicators which were 12% more, and 29% less sensitive than the original.

4. Conclusions

A general-purpose air pressure *colourimetric* indicator has been developed based on a very sensitive CO₂ indicator, which responds to the change in partial pressure of CO₂ in air. The indicator uses the pH indicator dye thymol blue (TB) and is green coloured in ambient air at ca. 1 atm, bright blue under high vacuum (< 0.01 atm) and bright yellow at high air pressures (> 10 atm). The TB indicator is cast from an ink and its change in colour can be monitored either spectrophotometrically, or using digital photography coupled with colour analysis, and the results related quantitatively to air pressure. The latter method is very inexpensive and ideal for monitoring, through the colour of the TB indicator, sub-ambient air pressures, such as found in vacuum packaging, and super-ambient air pressures, as found in aerodynamic studies. This is the first reported example of a general-purpose air pressure indicator capable of monitoring sub- and super-ambient air pressures, and, given its low cost and ease of use, it may prove useful in many areas other than packaging or aerodynamics, especially as the indicator can be probed using the digital camera in a mobile phone and an appropriate RGB measuring colour App.

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