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1   # A Smart Adhesive 'Consume Within' (CW) Indicator for Food Packaging

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5   **Abstract**

6   A CO_2-sensitive, smart adhesive is reported in which a CO_2-sensitive pigment, comprising the

7   pH-sensitive dye, phenol red, PR, coated onto nano-particulate silica particles, is dispersed

8   in a hot melt, pressure sensitive adhesive. A CO_2-sensitive, brightly coloured adhesive tape

9   is produced by coating the smart adhesive onto a polymer 'barrier' film substrate. When

10   placed inside on the plastic lidding of a CO_2 MAPed package, the smart adhesive-based

11   indicator changes to an orange/yellow colour due to the presence of the CO_2, and returns to

12   its original deep purple colour, upon exposure to air, at a rate that depends upon

13   temperature and the CO_2 permeability and thickness of the polymer barrier film. The smart

14   adhesive tape is used as a 'consume within', CW, indicator for refrigerated goods and briefly

15   compared in performance to the more complex 'After Opening Freshness' indicator

16   produced recently by Insignia Technologies Ltd. Other potential time-temperature

17   applications of this new technology are discussed briefly.

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1. Introduction

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26 Smart packaging is defined as 'packaging that provides additional levels of useful

27 functionality beyond protecting, containing and providing information about the product'

28 (Kerry & Butler, 2008). As part of smart packaging research many smart labels have been

29 developed for food packaging to help improve quality control and reduce waste.

30 A major part of smart food packaging is Modified Atmosphere Packaging (MAP) in which the

31 atmosphere within the food package is flushed with an inert gas, such as nitrogen or carbon

32 dioxide, thereby reducing the oxygen content to typically 0.3-3% (Kerry & Butler, 2008, p. 4).

33 Unlike nitrogen, carbon dioxide, CO_2, is classified as an active gas, since it affects most food-

34 spoiling microbes, reducing significantly their growth, even if some oxygen is present

35 (Brody, Strupinsky, & Kline, 2001). Both CO_2 and nitrogen slow the respiration rates of

36 foods, such as fruits and vegetables, and retard oxygen-based spoilage. As a consequence,

37 MAP is very effective at extending the shelf-lives of many foods and is widely used in

38 packaging. Some typical shelf-lives of MAPed, and non-MAPed, foods are given in Table 1

39 (Mills, 2009c).

40 **Table 1: Typical shelf-lives of some MAPed and unMAPed foods**

Food	Lifetime when air-packaged /days	Lifetime when MAPed /days
Beef	4	12
Pork	4	9
Poultry	6	18
Bread	7	21

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49 One of the problems with MAP is quality control, QC, in that it is impossible to check quickly

50 and cheaply that each package has been properly MAPed and sealed. Thus, MAPed food

51 packages are usually sampled by the package before shipping, typically every 300-400

52 packages, to ensure they are correctly packaged, and if a fault is found then the line is fixed

53 and the possibly compromised packages are scrapped/repackaged, resulting in a significant

54 degree of waste.

55 In order to improve MAPed package QC, in the early 90's Cryovac-Sealed Air Ltd. introduced

56 the Trufflex GS CO_2 indicator for individual and wholesale packages (Mills, 2009a). This CO_2

57 indicator used a solvent-based ink which contained an ion-pair of a pH indicating dye anion,

58 D^-, with a quaternary ammonium cation, Q^+, such as the tetraoctyl ammonium cation. This

59 ion-pair is usually represented as: $D^-Q^+xH_2O$ since such ion-pairs usually retain a few

60 molecules of water, even when dissolved in a lipophilic solvent, such as toluene. As a

61 consequence, the $D^-Q^+xH_2O$ ion pair readily dissolves in a solvent-based, i.e. non-aqueous,

62 ink and, when allowed to dry, produced an indicator film that responds to CO_2, as if the dye

63 is dissolved in water, *via* the following reaction:

64 $$D^-Q^+xH_2O + CO_2 \rightleftharpoons Q^+HCO_3^-(x-1)H_2O.DH \tag{1}$$
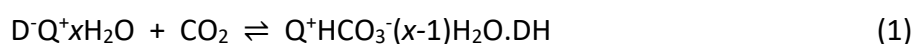
65 Colour **A** Colour **B**

66 where, $D^-Q^+xH_2O$ and $HCO_3^-(x-1)H_2O.DH$ are the differently coloured deprotonated and

67 protonated forms of the pH-indicating dye, D. In the Trufflex GS CO_2 indicator (Mills, 2009a)

68 the pH indicating dye *meta*-cresol purple was used and the polymer resin part of the ink,

69 used to encapsulate the ion-pairs, was ethyl cellulose.

70 Since this time many different CO_2 indicators have been reported (Mills, 2009b; Neethirajan,

71 Jayas, & Sadistap, 2009; Puligundla, Jung, & Ko, 2012), based on the above ion-pair

72 technology, but with different dyes, phase transfer agents (although most often tetrabutyl

73 ammonium hydroxide, TBAH) and encapsulating polymers. However, after an initial flurry

74 of interest, this smart ink technology for MAP QC failed to prosper commercially, possibly

75 because of the need to use solvent-based inks, since their water based equivalents would be

76 easily leached and possibly because most food package printing has turned away from using

77 solvent-based inks. Another problem with solvent-based, CO_2-sensitive inks is an inherent

78 shelf-life instability due to a slow dehydration process and/or an irreversible reaction with

79 the low levels of the acidic gases, NO_2 and SO_2 in air (Wolfbeis, Kovács, Goswami, & Klainer,

80 1998).

81 Recently, interest in CO_2-based indicators for MAP has been revived with the development

82 of CO_2-sensitive smart plastic films, in which very small (radius = ca. 9 nm) hydrophilic silica

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83   particles are coated with a layer of $D^-Q^+x H_2O$ ion pairs to create a CO_2-sensitive powder

84   pigment which is then mixed with a hydrophobic polymer, such as low density polyethylene,

85   LDPE, and extruded as a CO_2-sensitive plastic film (Mills & Yusufu, 2016a, 2016b). Unlike the

86   equivalent solvent-based CO_2 sensitive ink, the resulting CO_2-sensitive plastic film, when

87   stored in a cool, dark place is stable for years (Mills & Yusufu, 2016a, 2016b). Fig. 1 provides

88   a schematic illustration of the basic features of a CO_2-sensitive smart plastic film.

89   This technology has been used recently by Insignia Technologies Ltd. (Glasgow, UK), referred

90   to henceforth as 'Insignia', to create a variety of different MAP labels, including ones for: (i)

91   leak-detection/MAP QC, (ii) after opening freshness (AOF) indicating and (iii) stock

92   rotation/shelf-life monitoring (Insignia Technologies Ltd., 2019).

93   As can be seen from the types of smart indicators sold by Insignia and listed above, for stock

94   rotation or shelf-life monitoring, one promising area of application of the CO_2-sensitive

95   plastic films, illustrated in Fig. 1, is as a colour-based timer. Timers in food packaging are

96   not uncommon, especially time-temperature indicators, i.e. TTIs. A TTI is a smart label that

97   shows the accumulated time-temperature history of a product. TTIs are usually employed

98   to improve food distribution, reduce food waste and improve shelf-labelling by highlighting

99   any significant deviations from the recommended refrigeration temperature (Taoukis, 2001;

100 Wang et al. 2015). Probably the most well-known of the TTI's is the FreshCheck® Freshness

101 'You Can See®' indicator (FreshCheck® indicator, 2014) sold by the TempTime Corporation,

102 based on the thermal polymerisation of colourless diacetylenic monomers to yield very

103 dark, and conjugated polymers. The kinetics of the polymerisation depends not only on

104 temperature but also upon the type of substitution, thereby allowing the production of TTIs

105 with different temperature sensitivities. Fresh Check® indicators have been used in the

106 past by the Monoprix supermarket chain in France on selected refrigerated products as well

107 as other chain stores (Mills, 2009a). Most TTIs are full history, temperature-only activated

108 indicators, requiring deep-freeze storage of the label prior to their application, which is a

109 feature that limits their use mainly to frozen or chilled foods.

110 The Insignia CO_2-based TTIs are different from all other TTIs in several respects, in that they

111 do not require deep-freeze storage and are activated by simply exposing the indicator to air.

112 For example, the Insignia 'after opening freshness', AOF, label works by reacting reversibly,

113 *via* reaction (1), to the CO_2 within the MAPed package to produce the $HCO_3^-(x\text{-}1)H_2O.DH$

form of the dye (phenol red, PR), which is beige-coloured (Yusufu, Wang, & Mills, 2018). The label is activated as a time-temperature indicator by peeling back the lidding on which the indicator is attached, thereby letting the CO_2 escape and exposing the label to air. The Insignia stock rotation/shelf life monitoring labels work on the same principle, but are stored in a CO_2 flushed package and taken out (and so activated upon exposure to air) as required. In both cases, upon opening the CO_2-flushed package in which they are contained, the indicator slowly recovers its original colour, i.e. it turns from colour B (beige coloured for the AOF label) to colour A (deep purple for the AOF label) due to reaction (1) as the CO_2 slowly diffuses out of the indicator film into the ambient air (Yusufu, Wang, & Mills, 2018).

The kinetics of the above colour-changing process is largely diffusion-controlled, and so the time it takes for the colour of the indicator to completely change, depends upon: (i) the temperature and (ii) the CO_2 permeability, $Pm(CO_2)$, and the overall thickness, of the indicator layer plus any added barrier layer. If the temperature is fixed, as it is, at ca. 5 ^{o}C, for refrigerated products for example, then the time taken for the indicator to change colour can be tuned to a desired value, such as 4 days for the Insignia AOF label, through the careful choice of the barrier layer polymer CO_2 permeability, and its thickness, b. The main construction features of such CO_2 indicator based TTI labels, like the Insignia AOF label, are illustrated in Fig. 2(a). In the Insignia AOF label, a 70 μm Phenol Red, PR, LDPE CO_2-sensitive plastic film indicator layer is covered by a 30 μm barrier layer of white polyethylene terephthalate, PET, which has a low value for $Pm(CO_2)$ (Ashley, 1985), and sufficient thickness, that it ensures the MAPed packaged indicator at 5 ^{o}C will change from beige to a light purple colour after 4 days after opening (Yusufu, Wang, & Mills, 2018).

Most, if not all, the Insignia TTI label products work on the above principle and have the same structure as that illustrated in Fig. 2(a). However, the profit margins in packaging, especially food packaging are so tight that any additional costs, such as those for a smart label, are hard to bear unless they are very low. Achieving this necessary extremely low cost feature has proved a major hurdle in the commercialisation of most smart indicators for food packaging, including the Insignia AOF label. Interestingly, a brief inspection of Fig. 2(a) suggests that it might be possible to reduce markedly the number of components in the AOF label, and, for that matter, in any TTI with the same structure and principles of operation, by putting the smart CO_2-sensitive pigment into the pressure sensitive adhesive, as illustrated

145 in Fig. 2(b) and in this paper we report the first example of such a smart CO_2 sensitive

146 pressure sensitive adhesive and tape.

2. Experimental

2.1 Materials

149 Unless otherwise stated, all chemicals were purchased from Sigma Aldrich in the highest

150 purity available. All solutions were prepared fresh, and all aqueous solutions were made up

151 using double distilled and deionised water. The SiO_2 (Aerosil 130 hydrophilic fumed silica)

152 was provided by Evonik Industries (BET surface area = 130 ± 25 m^2 g^{-1}). Most of the

153 different plastic films used in this work as the barrier layer, namely: 25 μm thick

154 polytetrafluoroethylene (PTFE), low-density polyethylene (LDPE), polypropylene (PP) films

155 and Polyethylene terephthalate (PET) of different thicknesses, i.e. 5 μm, 13 μm, 25 μm,

156 were obtained from GoodFellow UK (Cambridge, UK). The one exception was 50 μm PET,

157 which was purchased from Adhesive Technical Services Ltd (London, UK). The PSA, a

158 synthetic styrene–isoprene–styrene (SIS) hot-melt, HM, adhesive (Tack Melt A43 A) was

159 purchased from Ichemco S.r.l. (Milan, Italy). The silicone-release film was purchased

160 ChemInstruments UK.

2.1.1 Smart Pigment preparation

162 0.2 g of phenol red and 3 mL of a 40 % tetrabutylammonium hydroxide solution in water

163 (TBAOH) were added to a 120 ml beaker containing 2 g of hydrophilic silica (BET surface

164 area = 130 ± 25 m^2 g^{-1}) dispersed in 100 ml double distilled, deionised water. The mixture

165 was stirred vigorously using a magnetic stirrer for 2 hours and the coated, dispersed powder

166 particles were then dried using a Buchi Mini Spray Dryer B-290. The final dry PR-SiO_2

167 pigment powder was purple coloured in air and changed to an orange/yellow colour upon

168 exposure to 100% CO_2, as illustrated in Fig. 3(a).

2.1.2 Smart adhesive preparation

170 10 g of the hot-melt PSA (Tack Melt A43 A) were placed in a 100 ml beaker and warmed to

171 120°C in an oven, where, after a period of 10 min, the adhesive melted to a viscous liquid,

172 and to which were then added 0.25 g of the PR-SiO_2 pigment and 2.5 mL of the 40 % TBAOH

173 aqueous solution. The mixture was stirred for 30 s and then placed in the oven for another

5 minutes. This procedure of warming in an oven and stirring was repeated three times to ensure the adhesive, pigment and base were fully mixed.

The final purple colour smart, hot, viscous adhesive solution was placed on a clear 50 μm PET film which was taped on a 110 °C hot plate. A K-bar 6 (K hand coater, 2019), a metal wire-wound rod, heated to 170 °C, which delivers wet film thickness of 60 μm, was then used to drawdown a film of the ink on the heated PET film. K-bar drawdown rods are routinely used in industry as a simple but effective way of applying reproducibly paints, printing inks, lacquers, adhesives and other surface coatings onto many substrates including paper, board, plastic films, foils, metal plates, glass plates and wood. Depending on the wire thickness used to wind the drawdown rod they can deposit wet film thicknesses between 4-500 μm (K hand coater, 2019). The final dried thickness of the K-bar coated smart adhesive on the PET film was found to be ca. 32 μm, as measured using Scanning Electron Microscopy, SEM. As with the pigment, the dried adhesive film appeared purple coloured in air and orange/yellow in CO_2 and photographic images of the hot melt (HM) PSA film in air, CO_2 and air again (after 1 h) are illustrated in Fig. 3(b).

The adhesive indicator strips were pressed onto a silicone release film and stored under ambient conditions in a cool dark place. Note that when the strips are pressed onto the silicone release film the grooves on the adhesive (due to the K-bar) are flattened out and in all subsequent work with these labels there is no evidence of lateral diffusion from the edge of the tape.

Pressure sensitive tack is the adhesive property related to bond formation that enables the adhesive to bond with the surface of another material upon brief contact under light pressure. A measure of this property can be gained from the rolling ball tack test (PSTC-6 Tack Rolling Ball, 2007), which involves rolling a steel ball down a set incline and along the adhesive and measuring how far it travels; a high tack PSA will yield a distance of 0-10 cm. The rolling ball tack test of the non-pigmented and pigmented HM adhesive yielded values of 2.1 and 3.3 cm which are similar to those reported for the adhesive (4 cm) (Ichemco, 2019) and suggest that the tack of the PSA HM adhesive used in this work is largely unchanged with the addition of 2.5 wt% of the smart pigment, so that both can be classified as high tack (pressure-sensitive) adhesives.

2.2 Measurements

205   All UV/ Vis absorbance measurements were made using an Agilent Technologies CARY 60

206   UV-vis spectrophotometer. All FT-IR spectra were recorded using a Perkin Elmer model

207   Spectrum 1 FT-IR spectrometer. All digital photographs were taken using a Cannon 600D

208   digital camera and all digital images were processed for their red, green and blue colour

209   space values (i.e. RGB values) using the freely available photo processing software, *Image J*

210   (Image J, 2019). All gases used were high purity and included pure CO_2 and Ar. Individual

211   mixtures of 1% CO_2/air, 5% CO_2/air and 25% CO_2/Ar mixture were purchased from BOC and

212   used as received. Different gases with different levels of CO_2 were generated using a Cole-

213   Parmer gas blender. Unless stated otherwise, all work was carried out at 22 ^{o}C.

214   **3. Result and Discussion**

215   3.1 *Smart pigment and adhesive film CO_2 sensitivity and responsivity*

216   From Eq. (1) it follows that the ratio, *R*, of the concentrations of the protonated and

217   depronated forms of the pH-sensitive dye is related to the %CO_2 *via* the following

218   expression:

219   $$R = [HD]/[D^-] = \alpha \times \%CO_2 \tag{2}$$

220   where [HD] and [D$^-$] are the concentrations of $Q^+HCO_3.HD.(x\text{-}1)H_2O$ and $Q^+D^-.xH_2O$,

221   respectively, α is a proportionality constant (units: %$^{-1}$), the value of which provides a

222   measure of the sensitivity of the CO_2-sensitive optical sensor under test. Experimentally,

223   the value of *R* can be calculated from the measured absorbance of the indicator film at a

224   known value of %CO_2, *A*, at the wavelength of maximum absorbance for, usually, D$^-$, i.e.

225   λ_{max}(D$^-$), since, from reaction (1) and Eq. (2) it follows:

226   $$R = (A_0 - A)/(A - A_\infty) = [HD]/[D^-] = \alpha.\%CO_2 \tag{3}$$

227   where, α is a measure of the CO_2 sensitivity of the indicator, A_0 is the value of absorbance

228   due to the pH-indicating dye at λ_{max}(D$^-$) when %CO_2 = 0 (i.e. when all the dye is in its

229   deprotonated form) and A_∞ is the absorbance of the film when all of D is in its protonated

230   form, i.e. as HD, i.e. when %CO_2 = ∞; the latter absorbance is assumed here to be that value

231   of *A* measured when the %CO_2 = 100 %.

232   Recent work by this group (Yusufu & Mills, 2018) and others (Knutson et al. 2015) has

233   shown that for such simple colour-changing systems, digital photography coupled with

234   colour analysis can be used to generate apparent absorbance values, A', based on either the

235   red, green or blue component values (which range from 0-255) of the digital image of the

236   indicator, i.e. RGB(red), RGB(green) and RGB(blue), respectively. Thus, A' values, derived

237   from digital images of the indicator, can be used as a substitute for the real absorbance

238   values at $\lambda_{max}(D^-)$ in Eq. (3) to yield the same value of α.

239   In this work, the pH-indicating dye used was phenol red, PR, and thus, in some parts of this

240   work, the RGB(red) component value of each digital image of the indicator was used to

241   calculate the apparent absorbance of the indicator using the following expression:

242   A'(red) = log{255/RGB(red)}   (4)

243   For example, in the study of the CO_2-sensitive 'naked' pigment, the latter was dispersed

244   onto 3M double-sided tape and attached on a microscope slide which was placed in a gas

245   cell. This allowed different, known CO_2/argon gas mixtures to be flowed over it and the

246   colour of the indicator to be captured using digital photography for each %CO_2. Digital

247   colour analysis of each image yielded, *via* Eq. (4), an apparent absorbance value based on

248   the red component, A'(red), which was used in Eq. (3) to calculate a value for R for each

249   %CO_2. The resulting plot of R vs %CO_2 is illustrated in Fig. 4(a) and reveals a good straight

250   line, as predicted by Eq. (3), with a gradient (i.e. α value) of 0.61 $\pm$ 0.01 (%CO_2)$^{-1}$, which, not

251   surprisingly, is similar to that reported for the AOF label (0.62 %CO_2^{-1}), in which the same

252   pigment, i.e. PR on silica, was used, although this time embedded in a thin,70 μm, layer of

253   LDPE, rather than a HM adhesive (Yusufu, Wang, & Mills, 2018).

254   The pigment exhibits a light purple transition colour about 60% into its change from its

255   original orange/yellow colour – in the presence of CO_2 – to its final deep purple colour, in its

256   absence, as illustrated by the photos in Fig. 4(a). As a consequence, the time associated

257   with this transition point (i.e. 60% into its colour recovery, $t_{60}\uparrow$) will be reported here in all

258   subsequent studies of the responsivity of the CO_2 sensitive pigment and the hot melt (HM)

259   adhesive film.

260   The variation in the value of A'(red) of the PR on silica based CO_2-sensitive pigment was also

261   monitored under an alternating cycle of 100% CO_2 and 100% argon gas streams and the

262   results are illustrated in Fig. 4(b) from which 60% response (to CO_2) and recovery times, i.e.

263    $t_{60}\downarrow$ and $t_{60}\uparrow$, of < 1 s and 2 s, respectively, were determined. The latter work reveals that

264   the naked, high surface area pigment particles, when not embedded in a highly viscous

265   encapsulation medium, such as a polymer or, in this work, an HM adhesive, are extremely

266   fast in terms of response and recovery to exposure to CO_2, as might be expected given the

267   large diffusion coefficient of gaseous CO_2 (0.16 cm^2 s^{-1} at 1 atm and 298 K) (Diffusion

268   coefficient, 2011).

269   A similar study to that above was then conducted on the CO_2-sensitive HM adhesive film (on

270   a 50 μm PET film) – with the adhesive uppermost, i.e. exposed to the gas stream, and the

271   results of this work are illustrated in Fig. 5. In this work the colour change exhibited by the

272   indicator at different %CO_2 levels was monitored by UV/Vis spectroscopy. The spectral data

273   in figure 5(a) coupled with Eq. (3) was used to construct the plot of R vs %CO_2 illustrated in

274   the insert diagram in figure 5(a), from which a value of α of 0.57 ± 0.017 %$^{-1}$ was derived

275   which is very similar to that found for the pigment alone, *vide supra*: 0.61 $\pm$ 0.01 (%CO_2)$^{-1}$.

276   The latter result suggests that encapsulating the PR on silica pigment in the HM adhesive

277   has little effect on its CO_2 sensitivity. In contrast, when exposed to an alternating cycle of

278   100% CO_2 and 100% argon gas streams, there was a significant increase in $t_{60}\downarrow$ and $t_{60}\uparrow$

279   values, 0.7 min; and 11 min, respectively, compared to those for the naked pigment, i.e. < 1 s

280   and 2 s, respectively, which is largely due to the much greater diffusion coefficient, D, of CO_2

281   in air compared to that in the adhesive film. Although the value for D is not known for the

282   HM adhesive, the recovery time of the CO_2-sensitive adhesive ($t_{60}\uparrow$ = ca. 11 min) is similar to

283   that reported for a CO_2-sensitive LDPE film loaded with the same pigment and of a similar

284   thickness, i.e. $t_{60}\uparrow$ = 26 min (Yusufu, Wang, & Mills, 2018). Thus, it seems reasonable to

285   assume that D for the HM adhesive is not too dissimilar to that for LDPE, i.e. ca. 3.7x10^{-7} cm^2

286   s^{-1}, which in turn is over 400,000 times less that in air (Pauly, 2005).

287   3.2 *Effects of different additional barrier layers: type and thickness, b*

288   As noted earlier, one possible use of the CO_2-sensitive adhesive films described above is in

289   the construction of a much simpler version of the Insignia AOF label (Yusufu, Wang, & Mills,

290   2018), *i.e.* that illustrated in Fig. 2(b), compared to the AOF label illustrated in Fig. 2(a). The

291   original AOF label was designed to help reduce household food waste by reassuring the

292   consumer through a series of colour changes that the food was 'fresh' (at which point the

293 label will be beige coloured), or 'still fresh' (brown), or warning that it was 'past best' (pale

294 purple) (Yusufu, Wang, & Mills, 2018). Obviously, the AOF label does not measure food

295 freshness directly, but rather the accumulated time-temperature history of the packaged

296 product, once the MAPed package, to which it is attached, has been opened. Thus, when

297 correctly refrigerated, the AOF label responds to how long the package has been opened

298 and in so doing provides advice as to the freshness of the product. It is argued by Insignia

299 (Insignia Technologies Ltd., 2019) that this advice will help stop the consumer throwing

300 away edible food because of unfounded concerns regarding its freshness, mostly due to

301 forgetting when the package was opened. It is also suggested that it encourages the

302 consumer to keep fresh food, which is still perfectly edible, for slightly longer than is

303 recommended by the very conservative 'consume within' advice of the food packager. For

304 example, when properly refrigerated, the Insignia AOF label suggests the packaged ham is

305 still good to eat after 4 days after opening, which is significantly longer than the packager's

306 recommendation of 2 days (Insignia Technologies Ltd., 2019).

307 Both indicators illustrated in Fig. 2 work on the same principle, and contain the same

308 pigment, and serve the same function, namely as a timer under refrigerated conditions. In

309 order to distinguish between: (i) Insignia's AOF label, see Fig. 2(a), and (ii) the simpler, two

310 component smart adhesive-based TTI described here, illustrated in Fig. 2(b), we shall refer

311 to the latter henceforth as a 'consume within', *i.e.* CW, indicator. This name also helps to

312 underline that its function is that of a timer, rather than a *direct* indicator of food freshness.

313 In order to demonstrate the key function of the polymer barrier layer in the CW indicator,

314 and the importance of the barrier layer's permeability towards CO_2, the purple-coloured PR-

315 based smart HM adhesive (thickness: 32 μm) was coated onto four different polymers

316 namely: PTFE, LDPE, PP and PET, all 25 μm thick. In each case, the product, a sticky purple-

317 coloured tape, was stuck onto a glass microscope slide. Each of these films was then

318 exposed to CO_2, as if placed in a CO_2 MAPed package, so that the adhesive indicator film

319 turned orange/yellow, due to reaction (1) and then exposed to air and the recovery from its

320 now orange/yellow coloured form to its original deep purple colour form monitored as a

321 function of time using UV/Visible absorption spectroscopy. Plots of the absorbance of the

322 deprotonated (deep purple) form of the PR in the HM adhesive, at its λ_{max} value of 580 nm,

323 *Abs*$_{580}$, for each of these films, including one *without* a barrier layer, as a function of

324   recovery time are illustrated in Fig. 6(a), from which values for $t_{60}\uparrow$, at which point the

325   indicator film is light purple in colour, were determined from the red broken line intercepts.

326   In the simplest model of gas diffusion into and out of a thin plane polymer (i.e. barrier layer)

327   sheet the response and recovery times are expected to depend directly upon b^2 and the

328   reciprocal of the diffusion coefficient, $D(CO_2)$. Although values of $D(CO_2)$ for some of the

329   polymers used here are not known, the values of $Pm(CO_2)$, which are proportional to

330    $D(CO_2)$, are known and have been used in the plot of $t_{60}\uparrow$ vs $P(CO_2)$ illustrated in Fig. 6(b),

331   which suggests the simple diffusion model is not quite appropriate as $t_{60}\uparrow$ appears to be

332   proportional to $-P(CO_2)$ and not its reciprocal. This is possibly not unexpected as

333   permeability is the product of the diffusion coefficient and solubility, and both will influence

334   the overall value of $t_{60}\uparrow$. However, the results in Fig. 6(a) do show the expected general

335   trend of an increase in the response time of the CW indicator with decreasing value of

336    $P(CO_2)$.

337   In another set of experiments, using the same system, the PR-based, smart HM adhesive

338   (thickness: 32 μm) was coated onto four PET films of different thicknesses which were then

339   each pressed onto a glass microscope slide. Each of these films – polymer barrier film facing

340   up - was then exposed to CO_2 until it had turned to its usual orange/yellow colour, due to

341   the full protonation of the dye *via* reaction (1). Once fully acidified by the CO_2, each

342   indicator was then exposed to air and the recovery of the initial, deep purple colour of the

343   CW indicator monitored as a function of time using UV/Visible spectroscopy. The results of

344   this work were used to construct the Abs_{580} versus recovery time profiles illustrated in Fig.

345   7(a), for all the different indicator films, including one without a polymer barrier layer.

346   These profiles enabled the determination of the value of $t_{60}\uparrow$, for all the indicator films

347   tested, from the broken red line intercepts in Fig. 7(a). The simple diffusion model suggests

348   that $t_{60}\uparrow$ should be proportional to b^2, whereas from the plot illustrated in Fig. 7(b), it

349   appears that instead, $t_{60}\uparrow$ is approximately proportional to $b^{0.5}$, for reasons that remain

350   unclear. However, once again the results show the expected general expected trend of an

351   increase in the response time of the CW indicator with increasing barrier film thickness, b.

352   *3.3 Shelf-life stability*

353   An important part of any indicator is shelf-life stability and in a study of this feature the CW

354   indicator (coated on 50 μm PET) was pressed onto a silicone-release film and tested

355   intermittently whilst being stored in a cool, dark place. Photos of the indicator, at 0, 30 and

356   60 days are illustrated in Fig. 8 and this and other work showed that the colour, response

357   and recovery characteristics and CO_2 sensitivity of the indicator remained unchanged with

358   storage time over this period. These results suggest that the CW indicator when stored

359   correctly is not inherently unstable and, as a result, has a reasonable shelf-life.

360   *3.4 Comparison of the CW indicator with the AOF indicator*

361   In an initial test of the CW indicator in a package, the PR HM adhesive was coated on PP and

362   then attached to the underside of the plastic film lidding (39μm thickness laminated PET and

363   PE), used to seal a MAPed food tray, using a RotoPack packaging machine and a flush gas of

364   100% CO_2. The otherwise empty package, with CW indicator, inside was placed in a

365   refrigerator set at 5 $^{\circ}$C and left for 24 h, by which time it had changed completely to an

366   orange/yellow colour . The package was then opened and the recovery of the CW indicator

367   monitored photographically until its original (CO_2 free) deep purple colour had developed.

368   The same experiment was repeated using an AOF label taken from a Sainsbury's cooked

369   ham package (Yusufu, Wang, & Mills, 2018). The results of this work are illustrated in Fig.

370   9(a) and (b).

371   The above photographic results show that the CW indicator exhibits a very similar colour

372   change as the Insignia AOF label (orange/yellow to purple) as it recovers its colour, at 5 $^{\circ}$C,

373   after opening the MAPed package. This is not surprising given that both employ the same

374   PR coated on silica pigment illustrated in Fig. 3(a), but whereas the AOF label has this

375   pigment embedded into an extruded LDPE film (Yusufu, Wang, & Mills, 2018), in the CW

376   indicator it is dispersed in a HM adhesive. The time scales of the colour change recovery

377   exhibited by the two indicators are also very similar, namely: $t_{60}\uparrow$ values of 3 and 4 days for

378   the CW indicator and AOF label, respectively. Note: the 25 μm PP barrier layer on the CW

379   indicator was selected so that the two films exhibited similar recovery times, in order to

380   allow a ready comparison between the two indicators. Obviously, the recovery of the CW

381   indicator can be increased, by simply increasing the thickness of the PP barrier layer, so that

382   its $t_{60}\uparrow$ value equalled that of the AOF label, i.e. 4 days. The above work shows that the very

383   simple CW indicator functions in the same way as the Insignia AOF label, but is of a much

simpler construction and, therefore, likely to be much less expensive to produce. Previous work carried out on the AOF label has shown that its response features are largely independent of humidity (Yusufu, Wang, & Mills, 2018) and this is also expected to be the case with the CW indicator, given the hydrophobic natures of the materials used in its construction. However, if adopted for food packaging, a study into the effects of humidity and flavour inside the package on sensor behaviour will need to be carried out. Note: none of the work described here, or elsewhere (Yusufu, Wang, & Mills, 2018), was carried out in association with or funded by Insignia.

Conclusions

The first smart adhesive is reported in which a CO_2-sensitive pigment, comprising the pH-sensitive dye, PR, coated onto nano-particulate silica particles, is dispersed in a hot melt, pressure sensitive adhesive. When the adhesive is coated onto a polymer 'barrier' film, the product is a purple coloured adhesive tape which, when placed on the inside of a CO_2 MAPed package, changes to an orange/yellow colour due to the presence of the CO_2. Upon opening the package, thereby releasing the CO_2, the indicator slowly recovers to its original deep purple colour, due to the diffusion of the CO_2 dissolved in the indicator film into the ambient air. The rate of this colour recovery depends upon temperature and the value of $Pm(CO_2)$ and thickness of the polymer barrier film. As a consequence this simple CO_2-sensitive adhesive/polymer barrier film combination can be used as a tunable 'consume within' indicator for food packaging, and is a direct competitor to the more complex 'After Opening Freshness' indicator produced by Insignia Technologies Ltd. This new, simple technology can be used to create a number of other different TTIs, such as: a timer for stock rotation, a Deli counter CW label and a MAP leak indicator. To our knowledge this is the first report of an indicator based on a smart adhesive and tape.

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