# Intelligent pigments and plastics for $CO_2$ detection

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**A novel $CO_2$ intelligent pigment is incorporated into a thermoplastic polymer to create a long-lived $CO_2$-sensitive plastic film which is characterised and then compared to a traditional solvent-based $CO_2$ indicator film.**

A number of optical indicators have been developed[1–7] in recent years to detect the presence of $CO_2$ at different levels, depending on the desired application. The majority of $CO_2$ indicators work *via* the change in pH which occurs when $CO_2$ dissolves in water. A pH-sensitive dye, $D^-$, changes colour when it reacts with the protons generated from the dissolution of $CO_2$ in water, *i.e.*,

$$D^- \text{ (colour A)} + H^+ \Leftrightarrow HD \text{ (colour B)} \quad (1)$$

where A is the colour of the dye (in its anionic, deprotonated form) before exposure to $CO_2$ and B is the colour of the dye (in its protonated form) after exposure to $CO_2$. Thus, upon exposure of such indicators to $CO_2$, the pH of the ambient environment decreases sufficiently to protonate the dye and so causes a measurable and observable change in absorbance of the indicator. The widespread detection of $CO_2$ by most thin-film, optical indicators has been hindered by their interaction with ambient acidic gas species (such as $SO_2$ and $NO_2$), which irreversibly acidify and markedly reduce the shelf-life of the indicator.[3] This paper identifies a route for producing $CO_2$ indicators with increased shelf-life stability, through the incorporation of a fast-acting, reversible, stable (>6 months) $CO_2$-indicating pigment into a flexible, extrudable, thermoplastic polymer.

To 2.0 g of hydrophobic silica (Degussa/Evonik Aerosil R812, specific surface area = 260 ± 30 m$^2$ g$^{-1}$, average particle size = 7 nm), 0.08 g of *m*-cresol purple (MCP), 100 ml of ethyl acetate and 1.5 ml of 1 M tetrabutylammonium hydroxide in methanol were added. (The silica employed has been rendered hydrophobic, by the manufacturer, by reacting the surface hydrophilic silanol groups (Si–OH) with dimethyldichlorosilane to produce hydrophobic Si–Me groups.) This mixture was mixed thoroughly and the solvent (ethyl acetate) then removed under reduced pressure using a rotary evaporator. The resultant powder was ground up using a pestle and mortar to generate a fine blue powder. The anionic form of MCP, $MCP^-$, is rendered hydrophobic by ion-pairing with the quaternary ammonium cation, $Q^+$, to form $Q^+MCP^- \cdot xH_2O$; note: the presence of a few molecules of water is known[3] to associate with such ion-pairs.

As a result, rotary evaporation of this solvent-soluble ion-pair with the hydrophobic silica generates particles with a coating of $Q^+MCP^- \cdot xH_2O$, which are able to respond rapidly and reversibly to the presence of $CO_2$ *via* the following equilibrium reaction:

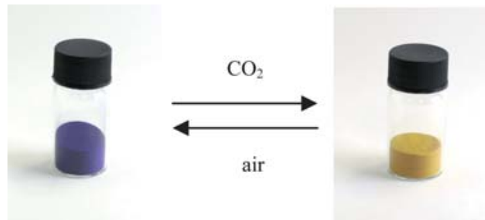


**Fig. 1** Colour change of $CO_2$-sensing pigment exposed to 100% $CO_2$.

$$\underset{\text{(blue)}}{Q^+MCP^- \cdot xH_2O} + CO_2 \Leftrightarrow \underset{\text{(yellow)}}{Q^+HCO_3^- \cdot (1-x)H_2O \cdot MCPH} \quad (2)$$

This same key reaction features[3] in MCP, solvent-based $CO_2$-sensitive plastic films. Thus, as illustrated by the photographs in Fig. 1, in the absence of $CO_2$ the MCP is in its blue anionic ($MCP^-$) state, but in the presence of $CO_2$ it is converted, *via* the reversible reaction (2), to its yellow, protonated form (MCPH).

The resulting $CO_2$-sensitive pigment is fast-acting (<1 s), reversible and very stable (>6 months), when stored in a darkened bottle under air.

In order to make the corresponding intelligent *plastic* $CO_2$ indicator, 0.6 g of the hydrophobic *pigment* was added to 4.0 g of powdered polyethylene (Alfa Aesar, LDPE, 1000 μm) and the mixture ground up using a mortar and pestle until the colour was a uniform blue. A small sample (*ca.* 0.3–0.4 g) of the powder mixture was heat pressed using a Specac Atlas™ Series Heated Platens at 115 °C to create a blue polyethylene film (0.1 mm thick) which was used in subsequent indicator work. The composition of the final $CO_2$ intelligent plastic, in terms of parts per hundred resin (pphr), was PE/MCP/$SiO_2$/TBAH = 100/0.6/15/2.9.

For comparison purposes, a similar solvent-based ink was prepared by dissolving 0.08 g of *m*-cresol purple in 3 ml methanol and 1.5 ml 1 M tetrabutylammonium hydroxide (TBAH) in methanol. This solution was stirred for 15 minutes, placed in a sonicating bath for 10 minutes, then stirred further until fully dissolved. This solution was added to 20 g of 10% w/v ethyl cellulose in toluene/ethanol (80 : 20), along with 2 ml of tributyl phosphate. The final ink solution

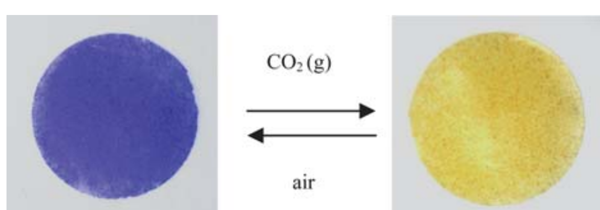


**Fig. 2** Colour change of $CO_2$-sensing pigment incorporated into polyethylene plastic film, when exposed to 100% $CO_2$.

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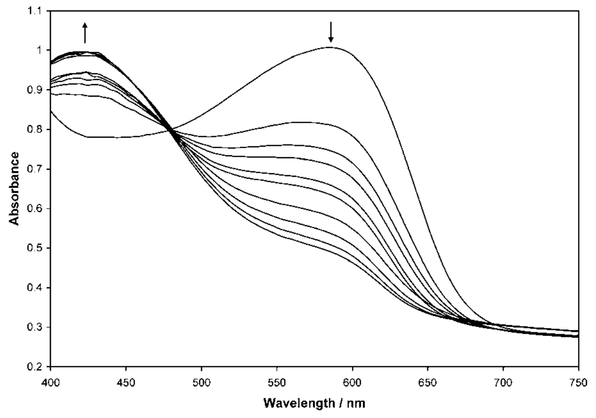


**Fig. 3** UV/visible absorption spectra of the MCP/silica/PE plastic film as a function of %$CO_2$, for %$CO_2$ (from top to bottom) of 0, 1, 2, 3, 4, 5, 20, 30, 60, 100%, respectively. $Abs_\infty$ is ~0.44.

was stirred for at least 30 minutes. The composition of the deposited dried ink film, 0.8 μm thick, in terms of pphr, was EC/MCP/TBAH/tributyl phosphate = 100/4/19.5/97.

The MCP/silica pigment in polyethylene plastic film is initially blue coloured but, as with the bare pigment (see Fig. 1), it changes to yellow upon exposure to carbon dioxide gas, as illustrated in Fig. 2. This characteristic, blue to yellow, colour change was also observed for the MCP solvent-based ink, which uses the same quaternary base.

Fig. 3 shows the recorded UV-visible spectra of the MCP/silica pigment plastic film as a function of %$CO_2$. As with its solvent-based film counterpart, the change in colour, due to $\lambda_{max}$ shifting from 592 to 424 nm, is a result of the $MCP^-$ forming MCPH *via* reaction (2). The variation in the absorbance due to the MCP in the plastic film as a function of %$CO_2$ is illustrated in Fig. 4.

It is useful to define the parameter, *R*, which is directly proportional to the ratio of concentrations [MCPH]/[$MCP^-$], *via* Beer's law, through the expression:

$$R = (Abs_0 - Abs)/(Abs - Abs_\infty) = [MCPH]/[MCP^-] \quad (3)$$

where $Abs_0$ is the value of absorbance of the dye at $\lambda_{max}$ ($MCP^-$) when %$CO_2$ = 0 (*i.e.* when the dye is fully in its deprotonated form)

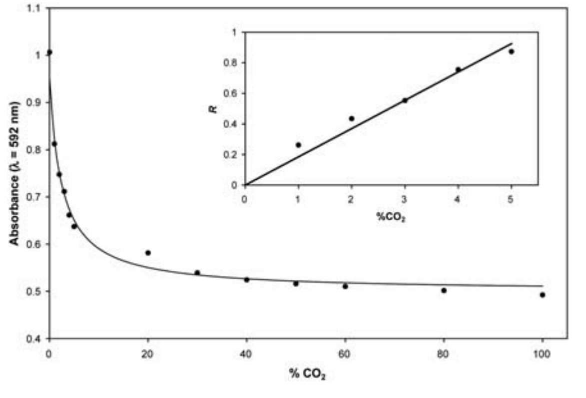


**Fig. 4** Plots of absorbance of MCP/silica pigment plastic film at 592 nm *versus* %$CO_2$. Data from Fig. 3. Solid lines were best fit to the data, revealing an $\alpha$ value of 0.185 ± 0.02%$CO_2^{-1}$.

and $Abs_\infty$ is the absorbance of the film when all the dye has been converted into its protonated form *i.e.* when %$CO_2$ = ∞. Since MCPH does not absorb at $\lambda_{max}$ ($MCP^-$), it is convenient to estimate $Abs_\infty$ at 592 nm. For such indicators it can be shown[3] that:

$$R = [MCPH]/[MCP^-] = \alpha\%CO_2 \quad (4)$$

and the linear relationship between *R* and %$CO_2$, as illustrated in the inset diagram in Fig. 4, reveals an $\alpha$ value of 0.185 ± 0.02%$CO_2^{-1}$. A similar experiment carried out on the solvent-based $CO_2$-indicator reveals an $\alpha$ value of 0.80 ± 0.08%$CO_2^{-1}$. Since $\alpha$ is a measure of indicator sensitivity, it appears that the solvent-based sensor shows a greater sensitivity (4 times) towards $CO_2$ compared to the MCP/silica pigment plastic indicator, possibly in part due to the greater permeability of $CO_2$ (by a factor of *ca.* 9) in ethyl cellulose compared to polyethylene.[8] Although the two indicator systems tested have markedly different dye levels ([dye] = *ca.* 7 times more—in terms of phr in the solvent based indicator), this is unlikely to be responsible for the difference in sensitivity for two reasons. Firstly, the sensitivity of such indicators is expected[9] to be independent of dye concentration, except at very high dye levels. Secondly, at high dye concentrations the dye will buffer the system and so the indicator would appear less sensitive (not more, as found for the higher dye-containing solvent-based indicator).

The MCP/silica pigment plastic indicator is fully reversible and responds quickly (within a few minutes) when exposed to 100% $CO_2$, but has a slow recovery time (*ca.* 2 hours to fully recover). In contrast the solvent-based $CO_2$-indicator has response and recovery times of both <1 and 3 s respectively. The above differences between the two indicators are due to the diffusion dependence of indicator film response and recovery times which, as a consequence, will depend upon film thickness and $CO_2$ permeability. Thus, the much slower recovery time of the polyethylene indicator will be due to its greater film thickness (100 compared to 0.8 μm) and lower $CO_2$ permeability (different by a factor of *ca.* 9). Both $CO_2$-indicators can be used repeatedly without any loss in performance.

As noted earlier, it is known[1,3,10] that most solvent-based $CO_2$-sensitive inks suffer irreversible acidification from interfering acidic gases, such as $NO_2$ and $SO_2$. Indeed, all optical $CO_2$ indicators that operate *via* a pH changing dye are non-selective with regard to other acidic gases and the indicators reported in this paper are no different. This is a particular problem when it comes to film storage since $NO_2$ and $SO_2$ are typically present in an urban environment at levels of 150 and 50 ppb, respectively.[10] And so it is an important feature of the MCP/silica pigment plastic $CO_2$-indicator films that they have a much greater longevity compared to that of a conventional solvent-based ink. For example, in our hands a solvent-based, indicator film will typically begin to acidify irreversibly, under ambient conditions within 1 week and be completely unusable within 5 weeks, when stored in a sealed container under ambient conditions. In contrast, the pigment/polymer composite film shows no visual sign of acidification after months of storage under the same sealed ambient, dark, conditions and works as if new. This is a significant advantage of the MCP/silica pigment plastic film indicators. Others[1] have shown the tolerance level of solvent based indicators for these acidic gases is only *ca.* 5 ppm. Interestingly, other work shows that the MCP/silica pigments have much higher tolerances (300 and 30 ppm for $NO_2$ and $SO_2$, respectively), which helps explain their greater longevity when stored under ambient air.

MCP/silica pigment plastic films over the range 20–40 °C show a decrease in sensitivity (*ca.* 0.06% per °C) with increasing temperature, similar to that of the solvent-based indicator[3] (*ca.* 7% per °C). This decrease is not unexpected given the nature of the key reaction (2).

It was also found that the MCP/silica pigment plastic indicator shows little or no sensitivity towards relative humidity, presumably due to the extremely hydrophobic nature of the indicator. In contrast, the MCP solvent-based indicator, whilst showing little or no sensitivity over a wide humidity range (typically 20–70%RH), does exhibit a slight decrease in sensitivity for %RH higher than 70%RH. Similar results have been found by others[6] studying other $CO_2$-sensitive, solvent-based indicators.

Fast-acting, reversible and stable, intelligent $CO_2$-sensitive pigments incorporated into thermoplastics, such as polyethylene, are easy and cheap to prepare. The resulting plastic films exhibit excellent reversibility, a striking colour change and a markedly longer shelf-life than similar, solvent-based $CO_2$-sensitive inks. As a consequence they have great potential for use in a wide range of applications—including food packaging.[11]



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