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# An intelligence ink for oxygen

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*Received (in Cambridge, UK) 5th May 2004, Accepted 10th June 2004*
*First published as an Advance Article on the web 9th July 2004*

**A generic ink formulation is described, comprising semiconductor photocatalyst particles, a brightly-coloured redox dye, a mild reducing agent, a polymer and a solvent, that creates an irreversible, reusable, UV-light-activated, colorimetric indicator or intelligence ink for oxygen.**

Oxygen is a key reactant in a myriad of processes, including animal and plant metabolism and oxidative decay and corrosion. It is no surprise, therefore, to note that there are many areas, particularly with regard to the preservation of materials, where the presence of oxygen is undesirable and the detection of oxygen is important.

One very good example of such an area is modified atmosphere packaging (MAP) in the food industry,[1] a popular form of which is when the atmosphere above the food is changed as it is packaged, by flushing the package with an inert gas, such as carbon dioxide or nitrogen, from one that contains 21% oxygen, *i.e.* air, to one that is largely free of oxygen, *i.e.* $< 1$–2%. Nowadays MAP is commonly employed in both the wholesale and retail food packaging industry since it has been shown typically to extend the shelf-life of many foods by a factor of 3–4 times that in air.[1,2]

In many cases, such as MAP, the detection of oxygen by conventional means, for example by using a Clark electrode or thermal conductivity gas chromatography, is too expensive and time-consuming to allow 100% quality assurance. Thus, of great interest to many, including the food-packaging industry, is the development of cheap, easy-to-use indicators that provide valuable and easily read information, such as the level of oxygen in a package, and are printable as inks; such inks are called ‘intelligence inks’.[2] To date, intelligence inks for oxygen have been largely limited to reversible, luminescence-based indicators, in which the key component is a luminescent dye, such as $Ru(bpy)_3^{2+}$ or a Pt(II) or Pd(II) porphyrin, that is readily quenched by oxygen.[3–6] However, such luminescence-based indicators are not easily ‘read’, requiring as they do interrogation by either specialized, or purpose-built, intensity or lifetime measuring systems in order to reveal their intelligence.[2]

Ideally all intelligence inks should be colorimetric since a change of colour is much easier to detect with a scanner or human eye. Not surprisingly, therefore, the biggest producer of oxygen scavengers in the food industry, the Mitsubishi Gas Corporation, has developed and commercialized a reversible colorimetric oxygen indicator, either in pellet and label form, comprising a strong reducing agent (typically a sugar, such as glucose, in alkaline or ascorbic acid) and a redox-indicator, such as methylene blue, that is colourless and readily re-oxidised by oxygen when in its chemically reduced form.[7–10] A number of similar indicators, that work on the same ‘indicator dye/strong reducing agent’ principle, have been reported by others.[2,11] A major problem with such indicators is the issue of storability, in that they require storage under anaerobic conditions since they quickly deteriorate in air, ceasing to work in a few hours as the strong reducing agent is used up in a direct, or indirect, reaction with oxygen. In the food packaging industry, another problem associated with this, and most oxygen indicators developed to date, is their reversible nature. Thus, consider the not-unlikely situation of a package that suffers only a very minor break in its integrity which causes the level of microbe metabolism inside the package to rise rapidly to such a level that the small rate of oxygen ingress is matched by the rate of oxygen consumption by the microbes. At that point the atmosphere inside the package will be almost oxygen free and this will be reflected by the colour, or fluorescence intensity, of the reversible oxygen indicator present in the package. The combination of a food package with a compromised integrity containing, as a result, unsafe food and an indicator showing an ‘oxygen-free’ condition is simply unacceptable; what is required is an irreversible oxygen sensor. The problems of oxygen indicator reversibility and storability are addressed in this communication, in which the initial details of an irreversible, reusable, UV-light-activated colorimetric oxygen intelligence ink/indicator are reported.

A typical oxygen intelligence ink comprised: 5 g of a 5 wt% aqueous dispersion of a semiconductor, $TiO_2$ (Degussa P25), 1 g of a 5 wt% aqueous solution of a redox-indicator dye, methylene blue (MB), 0.3 g of a mild sacrificial electron donor (SED) or reducing agent, triethanolamine (TEOA), and 20 g of a 5 wt% aqueous solution of an encapsulating polymer, hydroxyethyl cellulose (HEC). The ink components were mixed together by magnetic stirring, for 30 min and films of the ink were spin-coated on 22 mm diameter glass coverslips, using 2–3 drops (*ca.* 0.1 ml) of the ink and a spin-coater rotation speed of 6000 rpm for 30 s. The final film product, a clear, dry blue plastic layer, was ready to use and storable, for at least 1 year in the dark, under otherwise ambient conditions.

In air, under ambient room light conditions or upon visible-light irradiation, the $TiO_2$–MB–TEOA–HEC films do not bleach. However, upon irradiation with UV-A light (100 W BLB lamp) a typical film, which has an absorbance maximum due to MB at 610 nm, is bleached within 2.5 min of irradiation. The subsequent absorbance (at 610 nm) *versus* time profiles recorded for a film under an atmosphere of nitrogen, air and oxygen are illustrated in Fig. 1. Thus, upon UV-A illumination for 2.5 min (step (a)) the film loses its colour (changing from blue to white) and thus the absorbance drops to a constant lower value. After illumination, in an oxygen-free atmosphere ($N_2$), the bleached condition of the indicator persists (step (b)) and additional work shows that this

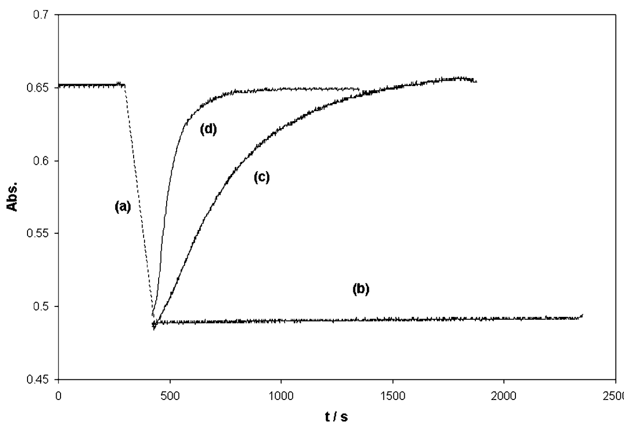


**Fig. 1** Variation in the absorbance (610 nm) of a typical $TiO_2$–MB–TEOA–HEC indicator as a function of time upon (a) illumination for 2.5 min with UV-A light (100 W BLB) in a gaseous environment of (b) nitrogen (where the photobleached state persists indefinitely), (c) air and (d) oxygen (where the film recovers its colour with increasing rate).

DOI: 10.1039/b406685e

condition holds for at least 7 days provided no significant (*i.e.* < 0.1%) levels of $O_2$ are present. In contrast, after illumination, in an air atmosphere the initial colour of the film returns (step (c)) and this recovery process is markedly faster in an oxygen atmosphere (step (d)), as illustrated by the results in Fig. 1. The results of other experiments show that the film does not function as an oxygen indicator if one or more of the key ingredients, namely: UV-A light, $TiO_2$ or TEOA, are omitted. In addition, the response characteristics of the indicator film, *i.e.* the kinetics of the photobleaching and dark-recovery-in-air steps, appear largely unaffected by humidity.

The basic principles by which the typical oxygen indicator described above works are illustrated in Fig. 2. Thus, ultra-bandgap illumination ($h\nu$)of the $TiO_2$ semiconductor particles creates electron–hole pairs, the photogenerated holes, $E°(h^+)$ = 2.91 V, of which oxidize the mild sacrificial electron donor (where, in this case, the SED = TEOA). The remaining photogenerated electrons, $E°(e^-)$ = −0.32 V, represented in Fig. 2 by $TiO_2^-$, reduce the dye, D, to a reduced form, $D^-$ that has a different colour to D. In the $TiO_2$–MB–TEOA–HEC film, D = MB which is blue, and $D^-$ is leuco-methylene blue, *i.e.* $D^-$ = LMB, which is colourless, $E°$(MB/LMB) = 0.53 V,. The above sequence of reactions represent a UV-light-activated step for the oxygen indicator film, since they effectively 'switch on' the indicator, rendering it oxygen sensitive. The SED and dye are chosen so that neither interact with each other in the dark (as occurs in the case of the Ageless Eye™, where the SED is a strong, rather than a mild, reducing agent),[2] or upon visible-light illumination (as occurs in the case of a range of riboflavine–EDTA oxygen sensors that have been reported by others[12,13]). In the absence of oxygen the reduced form of the dye, $D^-$, is stable indefinitely. Thus, in the $TiO_2$–MB–TEOA–HEC system, upon UV-activation in the absence of oxygen the film is converted into, and remains in, a photobleached state, as LMB, indefinitely. However, if the film is subsequently exposed to oxygen, the reduced form of the indicator dye, $D^-$, is re-oxidised to D and the original colour of the indicator film is restored.

The above generic system is irreversible, since following UV-A activation, and subsequent reaction with oxygen, the film, now restored to its initial colour, will not subsequently bleach, even if the atmosphere is changed from aerobic to anaerobic. A UV-A light activation step is required each time the oxygen indicator is required to function; without a subsequent UV-A activation step, it will only work once. It is also because a UV-activation step is required that these films (and ink) have an indefinite shelf-life under dark, but otherwise ambient, conditions, since the SED is only consumed when the film is activated.

The reusable nature of the $TiO_2$–MB–TEOA–HEC ink indicator is well illustrated by the repeated application of UV light (for 2 min)

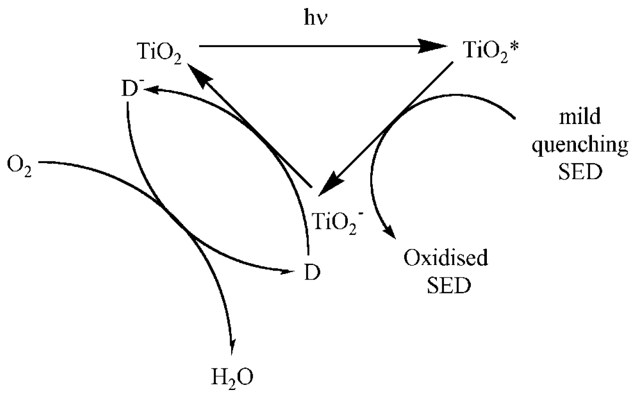


**Fig. 2** Schematic illustration of the key processes involved in the UV-activation and subsequent response towards oxygen of a $TiO_2$–MB–TEOA–HEC indicator.

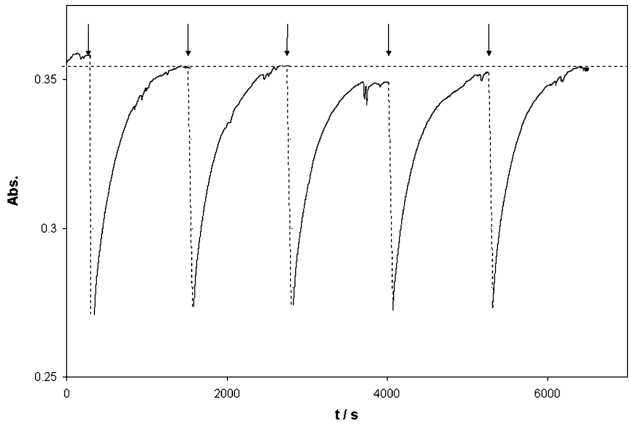


**Fig. 3** Absorbance (610 nm) *versus* time profile recorded for a typical $TiO_2$–MB–TEOA–HEC indicator upon repeated exposure (indicated by ↓) to 2 min of UV-A light (100 W BLB) under ambient aerobic conditions.

to a typical film in air and subsequent monitoring of the recovery of its colour, as measured by the absorbance of the film at 610 nm. The results of this work are illustrated in Fig. 3 for 5 cycles and in each the degree of photobleaching and the rate and extent of colour recovery in the dark, remain largely unchanged with repeated use of the film.

In conclusion, an example of a novel, ink formulation is described, that can be used to produce indicators for oxidants, such as oxygen. The $TiO_2$–MB–TEOA–HEC indicator is a first example of this type of irreversible, UV-activated, colorimetric system for the detection of oxygen. Many other examples, based on the same type of formulation can be made, both colorimetric and fluorimetric. Such inks are likely to find ready application in a number of areas, including modified atmosphere packaging in the food industry. If such an ink is to be used in the food industry several important questions need to be addressed regarding the indicator, including: where is it to be placed in the package and do any of the antimicrobial or antioxidant additives used in many foods, or possible microbial contaminants, interfere with its functionality? These questions are either the basis of current or further research. Based on current knowledge, this indicator technology continues to look very promising.

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