A novel reversible relative-humidity indicator ink based on methylene blue and urea

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A new relative-humidity sensitive ink based on methylene blue and urea is described which can utilise the deliquescent nature of urea.

Humidity sensors are used extensively in industry as well as for environmental monitoring. Their widespread applications cover a broad range of domestic, medical and industrial applications. For example, in food packaging, excess moisture in meat packaging can accelerate food spoilage, and as a consequence desiccants are often included in packaging to extend the shelf life. At low relative humidities (RHs) some dry grain products can undergo rapid free-radical oxidation and become rancid. Most fruit and vegetables are composed largely of water, consequently their optimum storage temperatures of the CoCl2-doped silica.

There have been a number of proposed colorimetric relative-humidity indicators, the majority of which are based on the use of inorganic salts such as cobalt(ii) chloride, CoCl2, which at a defined RH level (typically RH 40%) convert from their anhydrous form to their hydrated form, which is usually marked by a colour change, in the case of CoCl2, blue (anhydrous) to pink (hydrated). The sensitivity of this type of indicator can be tailored to the desired application by one of three methods: changing the concentration of the inorganic salt, adding a deliquescent synergic salt or, for systems with a silica support, altering the drying and activation temperatures of the CoCl2-doped silica. Such relative-humidity indicators have been proposed for a variety of applications including: refrigerated systems, clothes dryers, shoe storage, desiccant absorbent capacity indicators, electronic device storage and are often reversed by heating the hydrated salt to regenerate the anhydrous starting material. A typical commercial form, based on CoCl2, is the Humitector Humidity Indicator Card (Süd-Chemie Inc., USA).22

Recently, Matsushima et al. have proposed using thiazine and flavylium salts in gels as simple colorimetric humidity and temperature sensors.24–28 These salts exhibit reversible colour changes from blue (dry) to purple (humid), as a result of a change in relative humidity. This has been attributed to the absorption of water vapour by the gel in humid conditions which encourages the dye to form dimers and so leads to a shift in \( \lambda_{\text{max}} \) absorbance (ca. 10–20 nm) to a lower wavelength.

Whilst looking at this system, we have found that when the thia-zine dye, methylene blue (MB), is encapsulated within a polymer, such as hydroxy ethyl cellulose (HEC), with a notable excess of urea, (20 times w/w more than MB), the product ink is blue, but cast as a thin, opaque pink film, under ambient (RH = 60%, T = 20 °C) or dry conditions, and rapidly and reversibly is rendered blue coloured and clear when exposed to RH values >85%. Note that the observed colour changes for MB/urea/HEC films are the opposite of those observed by Matsushima et al. for their MB/gel films so the explanation for the effect is very different. It is also unusual to find a relative-humidity indicator which gives such a sharp, reversible colour change at high relative humidities. Consequently, this novel and promising relative-humidity indicator is the subject of this communication.

In this work, all relative humidities were measured at 20 °C unless otherwise stated. A typical relative-humidity sensor was made by spin coating an ink comprising 5 mg MB, 100 mg urea in 2 g of a 5% w/v HEC aqueous solution, for 30 seconds at 3500 rpm on to a 25 mm glass disc. Following the drying of the film at 70 °C for a few minutes, the final product is an opaque pink film (ca. 1.7 μm thick) under ambient conditions (40–60% RH) with a \( \lambda_{\text{max}} \) at 570 nm, which upon exposure to high relative-humidity conditions (>85% RH) turns rapidly blue (\( \lambda_{\text{max}} = 600 \) nm) and clear as illustrated in Fig. 1 and Fig. 2.

This colour change process occurs rapidly (response and recovery times: 10 s and 60 s respectively) and is reversible as illustrated by the

[Fig. 1 Photographs of a typical MB/urea/HEC relative-humidity indicator changing colour from pink (left) to blue (right) upon exposure to 100% RH air, from the bottom right.]
change in crystallinity of the urea when exposed to high relative humidities. Indeed a dye-free relative-humidity indicator based on optical clarity can be simply created using just urea in a polymer, such as HEC, since Fig. 3 shows that such a film is opaque at medium and low (<85%) RH levels, but clear at RH values >85% the process is entirely reversible. The polymer used, in this case HEC, does not appear to have any effect on the colour or opacity change, but merely acts as an encapsulation agent. This was confirmed by observing a similar effect in different polymers (such as polyvinyl alcohol, PVA and polyethylene oxide, PEO). Also in a polymer-free environment, achieved by grinding up a sample of urea with MB, the resulting pink powder exhibits a similar reversible colour change to blue when exposed to RH >85%.

The simplest explanation is that under ambient conditions (RH < 85%) MB is encapsulated in urea crystals as the pink trimmer and when exposed to high RHs the urea crystals dissolve, thereby releasing the MB into an environment in which its more stable form is the blue coloured MB dimer and monomer. In support of this, it is well known that urea is a hygroscopic compound which deliquesces under high RH conditions of >80% RH at 18 °C.\(^{26-28}\)

The notable features of this type of relative-humidity indicator are not only that it can be used exclusively for monitoring high (>85%) relative humidities, but it is quick to respond, highly reversible and has a good long-term stability. As it stands, such a >85% RH indicator has a potential application ensuring the correct RH conditions for the storage and ripening of fruit,\(^{29-31}\) for example. Further work is in progress developing this system using a series of hygroscopic, urea and non-urea-related, compounds which undergo deliquescent at different relative humidities (e.g. \(N,N\)-dimethylurea deliquesces at RH >63% at 18 °C) to generate a set of relative-humidity indicators for providing a sharp register at different, defined relative-humidity levels that span the RH scale.

**Notes and references**