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## Food Research International

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## Fadable ink for time–temperature control of food freshness: Novel new time–temperature indicator

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## ARTICLE INFO

## Article history:

Received 15 April 2008

Accepted 28 April 2008

## Keywords:

Time–temperature indicator

Color change

Red-ox

Multilayer structure

Fadable ink

## ABSTRACT

A novel new colorimetric time–temperature indicator, based on fadable ink has been developed. The printed sign is able to disappear in a defined time period. The color fading is based on the red-ox properties of anthraquinone derivative. Beige anthraquinone  $\beta$ -sulfonate can be easily reduced by sodium hydrosulfite and become red color. By contacting with oxygen, the red color turns back into beige. The time–temperature indicator comprises three thin layers materials either on paper or plastic substrate. The rate of color change is varied by the chemical composition of the polyacrylate. This multilayer structure time–temperature indicator can be easily made by knife coater and screen printing. The made indicator should be very useful to monitor freshness of food.

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### 1. Introduction

The control of elapsed time is very important for the storage of the food and pharmaceutical products. A number of time–temperature indicator (TTI), based on different chemical and physical processes, have been developed. Most of the products exhibit color change with elapse time. Such type of time monitoring is very simple and accessible to all users. For example, the Fresh-Check<sup>®</sup> time–temperature indicators based on color change as a result of solid state polymerization of substituted monomers. The Vitsab<sup>®</sup> time–temperature indicator is based on the time–temperature dependence of enzymatic reaction (Leak & Rönnow, 2000). Inside the indicator tag, a plastic outer compartment contains two mini-pouches, one contains a water solution of lipolytic enzyme, and the other is lipid substrate water solution containing a pH indicator. The TTI is activated by breaking the wall between two mini-pouches and the contents are mixed by outside force. A color change from green to clear yellow appears due to the controlled enzymatic hydrolysis of a lipid substrate with a decrease in pH.

A number of time–temperature indicators are based on the diffusion processes (Arens et al., 1997; Haas, 1990; Haas & Haas, 1997; Haas, Holt, & Davis, 2006; Manske, 1976). Time-indicating technology based on the red-ox dye can also monitor elapsed time. This principle has been used in many patents. All of these inven-

tions have different construction and indicate time duration in different way. Hu and Loconti (1973) and Gohil (2006) have reported a receptacle that contained a metered amount of oxidized red-ox dye and an effective amount of reducing agent in an alkaline medium, solvent or moisture retainer. The conversion of the oxidized red-ox dye into its reduced form occurs inside the sealed receptacle. The color change can also come from the oxygen diffusing through the barrier film and react with the reduced dye. Lewis (2002) invented a time indicator that consists of a tissue paper saturated with reduced dye and covered with a plastic cap. The oxygen diffuses through the plastic cap that leads to a color change from the oxidation of the dye. The plastic cap is thick in the center and gradually thinner toward the edge. This construction provides a gradual color transition from the edge to the center with the elapse of time.

Many new types of time–temperature indicators have been developed recently. Rani and Abraham (2006) reported new enzyme reactions for a low cost time–temperature indicator strip. Sun et al. (2008) developed a new amylase type TTI based on the reaction between amylase and starch. Bauer and Knorr (2005) reported a pressure induced starch gelation as a pressure time temperature indicator (PTTI). The OnVu<sup>®</sup> (2006) time–temperature indicator from Ciba Specialty Chemicals and Fresh Point relies on the properties of pigments that change color over time and temperature. The OnVu<sup>®</sup> is activated by UV light first to become dark blue and then gradually changes to light color as time passes.

We are reporting a novel time–temperature indicator here. The indicator is made from oxygen sensitive printing ink that will disappear with time. The convenient form of new time–temperature

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indicator allows it to be placed on the packages of food or bottle easily by either printing or coating process.

## 2. Materials and methods

### 2.1. Materials

Anthraquinone-2-sulfonic acid, sodium salt, monohydrate (sodium anthraquinone  $\beta$ -sulfonate), sodium hydrosulfite, sodium hydroxide and hydroxypropylcellulose (Average M.W. 100.000) used throughout this work were obtained from Acros Organics (Belgium). Photoinitiator: 2,2-dimethoxy-2-phenyl acetophenone – benzil dimethyl ketal (DBK) was obtained from Ciba Specialty Chemicals (Switzerland). 2-Hydroxyethyl methacrylate (HEMA) was obtained from Sigma Aldrich (USA). Ethoxylated (15) trimethylolpropane triacrylate (EO(15)TMPTA), tetraethylene glycol diacrylate (TEGDA), propoxylated (2) neopentyl glycol diacrylate (PO(2)NPGDA), ethoxylated (3) bisphenol A diacrylate (EO(3)BPADA), tricyclodecane dimethanol diacrylate (TCDDA), tris (2-hydroxy ethyl) isocyanurate triacrylate (THEICTA), polyethylene glycol (400) diacrylate (PEGDA), ethoxylated (9) trimethylolpropane triacrylate (EO(9)TPTA), highly propoxylated (5.5) glyceryl triacrylate (HPO(5.5)GTA) were obtained from Sartomer Co. (USA). All chemicals were used as received without any purification.

### 2.2. Construction of time and temperature indicator

The present time–temperature indicator has multilayer structure. Fig. 1 illustrates the layers of its construction that comprises

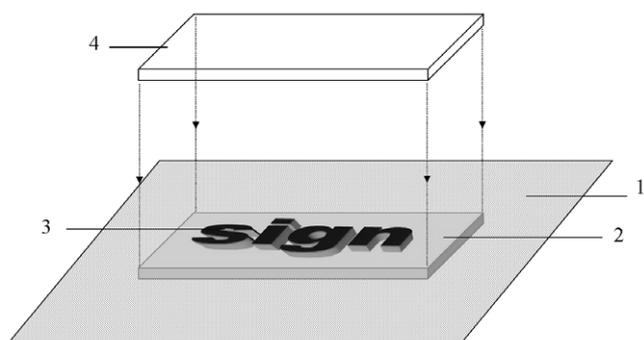


Fig. 1. The construction of time–temperature indicator (1 – substrate, 2 – background for printing, 3 – printed sign, 4 – transparent polymeric coating).

a polymeric background for printing 2, printed sign 3 and transparent polymeric coating 4. This time–temperature integrator can be easily printed on any flexible or rigid substrate 1.

### 2.2.1. Red-ox compound

The indicator contains beige color anthraquinone derivative – sodium anthraquinone  $\beta$ -sulfonate that is able to be reduced to colored molecules with deep red. The reduced molecules react with oxygen and lost its intense color thereby return to its original color. The time of the oxidation depends on many factors described below that can be calculated and predicted. The reduction reaction of sodium anthraquinone  $\beta$ -sulfonate by sodium hydrosulfite in alkali media is shown in Fig. 2. The fadable ink is prepared from the reduced form of anthraquinone derivative.

### 2.2.2. Fadable ink

The reduced anthraquinone derivative was mixed with polymer binder to obtain the ink. The binder is water soluble or water dispersible polymer. Water is a necessary component in the reduction process. We have used hydroxypropylcellulose as a binder that dissolves in water–alcohol mixture. The printing ink composition for the fadable sign is summarized in Table 1. The fadable ink should be kept in an oxygen free environment. The fabrication of the device including printing and protective layer coating needs to be operated in the oxygen free environment.

### 2.2.3. Background layer

The color of the sign in the presence of air changes from red to beige as shown in Fig. 3. To make beige color “invisible” or to mask it, we have used a background layer for printing. The background layer should have a similar color as the ink sign after oxidation that will makes the oxidized sign invisible. The background layer consists of polyvinyl alcohol (PVA) containing some amount of anthraquinone compound that is similar as used in the ink. For that 20% (by wt.) water–alcohol solution of PVA was blended with 8% (by

Table 1  
Composition of fadable ink

Component	Amount (wt%)			
	I	II	III	IV
AQS	0.64	0.62	0.61	0.59
Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	2.55	4.97	7.27	9.47
NaOH	2.04	1.99	1.94	1.89
HPC	7.64	7.45	7.27	7.10

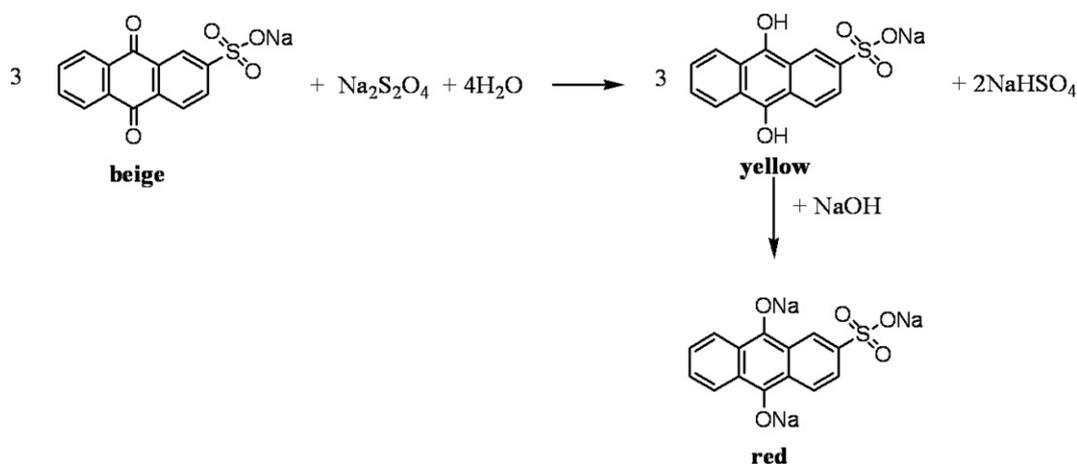


Fig. 2. Reduction reaction of sodium anthraquinone  $\beta$ -sulfonate with sodium hydrosulfite and sodium hydroxide.

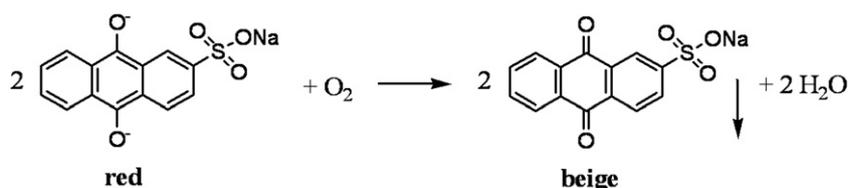


Fig. 3. Oxidation reaction of fadable ink.

wt.) of sodium anthraquinone β-sulfonate. A thin film was obtained on the glass substrate using this ink solution with a draw down rod and then dried. The background layer was printed by ink in a glove box filled with nitrogen using screen stencil with specific designed sign.

2.2.4. Protective coating

The sing was covered by polyacrylates protective coating with two functions. First, it keeps off the moisture to smear the ink. Second, the polymeric coating controls the rate of oxidation. Different acrylates have different oxygen permeability that varies the color change rate with its chemical composition and film thickness. We have used UV-curing technology to prepare acrylate protective coating. The process is energy saving and environmental friendly due to its fast curing rate and solventless system. All UV irradiation was conducted using UV light, provided by 4-watts UVGL-25 Mineralight® lamp (UVP, Inc., San Gabriel, CA), λ = 365 nm for 2 min.

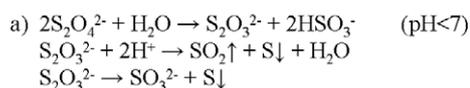
2.2.5. Substrate

This time–temperature indicator can be easily printed on different materials (substrates). The oxygen is required for color transition through the protective coating. However, the oxygen also can come through substrate, so the rate of color change will be increased. The rate of oxygen diffusion depends on the type of substrate material. Glass or aluminum foil does not permeate oxygen but polymer can. It is preferred to use glass, aluminum foil and other metallized material or low permeable plastic as substrate, so the color change will depends only on the oxygen diffusion through the protective layer.

2.3. Characterization and analysis

The color change of the samples was monitored by Perkin Elmer Lambda 35 UV/VIS Spectrometer from 300–900 nm. The samples

I. “Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> + H<sub>2</sub>O” + “AQS” + “NaOH”



II. “Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> + NaOH + H<sub>2</sub>O” + “AQS”

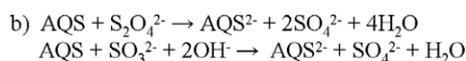
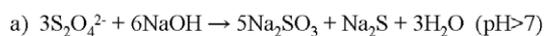


Fig. 4. Reaction mechanism of fadable ink prepared by different mixing order of each component.

were prepared on the glass substrate and measured at 25 °C and 75% RH in air.

The glass transition temperature of polyacrylates was determined by differential scanning calorimeter (Diamond DSC, Perkin Elmer). The samples were scanned by a ramping rate of 10 °C/min from 50 °C to 100 °C or 150 °C and the furnace was heated and purged by N<sub>2</sub> with a flux of 20 ml/min.

3. Results and discussion

3.1. Composition of the ink

The ink composition as well as the order of components mixing determines the ink color and the time of color transition. The

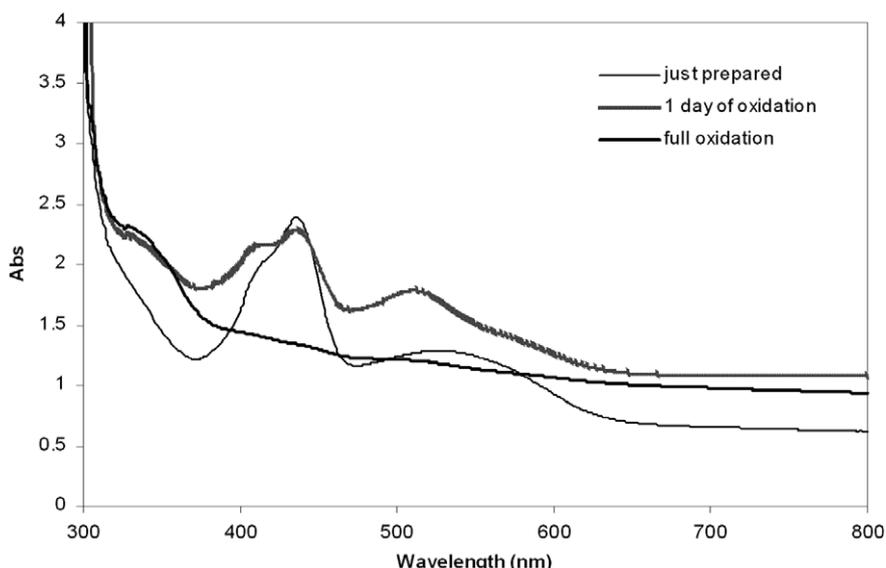


Fig. 5. UV–vis spectra of thin films (40 μm) prepared from ink composition 2.

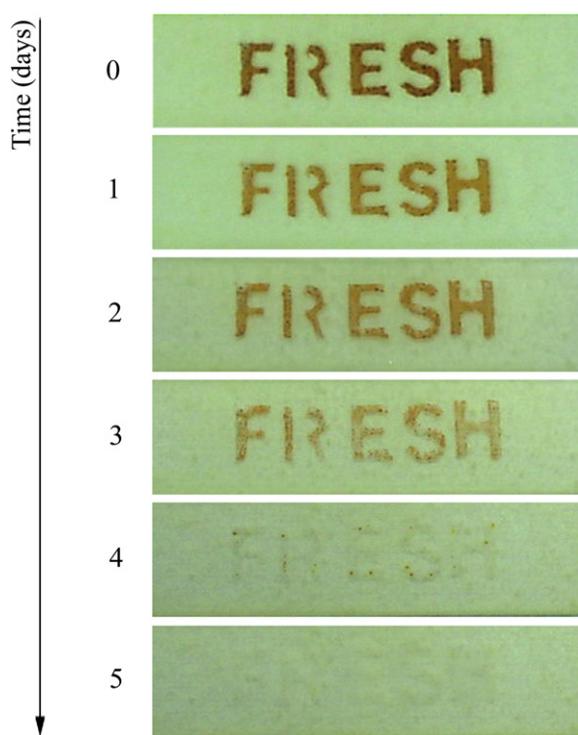


Fig. 6. Fading of the color in time-temperature indicator at 25 °C.

reduction of sodium anthraquinone  $\beta$ -sulfonate by sodium hydro-sulfite in water leads to a bright yellow compound. The alkali media is responsible for the red color of the reduction product, as shown in Fig. 2. The order of mixing is very important for the ink preparation. If, we mixed the  $\text{Na}_2\text{S}_2\text{O}_4$  with water first, undesirable by products of sulfur and  $\text{SO}_2$  were formed with acidic pH (Fig. 4I, a). The anthraquinone  $\beta$ -sulfonate can be reduced to yellow hydroanthraquinone  $\beta$ -sulfonate ( $\text{H}_2\text{AQS}$ ) in acid media.  $\text{H}_2\text{AQS}$  further reacted with alkali and formed red sodium salt of hydroanthraquinone  $\beta$ -sulfonate ( $\text{Na}_2\text{AQS}$ , or in ionic form  $\text{AQS}^{2-}$ ) (Fig. 4I, c). This order of mixing wastes  $\text{Na}_2\text{S}_2\text{O}_4$  reductants and produces by products. Thus, we mixed the reductant in NaOH and water first, and

then added sodium anthraquinone  $\beta$ -sulfonate into the alkali media. The reduction mechanisms of reduction the sodium anthraquinone  $\beta$ -sulfonate in alkali media are shown in Fig. 4II. The side chemical reactions are prevented, and all of the reductant is used for reduction of anthraquinone derivative only. The second order of mixing makes the ink with better stability due to the excess of reductant. The different ink compositions used in this study are summarized in Table 1.

The oxidation reaction of  $\text{AQS}^{2-}$  is shown in Fig. 3. The reaction can be observed by normal eye with the color fading of the ink's sign. The amount of fading in the ink can be monitored by the UV-vis spectroscopy to measure the decrease in absorption at 510 nm as shown in Fig. 5. The transparency of the ink film decreases with time due to the formation of insoluble anthraquinone  $\beta$ -sulfonate.

The color of the sign made from compositions 1–4 are fading by different amount of time. Thus, the printed signs with a thickness of 40  $\mu\text{m}$  fade in 12, 30, 48 and 50 h for compositions 1–4, respectively at 25 °C. The composition with the highest amount of  $\text{Na}_2\text{S}_2\text{O}_4$  exhibits the longest time of fading as we expected.

### 3.2. Polymer protective coating

The time of oxidation can be slowed down by the usage of polyacrylate protective coating. The oxidation kinetics of ink is controlled by oxygen diffusion through polymer coating. The diffusion process is affected by the chemical structure of the polyacrylate and their thickness. We have determined the rate of air diffusion in different polyacrylate films, the results will be published separately (2008). The activation energy of diffusion is different for different polyacrylate films that are possible due to the differences in the crosslinking density and rigidity of the polyacrylates. We have founded the diffusion properties of the polyacrylates depend on the chemical structure of monomer and its  $T_g$ , functionality and molecular weight per active functional group.

We have applied the knowledge about air diffusion through polyacrylates for this time-temperature indicating system. The polyacrylate coating was covered for the sign with a thickness 40  $\mu\text{m}$  made from the composition 2 (Table 1). The polyacrylate coating can be made by mixing propoxylated(2)neopentyl glycol diacrylate (3 g), 2-hydroxyethyl methacrylate (3 g) and benzil dimethyl ketal (0.12 g) for about 10 min, then a thin acrylate film

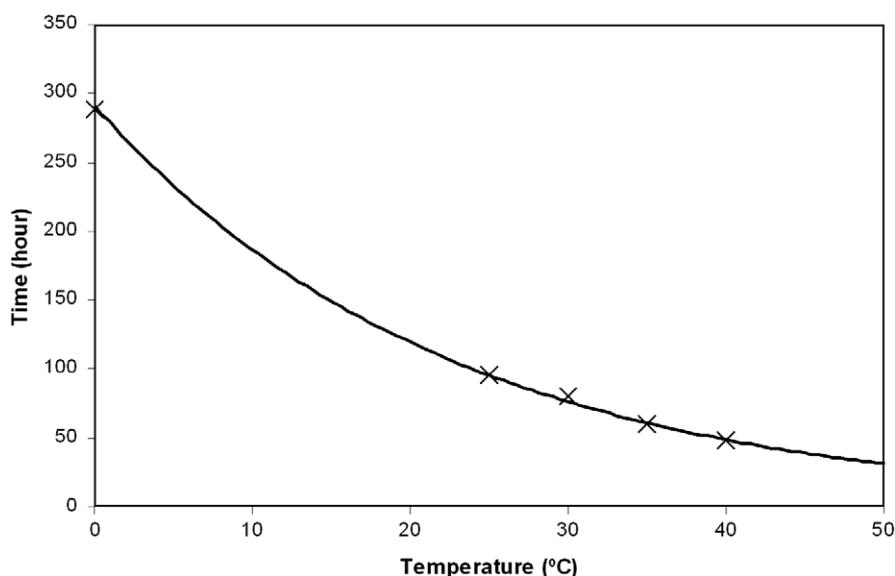


Fig. 7. Time-temperature relationship in time-temperature indicator using HEMA:PO(2)NPGDA 100  $\mu\text{m}$  polyacrylate coating.

**Table 2**

Glass transition temperature of polyacrylates and fading time of ink covered with different polyacrylate at 25 °C

Sample	$T_g$ (°C)	Time of color fading (h)
HEMA: EO(15)TMPTA	9.8	63
HEMA: PEGDA	-5.5	58
HEMA: EO(9)TPTA	10.4	72
HEMA: HPO(5.5)GTA	48.2	132
HEMA: TEGDA	17.2	80
HEMA: PO(2)NPGDA	46.4	120
HEMA: EO(3)BPADA	44.5	108
HEMA: TCDDA	96.1	288
HEMA: THEICTA	112.3	384

(about 100  $\mu\text{m}$ ) was covered the printed background layer using a draw down rod and curing with a UV light (4-watts UVGL-25 Mineralight<sup>®</sup> lamp,  $\lambda = 365$  nm) about 2 min. Both printing and coating processes are carried out in the nitrogen or argon purge glove box to exclude air. The made TTI is placed in the air and is ready to monitor time. The color of TTI faded completely into background in five days at 25 °C and looked invisible as shown in Fig. 6. For a more flexible protective coating made from 100  $\mu\text{m}$  of HEMA:-PO(2)NPGDA provides a fading time of 3 days (72 h) at 25 °C. The time-temperature relationship of color fading for this system is represented in Fig. 7. As we expected, the time of fading decreases with increasing of temperature from reaction kinetic point of view. Table 2 shows different polyacrylate coating provide different time of color fading due to the different rate of oxygen diffusion. The thickness of polyacrylate coating is fixed at 100  $\mu\text{m}$ , because the variations in thickness also can lead to changes in the time of color fading.

#### 4 Conclusions

We have presented a new novel type of colorimetric time-temperature indicator that can be used for monitoring time-tempera-

ture sensitive products such as the freshness of food. The indicator is based on fadable ink, and the sign made by this ink is able to disappear in a defined time period. The fading time is determined by the oxygen diffusion rate through the polyacrylate protective layer of ink and temperature. Different polyacrylates have different rate of air diffusion coefficient which is correlated with the glass transition temperature of polyacrylates. This time-temperature indicator can be easily fabricated for monitoring elapsed time and temperature.

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