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The Quantitative Analysis of the Light Stability of Insoluble Singlet Oxygen Sensitizers

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SUMMARY

Evaluation of insoluble sensitizing materials for further technological development must include tests of their energy transfer efficiency as well as of their light stability. A procedure for the determination of the light stability of insoluble sensitizer particles including the preparation of surfaces to be irradiated and analysed is given. A close link to the widely adopted analytical methods used in industrial dyestuff, pigment and polymer laboratories (Xenotest irradiation, Cielab analysis) assures its easy implementation. The procedure may also be used for sensitizing materials already irradiated in suspensions. Standardized irradiations of blue wool patterns facilitate those determinations for procedures involving the irradiation of photoactive surfaces.

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1. INTRODUCTION

In recent years several insoluble photoactive materials have been described and proposed as sensitizers of photochemical reactions in heterogeneous systems.[1] Of all the materials proposed, only those consisting of entirely insoluble particles or chemically bound to an insoluble and chemically inert support are considered suitable for use in heterogeneous reaction mixtures.

Two examples of a singlet oxygen sensitizer (Rose Bengal) bound to two different polymers have been commercialized.[1e,1i] The interest in insoluble sensitizers is based on their easy separation from the reaction mixture by either filtration or centrifugation and their potential recyclization. However, the light stability of insoluble sensitizers is not very satisfactory at the present time and further development in this direction is needed.

We report in this paper a method of quantifying the light stability of photoactive surfaces using the same industrial testing procedures as are applied on dyestuffs, pigments and polymers.[2] This method consists of the preparation of planar surfaces of a convenient size, irradiated in standard Xenotest equipment and subsequently analysed using a reflection spectrophotometer.

Clearly this method does not take into account potential solvent interactions of excited states in the solid surface, and the analysis is considered as part of an early evaluation in order to eliminate unsuitable materials.

2. MATERIALS

2.1. Polymer-based insoluble materials

Sensitox[1c,g] (1, Hydron Laboratories Inc., New Brunswick, NJ 08902, USA) consists of Rose Bengal as sensitizer (0·25 g/g polymer support[1g]) esterified to chloromethylated beads (diameter 5×10^{-5} m) of a copolymer of styrene and divinylbenzene (Bio-Rad S-XI, Bio-Rad Laboratories, Richmond, CA 94804, USA).

P-HP[1h,3] (2) is a polymer-bound hematoporphyrin. The polymer support used is a polyepoxy resin of the Araldite type which consists of propane-2,2-di(4,4'-phenylglycidyl ether) (Araldite F, Ciba–Geigy AG, 4002 Basle, Switzerland) and phthalic anhydride.

P-RB[1h,3] (3) is a polymer-bound Rose Bengal having the same Araldite type support.

Particles of 5×10^{-5} m diameter with sensitizer concentrations of 0·23 (2) and 0·24 (3) g/g support, respectively, were used.

Sensitox II[li] (4) is an insoluble Rose Bengal sensitizer bound to a copolymer of chloromethylstyrene and ethylene glycol monomethacrylate with ethylene glycol bismethacrylate as a cross-linking agent. Beads of $\sim 5 \times 10^{-5}$ m diameter contain 0·093 g sensitizer per g polymer support.

2.2. Spacer materials

CaF_2 (99·8 %, coating material, Balzers AG., 9496 Balzers, Liechtenstein) tablets were milled to a fine powder before being mixed and finally milled with the insoluble sensitizer.

KBr (for IR spectroscopy, Fluka AG, 9470 Buchs, Switzerland) was used directly for the mixtures indicated below.

Lakes containing the finely suspended insoluble sensitizers were prepared from 10% aqueous poly(vinyl alcohol) and painted on aluminized cardboard.

3. PROCEDURE

3.1. Preparation of surfaces

Particles providing photoactive surfaces were dust-powdered in an agate ball mill and pressed into pellets using the appropriate equipment for KBr pellets in IR spectroscopy. Whereas the Bio-Rad-based material[1e-g] was easily transformed into such pellets, Araldite[1h], methacrylate copolymers[li] as well as silica gel-supported[4] sensitizers needed binding additives such as CaF_2 or KBr.

It must be pointed out that the use of those binding materials yields a macroscopic dilution (spacing) of the particles functionalized at their surfaces with photoactive compounds (chromophores). However, the concentration of chromophores on a particular surface and, thus, eventual chromophore–chromophore interactions are not affected.

The total amount of powder used for one pellet was ~0·2 g. The pellet was formed in a KBr pellet module using a pressure of 18 t cm^{-2}. During this procedure a vacuum of ~1 Torr was applied.

3.2. Preparation of lakes

Suspensions of dust-powdered photoactive surfaces were prepared in a glass ball mill (1 mm diameter, 2–3 h). Additional milling with quartz sand (1 h) was necessary for suspensions containing Araldite type materials.

3.3. Irradiation

The pellets were mounted into suitable cardboard or metal holders which were placed on the sample-holding device of a Xenotest 450 (Original Hanau Quarzlampen GmbH, 6450 Hanau, W. Germany). A lightfastness standard[5] (blue wool patterns) was irradiated under the same conditions with each series of samples.

The emitted light from a xenon lamp (4500W) was filtered by an alternating combination of six IR filters (01176) and one UV filter (011677, Heraeus Laborgeräte AG, 8045 Zürich, Switzerland) generally used for the simulation of the spectral distribution of solar irradiation.

Temperature and humidity during irradiation were kept at 30 °C and 60 ± 5 %, respectively.

Radiometric experiments on blue wool patterns were made on an optical bench using a 1000W xenon lamp (Oriel GmbH, 6100 Darmstadt, West Germany) and a 10 cm water filter for IR protection. The light was filtered by the same combination of filters as indicated above, mounted on a rotating wheel. Irradiation time and irradiance were controlled by a bolometer (YSI 6551, Yellow Springs Instrument Co., Yellow Springs, OH 45367, USA) linked to an integrating actinometer.[6]

3.4. Evaluation of light stability and lightfastness[5b]

The irradiated pellet or lake surfaces were compared in a qualitative analysis with the jointly irradiated blue wool patterns showing eight differently dyed textile strips of different but defined light stability (levels 1 to 8).[5] Colour changes (e.g. bleaching) were evaluated visually by comparing irradiated samples with irradiated blue wool patterns and standards kept in the dark; marks of 1 (very unstable) to 8 (very stable) were attributed according to the lightfastness of that level of the blue wool pattern which corresponded best to the observed colour change of the sample.

Quantitative analysis involved the recording of spectral radiance factors (β) of the irradiated samples as well as of those kept in the dark and the calculation of the corresponding Cielab values.

Changes of sample colours may be recorded quantitatively by the Cielab colour system.[8] This system defines within a space of either rectangular or cylindrical coordinates the colour point of any coloured light. The rectangular coordinates L^*, a^*, b^* represent by a^* the red ($a^* > 0$) to green ($a^* < 0$), by b^* the yellow ($b^* > 0$) to blue ($b^* < 0$) and by L^* (always >0) the lightness contribution of a given colour. The L^*-axis ($a^* = b^* = 0$) represents achromatic colours ranging from ideal black ($L^* = 0$) to ideal white ($L^* = 100$). The representation in cylindrical coordinates L^*, C^*_{ab}, and h_{ab} is closely connected with the idea of lightness, chroma and hue and therefore more intuitive. The length of the vector C^*_{ab} between the L^*-axis and a colour point represents the chroma of this colour, and the angle h_{ab} between the a^*-axis and the vector determines its hue. Thus, points placed along the same vector represent colours of the same hue, and points placed on a circle centered on the L^*-axis stand for colours of the same chroma.

The Cielab coordinates are calculated from the spectral radiance factors (β)[8,9] using the standard illuminant D65 and the 1964 supplementary standard colorimetric observer (10°).

Colour changes of wool patterns, sample pellets or lakes as a function of irradiation time may be observed by reflection spectrophotometry. Spectral radiance factors (β) are measured every 20 nm in the wavelength range from 400 to 700 nm (Fig. 1). The Cielab coordinates are calculated from those values for CIE illuminant D65 and CIE 1964 supplementary standard colorimetric observer (Table 1). The L^*, a^*, b^* values enable us to present the quantitative analysis of colour changes by means of two relationships. The first shows differences of L^* values representing pure bleaching or darkening effects (Fig. 2), the second indicates changes in chroma (C^*_{ab}; Table 1) and hue (h_{ab}, Table 1, Fig. 3). The combination of the two graphs ($L^* = f(t)$ and $b^* = f(a^*)$) provides a qualitative but comprehensive view on the light stability of the different samples investigated. Quantitative values of the distances between two colour points within the three-dimensional Cielab system are given by ΔE^*_{ab} (Table 1, footnote *d*) and are listed in Table 1.

Figure 2 reflects the strong bleaching of the dyed wool strip, whereas Fig. 3 shows a very dominant shift of the colour from blue to yellow.

Cielab analysis provides a very clear and convenient way to explain,

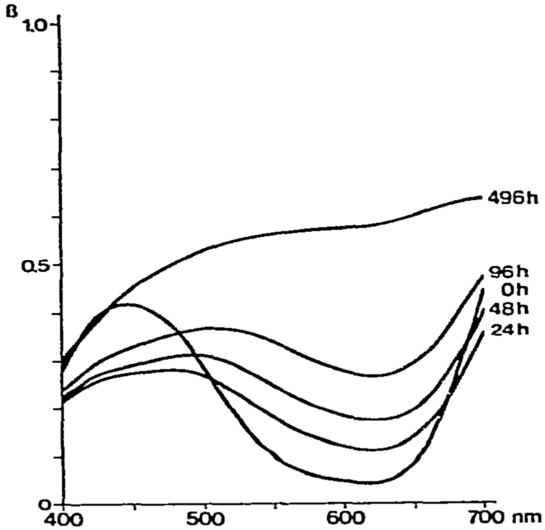

Fig. 1. Spectral radiance factors (β) of the least stable strip (level 1) of blue wool patterns irradiated in a Xenotest 450 apparatus for different irradiation times.

TABLE I

Cielab Data of the Samples Shown in Figs. 1, 2 and 3

Irradiation time, t (h)	L^*	a^*	b^*	C^*_{ab}	h^a_{ab} *(degrees)*	ΔH^{*b}_{ab}	ΔE^{*c}_{ab}
0^d	44	−4·1	−42·0	42	264	—	—
24	50	−10·8	−14·8	18·3	234^e	−14·6	29
48	57	−10·1	−7·3	12·5	216^e	−19·0	38
96	64	−8·5	−0·1	8·5	181^e	−25·0	47
496	79	−1·6	−11·1	11·3	98^e	−43·0	64

[a] $h_{ab} = \arctan (b^*/a^*)^{8b}$

[b] $\Delta H^*_{ab} = \sqrt{(a^*_t - a^*_{t_0})^2 + (b^*_t - b^*_{t_0})^2 - (C^*_{ab_t} - C^*_{ab_{t_0}})^2}$, contribution to the hue; the sign attributed to this quantity conforms with the official definitions.[8b]

[c] $\Delta E^*_{ab} = \sqrt{(L^*_t - L^*_{t_0})^2 + (a^*_t - a^*_{t_0})^2 + (b^*_t - b^*_{t_0})^2}$

[d] Standard, t_0

[e] Calculated[a] for Fig. 5, differences between these data and h_{ab} of the standard[d] are not to be confused with the results of ΔH^{*b}_{ab}.

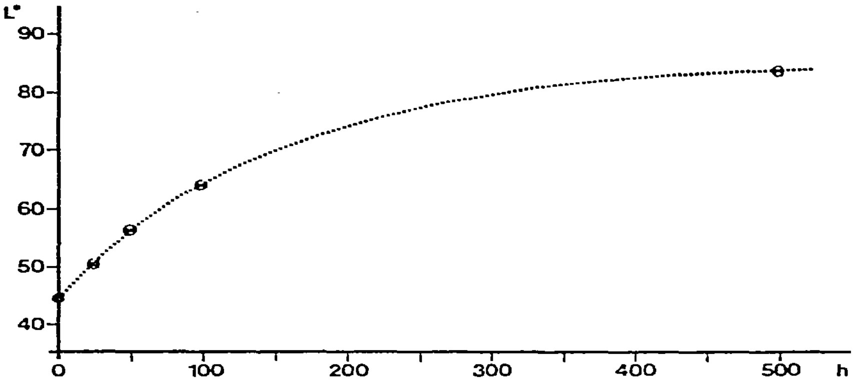

Fig. 2. Bleaching of the blue wool pattern (level 1) shown as a function of L^* vs. irradiation time (see also Fig. 1).

display and evaluate colour changes of photoactive surfaces and the results on the light stability of insoluble photoactive materials are presented accordingly.

The reflection spectrophotometer used (Zeiss RFC 3) was linked to a HP 2100A computer. In taking spectral radiance factors of the surface, a mask of 5 mm diameter was used. The Cielab data were calculated automatically from the measured radiance factors.[10]

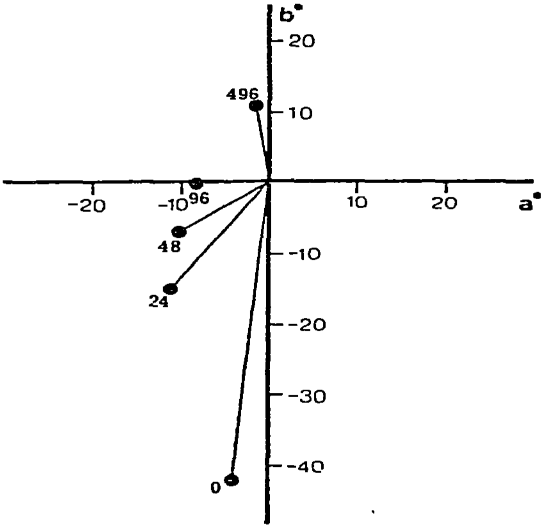

Fig. 3. Colour changes of the blue wool pattern (level 1) shown in a Cielab a^*, b^* diagram at different irradiation times (h).

4. RESULTS AND DISCUSSION

The polymer-based insoluble sensitizers mentioned above have been tested by this procedure in order to establish a classification of those materials with regard to their light stability. In addition to pellets of pure photoactive material (where possible), different mixtures with KBr and CaF_2 as spacers have been prepared.

Irradiation of pellets consisting of pure Bio-Rad S-XI or of KBr or CaF_2 mixtures with Bio-Rad S-XI, Araldite F–phthalic anhydride and chloromethylstyrene–methacrylate copolymers did not show any colour changes, and, thus, no corrections of the reported ΔE^*_{ab} values of the irradiated sensitizer samples were needed.

4.1. Bleaching and colour changes

There was practically no bleaching of pure Sensitox pellets (Fig. 4), and colour changes were only found when the sensitizer was mixed with spacers, e.g. 50% CaF_2 (**1d**, Fig. 5).

The evolution of bleaching and colour changes of different Sensitox spacer mixtures is represented by the Cielab parameters in Table 2 and visualized in Fig. 6.

No pellets could be made, either with Sensitox II or with pure Araldite F–phthalic anhydride copolymer.

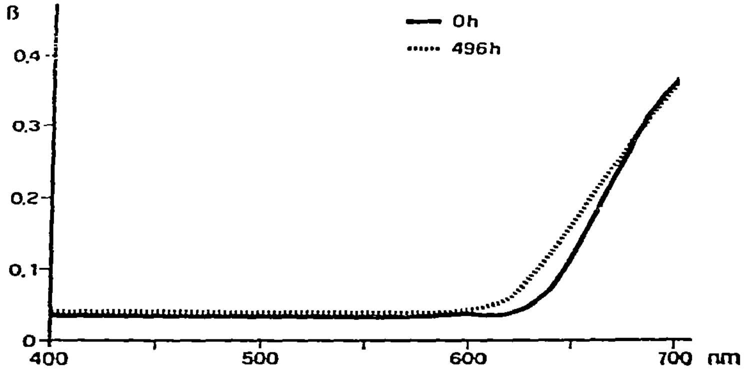

Fig. 4. Spectral radiance factors (β) of Sensitox pellets (**1a**) kept in the dark and after 496 h of Xenotest irradiation.

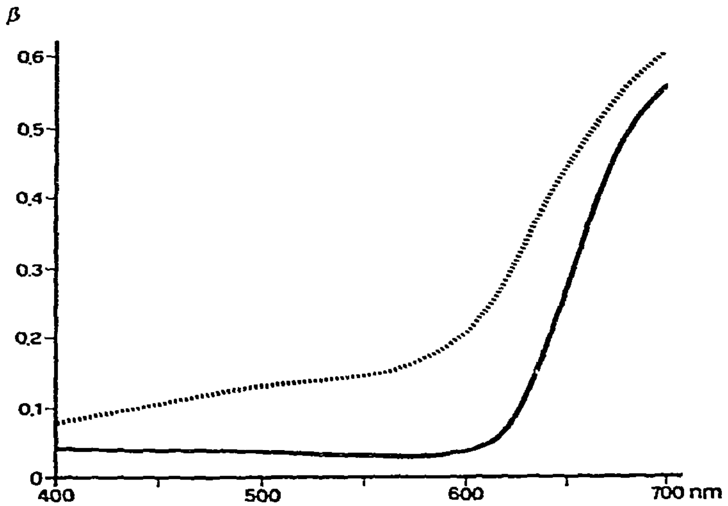

Fig. 5. Spectral radiance factors (β) for pellets made from a 50% Sensitox/50% CaF_2 mixture (**1d**) kept in the dark and after 496 h of Xenotest irradiation. Key as for Fig. 4.

TABLE 2

Cielab Data for Pellets Containing Sensitox at Different Irradiation Times

Pellets	*Irradiation time, t (h)*	L^*	a^*	b^*	C^*_{ab}	h_{ab}	ΔH^*_{ab}	ΔE^*_{ab}
100% Sensitox (**1a**)	0	22·7	8·2	1·7	8·3	11·7	—	—
	24	24·2	8·3	1·6	8·5		−0·1	1·4
	48	24·1	8·5	1·7	8·6		−0·0	1·3
	496	24·3	9·2	2·4	9·5		0·5	2·0
50% Sensitox/ 50% KBr (**1b**)	0	22·5	10·8	1·3	10·9	6·8	—	—
	24	28·2	10·0	2·7	10·3		1·5	6·0
	48	28·7	10·2	2·6	10·5		1·4	6·4
	496	26·5	10·4	3·1	10·8		1·9	4·5
5% Sensitox/ 95% KBr (**1c**)	0	21·3	14·0	1·8	14·2	7·2	—	—
	24	27·8	14·5	3·4	14·8		1·5	6·8
	48	28·4	12·6	3·1	13·0		1·5	7·3
	496	31·4	13·6	5·2	14·5		3·5	10·7
50% Sensitox/ 50% CaF_2 (**1d**)	0	23·9	20·2	1·7	20·3	4·7	—	—
	24	34·2	18·8	5·3	19·4		3·8	11·1
	48	36·5	16·0	4·6	16·6		3·6	13·6
	496	47·0	14·4	14·5	20·3		14·1	27·1

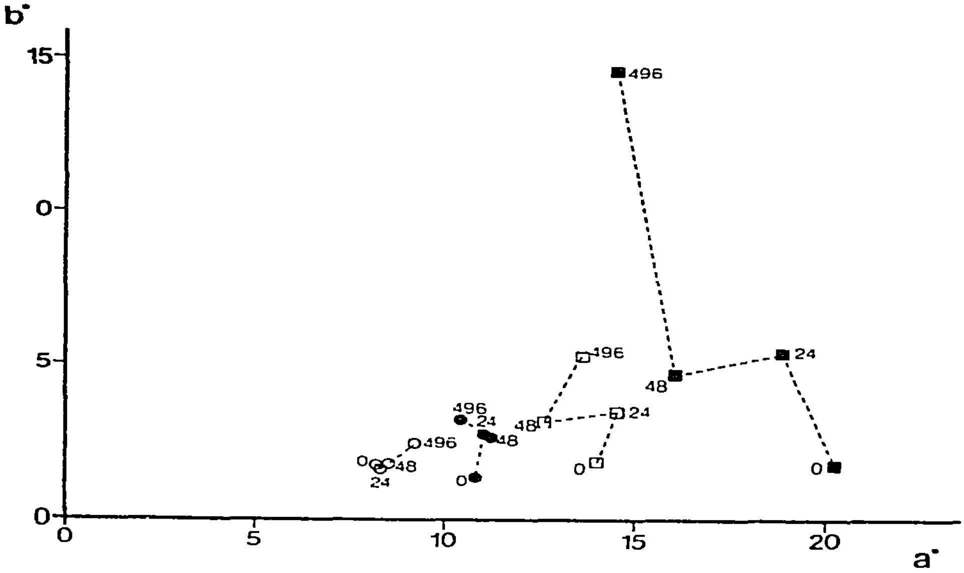

Fig. 6. Cielab a^*, b^* diagram for pellets containing Sensitox (**1a–d**) at different irradiation times (h). ○, 100 % Sensitox (**1a**), ΔE^*_{ab} (496 h) = 2·0; ●, 50 % Sensitox/50 % KBr (**1b**), ΔE^*_{ab} (496 h) = 4·5; □, 5 % Sensitox/95 % KBr (**1c**), ΔE^*_{ab} (496 h) = 10·7; ■, 50 % Sensitox/50 % CaF_2 (**1d**), ΔE^*_{ab} (496 h) = 27·1).

Those of different P-HP, P-RB and Sensitox II spacer mixtures are shown in a selection of reflection spectra (Figs. 7–9), Cielab data (Tables 3–5) and corresponding diagrams (Figs. 10–12).

Pure Sensitox pellets are apparently far too concentrated for the macroscopic observation of any colour difference due to the decay of a

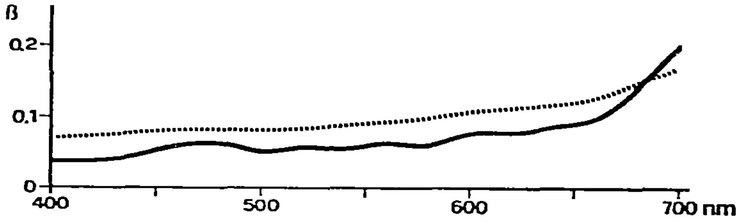

Fig. 7. Spectral radiance factors (β) of pellets made from a 5 % P-HP/95 % KBr mixture (**2c**) kept in the dark and after 496 h of Xenotest irradiation. Key as for Fig. 4.

TABLE 3
Cielab Data for Pellets Containing P-HP at Different Irradiation Times

Pellets	*Irradiation time, t (h)*	L^*	a^*	b^*	C^*_{ab}	h_{ab}	ΔH^*_{ab}	ΔE^*_{ab}
50% P-HP/ 50% KBr (**2b**)	0	36·6	2·2	6·0	6·4	70·4	—	—
	24	42·1	0·6	7·7	7·6		1·9	6·0
	48	43·7	0·7	8·9	8·8		2·2	7·8
	496	52·6	4·4	21·7	22·0		2·3	22·5
5% P-HP/ 95% KBr (**2c**)	0	28·3	4·0	3·3	5·2	39·2	—	—
	24	31·7	2·8	3·4	4·4		0·9	3·6
	48	38·7	2·7	5·1	5·7		2·2	10·7
	496	35·8	3·9	4·4	5·9		0·9	7·7
50% P-HP/ 50% CaF_2 (**2d**)	0	42·3	2·0	6·3	6·6	71·9	—	—
	24	63·4	0·3	7·2	7·0		2·5	21·2
	48	69·0	0·5	9·9	9·8		3·1	27·0
	496	75·7	0·3	14·4	14·3		3·1	34·4

TABLE 4
Cielab Data for Pellets Containing P-RB at Different Irradiation Times

Pellets	*Irradiation time, t (h)*	L^*	a^*	b^*	C^*_{ab}	h_{ab}	ΔH^*_{ab}	ΔE^*_{ab}
50% P-RB/ 50% KBr (**3b**)	0	31·7	25·6	7·1	26·6	15·4	—	—
	24	31·9	27·6	12·9	30·4		4·8	6·2
	48	30·3	27·1	11·7	29·4		3·9	5·1
	496	32·2	26·8	14·4	30·3		6·4	7·5
5% P-RB/ 95% KBr (**3c**)	0	24·6	22·4	6·5	23·3	16·1	—	—
	24	35·9	22·1	8·0	23·5		1·5	11·7
	48	39·8	20·8	8·1	22·3		2·1	15·4
	496	43·6	22·8	14·4	26·9		7·0	20·6
50% P-RB/ 50% CaF_2 (**3d**)	0	35·4	27·1	5·2	27·6	10·9	—	—
	24	42·0	26·7	12·9	29·6		7·5	10·2
	48	42·8	26·6	14·7	30·2		9·1	12·1
	496	52·3	21·6	21·1	30·0		16·6	23·9

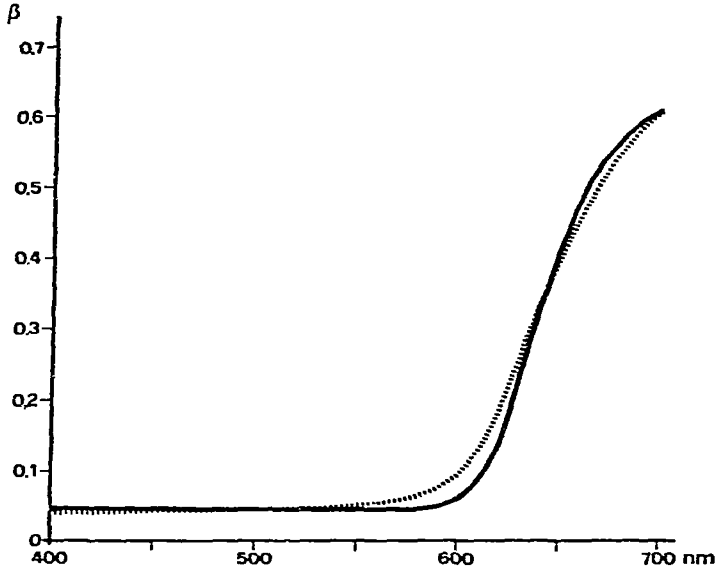

Fig. 8. Spectral radiance factors (β) of pellets made from a 50% P-RB/50% KBr mixture (3b) kept in the dark and after 496 h of Xenotest irradiation. Key as for Fig. 4.

TABLE 5
Cielab Data for Pellets Containing Sensitox II at Different Irradiation Times

Pellets	*Irradiation time, t (h)*	L^*	a^*	b^*	C^*_{ab}	h_{ab}	ΔH^*_{ab}	ΔE^*_{ab}
50% Sensitox II/ 50% KBr (4b)	0	31·6	41·3	10·8	42·7	14·7	—	—
	24	50·4	28·1	13·8	30·6		6·1	23·2
	48	53·2	24·4	18·8	29·5		13·2	28·6
	496	68·9	10·3	28·7	28·3		32·7	51·7
5% Sensitox II/ 95% KBr (4c)	0	29·0	34·0	10·0	35·4	16·4	—	—
	24	39·4	39·0	16·4	42·2		4·5	13·2
	48	45·0	35·2	18·5	39·6		7·5	18·2
	496	55·5	24·0	29·8	38·2		21·9	34·5
50% Sensitox II/ 50% CaF_2 (4d)	0	32·2	39·2	4·0	39·4	5·8	—	—
	24	45·8	27·5	10·6	28·6		8·1	19·1
	48	52·0	22·3	14·5	25·1		13·9	28·1
	496	68·1	9·7	30·6	29·4		38·5	53·6

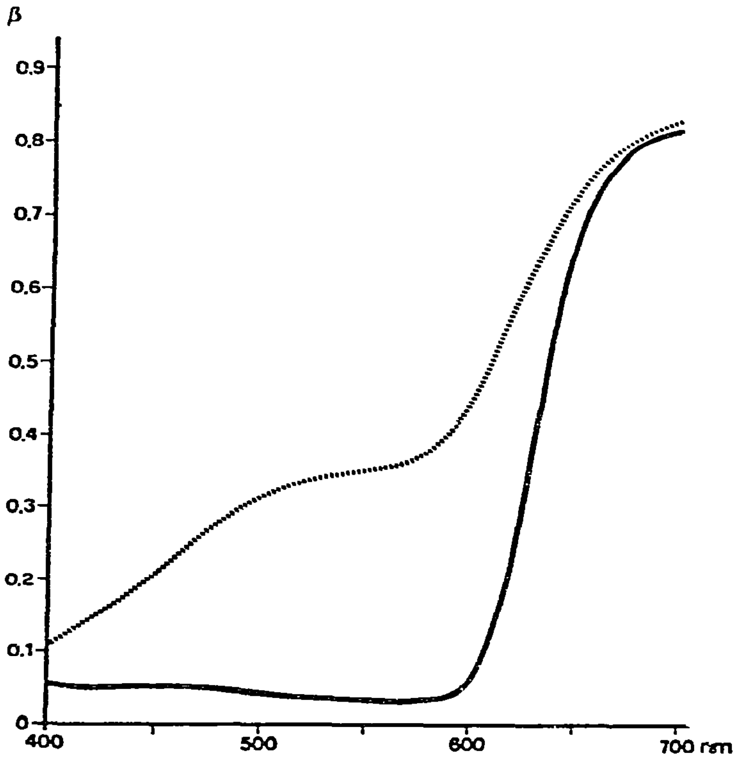

Fig. 9. Spectral radiance factors (β) of pellets made from a 50 % Sensitox II/50 % KBr mixture (**4b**) kept in the dark and after 496 h of Xenotest irradiation. Key as for Fig. 4.

relatively minute fraction of the chromophore. Changes in lightness, chroma and hue therefore remain within a maximal range of less than 2 units ($\Delta E^*_{ab} = 2{\cdot}0$) of the Cielab system (Table 2, **1a**). A dilution of the coloured material by spacer substances such as KBr or CaF_2 makes colour changes more visible, and the maximal dimensions of the space travelled by the colour point upon irradiation of the pellets increase to 4 ($\Delta E^*_{ab} = 4{\cdot}5$, Table 2, **1b**) and 10 ($\Delta E^*_{ab} = 10{\cdot}7$, Table 2, **1c**) Cielab units for KBr contents of 50 and 95 %, respectively.

The same effect of dilution is found with P-RB/KBr mixtures: there ΔE^*_{ab} values increase from 7·5 (Table 4, **3b**) to 20·6 (Table 4, **3c**) at an irradiation time of 496 h when KBr is increased from 50 to 95 %.

Coloured surfaces containing 95 % KBr show a better light stability (smaller ΔE^*_{ab} values) than those containing 50 % of the same spacer

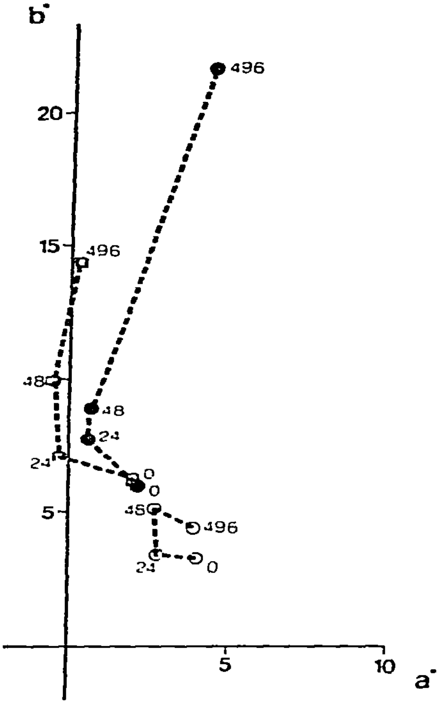

Fig. 10. Cielab a^*, b^* diagram for pellets containing P-HP (**2b–d**) at different irradiation times (h). ●, 50% P-HP/50% KBr (**2b**), ΔE^*_{ab} (496 h) = 22·5; ○, 5% P-HP/95% KBr (**2c**), ΔE^*_{ab} (496 h) = 7·7; □, 50% P-HP/50% CaF$_2$ (**2d**), ΔE^*_{ab} (496 h) = 34·4.

material in the cases of Araldite F-bound hematoporphyrin as well as of Sensitox II: the combined changes in lightness, chroma and hue of P-HP surfaces containing 50% KBr cover a range of up to 22 Cielab units ($\Delta E^*_{ab} = 22{\cdot}5$, Table 3, **2b**), whereas changes for pellets containing 95% KBr remain within the same limits observed for Sensitox (<8 Cielab units, $\Delta E^*_{ab} = 7{\cdot}7$, Table 3, **2c**). The same increase of KBr spacer material reduces colour changes from 52 ($\Delta E^*_{ab} = 51{\cdot}7$, Table 5, **4b**) to 35 ($\Delta E^*_{ab} = 34{\cdot}5$, Table 5, **4c**) Cielab units in the case of the rather unstable Sensitox II surfaces.

The results indicate that there is neither a chromophore- nor a support-specific stabilizing effect of KBr.

Comparing colour point changes in Tables 2–5 and in the corresponding Figs. 6 and 10–12, it can be seen that the addition of CaF$_2$ gives a stronger dilution effect than the addition of the same quantity of

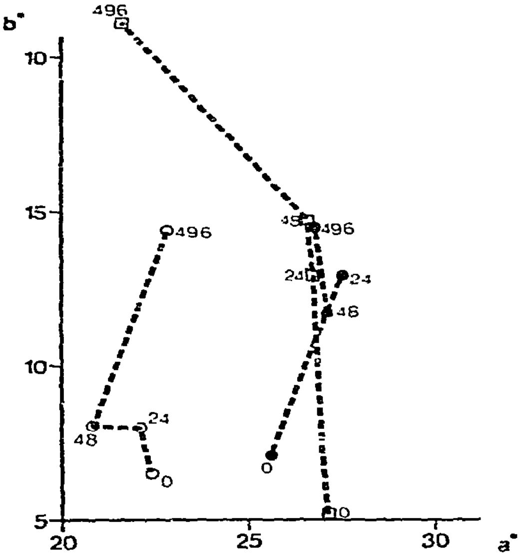

Fig. 11. Cielab a^*, b^* diagram for pellets containing P-RB (3b–d) at different irradiation times (h). ●, 50% P-RB/50% KBr (3b), ΔE^*_{ab} (496 h) = 7·5; ○, 5% P-RB/95% KBr (3c), ΔE^*_{ab} (496 h) = 20·6; □, 50% P-RB/50% CaF_2 (3d), ΔE^*_{ab} (496 h) = 23·9.

KBr. So far there is no proof for a destabilizing effect of the added CaF_2. In fact, only in the case of Sensitox II is there an appreciable colour effect (h_{ab}(4b) = 14·7 vs. h_{ab}(4d) = 5·8) which has to be explained by a chromophore–spacer interaction and might point in this direction.

An alternative method for the study of the light stability of coloured powders is already well known in the evaluation of pigments. These are mixed with colourless liquid polymer materials and milled to lakes which are painted on aluminized surfaces, dried and irradiated. Figure 13 shows the spectral radiance factors of a lake suspension of Sensitox prepared according to such a procedure. The unexposed lake shows significant spectral changes when compared with the corresponding spectral radiance factors of Sensitox (Figs. 4 and 5). Radiance factors (β) start to increase at $\lambda \simeq 600$ nm, and, furthermore, an additional reflection with a $\beta_{max} \simeq 460$ nm is observed indicating some lake–chromophore interaction. Sensitox suspended in poly(vinyl alcohol) is far less stable compared with pellets with or without spacer materials used in the preceding tests. Therefore the testing of paint surfaces was not pursued further.

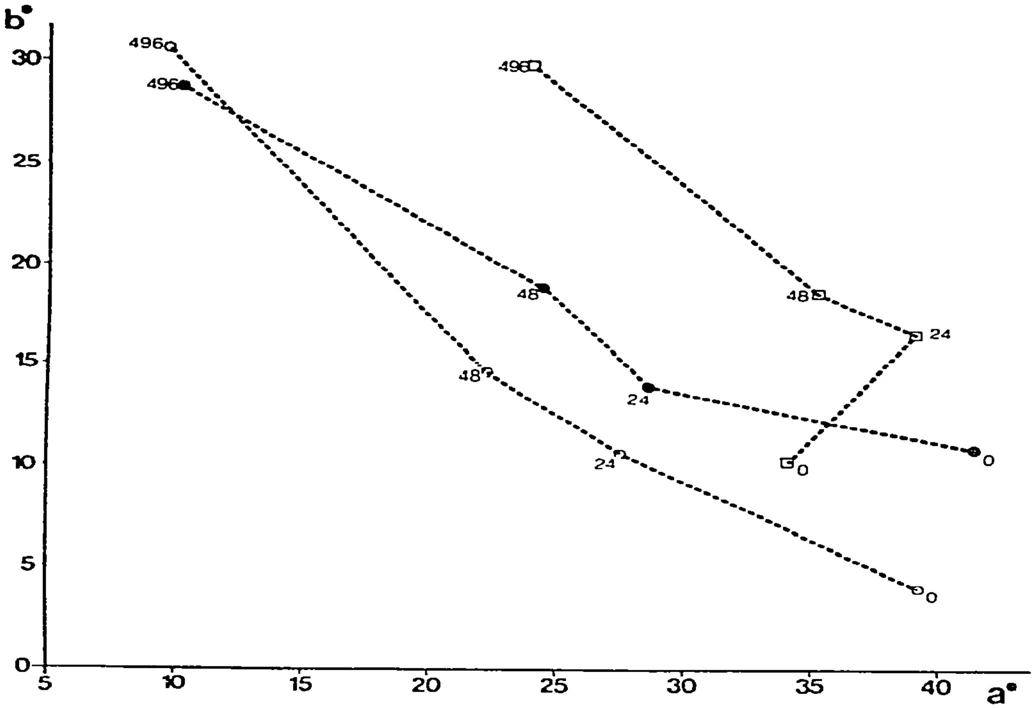

Fig. 12. Cielab a^*, b^* diagram for pellets containing Sensitox II (**4b–d**) at different irradiation times (h). ●, 50% Sensitox II/50% KBr (**4b**), ΔE^*_{ab} (496 h) = 51·7; □, 5% Sensitox II/95% KBr (**4c**), ΔE^*_{ab} (496 h) = 34·5; ○, 50% Sensitox II/50% CaF$_2$ (**4d**), ΔE^*_{ab} (496 h) = 53·6.

4.2. Evaluation of photoactive surfaces

Limits of light stability within which insoluble photoactive materials would be considered for further development may be described as volumes (e.g. spheres, ellipsoids, etc.) within the three-dimensional Cielab system. Their dimensions are to be defined according to the specific requirements.

In order to compare different materials and to attribute a certain order to a series of substances tested, the measurement of the dose of irradiation (energy fluence[11]) applied in a Xenotest apparatus is of great importance. It may be measured by a specifically designed Xenometer or by any radiometer. However, those instruments are not always available, and their results may vary considerably when different systems are compared.

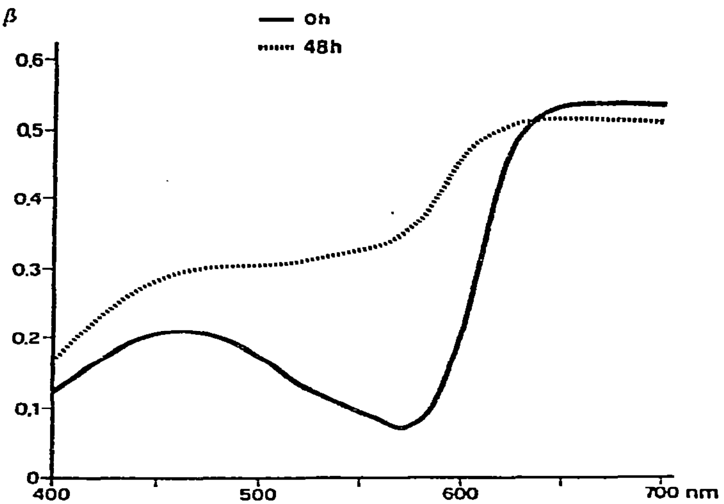

Fig. 13. Spectral radiance factors (β) of lake samples of Sensitox in 10% aqueous poly(vinyl alcohol) kept in the dark and after 48 h of Xenotest irradiation.

We therefore took the lightfastness of the widely used blue wool pattern as a means for dose measurement.

Bleaching and colour changes of this blue wool pattern can be related to defined doses of irradiation by plotting radiance factors at defined wavelength (β_λ) vs. dose determined by radiometric experiments (see section 2). For example, curve-fitting parameters for level 1, using

$$a\beta_\lambda^2 + b\beta_\lambda + c = \text{dose}$$

are $a = 3{\cdot}094\ (\pm 0{\cdot}465) \times 10^5$, $b = 1{\cdot}22\ (\pm 0{\cdot}214) \times 10^5$, $c = -1{\cdot}86\ (\pm 0{\cdot}23) \times 10^4$. Values of β_λ measured for levels 1 and 2 after Xenotest irradiation are correlated with the corresponding curves and an irradiance of 645 ($\pm 20\%$) W m^{-2} of the Xenotest apparatus has been calculated for the experiments reported. This analysis makes it possible to evaluate applied doses from simple reflection measurements of simultaneously irradiated blue wool patterns. As in actinometry, these correlations have to be made for relatively small doses ($< 5 \times 10^4$ W h m^{-2} for level 1) and results of the different levels of the blue wool pattern may not be mixed in order to prevent artefacts due to variations of irradiance, dye–fibre interaction and chemical reactivity as absorption spectra and absorbance of the surface change.

TABLE 6

Differences of Cielab Quantities of a Series of Insoluble Sensitizers and Corresponding Lightfastness Marks[5b] for Sample Surfaces Irradiated with a Dose of 3·20 ($\pm$0·65) $\times 10^5$ W h m^2

	ΔL^*	ΔC^*_{ab}	ΔH^*_{ab}	ΔE^*_{ab}	*Lightfastness*
1b	4·0	−0·1	1·9	4·5	7
3b	0·5	3·7	6·4	7·5	6
2b	16·0	15·6	2·3	22·5	4
4b	37·3	−14·4	32·7	51·7	2
2c	7·5	0·7	0·9	7·7	6·5
1c	10·1	0·3	3·5	10·7	6
3c	19·0	3·6	7·0	20·6	5
4c	26·5	2·8	21·9	34·5	3·5
3d	16·9	2·4	16·6	23·9	4
1d	23·1	0	14·1	27·1	3·5
2d	33·4	7·7	3·1	34·4	2
4d	35·9	−10·0	38·5	53·6	2

These radiometric measurements enable Cielab data (e.g. E^*_{ab}) from different experiments and laboratories to be related and, thus, orders of light stability can be established for a given irradiation dose (Table 6). It is interesting to note from Table 6 that marks given for individual pellets do not vary extensively from ratings made on the basis of ΔE^*_{ab} values. Differences are observed in cases of relatively small changes of hue (ΔH^*_{ab}) and chroma (ΔC^*_{ab}) compared with the corresponding ΔL^* values, indicating that comparisons of samples and corresponding standards (blue wool pattern) made by the human eye are more influenced by the bleaching than by colour changes.

Light stability tested as described here is certainly not the only parameter to be considered in evaluating the usefulness of photoactive surfaces, for example as insoluble singlet oxygen sensitizers. The interactions of a polymer support and/or of the electronically excited chromophore with the solvent as well as the variable sensitizing efficiency of non-irradiated and irradiated materials and, thus, of bleached or differently coloured materials are not taken into account. In addition, the chemical inertness of surface-bound and homogeneously dissolved sensitizers might also be different. A colour point analysis according to the procedure given in this paper can also be made with insoluble sensitizers isolated from suspensions irradiated in photochemical reactors.[12]

A thorough investigation of the usefulness of an insoluble sensitizer for industrial purposes must certainly include efficiency measurements of a specific energy transfer process in measuring corresponding reaction rates.[3] We think that the combination of light stability and efficiency tests provides the data necessary to evaluate photoactive materials at an early instance of development. Furthermore, the link with the Cielab system yields an easy and well-understood quantitative description of colour changes related to photochemically induced molecular transformation in surfaces.

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REFERENCES

1. (a) R. E. Moser and H. G. Cassidy, *Polym. Lett.*, **2**, 545 (1964).
    (b) P. A. Leermakers and H. T. Thomas, *J. Amer. Chem. Soc.*, **87**, 1620 (1965).
    (c) G. R. de Maré, M.-C. Fontaine and P. Goldfinger, *J. Org. Chem.*, **33**, 2528 (1968).
    (d) A. M. Braun and F. Lohse, CH 3862/71 (16.3.1971), to Ciba–Geigy AG.
    (e) E. C. Blossey, D. C. Neckers, A. L. Thayer and A. P. Schaap, *J. Amer. Chem. Soc.*, **95**, 5280 (1973).
    (f) R. Nilsson and D. R. Kearns, *Photochem. Photobiol.*, **19**, 181 (1974).
    (g) A. P. Schaap, A. L. Thayer, E. C. Blossey and D. C. Neckers, *J. Amer. Chem. Soc.*, **97**, 3741 (1975).
    (h) G. A. Graf, Thesis, Université de Haute-Alsace, Mulhouse, 1978.
    (i) A. P. Schaap, A. L. Thayer, K. A. Zaklika and P. C. Valenti, *J. Amer. Chem. Soc.*, **101**, 4016 (1979).

2. (a) R. S. Sinclair, *Photochem. Photobiol.*, **31**, 627 (1980) and literature cited therein.
   (b) N. S. Allen, J. F. McKellar, B. M. Moghaddam and G. O. Phillips, *J. Photochem.*, **11**, 101 (1979) and literature cited therein.
3. G. A. Graf and A. M. Braun, to be published.
4. E. Gassmann and A. M. Braun, to be published.
5. (a) SNV-Norm 95 809-1961.
   (b) E. McAlpine and R. S. Sinclair, *Textile Res. J.*, **47**, 283 (1977).
6. This actinometer is a new version[4] of the apparatus developed by K. Schaffner *et al.*[7]
7. W. Amrein, J. Gloor and K. Schaffner, *Chimia*, **28**, 185 (1974).
8. (a) Publication CIE No. 15.2 (TC-1.3), 1982.
   (b) DIN 6174.
9. DIN 5033.
10. For example D. Balkow, Diplomarbeit (Prof. J. Krochmann), TU Berlin, 1971.
11. J. Jagger, Phototechnology and biological experimentation, in *The science of photobiology*, ed. K. C. Smith, p. 16. New York, Plenum/Rosetta, 1971.
12. M.-T. Maurette, E. Oliveros, M. Metzger and A. M. Braun, to be published.