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Spectral Studies of Lithol Red Pigments

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SUMMARY

The origins of the colour changes in different metal salts of Lithol Red pigments have been investigated by spectral methods. The results indicate that all the examined pigments exist, both in solution and in the crystal state, in the hydrazone form. All the products had very similar spectra in solution. In the crystal state intermolecular interactions influenced by the crystal structure and by the size of the metal cation may be the factors which cause the observed colour of the pigments.

1 INTRODUCTION

The Lithol Red pigments are one of the oldest types of organic pigments (P. Julius, 1899) but are still extensively produced. Although the barium toner (CI Pigment Red 49, CI 15630, **I**) is the most important and has the highest production volume, the sodium, calcium and more recently the strontium salts are now produced by many manufacturers. The colour properties of these pigments vary from the yellowish red sodium salt, the bright red barium and strontium salts to the bluish red calcium salt. The hue of a particular metal salt can also be varied by changes in the methods of preparation, especially by the so-called resination process. According to Patton,[1] five distinct hues of the resinated barium salt and two different hues of the calcium salt can be obtained. No information on the origin of these colour changes has been reported in the literature.

The purpose of this present work was to carry out detailed

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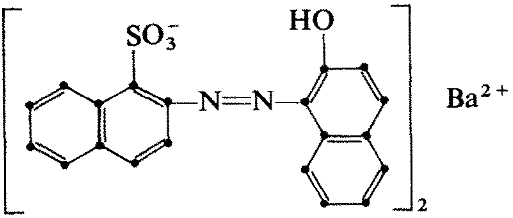

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spectrophotometric studies of selected salts of the dye **I**, both in solution and in stretched PVA films. In this way, it was hoped to examine the dependence between structure and colour of these pigments. The possibility of dichroism as the origin of colour changes has also been investigated.

2 EXPERIMENTAL

The syntheses of all monovalent metal salts of the dye **I** were carried out by reaction of the dye in the form of its sulphonic acid with a corresponding metal carbonate. The latter were used in 1·5 mol/mol excess and the reactions were carried out in aqueous medium at 70–80°C for 1 h. Excess of mineral salts were then removed by filtration of the pigment samples and washing with cold distilled water. The barium, calcium and strontium salts were prepared from the sodium salt of the dye as described in a typical commercial method.[2]

Two model compounds were also synthesized. These were the sulphonic acid of the dye, prepared from an aqueous solution of the sodium salt by precipitation from dilute acidified solution and 2-hydroxy-1,2′-azonaphthalene, prepared by coupling diazotized 2-naphthylamine with 2-naphthol.

Spectrophotometric studies in the visible region were carried out on a Specord UV–VIS spectrophotometer (Carl Zeiss, Jena, GDR). In all cases solutions of the concentrations of $5{\cdot}00 \times 10^{-5}$ mol dm^{-3} were used. Ethanol, dimethylformamide and their mixture with water (1:1) were used as solvents. In some cases, acetone, toluene, chloroform and methanol were also used. The same spectrophotometer was used for spectral measurements of pigment particles dispersed in poly(vinyl alcohol) films. In this work, pigment concentrations in dry films were 1·0–2·0% by wt and a stretching ratio of 3·5–4·0 was used. Preparation and stretching of the PVA films were carried out using techniques previously reported.[3]

3. RESULTS AND DISCUSSION

The prepared products exhibited, as do most of the commercial pigments, a rather low solubility in water and organic solvents. More extensive spectrophotometric studies were possible only for products with sufficient solubility (e.g. the sodium salt) or in disaggregating-type systems such as water–pyridine or water–dimethylformamide mixtures (Table 1.).

From the data shown in Table 1, it can be seen that all the pigments have similar λ_{max} values in water–ethanol solutions and the same λ_{max} value in water–dimethylformamide. Molar extinction coefficients were also similar although a slight increase of ε_{mol} with increasing molecular weight of the monovalent cation can be observed.

In the case of the relatively soluble sodium salt of the dye, a slight hypsochromic shift of λ_{max} with increasing polarity of the solvent was observed. In the weakly polar chloroform (dielectric constant 4·8), the λ_{max} of this salt is at 510 nm but in the more highly polar methanol (dielectric constant 33·6) it was at 496 nm. This shift towards shorter wavelengths is accompanied by an increase in the molar extinction coefficient, as in the case of other aggregated dyes.

It was also observed that when acetone or dimethylformamide were used as solvents some broadening of the main absorption band, accompanied by the appearance of a new fused band of similar intensity at about 510 nm, occurred. Since no such phenomenon was observed in mixtures of these solvents with water it may be presumed that the new band is due to the

TABLE 1
Values of λ_{max} and ε_{max} for Water–Ethanol and Water–Dimethylformamide Solutions of Lithol Red Pigments

Salt of Dye I	*Water–ethanol, 1:1*		*Water–dimethylformamide, 1:1*	
	λ_{max} *(nm)*	ε_{max}	λ_{max} *(nm)*	ε_{max}
Li	497	22 600	500	23 300
Na	498	24 800	500	24 000
K	—	—	500	24 800
Rb	—	—	500	26 600
Cs	498	25 900	500	25 200
Ca	—	—	500	25 400[a]
Sr	—	—	500	25 000[a]
Ba	—	—	500	22 700[a]

[a] Calculated per mol of the azo dye.

formation of charge-transfer (CT) complexes in the case of solvents containing carbonyl groups.

Comparison of the absorption curves of the examined salts with those of the 'unmetallized' sulphonic acid of the dye and of 2-hydroxy-1,2'-azonaphthalene give evidence that all the examined salts exist, in solution, predominantly in the hydrazone form. Only the non-ionic 2-hydroxy-1,2'-azonaphthalene, in solvents of low polarity, shows the presence of the azo form of the dye (Fig. 1). In other products there is a slope of the absorption curve in the region 420–440 nm where one may expect the appearance of the absorption peak specific for the azo form of the dye. Similar phenomena have been previously reported in the case of phenylazo-2-naphthols, which, in polar solvents, exist predominantly in the hydrazone form. Longest wavelength absorptions are at 415 nm for the azo form and 490–500 nm for the hydrazone form.[4-7]

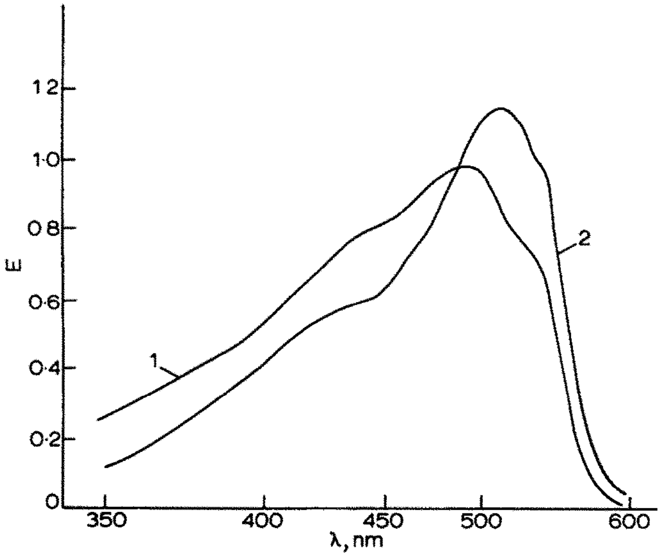

Fig. 1. Absorption curves of 2-hydroxy-1,2'-azoenaphthalene in toluene (1) and in water–dimethylformamide (1:1) (2). Concentration of dye, $5{\cdot}0 \times 10^{-5}$ mol dm^{-3}.

More relevant to the observed colour of the examined pigments in the solid state are spectra measured in PVA films (Table 2).

From the data in Table 2 it can be seen that all the examined products have two long-wavelength absorption bands. The first, usually the more intense band, occurred in the range 500–530 nm and the second, sometimes apparent as a slope on the main absorption curve, is present at 550–570 nm.

TABLE 2
The Long-Wavelength Absorption Bands in Spectra of Lithol Red Pigments
(1·5% Dispersions in PVA Films)

*Salt of Dye **I***	*Unpolarized light*			*Polarized light*					
				Parallel			*Perpendicular*		
	λ_{1max}	λ_{2max}	E_1/E_2	$\lambda^{\parallel}_{1max}$	$\lambda^{\parallel}_{2max}$	$E^{\parallel}_1/E^{\parallel}_2$	$\lambda^{\perp}_{1max}$	$\lambda^{\perp}_{2max}$	$E^{\perp}_1/E^{\perp}_2$
Li	526	568[a]	1·54	520	—	—	527	572	1·27
Na	510	546	0·98	508	536	1·04	510	558	0·85
K	527	551[a]	1·21	523	—	—	530	548	1·07
Rb	527	550[a]	1·14	525	550[a]	1·33	527	552	1·08
Cs	502	530	1·06	500	523[a]	1·07	506	532	1·03
Ca	532	576	0·97	524	576	1·03	532	576	0·93
Sr	527	565	1·03	525	563	1·11	529	568	0·95
Ba	528	565	0·87	527	563	0·91	528	565	0·80
Ba_{rosin}	532	568	0·91	527	565	0·95	527	570	0·84
Sulphonic acid of I	525	551[a]	1·25	520	—	—	530	551	1·04
2-Hydroxy-1,2′-azo-naphthalene	532	578	0·86	532	581	0·84	532	578	0·84

[a] Approximate value estimated from slope of absorption curve.

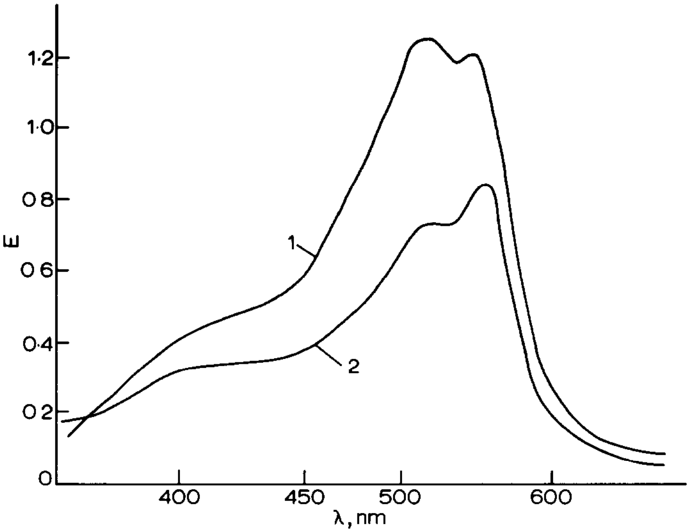

Fig. 2. Dichroic spectra of sodium salt of Lithol Red R. Light polarized parallel (1) and perpendicular (2) to direction of stretching.

Both of these bands are more clearly visible when measurements were carried out in polarized light (Fig. 2).

The intensity of the first absorption band increased rapidly when measurements were taken in light polarized parallel to the direction of stretching, i.e. to the longer axis of the pigment crystals. According to the literature, the most intense absorption band would be the result of an electron transition directed along the chromophore system of the dye. The observed bathochromic shift of this band in comparison with solvent-spectrophotometry data (Table 1) indicates that all the examined products also exist in the hydrazone form in the crystal state. Similar results have been previously reported in the case of other azo dyes, e.g. 1-phenylazo-2-naphthol,[8,9] CI Pigment Red 31 [9,10] and CI Acid Orange 7.[7] All these dyes are also based on 2-naphthol or its derivatives.

The second absorption band is more apparent in light polarized perpendicular to the direction of stretching. The absence of this band in solution spectra and its usually lower intensity suggest that it is a charge-transfer type.

The largest bathochromic shift of this band occurs in the case of unsubstituted 2-hydroxy-1,2′-azonaphthalene ($\lambda_{2\text{max}}^{\perp} = 578$ nm). Introduction of a sulphonic group into the dye molecule causes a hypsochromic shift to 551 nm. The location of this band in various metal salts changes, although some correlation between $\lambda_{2\text{max}}^{\perp}$ and the ionic radius of the metal cation can be observed (Fig. 3).

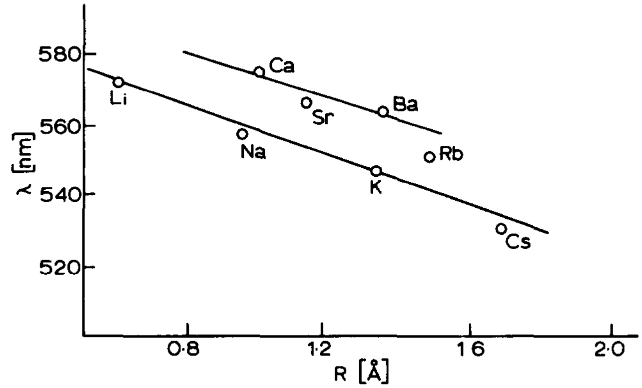

Fig. 3. Dependence between λ_{max} of the CT absorption band and ionic radius of metal cation of different salts of Lithol Red R.

This observation suggests that the CT interactions are of the intermolecular type. All the examined pigments probably have a crystal structure typical of other ionic substances, i.e. metal cations are located in vacancies formed between close-packed large anions of the dye. In such a structure, intermolecular interactions would be more intense in the case of small metal cations. In Fig. 3, such a correlation is apparent: for example, compare the small lithium cation, $\lambda\frac{1}{2}_{max}$ 572 nm, with the large caesium cation, $\lambda\frac{1}{2}_{max}$ 532 nm. Moreover, there can also be observed another type of correlation for the bivalent metal salts connected probably with change of crystal structure in which only half of the vacancies are occupied by bivalent cations.

Observed correlation between λ_{max} values of CT bands and ionic radii of metal cations are probably the result of the similarity of the crystal structure of all the pigments examined. It was found that all the monovalent and bivalent metal salts of the dye had almost identical X-ray diffraction spectra, similar to those previously reported in the case of the sodium and barium salts.[11] In some cases only minor changes of interplanar spacings and some differences in intensities of the diffraction peaks were observed. However, when the crystal structure of a particular pigment has been deliberately changed, different dichroic spectra have been obtained. Figures 4 and 5 show a comparison of the dichroic spectra of the potassium salts of the dye prepared from the sulphonic acid (Fig. 4) and then recrystallized from 50% dimethylformamide (Fig. 5). X-ray data analysis of these salts are listed in Table 3. It can be seen that even minor differences in crystal structure may thus be one of the factors which can produce the observed changes in the colour of a particular pigment.

No correlation between the crystal shape and the colour of these

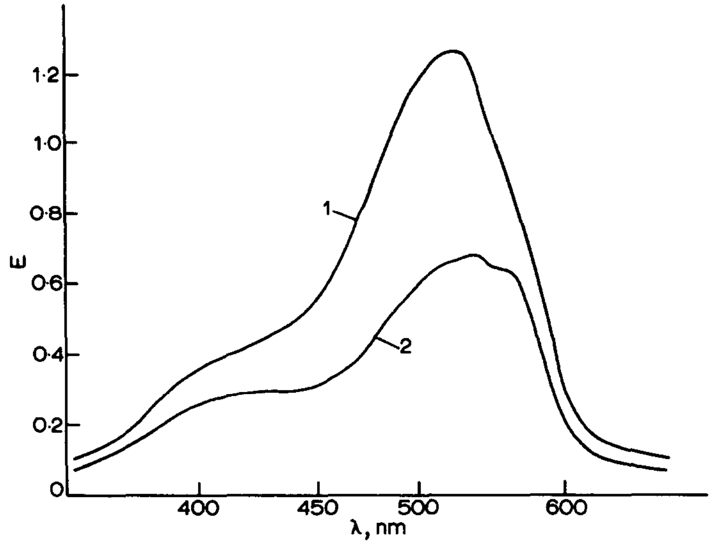

Fig. 4. Dichroic spectra of potassium salt of Lithol Red R (derived from the sulphonic acid of the dye). Light polarized parallel (1) and perpendicular (2) to direction of stretching.

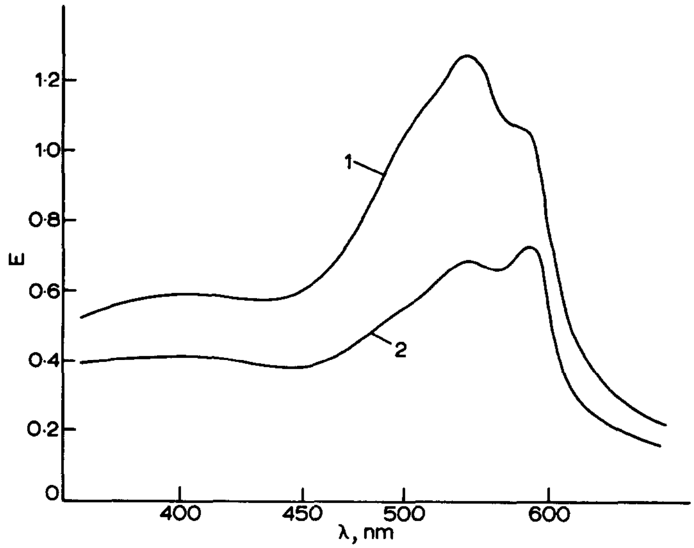

Fig. 5. Dichroic spectra of potassium salt of Lithol Red R (sample from Fig. 4 recrystallized from 50% DMF). Light polarized parallel (1) and perpendicular (2) to direction of stretching.

TABLE 3
X-Ray Diffraction Patterns of Potassium Salts of the Dye I

Potassium salt of I		*Potassium salt of I recrystallized from 50% DMF*	
d (*Å*)	*I*[a]	*d* (*Å*)	*I*[a]
17·68	vs	17·68	vs
8·84	ms	8·84	vs
8·04	ms	8·12	ms
5·90	m	5·90	ms
5·09	m	3·81	w
4·15	ms	3·70	w
3·43	ms	3·40	ms
		3·22	w

[a] vs, very strong; ms, medium strong; m, medium; w, weak.

pigments has been previously reported. Samples of resinated and non-resinated barium salts of the dye, which exhibit the same crystal structure but a different morphology of pigment particles,[11] had almost identical dichroic spectra. A slight bathochromic shift of the CT band (2–5 nm) in the dichroic spectra of the resinated pigment sample is probably too small to be responsible for the observed colour change. In previous work on copper phthalocyanine, Hauser and co-workers[12] observed a more definite shift of the absorption bands in the dichroic spectra (ca 20 nm). This shift was also connected with the rather minor colour change from reddish-blue (acicular) to greenish-blue (isometric pigment particles).

The observed colour change during the resination of Lithol Red pigments is thus probably due to the variation in the particle sizes of both samples and thence to the differences between light absorption and scattering. This assumption would however require further investigation.

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