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Electronic Spectroscopy and Trichromaticity Colorimetry of Some Inorganic Pigments and their Mixtures

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ABSTRACT

Electronic spectroscopy and trichromaticity colorimetry were applied to study chrome yellow and iron blue mixtures. The colour of these pigment mixtures was determined on the basis of reflectance spectra and described in the CIE, CIELAB, CIELUV colour spaces. It was found that various ratios of the components change the intensity of the reflectance spectra, whereas the band positions exhibit only small deviations from those of the pure components. The changes in the pigment concentrations give rise to a nonlinear variation of chromaticity coordinates. In the samples of mixtures containing an identical quantity of iron blue, the same colour differences were observed. Our experimental data suggest that this method can be applied to improve the analysis of the colorant compounds.

INTRODUCTION

Colorants are characterized by their ability to selectively absorb light in the visible region (380–780 nm). Electronic (absorption and reflection) spectra have been used to investigate some correlations between chemical structure and colour of the species.[1,2] The characteristic parameters of the spectrum, i.e. the positions of absorption bands and their intensity and shape, are important factors in the determination and prediction of colour and these parameters are dependent upon the electronic structure and symmetry of the molecules. Theoretical problems connected with the nature of colour have been studied very extensively, especially in the case of organic dyes.[3]

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One of the most important problems in colour technology is how to attain a specified colour using a mixture of colorants.[2] An objective method is necessary to specify colour accurately and a colour measurement system based on a mathematical analogue of the human eye has been proposed by the International Commission on Illumination.[4] The application of trichromaticity colorimetry and chromaticity coordinates creates possibilities for studying colour and its changes and this method has been used in investigations of dyes,[5,6] archaeological glass,[7] marine sediments[8] and brown coal,[9] and in restoration works of frescoes.[10,11] The adaptation of colour measurement systems falls into the following areas: computer colour matching, colour quality monitoring, colorant solution evaluation and colour communication. The purpose of computer colour matching is to select and determine the correct proportions of several colorants that, when combined, match the colour of a standard of typically known composition. To obtain accurate results it is necessary to input into the computer basic information on the behaviour of individual pigments in particular systems.

This paper describes an evaluation of the colour of pigment mixtures using chromaticity coordinates, and a study on the relation between the component concentrations and colour parameters. Pigments were selected which exhibited principal visible absorption bands at widely different wavelengths (chrome yellow and iron blue).

EXPERIMENTAL

Colorimetric and spectroscopic investigations were carried out with the industrially utilised chrome yellow and iron blue. The main components of these pigments are transition metal compounds. The chrome yellow pigment contains $PbCrO_4$. The iron blue components are ferric ferricyanide,

TABLE 1

Chromaticity Coordinates of the Chrome Yellow (A)/Li_2CO_3 Systems

Weight fraction A	x	y	Y	L^*	a^*	b^*	u^*	v^*	h_{ab} *(deg)*
0·01	0·3698	0·4055	88·0395	111·178	−6·548	38·660	14·090	63·287	99·387
0·015	0·3745	0·4105	87·3599	110·891	−6·484	41·371	15·683	66·919	98·908
0·025	0·3882	0·4238	84·6135	109·716	−5·775	48·933	20·856	76·309	96·731
0·03	0·3945	0·4310	82·1883	108·658	−5·840	52·654	22·481	80·636	96·329
0·04	0·4000	0·4351	80·1878	107·769	−5·110	55·119	24·924	83·134	95·297
0·05	0·4053	0·4403	78·6607	107·081	−4·907	58·095	26·591	86·245	94·829

TABLE 2

Chromaticity Coordinates of the Iron Blue (B)/Li_2CO_3 Systems

Weight fraction B	*x*	*y*	*Y*	*L**	*a**	*b**	*u**	*v**	h_{ab} *(deg)*
0·005	0·2933	0·2826	41·7204	86·678	−7·145	−21·899	−28·746	−40·638	251·930
0·01	0·2420	0·2701	34·7743	81·573	−6·884	−25·844	−31·536	−48·868	255·084
0·015	0·2368	0·2626	29·5759	77·287	−5·775	−27·340	−31·122	−52·298	258·072
0·02	0·2418	0·2626	28·3323	76·188	−3·458	−26·431	−26·930	−50·841	262·546
0·025	0·2383	0·2551	24·2808	72·368	−1·812	−27·655	−25·556	−53·796	266·251
0·03	0·2328	0·2501	20·1851	68·046	−2·025	−27·953	−26·181	−54·580	265·856

potassium ferrocyanide and ferric ferrocyanide; the percentage content of $[Fe(CN)_6]^{4-}$ ions in this mixture is about 55%.

Reflectance spectra in the wavenumber range 12000–47000 cm^{-1} were recorded with a Hitachi 356 UV/VIS spectrophotometer connected to an IBM PC microcomputer. Li_2CO_3 was used as the white standard (non-absorbing matrix). Samples (1 g) were prepared by mixing and grinding the individual pigments or mixtures of chrome yellow and iron blue with the matrices and pressing them under pressure (up to 200 kg cm^{-2}). The pigments were mixed with Li_2CO_3 in different proportions (Tables 1–4). The band positions were determined with the digital filter method described in detail elsewhere.[12] The filter acts by a single convolution of the spectral data with filter functions. Two characteristic parameters, α and N, determine the degree of resolution enhancement and filter width, respectively.

TABLE 3

Chromaticity Coordinates of the Chrome Yellow (A)/Iron Blue (B)/Li_2CO_3 Systems

Weight fraction	*x*	*y*	*Y*	*L**	*a**	*b**	*u**	*v**	h_{ab} *(deg)*
A 0·05 B 0·005	0·3171	0·4886	38·7106	84·541	−23·818	21·701	−25·669	41·289	137·663
A 0·05 B 0·01	0·2930	0·3848	29·2380	76·991	−23·632	11·127	−31·170	24·201	154·787
A 0·05 B 0·015	0·2840	0·3621	25·9354	73·976	−19·772	4·510	−29·044	12·043	167·151
A 0·05 B 0·02	0·2792	0·3614	22·4628	70·515	−20·294	3·632	−30·324	10·577	169·854
A 0·05 B 0·025	0·2750	0·3387	21·1705	69·136	−15·253	−1·861	−26·062	−0·367	186·956
A 0·05 B 0·03	0·2701	0·3323	18·7911	66·442	−14·653	−3·663	−26·163	−3·873	194·035

TABLE 4

Chromaticity Coordinates of the Chrome Yellow (A)/Iron Blue (B)/Li_2CO_3 Systems

Weight fraction	x	y	Y	L^*	a^*	b^*	u^*	v^*	h_{ab} *(deg)*
A 0·03 B 0·005	0·3026	0·3795	43·4173	87·837	−21·537	12·686	−27·011	26·497	149·501
A 0·03 B 0·01	0·2791	0·3582	29·3843	77·119	−21·324	3·188	−32·312	10·001	171·498
A 0·03 B 0·015	0·2721	0·3423	25·9450	73·985	−18·453	−1·447	−30·973	1·014	184·484
A 0·03 B 0·02	0·2579	0·3260	21·7646	69·776	−17·861	−6·542	−33·177	−8·725	200·111
A 0·03 B 0·025	0·2616	0·3200	20·8028	68·733	−14·522	−7·462	−28·774	−11·102	207·196
A 0·03 B 0·03	0·2538	0·3157	17·3731	64·727	−15·124	−8·693	−30·431	−13·431	209·889

The determination of the number of component bands and estimation of their positions by second derivatization followed the least-square curve fitting procedure. All the spectra were resolved using the same filter parameters: $\alpha = 300$, $N = 20$.

The colour parameters of the samples diluted with matrix were calculated from the reflectance spectra using trichromaticity colorimetry methods. This method has been previously applied to characterize some transition metal compounds.[13–16] The CIE, CIELAB and CIELUV colour systems were used for quantitative description of the colour. The calculation of chromaticity parameters was accomplished using COLOR and REFLEKS computer programs (J. Myrczek, unpublished).

RESULTS AND DISCUSSION

Spectroscopic investigations

There are three main sources of the colour of transition metal compounds. First of all there are *d–d* electronic transitions between energy levels of the d^n electronic configuration, then ligand to metal charge transfer (LMCT) and the reverse MLCT transitions, and finally the transitions in the ligand itself. The colour of iron blue is related to the energy of the electronic transitions within the configurations d^6 (Fe^{2+}) and d^5 (Fe^{3+}), as well as to charge transfer transitions.[17] MLCT and LMCT

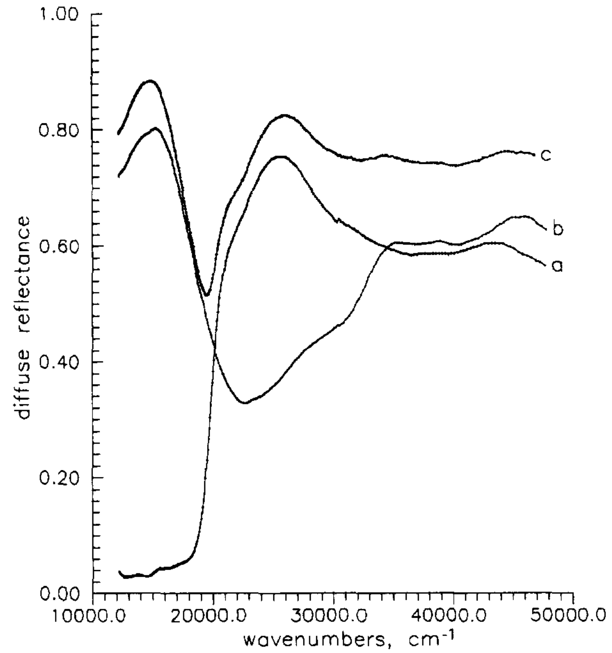

Fig. 1. Diffuse reflectance spectra of (a) chrome yellow, (b) iron blue and (c) mixture of chrome yellow and iron blue with Li_2CO_3 matrix.

transitions involving the cyanide groups may be anticipated. In chrome yellow the chromophore is the CrO_4^{2-} (d^0) anion.[17,18] The isolated chromate ion possesses four equivalent Cr–O bonds of a T_d symmetry and the electronic transitions are due to charge transfer transitions from the oxygen orbitals to unoccupied chromium orbitals.

The reflectance spectra of the investigated pigments are shown in Fig. 1. Digital filtration of the spectra was found to be an essential condition for estimation of the band maxima.[12] In the chrome yellow/Li_2CO_3 system the following band positions were found in the filtered spectra (cm^{-1}): 21300, 25200, 31800, 38800. In iron blue, a 24600 cm^{-1} shoulder and bands at 15200, 27600, 34400 and 38700 cm^{-1} were present.

The digital filtration method applied to the spectrum of the chrome yellow and iron blue mixture revealed bands at 15200, 21200, 25200, 31300, 34400 and 38700 cm^{-1}. Generally, it was found that for various concentrations of chrome yellow and iron blue in the mixture, the band positions showed only small deviations from the individual components, which can be explained by some perturbation caused by the host lattice. However, when using various ratios of the components, changes in the intensity distributions of the reflectance spectra were apparent. The changes were not linear with respect to pigment concentration, because the linearity

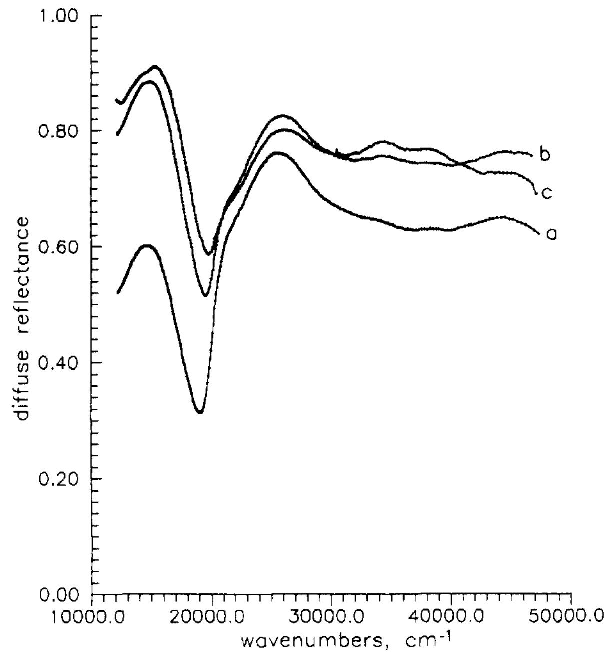

Fig. 2. Diffuse reflectance spectra of various mixtures of chrome yellow (A) and iron blue (B) in Li_2CO_3 (in weight fractions); (a) A 0·05, B 0·005; (b) A 0·05, B 0·02; (c) A 0·05, B 0·03.

depends not only on the chemical composition of the mixture but also on the wavelength.[19] Figure 2 shows the reflectance spectra for different mixtures of chrome yellow and iron blue with matrices.

In the studied pigment mixtures the band positions can be related to the band positions in simple pigments. However, the 27600 cm^{-1} band of the iron blue was not observed in the mixture. We cannot fully explain this observation, but most probably the weak 27600 cm^{-1} band of iron blue is completely overlapped by the strong 25200 cm^{-1} band of chrome yellow. For the filter parameters used in the study, this band could become unobservable. The 31300 cm^{-1} band observed in the mixture of pigments is shifted to lower energy by 500 cm^{-1} in comparison with the results for chrome yellow.

Colorimetric investigations

Colorimetric analysis was performed with the CIE system (*x*, *y*, *Y*) using the latest CIE recommendation with CIELAB (*L**, *a**, *b**) and CIELUV (*L**, *u**, *v**) chromaticity coordinates. *L** is closely related to the lightness of the sample, while *a** and *b** correspond to two antagonistic chromatic

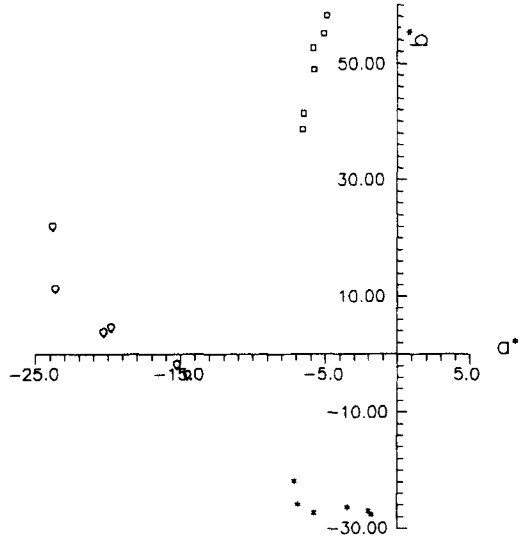

Fig. 3. Positions of colour points on the CIELAB plane: □, chrome yellow; *, iron blue; ○, mixture of pigments.

processes (red–green and yellow–blue). The values of the colour parameters for the systems chrome yellow/Li_2CO_3, iron blue/Li_2CO_3 and chrome yellow/iron blue/Li_2CO_3 were calculated directly from recorded reflectance spectra. These chromaticity coordinates are summarized in Tables 1–4. The positions of colour points for the chrome yellow/iron blue/Li_2CO_3, chrome yellow/Li_2CO_3 and iron blue/Li_2CO_3 systems on the CIELAB plane are presented in Fig. 3.

The changes in the pigment concentrations give rise to a nonlinear variation of chromaticity coordinates. This is related to the dichromatic behaviour which occurs in the majority of all coloured systems depending upon the experimental conditions. A similar dependence has been observed for pigments mixed with TiO_2 and for solutions.[5,13,20] The largest changes were observed for the values Y and L. Y represents the percentage luminance factor and this is an approximate correlation to the perceptual attribute of lightness. The Y values range from 100 for white objects (no light absorbed) to zero for objects that absorb all the light.[4] Increasing the pigment concentrations in the mixture caused a decrease in Y. As an example, the relationship between Y and molar fraction of iron blue is illustrated in Fig. 4.

The colour resulting from a mixture of colorants cannot be predicted accurately from the chromaticity coordinates of the individual components.[5] Adding iron blue to the chrome yellow/Li_2CO_3 system does change all the chromaticity values in a uniform manner. Figure 5 shows the changes

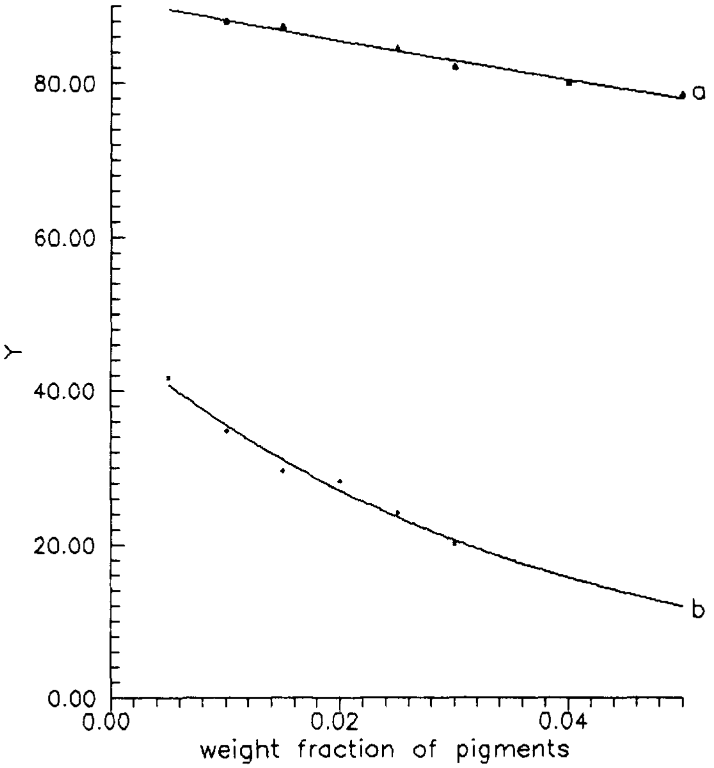

Fig. 4. Reaction between luminance Y and pigment concentration for (a) chrome yellow and (b) iron blue.

of the hue angle h_{ab} with the increase in concentration of iron blue; h_{ab} is defined as follows:

$$h_{ab} = \arctan(b^*/a^*).$$

h_{ab} lies between 0 and 90° if a^* and b^* are both positive; between 90 and 180° if b^* is positive and a^* negative; between 180 and 270° if a^* and b^* are both negative; and between 270 and 360° if b^* is negative and a^* is positive. For two experimental series, differences in h_{ab} in the range 137–210° were found for the pigment mixture chrome yellow/iron blue/Li_2CO_3. For chrome yellow/Li_2CO_3 the differences were between 94 and 100° and for iron blue/Li_2CO_3 between 250 and 266°.

The colour changes between samples of mixtures containing various quantities of the pigments can be evaluated by chromaticity differences. If the differences between two colours in L^*, a^*, b^* are denoted by ΔL^*, Δa^* and Δb^*, respectively, then the colur difference may be evaluated as the CIELAB colour difference ΔE^*_{ab}:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)]^{1/2}.$$

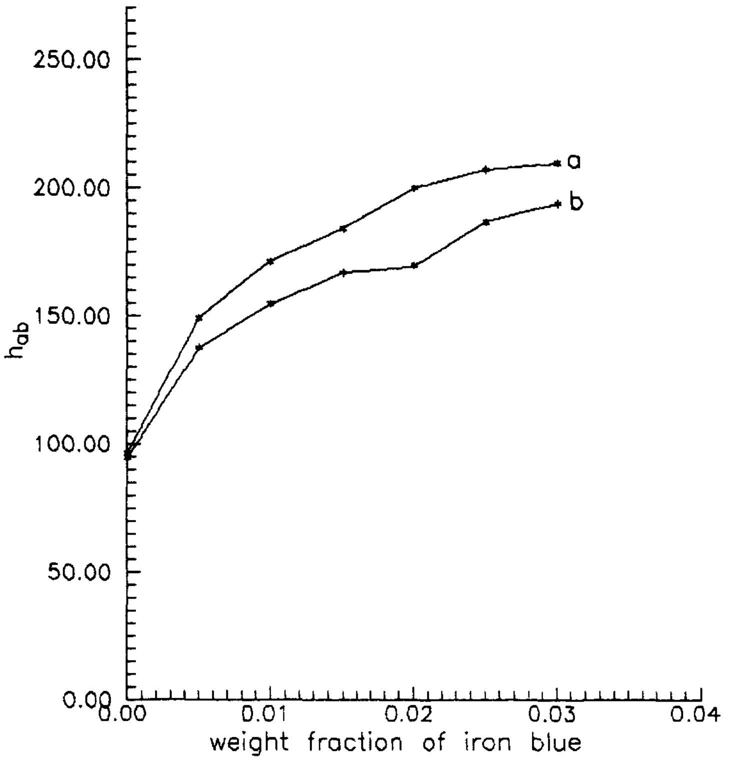

Fig. 5. The effect of iron blue concentrations (in weight fractions) on the hue angle h_{ab} for mixtures with (a) 0·03 and (b) 0·05 weight fractions of chrome yellow.

ΔE^*_{ab} is due to the change of all three quantities and is equal to the distance between two points representing the colours in the CIELAB space; similar measures can also be evaluated in the CIELUV space.

For quantitative evaluation of ΔE^*_{ab}, ΔL^*, Δa^*, Δb^* were calculated from the characteristic colour parameters of the mixtures of both pigments and the values for chrome yellow with the matrix as the reference sample. Table 5 presents the ΔE^*_{ab} values as a function of the iron blue concentrations obtained for two series of samples where the chrome yellow content is constant. It can be seen that if the samples contain an identical quantity of iron blue the ΔE^*_{ab} values are practically the same. This good correlation implies that the concentration of iron blue can be designated if the ΔE^*_{ab} value and the concentration of chrome yellow are known.

Thus, a study of pigments by electronic spectroscopy together with trichromaticity colorimetry allows information to be readily obtained about the composition of the mixture. The determination of band positions by the digital filter method is helpful in qualitative analysis and enables

TABLE 5

ΔE^*_{ab} Values for Chrome Yellow/Iron Blue/Li_2CO_3 and Chrome Yellow/Li_2CO_3 Systems for Two Weight Fractions of Chrome Yellow (A, 0·03; B, 0·05)

Weight fraction of iron blue	ΔE^*_{ab} *(A)*	ΔE^*_{ab} *(B)*
0·005	46·799	47·722
0·010	58·838	60·774
0·015	64·717	65·484
0·020	67·379	67·699
0·025	71·705	73·132
0·030	73·072	76·023

identification of the pigments used. The colour differences can be applied to the quantitative analysis of colorant composition.

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