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Industrial Photochemistry: XII High Contrast by Luminescence of Copy-Resistant Paper

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ABSTRACT

It is well known that the contrast of photocopies is lowered by the use of coloured paper. However, at the same time, the original data are often difficult to read. We show in this present paper that the use of coloured, luminescent paper leads to a satisfying contrast for the original and often to copy-resistant paper.

1 INTRODUCTION

Light can be used for its synthetic[1,2] or destructive properties.[3] It can also be used to form objects such as holograms,[4] three-dimensional objects,[5,6] photographs, and photocopies.

Photoreproduction is almost exclusively a photophysical process, derived from the Rank Xerox process, a method based on transfer electrocopy and which comprises the disappearance of an electrostatic charge (or its appearance) induced by light. A coloured powder is attracted to the charged region, its adhesion often being due to the powder fusion. This process is widely used, and consequently duplication of even unauthorized black and white data is very easy because almost all public or private offices have photocopiers.

In order to prevent unauthorized copying, several techniques have been patented. These are mainly based on three basic concepts:

(1) *Optical physical methods* using supports which are either striped films,[7] diffuse materials[8] or metallic coatings which reflect light.[9]

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(2) *Photochemical methods* using photochromic reactions. An intensive light flux will make ink white, thus preventing duplication. This invention has been patented.[10]

(3) *Optical chemical methods* using both coloured paper and ink. With white light, the eye is able to discriminate between the text and a coloured support, and to detect the existence of one or more colours, even if they are or not juxtaposed. In contrast, the more-or-less monochromatic light source of the photocopier corresponds to a wavelength for which the text and the support have identical reflection properties, thus preventing copying with a special material. This technique has been patented several times.[11-14] The use of coloured paper, especially red, with classical black inks shows that effectively copying is difficult to perform. This is due to too low a contrast between the text and the support in the wavelength range of the copier, especially in the case of selenium photocopiers (because selenium is only sensitive up to 600 nm). Under these conditions, the selenium copier cannot distinguish black print from the red background, but the eye can. The practice of this technique, however, shows that it can be very tiring for the eyes, when a large number of lines or pages have to be read.

The contrast which is essential for easy reading can be improved by the addition of compounds which absorb and re-emit light. These luminescent substances have the property of light emission by fluorescence or phosphorescence. The following descriptions are pertinent to paper in which such emissive substances have been incorporated.

2 DISCUSSION: THE USE OF EMISSIVE SUBSTANCES LEADING TO A BETTER CONTRAST FOR READING AN ORIGINAL DOCUMENT

2.1 With a white background

In the case of a white paper which does not absorb visible light, the corresponding support response at wavelength λ can be defined as:

$$R_0(\lambda) = \text{reflected flux } (\lambda)/\text{incident flux } (\lambda)$$

If $I(\lambda)$ is the light source spectrum, in particular related to white light, and $S(\lambda)$, the eye response curve (see Fig. 1), then the average response of the system is:

$$\langle R_0 \rangle_{\text{support}} = \frac{\int_0^\infty R_0(\lambda) I(\lambda) S(\lambda)\,\mathrm{d}\lambda}{\int_0^\infty I(\lambda)\,\mathrm{d}\lambda} \quad \text{where} \int_0^\infty S(\lambda)\,\mathrm{d}\lambda = 1$$

If the chosen ink has an apparent response $\langle R \rangle_{\text{ink}}$, the contrast with white background can be defined as:

$$C_0 = \langle R_0 \rangle_{\text{support}} / \langle R \rangle_{\text{ink}}$$

In the case of photocopier use, the source has a different spectrum $\overline{I(\lambda)}$ and the detector sensitivity is $\overline{S(\lambda)}$, which is different compared to the eye sensitivity. The photocopier response is then

$$\langle \overline{R_0} \rangle_{\text{support}} = \frac{\int_0^\infty R(\lambda)\overline{I(\lambda)}\,\overline{S(\lambda)}\,\mathrm{d}\lambda}{\int_0^\infty \overline{I(\lambda)}\,\mathrm{d}\lambda} \quad \text{where} \int_0^\infty \overline{S(\lambda)}\,\mathrm{d}\lambda = 1$$

This leads to a contrast $\overline{C_0}$:

$$\overline{C_0} = \langle \overline{R_0} \rangle_{\text{support}} / \langle \overline{R} \rangle_{\text{ink}}$$

This contrast, which depends on the copier, is lower than C_0. However, actually the quality of the copiers is such that $\overline{C_0} \simeq C_0$ and sometimes $\overline{C_0} > C_0$.

2.2 With a non-fluorescent coloured background

If $R_\infty(\lambda)$ is the response of a black support (for example, black ink) and $R_0(\lambda)$ is the response of a white one, in the first approximation, one obtains for a coloured background the response $R_c(\lambda)$:

$$R_c(\lambda) = R_\infty(\lambda) + [R_0(\lambda) - R_\infty(\lambda)][1 - a(\lambda)]$$

where $a(\lambda)$ is the absorption of the coloured material at the wavelength λ, with $0 \leq a(\lambda) \leq 1$.

Under these conditions for the original the response becomes:

$$\langle R_c \rangle = \frac{\int_0^\infty R_c(\lambda) I(\lambda) S(\lambda)\,\mathrm{d}\lambda}{\int_0^\infty I(\lambda)\,\mathrm{d}\lambda}$$

which leads to a decrease of the contrast C_c for the eye ($\langle R_c \rangle < \langle R_0 \rangle$).

For a copier, if its observation wavelength range corresponds to the absorption wavelength of the coloured substance, then the copy contrast $\overline{C_c}$ can be very low. This situation is particularly true in the case of a red background with a black ink impression, in which case $C_c > \overline{C_c}$. However, if no wavelength overlap intervenes between the copier and the coloured substance, then the copier analyses the background as a white one and consequently the copy is more contrasted than the original, i.e. $\overline{C_c} > C_c$.

2.3 With a luminescent coloured background

Generally, the analysis wavelength range of the copier is narrow, which means that the $\overline{C_c}$ variation is low, irrespective of whether the background is fluorescent or not. The eye, however, has a large spectral observation range and a fluorescent background for an original can increase its contrast. In order to illustrate this case, we have developed a simplified model. The corresponding assumptions, which are illustrated in Fig. 1, are:

(1) The coloured compound used in the background absorbs with a constant value $a(\lambda)$ for $\lambda < \lambda_1$, where λ_1 represents the cutting wavelength:

$$a(\lambda) = a \quad \text{for } \lambda \leq \lambda_1$$
$$a(\lambda) = 0 \quad \text{for } \lambda > \lambda_1$$

(2) The emission quantum yield Φ does not depend on the wavelength.
(3) Emission, like absorption, has a simplified distribution:

$$F(\lambda) = \Phi/\Delta\lambda \quad \text{for } \lambda \in [\lambda_1, \lambda_1 + \Delta\lambda]$$
$$F(\lambda) = 0 \quad \text{for } \lambda > \lambda_1 + \Delta\lambda$$

(4) The spectrum which defines $I(\lambda)$ is the solar spectrum, as pictured in Fig. 1.
(5) The copier has a monochromatic excitation source, with an analysis at wavelength λ' (in Fig. 1, λ' can occupy two positions λ'_1 and λ'_2, which are defined as 'condition 1': $\lambda'_1 < \lambda_1$ and 'condition 2': $\lambda'_2 > \lambda_1$).

For a coloured background, non-fluorescent, the contrast is of poor quality.

Taking into account the preceding assumptions, Figs 2 and 3 show the expected $\langle R_c \rangle$ variations with λ_1 for different values of $a(\lambda)$.

Under these conditions, where Φ can be equal to zero, if $\lambda' < \lambda_1$ (condition 1) ($\lambda' = \lambda'_1$, cf. Fig. 1), it is possible to have a notable lowering of the contrast for the copy. On the contrary, according to Section 2.2, if $\lambda' > \lambda_1$ (condition 2), the copier analyses the background as a white one and for these particular conditions, the copy can be more contrasted than the original.

To prevent copying, it is necessary to choose a maximal absorption wavelength λ_1 greater than λ' (see condition 1), which involves the use of colours. This property is well known and is the subject of several industrial protection methods (cf. Section 1).

However, as shown in Figs 2 and 3, if the copy is difficult to read, the reading of the original document can also become very tiring.

Our aim in this paper is to show that the use of a luminescent background for the original leads to both a good contrast for its reading and a good

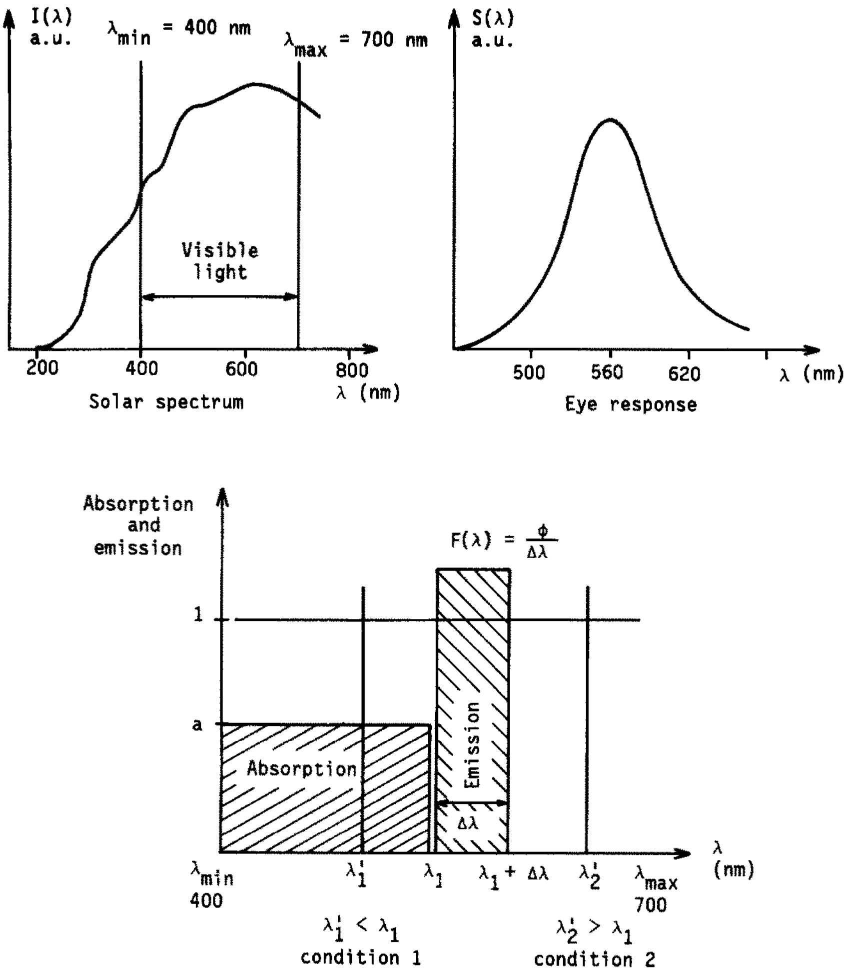

Fig. 1. Visualization of the assumptions and conditions 1 and 2 described in Section 2.3.

resistance to copying it, as long as the photodetector stays insensitive to the fluorescence emission of the background and with condition 1 assumed at the beginning of this section (see also Fig. 1).

In the case of an emissive background, the corresponding value of the contrast, C_f was calculated.

The absorption of the paper is:

$$\text{Abs.} = \int_0^\infty a(\lambda) I(\lambda)\, d\lambda$$

and the corresponding emission intensity is defined as:

$$I_f(\lambda) = \text{Abs.}\, \Phi F(\lambda)$$

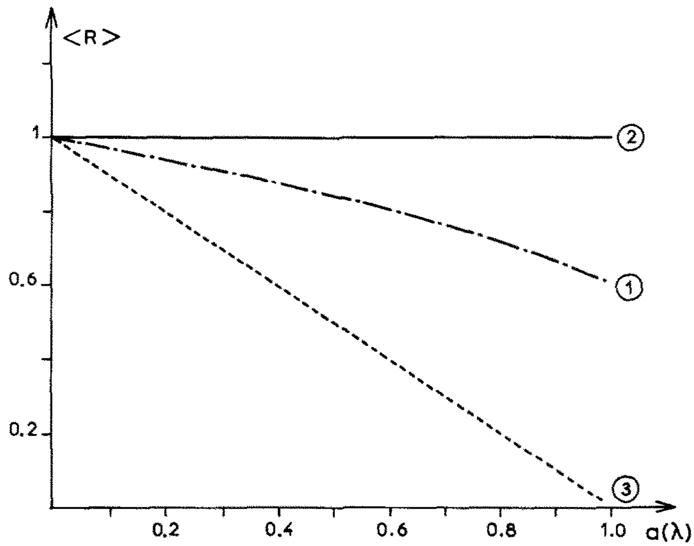

Fig. 2. Influence of $a(\lambda)$ on $\langle R \rangle$ for the following conditions: $\Phi = 1$, $\Delta\lambda = 30$ nm, $\lambda_1 = 550$ nm (cf. Fig. 1), $R_0(\lambda) = R_0$ and $R_\infty(\lambda) = R_\infty = R_0/100$: curve 1 for $\langle R_f \rangle$; curve 2 for $\langle R_c \rangle$ with condition 2 of Fig. 1; curve 3 for $\langle R_c \rangle$ with condition 1 of Fig. 1.

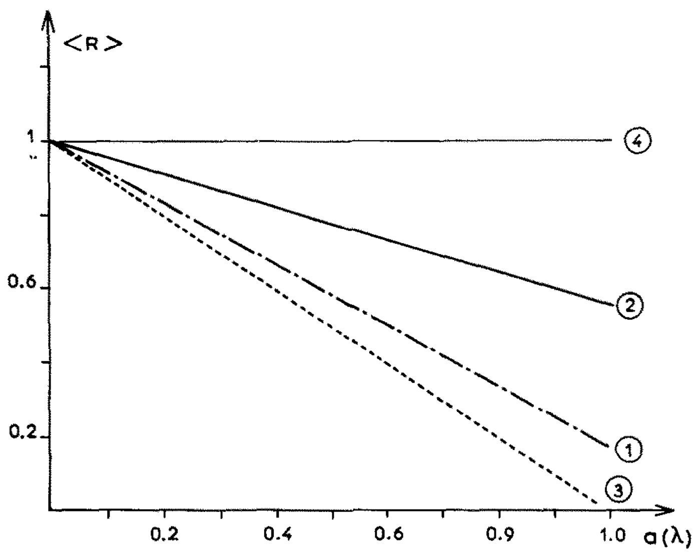

Fig. 3. Influence of $a(\lambda)$ on $\langle R \rangle$ for the following conditions: $\Phi = 1$, $\Delta\lambda = 30$ nm, $\lambda_1 = 600$ nm (cf. Fig. 1), $R_0(\lambda) = R_0$ and $R_\infty(\lambda) = R_\infty = R_0/100$: curve 1 for $\langle R_c \rangle$; curve 2 for $\langle R_f \rangle$; curve 3 for $\langle R_c \rangle$ with condition 1 of Fig. 1; curve 4 for $\langle R_c \rangle$ with condition 2 of Fig. 1.

where $F(\lambda)$ is the emission spectrum of the background. If we consider the eye sensitivity, the response is:

$$\langle R_1 \rangle = \Phi \,\text{Abs.}\, \frac{\int_0^\infty F(\lambda) S(\lambda)\, \mathrm{d}\lambda}{\int_0^\infty I(\lambda)\, \mathrm{d}\lambda}$$

and then C_f is:

$$C_f = \frac{\langle R_f \rangle_{\text{support}}}{\langle R \rangle_{\text{ink}}} = \frac{[\langle R_c \rangle + \langle R_1 \rangle]_{\text{support}}}{\langle R \rangle_{\text{ink}}}$$

The results presented in Figs 2 and 3 show that it is possible to find conditions where $\langle R_f \rangle$ is greater than $\langle \overline{R_c} \rangle$ and then $C_f > \overline{C_c} = \overline{C_f}$. However, it must be noted that C_f cannot be so large in comparison with C_0 and then, under our conditions, the maximal observed contrast would not be so high. Nevertheless, according to the results shown in Figs 2–4, it is possible to keep a satisfying contrast for an original, if one adds fluorescent compounds to its background.

2.4 With a coloured ink

Until now, we have only considered the case of a background for which the ink response was almost constant with varying wavelength and consequently we have only taken into account the response of the background, luminescent or not.

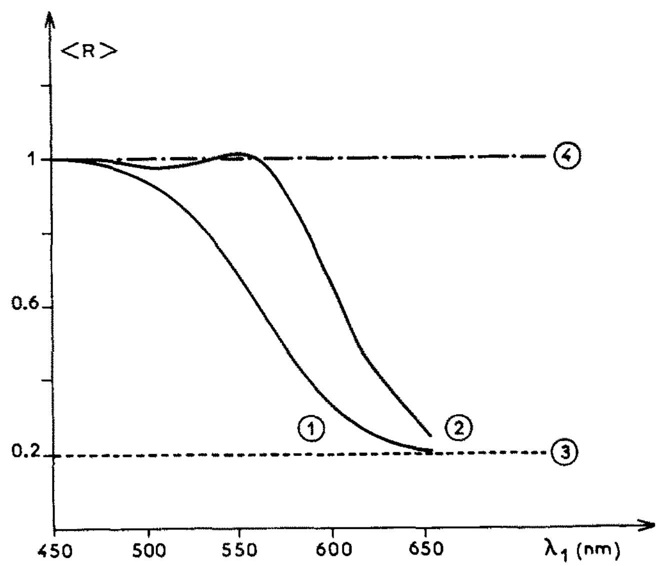

Fig. 4. Variations of the responses $\langle R_c \rangle$ (curve 1) and $\langle R_f \rangle$ (curve 2) with λ_1. The conditions are: $\Phi = 1$, $\Delta\lambda = 30$ nm, $a = 0{\cdot}8$, $R_0(\lambda) = R_0$ and $R_\infty(\lambda) = R_\infty = R_0/100$. The straight lines 3 and 4 correspond for $\langle R \rangle$ under the conditions $\lambda' < \lambda_1$ and $\lambda' > \lambda_1$ respectively.

It is possible to consider the use of coloured inks with a response which is variable with the wavelength. If we make the following assumptions for the absorption of the ink:

$$\text{for } \lambda \leq \lambda_2 \quad a_{\text{ink}} = \text{constant}$$
$$\text{for } \lambda > \lambda_2 \quad a_{\text{ink}} = 0$$

with preferentially $\lambda_2 \geq \lambda_1$, then the variations of C_0, C_f and C_c with the different parameters of the system can be calculated.

Evidently, the C_c and C_f values are lower, compared with the values for a black ink. However, if λ' is greater than both λ_1 and λ_2, the background and the ink will appear 'white' to the copier, which will lead to a complete loss of the contrast. Several patents are based on this principle.

In the experimental section, we have tested this principle. As expected, it leads to satisfactory results with respect to the difficulty of copy, but the use of the technique is limited because of the relative difficulty of reading.

3 EXPERIMENTAL

The object of the work was to verify the difficulty of copying a text, whilst keeping a satisfactory contrast. We used commercial fluorescent paper and did not consider the chemical nature of the luminescent coating. Typical commercial luminescent papers used were red (1), orange–red (2), orange (3), yellow–green (4), green (5) and white (6) [from Macline].

Emission and excitation spectra were recorded with an ISA Jobin–Yvon JY3 spectrofluorimeter (see Figs 5–10).

Photocopy tests with these supports were run, using two types of ink writing; black ink (A) and non-fluorescent coloured ink, similar to the support colour (B). Results are summarized in Table 1. The copier used was

TABLE 1
Photocopy Tests

Fluorescent paper	*Black ink A*	*Coloured ink B*
1 Red	Unreadable	Unreadable (original with not enough contrast)
2 Orange–red	Unreadable	
3 Orange	Readable	
4 Yellow–green	Readable	
5 Green	Readable	
6 White	Readable	Unreadable (improved contrast; with ultraviolet irradiation, acceptable contrast)

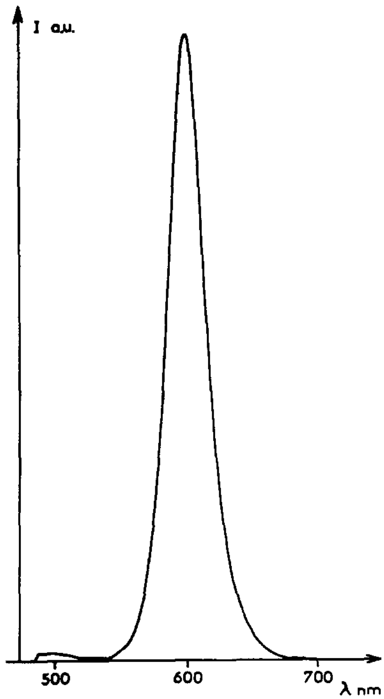

Fig. 5a. Fluorescence spectrum of red compound 1; excitation at 450 nm; maximum at 600 nm.

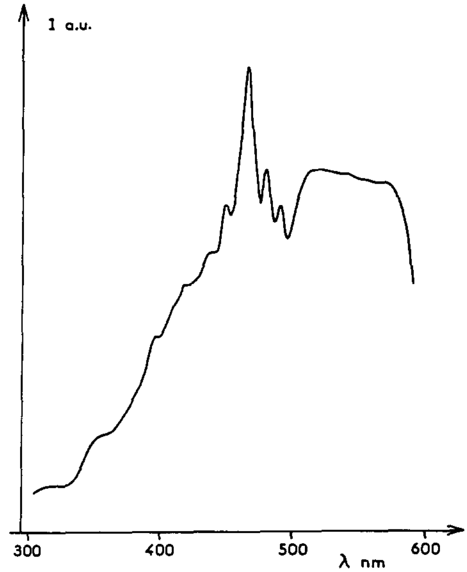

Fig. 5b. Excitation spectrum of red compound 1; analysis at 600 nm; maximum at 466 nm.

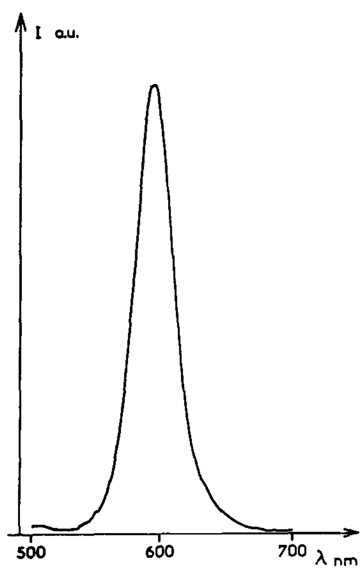

Fig. 6a. Fluorescence spectrum of orange–red compound 2; excitation at 450 nm; maximum at 600 nm.

Fig. 6b. Excitation spectrum of orange–red compound 2; analysis at 600 nm; maximum at 466 nm.

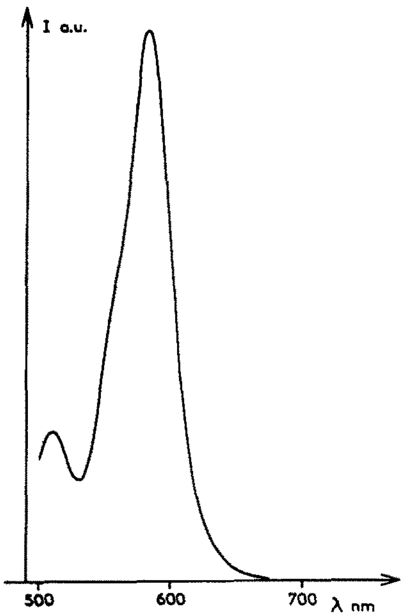

Fig. 7a. Fluorescence spectrum of orange compound 3; excitation at 450 nm; maximum at 585 nm.

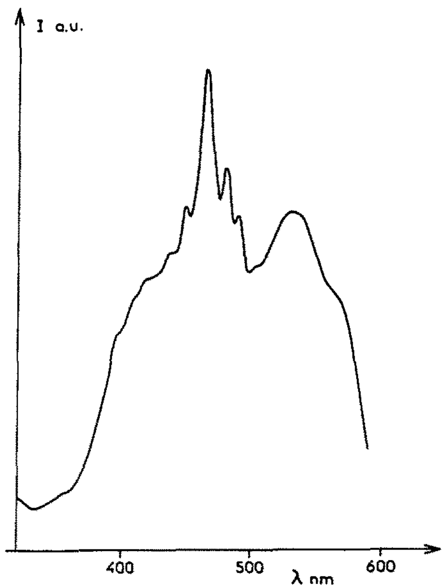

Fig. 7b. Excitation spectrum of orange compound 3; analysis at 600 nm; maximum at 468 nm.

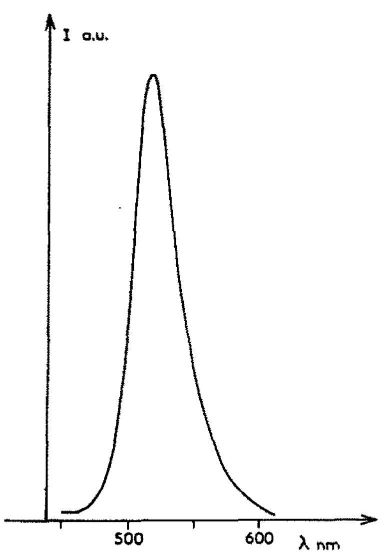

Fig. 8a. Fluorescence spectrum of yellow-green compound 4; excitation at 400 nm; maximum at 515 nm.

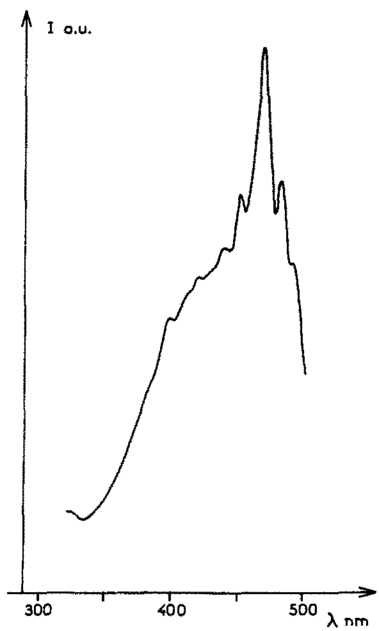

Fig. 8b. Excitation spectrum of yellow-green compound 4; analysis at 515 nm; maximum at 469 nm.

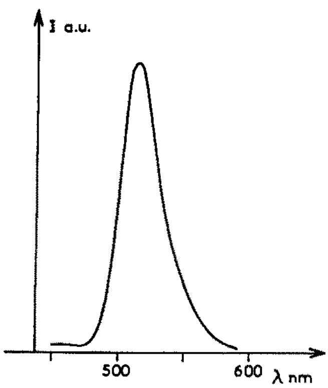

Fig. 9a. Fluorescence spectrum of green compound 5; excitation at 400 nm; maximum at 515 nm.

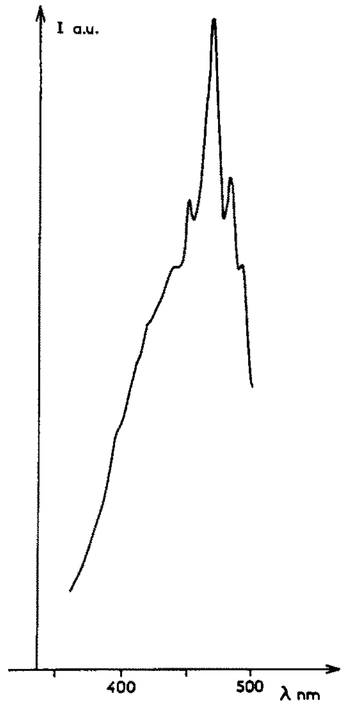

Fig. 9b. Excitation spectrum of green compound 5: analysis at 515 nm; maximum at 466 nm.

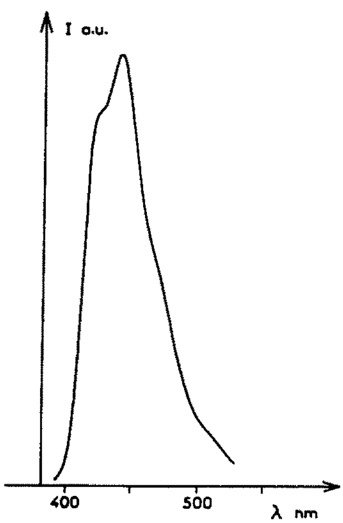

Fig. 10a. Fluorescence spectrum of white compound 6; excitation at 370 nm; maximum at 440 nm.

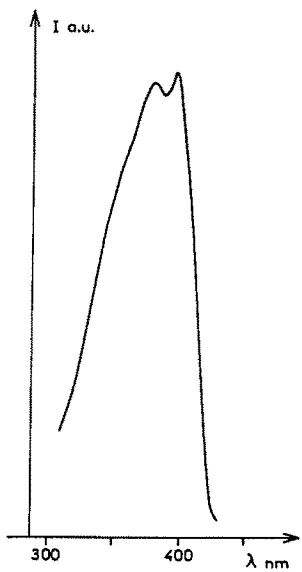

Fig. 10b. Excitation spectrum of white compound 6; analysis at 440 nm; maxima at 380 and 396 nm.

an OCE 1630 with selenium-dye photoconductor and halogen lamp light source.

In a further experiment, we used a non-emissive white ink on a white paper, with an ultraviolet light source. Almost all the commercial papers contain optical brighteners which induce a blue fluorescence. Some positive results were obtained, but, they were not developed and the main focus of our studies was on daylight experiments.

4 CONCLUSION

In order to reduce the copy quality, a concept based on the use of coloured products has been developed, and in particular the use of red products. With these conditions, for non-luminescent backgrounds, the contrast of the original document is itself of poor quality. However, by the use of fluorescent backgrounds, the contrast of the original is satisfactory, but the quality of the copy is not.

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