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Some Spectral Observations of Infrared Luminescence

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ABSTRACT: The fluorescence spectra of several components having fluorescence in the vis-near infrared (IR) region were obtained. Several of these components were obtained from IR luminescent inks. The spectral features (excitation and emission spectra and their intensities) explain the observed emission when these components are analyzed with an IR luminescence apparatus (excitation with blue green light/emission detected with IR sensitive television (TV) tube) or a laser induced fluorescence system (514.5-nm excitation with argon ion laser/emission detected with laser light absorbing goggles or with IR sensitive TV tube). The emissions from these methods are part of the same fluorescence emission peak. The emission response for each of the methods is dependent on the division of this peak between the vis and near IR region and its intensity in these regions. The intensity is dependent on the excitation source.

KEYWORDS: forensic science, luminescence, lasers, infrared luminescence, visible fluorescence, spectrofluorimetry, inks, chlorophyll, no carbon required (NCR) paper

What is normally called *infrared luminescence* by the forensic science community is simply a fluorescence emission in the near infrared (700 to 2000 nm) when the excitation light is any light of lower wavelength than the beginning of the near infrared (IR), that is, 700 nm. Sometimes the near infrared is extended to include some visible red (for example, 650 to 700 nm). In such cases, the excitation light must not extend beyond 650 nm.

Conventionally, the excitation source is the broadband blue-green light produced by filtering incandescent light with a Corning 9780 filter (permits 350- to 650-nm light). The emission is traditionally observed using infrared sensitive film in a camera having an IR-barrier filter that allows only IR light into the film or, as more recently done [*1*], using a television camera having a tube sensitive in the IR and having an IR-barrier filter (Fig. 1).

Recently, the three basic lasers used in fingerprint work (argon ion, copper ion, and frequency-doubled neodymium:yttrium aluminum garnet [Nd:YAG]) are being explored as narrow-band excitation sources. The emitted florescence in this case can be observed visibly by using the laser goggles (which filter the lasing wavelength) or in the near infrared using the photographic camera or the television camera mentioned above (Fig. 2) [*2-7*].

This work will show that the visible emission resulting from laser excitation and the near-infrared emission resulting from laser excitation or blue-green (Corning 9780 filter) excitation (Fig. 3) are part of the same fluorescence emission. Also, the reasons why some excitation sources are better than others will be explained in terms of the absorption (excitation) spectrum of the specimen being studied. Tappolet [*4*] considered similar investigations.

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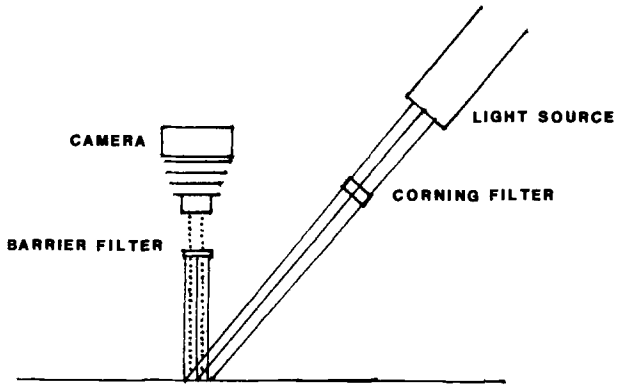

FIG. 1—*Excitation with blue-green light (broadband) light produced by filtering incandescent light with a Corning 9780 filter. The camera for observing emission can be a photographic camera with IR film or a TV camera with an IR sensitive tube. The barrier filter is a Kodak 89B Wratten filter.*

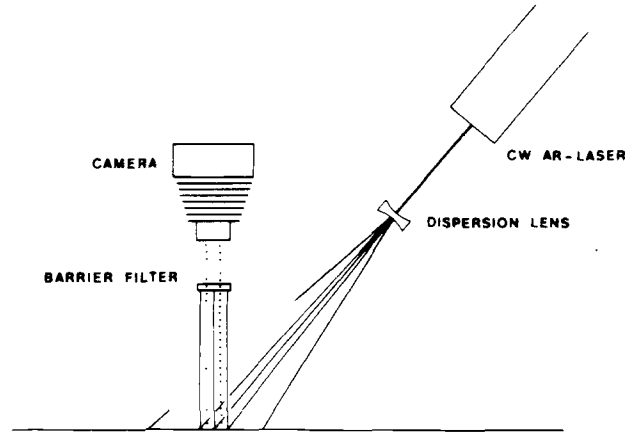

FIG. 2—*Excitation with 514.5-nm argon ion laser line. The camera can be a photographic camera with regular color film (or IR film) or a TV camera with an IR sensitive tube. The barrier filter is the Fisher 11-409-50A filter. The camera can be replaced with eye goggles having the Fisher filter. Figure is from Dalrymple, et al.* [2].

Before proceeding, we outline some basic principles of fluorescence. In any fluorescence phenomenon, two characteristics dominate the observed emission behavior:

The spectra: These spectra consists of two components:

(a) the emission spectrum obtained by exciting at the optimum excitation wavelength and
(b) the excitation spectrum obtained by observing the emission at the optimum emission wavelength.

The intensity of the spectra: The excitation and emission spectra have the same maximum intensity. This is dependent on:

(a) the intensity of the excitation source and
(b) the quantum efficiency of the fluorescence process.

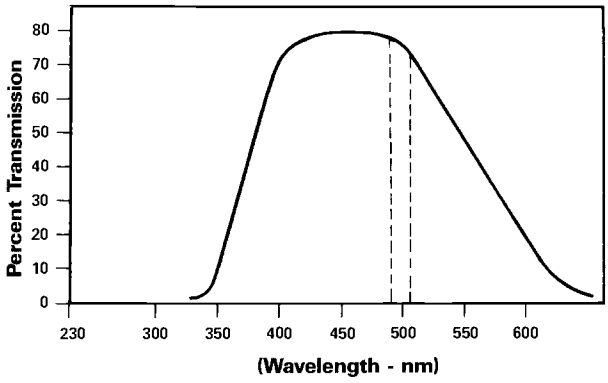

FIG. 3—*The broadband light permitted by the Corning 9780 filter* (solid line) *compared with the two major narrow band lines of the argon ion laser (488 and 514.5 nm)* (dotted lines).

The spectra dictate where optimum emission and excitation exists, and the maximum intensity determines how much of the overall emission can be observed.

In this work, comparative examination of several near-IR luminescent components used in ballpoint inks were performed. Chlorophyll from a single leaf was examined since it is highly fluorescent (high quantum efficiency) in the near infrared.

Also, the leuco dye in "no carbon required" (NCR) paper was examined because of its high fluorescence. This fluorescence is observed when NCR paper with a (leuco dye) coated back is placed over regular (for example, bond) paper and one writes on the front of the NCR paper. The leuco dye transfers onto the regular paper; it is invisible under ultraviolet (UV) and visible illumination, but is very luminescent in the near IR. Document examiners frequently encounter documents having writing only seen when seen in the near IR. Some disappearing inks exhibit similar behavior [*8,9*].

Experimental Procedure

Samples Examined

- Four ballpoint inks: Bic Black (U.S.-made), Bic Black (U.K.- and European-made), Bic Blue, and Skilcraft (U.S. Government) Black;
- NCR Paper (FBI FSRTG Service/Work Request form);
- Leaf from an African Violet pot plant.

Sample Preparation

Inks—Each of the inks was scribbled in a similar way on nonfluorescent paper. A single-hole punch disk (approximately 6 mm in diameter) was removed and placed in a 1-dram vial to which 30 μL methanol was added to extract the ink. With the extract a streak thin-layer chromatography (TLC) was prepared using E. Merck Silica Gel 60 plates. This was done for each ink in a similar way. The plate was developed in Solvent System I (ethyl acetate: ethanol : water = 70 : 35 : 30) until the solvent front moved about 10 cm from the line of application (Fig. 4).

The plate was then viewed using an IR luminescence system, and the most luminescent streak of the series of streaks for a given ink was noted (Fig. 5). The IR luminescence system used is the Richard's IR Camera System [*1*] with a Wratten 89B barrier filter for the emission and the Corning 9780 filter for the excitation. This most luminescent streak was then

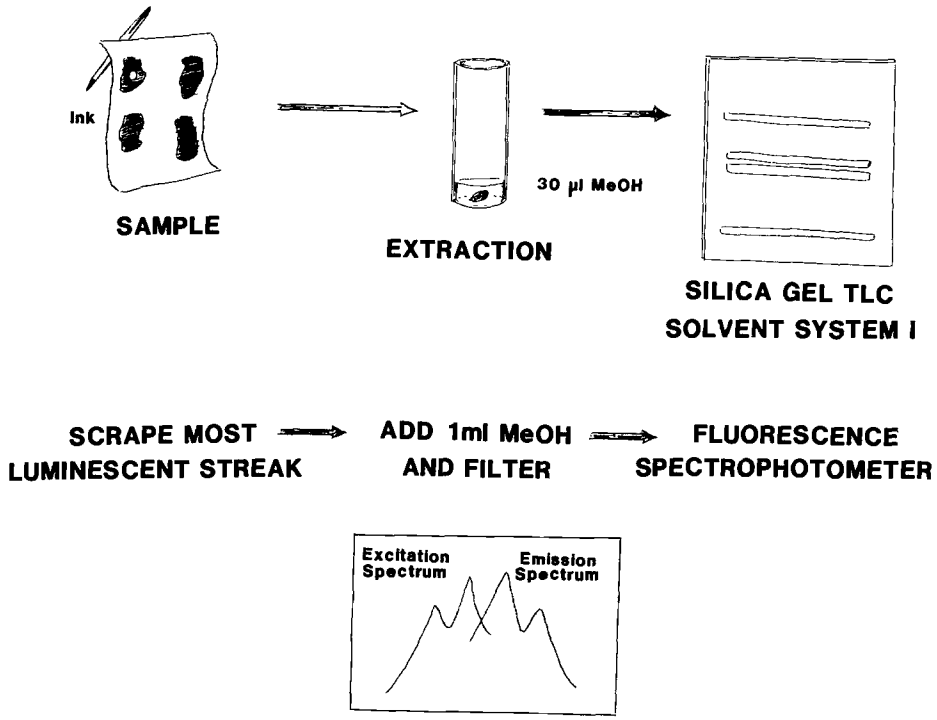

FIG. 4—*Schematic of method for selecting luminescent component in inks.*

scraped off, placed in a 1-dram vial to which 1 mL of methanol was added. The solution was filtered with a Millipore vacuum filter system to remove all suspended material. The resulting solution was then analyzed using a Perkin-Elmer (Hitachi) 650-40 fluorescence spectrophotometer.

Chlorophyll from Leaf—A hole punch from a single African violet leaf was cut into small pieces and placed in a 1-dram vial to which 1 mL of methanol was added. It was crushed using a glass stirring rod, and the solution was then filtered as described above for the inks. The fluorescence characteristics of the filtrate were then determined.

Leuco Dye in NCR Paper—The first sheet of a NCR stack is usually plain paper on the front side and coated paper on the back side where the coating contains a leuco dye. When this dye comes in strong contact with the coating on the front side of the next sheet, the leuco dye develops a color on this second coating. This second coating contains clay with sites of varied acid levels, which is what develops the dye. Also, the leuco dye is encapsulated so that the strong contact has to break the capsule in order for its content to enter the second coating [*10*].

A 1-cm^2 sample of the paper containing the leuco dye was used. This is treated as the leaf discussed above. The crushing with the glass stirring rod to release the leuco dye.

Instrumental Parameters

IR Luminescence System—The Richard's IR Camera System [*1*] was used with an 89B Wratten barrier filter for viewing the emission and a Corning 9780 filter for the excitation source. The heart of the system is the silicon-viticon IR-sensitive cathode ray tube (CRT) (sensitive up to about 1200 nm). For simplicity we shall call this the *broadband/TV system.*

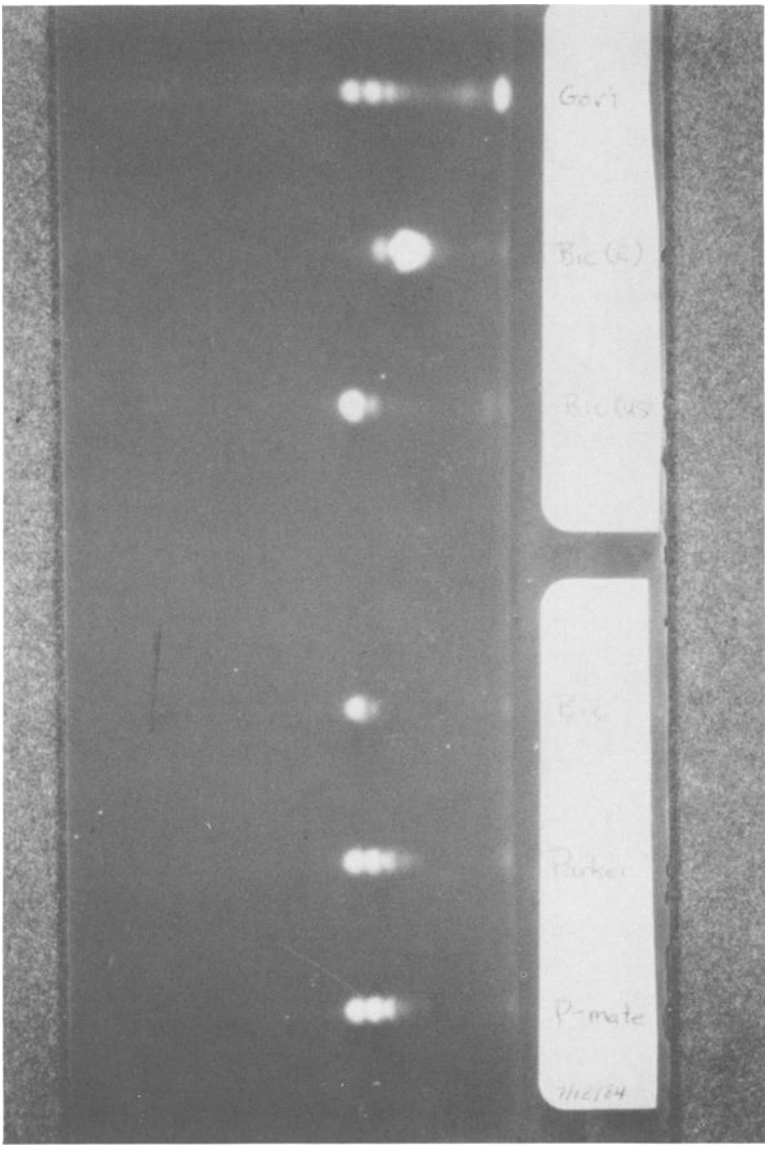

FIG. 5—*IR luminescence of TLC plate of three blue and three black ballpoint inks photographed using the broadband/camera system. From left to right these ballpoint inks are: blue Papermate, Parker, and Bic inks followed by Black U.S. Bic, European Bic, and Skilcraft (U.S. Government) inks.*

Laser Fluorescence System—The 514.5-nm line of the Spectra Physics Argon Ion laser was used as an excitation source at an operation power of 15 W. The goggles used contained Fisher 11-409-50A filters. We shall call this the *laser/goggle system.* When the laser is coupled with the TV component mentioned above to view in the near IR, this composite system shall be called the *laser/TV system.*

Fluorescence Spectrophotometer—The Perkin Elmer (Hitachi) 650-40 instrument was used with the same excitation and emission slit widths. It was operated at high gain, in the

ratio mode, and the spectra obtained is uncorrected (for the lamp spectral distribution and photomultiplier response). A glass filter was used by the excitation slit for visible excitation to avoid any second-order UV excitation peaks.

Results and Discussion

Figures 6 through 11 show the fluorescence spectra of the six samples examined. Four of these samples exhibit two fluorescence spectra, one in UV region and the other in the vis-near IR region. We shall only be concerned with the latter spectrum. The first (UV) spectrum is probably due to fluorescence emission from excitation to the second (higher energy) excited singlet state of the system.

The fluorescence spectra in Fig. 6 of the leaf extract is essentially that of chlorophyll. A leaf is extremely luminescent when using the IR luminescent system. However, when excited with the laser, the visible (bright red) fluorescence is poor; even the IR luminescence, when viewed with the IR camera, is poor. This is due to the laser illumination used: it has a very narrow band width and the wavelength is 514.5 nm. This wavelength is around the minimum absorption between the two principle absorptions of chlorophyll. Consequently, since little of the powerful laser light is absorbed, the fluorescence is low. The excitation source of the IR luminescent system is not as intense as the laser, but it is a broadband (350- to 650-nm light). When used in conjunction with the goggles (visible fluorescence) it shows some "red" fluorescence, but as noted, when used with the IR sensitive camera, it is highly intense.

Figures 7 through 10 are the fluorescence spectra of the four inks studied. Figure 7 of the Skilcraft black ink has the second strongest excitation peak at 525 nm, which is the laser frequency. Also, the maximum emission at 621 nm is well into the visible red range. This shows why the fluorescence emission is so strong when seen with the laser/goggle system. Also, the luminescence observed with the broadband/TV system (which led to selecting the most luminescent dye in this ink) is due to emission carried beyond 700 nm into the near IR. Note that this "carryover" appears to be small in Fig. 7; however, the degree of this carryover is governed by the overall intensity (recorder range). In this case a recorder range value of 261 gave "strong" luminescence in the near IR with either the broadband/TV or laser/TV system.

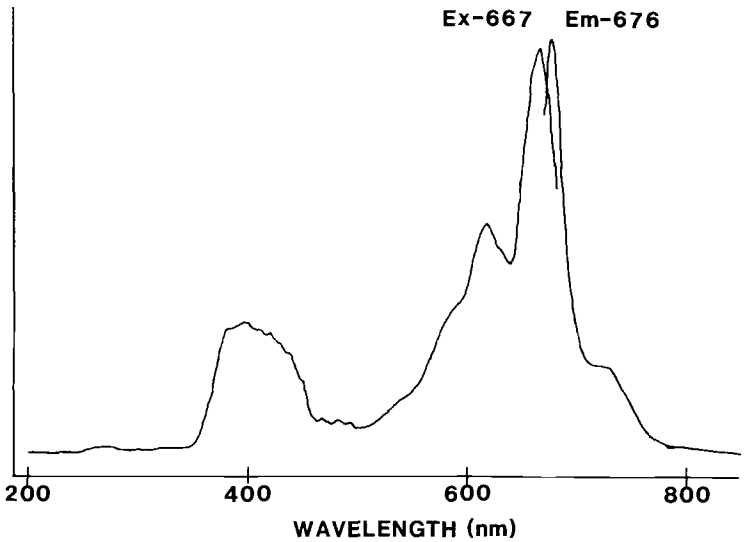

FIG. 6—*Excitation/emission spectra of green leaf (African violet).*

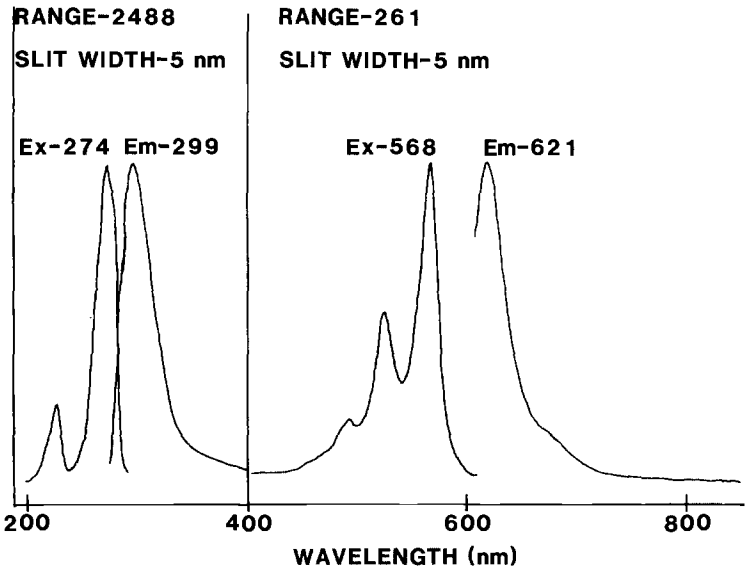

FIG. 7—*Excitation/emission spectra of the most luminescent component of the Skilcraft (U.S. Government) black ballpoint ink.*

The sample in Fig. 8 (U.S. Bic black) has similar features to those of Fig. 7. The emission should show up well with laser/goggle system and should also be seen with the wide band/TV system. Both of these predictions are observed. The Fig. 8 sample has a lower overall intensity (recorder range of 14.3) than that of Fig. 7; but the carryover into the near IR is much greater. That there are no masking components present [*11*] makes this ink one of the most IR luminescent inks.

Figure 9 displays the fluorescence spectra of the rhodamine dye used in the European and British made Bic black ballpoint ink. The fluorescence emission is observed with both the laser/goggle system and the broadband/TV or laser/TV system. From Fig. 9 it appears there is little carryover of the emission into the near IR and thus little to no emission observed with the broadband/TV or the laser/TV system. The reason for observing it strongly is the extremely large intensity (recorder range of 1549) it has. Note that the absorbance in the UV is the cause of the fluorescence one observed when irradiating with UV light. This absorbance, however, is small compared with that at 529 nm.

Figure 10 of the Blue Bic ink clearly shows why the fluorescence emission is mostly seen with the laser/TV or broadband/TV system. The emission is mostly in the near IR region, and there is some small carryover into the visible red range. This, along with the fact that the overall intensity (recorder range of 21) is small, shows why viewing with the laser/goggle system is poor.

The fluorescence of the NCR paper extract in Fig. 11 has the most narrow excitation and emission peaks observed. Laser induced fluorescence is small since there is little absorption of the laser light at 514.5 nm. Also, detection of this fluorescence is best done in the near IR since emission is at 715 nm and the carryover into the visible range is small. The fluorescence is thus best observed using the broadband/TV system. When a document containing writing done with NCR leuco dyes is analyzed with the laser/goggle system, a faint orange image emerges, while the broadband/TV system shows a strong luminescent image.

Another interesting observation about the NCR leuco dye is that there is absorption at 589 nm, and yet the compound is colorless. Normally absorption of visible light implies the

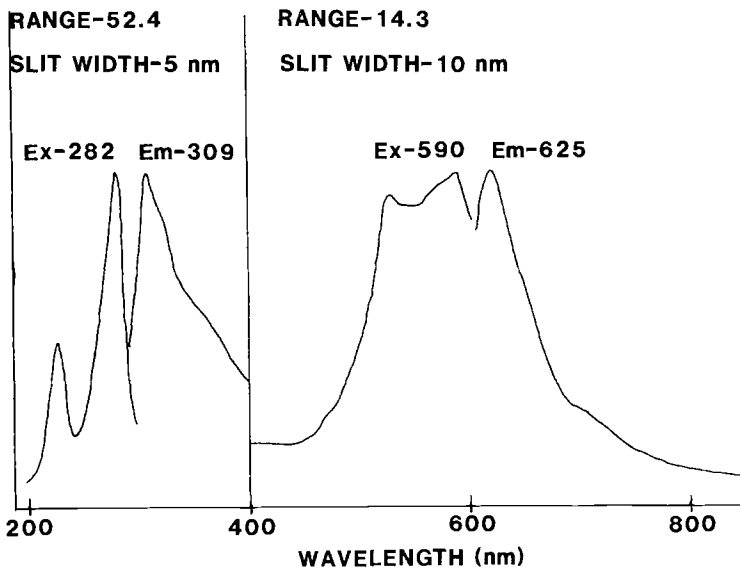

FIG. 8—*Excitation/emission spectra of the most luminescent component of the U.S. Bic black ballpoint ink.*

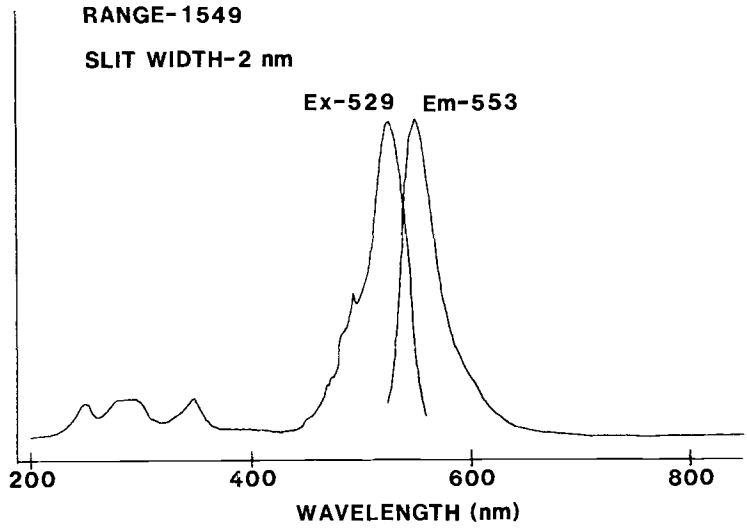

FIG. 9—*Excitation/emission spectra of the most luminescent component (rhodamine) of the European Bic black ballpoint ink.*

presence of color when the absorptivity coefficient is sufficiently high. For the NCR leuco dye, the coefficient must be extremely small since it is colorless. We should recall that a fluorescence excitation spectrum magnifies the amplitude of the corresponding absorption spectrum.

In each of these cases we studied the individual fluorescent compound. In the case of inks, they are often found in conjunction with "masking" components that hinder their fluorescence. These masking compounds can mask the excitation light (primary absorption) or the

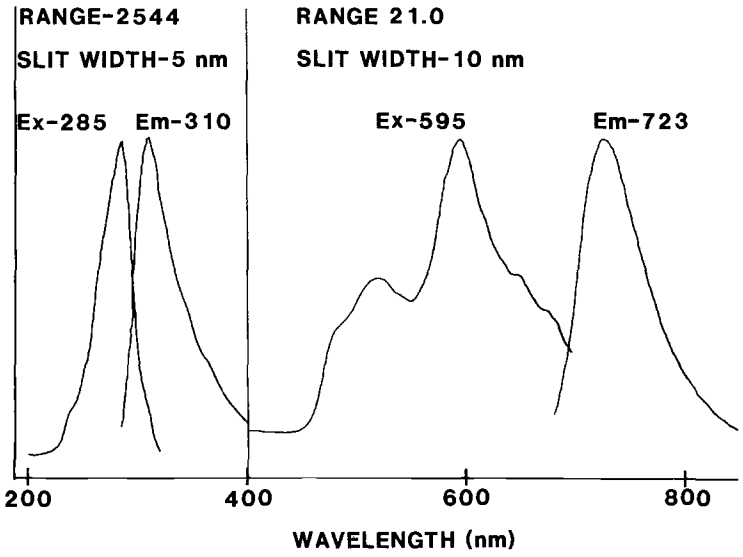

FIG. 10—*Excitation/emission spectra of the most luminescent component of the Bic blue ballpoint ink.*

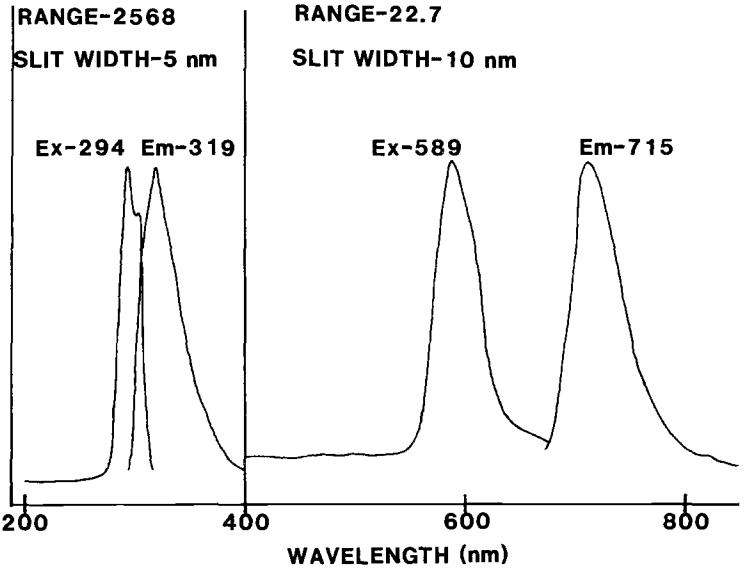

FIG. 11—*Excitation/emission spectra of the Leuco dye in NCR paper.*

emission light (secondary absorption). Sensi and Cantu [*11*] showed that inks which contain luminescent components, but do not luminesce in the IR as a result of the presence of masking compounds, sometimes become luminescent when the fluorescent compound is leached out from the masking compounds. In many cases it takes very little effort to effect this leaching; sometimes simply touching the ink line provides sufficient body fluids to cause the effect. For the blue "Eraser-Mate," Throckmorton [*12*] observed a natural increase in luminescence with age which, when tried to be erased, increased dramatically.

Degradation of the fluorescence has also been observed. The U.S. Bic black fluorescence on standard Government 3 by 5-in. (8- by 13-cm) pad paper disappears after one year. For other inks, Zimmerman and Mooney [7] observed the disappearance after several minutes. We also observed such fast disappearances with several Formulab 904 blue ballpoint inks. We do not know what causes this degradation when it occurs but speculate that, among other things, it could be caused by light (photodecomposition), oxygen (oxygen quenching), the acid in the paper, or chemicals in the air, or some combination of these.

Conclusion

The laser/goggle system has a very intense and narrow band excitation and observes only visible fluorescence. The broadband/TV system has a moderately intense and broadband excitation and observes vis-near IR or just near IR fluorescence depending on the IR cut-off filter used. The laser/TV system permits higher narrow band excitation intensity and, if the sample absorbs this light, it observes what the broadband/TV system observes but with higher intensity.

The excitation/emission spectra of a compound known to exhibit IR luminescence predicts how this compound will behave when observed with the difference viewing systems. This work shows that the different observations of the same compound are not independent but are part of the same fluorescence emission.

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