

August 2003

Measuring and Assessing UV Inks and Security Paper

It is said that at the time the first Spanish ships reached the South Pacific islands they made contact with societies where the concept of economical value attached to objects was totally unknown. Due probably to benign climatic conditions there was no scarcity of food and shelter and natives just shared resources as a general principle, an alien concept for the freshly arrived European adventurers. A cultural clash resulted as the natives started "sharing" whatever objects Europeans had brought; the place was known to later generations as "Islands of Thieves".

Most cultures have had some economical system based on some scarce object; Western and Eastern societies have for centuries utilized gold and silver as basis of their economic systems. Because of the difficulty of transport a metal in large quantities it was replaced first by certificates that evolved to checks and later to paper money; since most economies have abandoned the gold standard i.e. paper money is not longer equivalent to some amount of metal, the principle of scarceness is preserved by giving the State the total monopoly of emitting and printing money.



Fig. 1: Stamp used by the German Mail Office observed under natural light (left) and under UV light (right); while the paper background turns lightly violet due to the FWA present, the stamp turns to a vivid yellow as result of excited fluorescence. The UV content in natural light is not sufficiently high to excite the fluorescent pigment to detectable levels providing an easy way to prevent forgery.

There are many other objects in today's society that possess intrinsic value well above than the material it is made of, for example certificates of stock, diplomas from renowned Universities, ID cards, passports and passes to restricted areas, stamps, entrance tickets to notorious exhibitions or presentations, etc. Using modern electronic reproduction techniques

it is relatively easy to forge documents such that at first sight are not distinguishable from the original; for this reason there is an urgent need to add security features that authenticate the object (the newly emitted Euro exhibits about 7 different security features to prevent forgery of the currency).

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One of the oldest and easiest ways of authentication is the use of luminescent pigments that are excited by UV radiation producing colors in different shades that are characteristic of the object under examination; this is one of the most salient features to combat forgery of paper objects.

Production of UV fluorescent pigments is restricted and controlled, purchasing allowed only to registered users who must maintain a logbook on quantities and applications; this preserves the scarcity principle mentioned above.

The appearance of a color under proper excitation is an extremely easy and effective way to prevent forgery, since it

can be used by anyone without any intensive training; color excitation is done by a cheap UV lamp (today also by a miniaturized UV laser that can be attached to a keychain) available at any store.

The system relies however on an exact quality control mechanism during manufacturing of paper and printing; the levels of color emission must be constant enough in order not to introduce any doubt during assessment (see figure 1).

Since excitation of the pigment results from absorption of UV light, instruments must be able to produce variable amounts of UV intensity to determine and quantify fluorescence

Fluorescence and phosphorescence: “now you see it, now you don’t”

Luminescence is the general name for the emission of light that is the result of certain excitation at molecular level.

If the excitation is done with light the resulting luminescence is denoted as fluorescence or as phosphorescence depending on their nature (although generally used in these terms, there are also fluorescence and phosphorescence

originated from excitation by mechanical or thermal means, by ion bombardment, etc). The processes involved are visualized using the Jablonski diagram (see figure 2); electronic structure of molecules can be visualized as energy ladders representing the different energy levels attainable by a given electronic configuration.

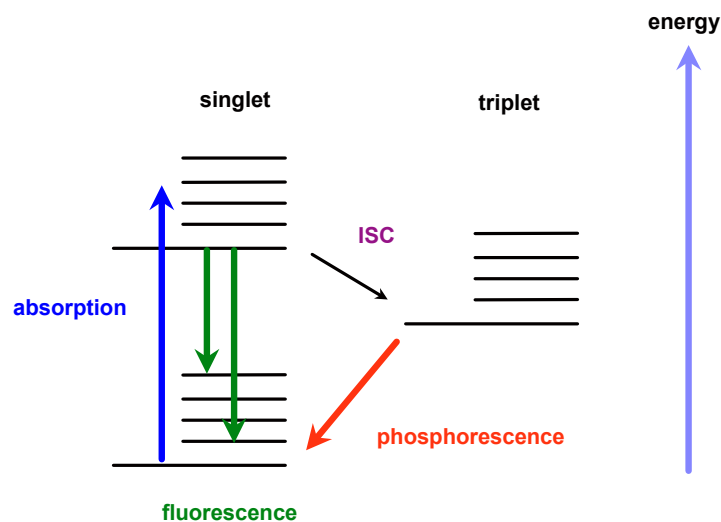


Fig. 2: The Jablonski diagram gives an overview of the processes leading to luminescence

For optical spectroscopy in the visible region it is important the existence of different electronic energy levels (denoted as long lines in figure 2), each contains a number of sub-levels corresponding to different vibrational, rotational and translational states. The left-hand ladder corresponds to singlet states (electron pair

is paired i.e. different spin directions) and the right-hand ladder corresponds to triplet states (both electrons have the same spin direction); both ladders continue further into high energies until the continuum is reached. Formally speaking, transitions between singlet and triplet states are “forbidden”; in the nature one prefers to

speak that they have a very low probability to occur, but this figure is finite and transitions are in fact observed.

With some exceptions all molecules are found to be at their ground singlet state and this level is assumed as starting point for any luminescence process. This starts by the absorption of a photon with enough energy to allow the transition of one of the electrons into one of the excited states (blue arrow process in figure 2); after whatever sub-level has been reached by the transition, the electron loses energy (as heat) to reach the lowest level of the corresponding excited state.

Three different processes are possible:

- the electron emit the excess energy as heat and falls down into the ground state, this is called “radiationless transition”
- the electron emits a photon corresponding to the energy difference from the excited state and one of the sub-levels of the ground state; this is called fluorescence and its energy will always be smaller than the absorbed photon i.e. fluorescence

Luminescence mechanism used in “UV inks”

Looking at the Jablonski diagram it is evident that fluorescence lies quite close to the absorption peak, only the phosphorescence can lie far apart from the absorption maximum (the wavelength difference between absorption and emission maxima is known as Stokes shift). This poses a problem when selecting fluorescent pigments for security applications, since it is desired that the pigment shows no color under “normal” illumination conditions i.e. daylight but shows a strong and luminous color under UV irradiation; this property is particularly important in those cases where the luminous pigment is printed forming some pattern that is visible only under UV light (one speaks normally about “invisible ink”). On the other hand long lifetimes for the emission i.e. phosphorescence are also not desired because the security pattern or color will persist for some time after examination, this is not a desirable property.

will always appear at higher wavelengths. The lifetime of fluorescence is of the order of femto- to microseconds

- the electron changes its spin in a process called “intersystem crossing” (ISC) and ends up in a triplet state; triplet states are quite stable and show slow decay, eventually a photon is emitted in the range of milliseconds to hours scale; the observed light is called phosphorescence and it appears at lower energies than fluorescence

There is no easy way to distinguish fast phosphorescence from fluorescence by just observing the emitted light, but only by conducting careful measurements.

Both phenomena are applied as security feature using pigments that absorb in the UV region and emit in the visible; while color of the observed emission depends on the nature of the pigment, its intensity is directly proportional to its concentration on the surface.

To produce the whole palette of colors by just excitation in the UV region other mechanism must be applied than rather a pure UV fluorescence process; this may introduce however serious problems to the instrumental determination since the luminescence mechanism must be taken into account.

Since increasing the Stokes shift is possible only within a reduced scale, the absorbed energy is normally used to excite different electronic states either within the molecule, transfer excitation to a different molecule (energy hopping) or formation of excited state complexes with a different electronic structure.

- homogeneous excitation: not all electronic states can be reached by absorption of light; selection rules (mostly based on symmetry arguments) dictate the transition probabilities, that can be very low (one speaks of “forbidden” transitions, see phosphorescence above). Such an electronic level

can be reached however through absorption to a higher lying state and radiationless transition to the lower excited state that then fluoresces (see figure 3, left picture). The “forbidden” transition is then “bypassed” and one achieves a large difference between absorption (UV region) and fluorescence (well in the visible region).

- energy hoping mechanism: the process is similar as the one just described, the energy absorbed is however transferred to a different molecule that becomes excited and emits light
- three-level mechanism: energy is absorbed to a first excited state, that populates the corresponding

triplet through ISC; now the excited triplet state absorbs light and fluoresces from the further excited triplet state. The fluorescence is active as long as the triplet state remains populated (see figure 3, right picture).

- excited-state complexes: some compounds can form complexes in the excited-state with unexcited (auto-complex) or other molecules, forming a totally new species with their own characteristics; some of these excited-state complexes show fluorescence located far from the original absorption wavelength. Fluorescence persists as long as the excited-state complex exists

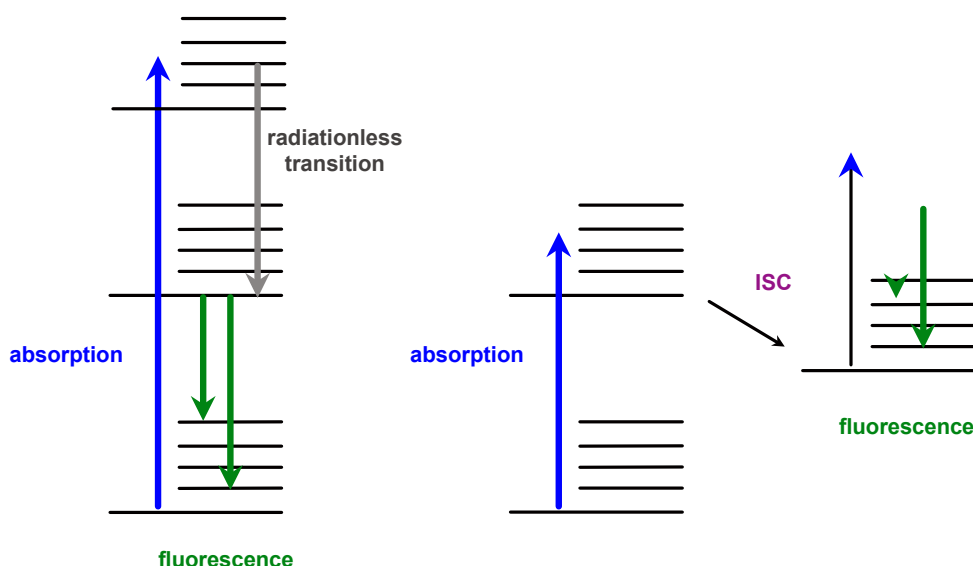


Fig 3. Different mechanism for fluorescence excitation: indirect excitation through a higher excited state (left) and fluorescence from a populated triplet state (3-level system, right)

Most of the materials used in UV luminescence are pigments, dyes are rare because the rigid crystal structure favors channeling the energy to radiative

Measuring UV fluorescence

Contrary as with colored materials, the measurement of luminescent colors demands special instrumentation because of the general rule “fluorescent colors can be measured only with a light source with

processes resulting in good efficiencies; by their nature dyes have normally flexible structures that tend to lose much of the energy invested in the excited state.

similar spectral distribution as the illuminant used for visual assessment”. The usual technique is to use a two-monochromator instrument that consists of two parts:

- first monochromator is used to illuminate the sample with monochromatic light; after the first monochromator is set to a given wavelength, light coming from the sample consists of the reflectance at the given wavelength and (if applies) the excited luminescence
- second monochromator scans the wavelength range while the first monochromator remains at the exciting wavelength

The process is repeated for each exciting wavelength of the first monochromator resulting in a two-dimensional excitation-emission matrix (also known as Donaldson matrix) that contains the full information of the process and can be used to calculate spectral profiles for different illuminants.

The technique can be used with all those materials where luminescence is produced by absorption at one wavelength only, systems that show three-level mechanism or luminescence from excited-state complexes cannot be measured using this

An example

Following are the results of measuring a UV luminescent postal stamp as used by the German Mail Office (see figure 1).

The sample shows a strong yellow luminescence when illuminated with a UV lamp (black light).

technique because the excitation wavelength is used only to create the luminescent species that must be excited by a second wavelength to produce emission.

Since the emission has its origin in the UV region, UV luminescent samples can be measured using the “Polaris White Star” system (produced by Axiphos GmbH, Germany for assessment of optically brightened fluorescent white samples). The measurement principle is based on illumination of the sample with two different UV spectral profiles that excite the luminescent compounds to different extents. Since the illumination remains polychromatic the system has the advantage to be able to measure those samples that show luminescence from a transient state.

Furthermore since it needs the operation of just two flashlights the measurement takes only seconds, contrary to minutes to hours needed by two-monochromator instruments.

Colorimetric results are shown in the table as (L*,a*,b*) without UV and for levels corresponding to daylight conditions. The shift to yellow color is evident (b* goes from negative to positive values) as well as that the material is luminescent (fair increase in L*).

Color coordinates of luminescent sample

	without UV	D ₆₅
L*	76.62	78.32
a*	1.2089	-0.6061
b*	-0.4606	1.1626

Figure 4. Reflectance values under different UV filters

Color values without UV give information about the perceived color of the substrate under low UV level; in the present case the total color difference induced by the UV luminescence is $\Delta E = 2.97$, taking into consideration the high L* value and the yellow shade, it is hardly perceived as

colored under daylight conditions. This is a very important result because the Quality Assurance System for the product demands that the luminescence does not interfere with the substrate color under normal daylight conditions. “Polaris White Star” is calibrated to give color coordinates

under UV levels corresponding to D_{65} (among other illuminants). Spectral values are shown in figure 5, where also the profile and relative amount of fluorescence is appreciated. The reflectance spectrum shows the beginning of the absorption of the pigment and some shading agent (absorption around 560 nm)

to improve the whiteness of the substrate (compensation of the long tail absorption of the luminescent pigment). The luminescence spectrum is relatively low (compared to fluorescence levels from fluorescent whitening agents) but is well above the noise of the detector and can be consistently determined.

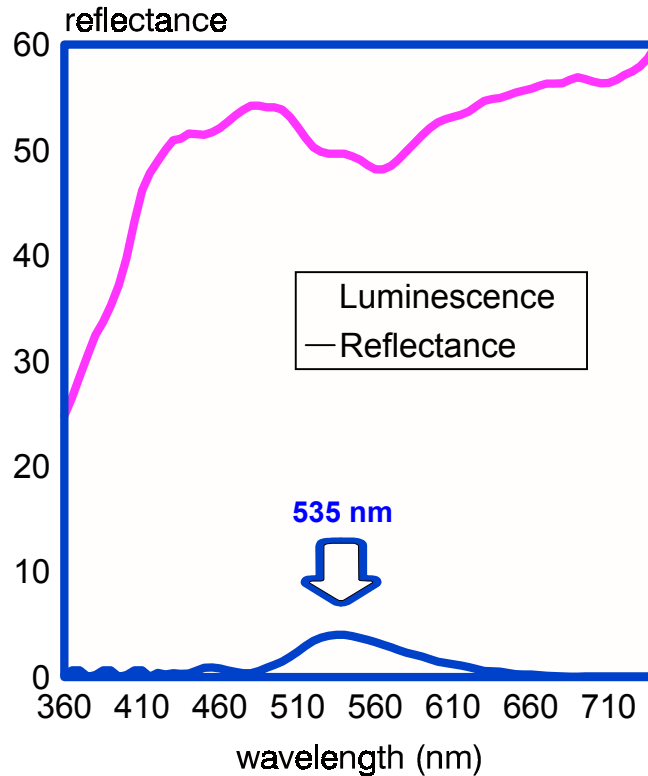


Figure 5. Reflectance and luminescence spectra of the stamp sample (see figure 1). Notice the presence of shading agent (absorption at 560 nm of the reflectance curve) and the low level luminescence (peaking at 535 nm) from the UV pigment.

The level of luminescence shown corresponds to a level of UV comparable to that encountered in daylight conditions and gives good information about the perceived color of the material; data can

effectively been used to establish dosage of the luminescent pigment and to build a consistent quality assurance system for manufacturing..

Other applications

While the need of fluorescent pigments as a security feature is certainly an spectacular area of applications, there are many other fields where luminescent pigments are applied mainly with the purpose of control. Some examples are listed:

- Luminescent labels: packaging of medicaments in pharmaceutical area poses high demands on reliability of the packing line; the

use of luminescent labels allows a premature detection of false packaging that could have disastrous consequences.

- Positioning: equipment for filling bottles, cups or buckets require certain given position of the object before the process sets on; this is normally achieved by marking certain positions of the object with "invisible inks" to achieve correct positioning before filling. An

interesting application is the positioning of letters prior to the address reading machine; the letter is turned so many times needed to orient it with the stamp at the right upper corner, for this the fluorescence of the stamp is used as orientation.

- Fluorescent marking: this a versatile area containing a large number of applications, for example invisible inks are used to

control the electrical knife in the textile industry to cut along a given pattern; fluorescent “penetrating” light oils are applied to welded joints to proof for non-porosity; “fluorescent water” is used to follow water lines or detect sewage losses; fluorescent materials are added to some oils and greases to detect improper disposal; the list is long and gets longer as new applications are discovered.

Conclusions

The software package “Polaris White Star” measures using lamps with variable UV content that allows the determination of fluorescence originated from absorption of UV light.

While the prime application is the determination of fluorescent whitening agents (FWA), fluorescent inks can be effectively be determined by the system. Although fluorescence levels are much lower than with the former compounds, the

sensitivity of the instrument allows a reliable determination of fluorescence levels and a quantification of the material present.

Since the measurement takes only seconds to perform, “Polaris White Star” is definitely an excellent tool for quality control during manufacturing of objects using “invisible inks” and other UV luminescent materials.