Extended Paper

Non-diffractive optically variable security devices

Rudolf L. van Renesse

TNO Institute of Applied Physics
P.O.Box 155, 2600 AD, Delft, The Netherlands

ABSTRACT

At the past optical security conferences attention was focused on diffractive structures -e.g. holograms, embossed gratings and thin-film devices- as security elements on valuable documents. The main reasons for this emphasis are, that the iridescent effect of such diffractive optically variable devices (OVD's) can be easily observed by the naked eye and that their fraud-resistance is considered excellent. No attention has been paid to non-diffractive optically variable phenomena like reversible photosensitivity, e.g. luminescence and photochroism. These may be employed in non-diffractive OVD's which may be readily authenticated and may provide excellent fraud-resistance as well. In order to survey the enormous variety of document security features the library SECURIDAT was compiled from a number of public domain databases. This paper discusses a few security applications of reversible photosensitivity that resulted from a search in SECURIDAT, viz. dual fluorescence with longwave remanence, thermochroism, stimulation of mixed inorganic phosphors and photochroism.

1. INTRODUCTION

An overwhelming number of optical security features for documents of value, e.g. passports, identity cards, credit cards, cheques, banknotes, has been applied in the course of time. Intaglio printing -on itself optically detectable as a relief structure$^{1)}$ - under certain conditions reveals hidden images when obliquely viewed.$^{2)}$ The printed image may be further spatially organized so that moiré and other effects are likely to arise on a copy as a result of interference with the scanning grid of copying-machines$^{3)}$. A watermark is included in most respectable banknotes, or various types of security thread, partly or wholly embedded in the paper structure. Security threads may furthermore be provided with micro-print (beyond the resolution of copying-machines), or with fluorescent substances or they may have a metal-glossy or lustrous appearance$^{4)}$. The base of valuable documents mostly consists of non-fluorescent paper frequently supplied with fluorescent print, fibres or planchettes. The presence of optical effects like fluorescence, metal-gloss or lustre can be readily verified. Although (non-)fluorescence is not considered a first-line protection, simple uv-sources are frequently applied in retail stores and at counters and are also available as handy pocket-devices. Documents of value may be further protected by lamination with transparent plastic foils. Such foils on their turn may contain embossed, fluorescent or retro-reflective markings.

This concise enumeration, by no means being limitative, concerns security features having in common that they are not of a diffractive nature but cannot be copied on current copying-machines. In view of the enormous variety in optical security features it seems surprising that in the past years attention has been almost exclusively focused on diffractive structures as security elements, e.g. holograms, kinegrams, embossed gratings and thin-film devices[5,6,7]. Because of their iridescent appearance such devices are generally called optically variable devices (OVD's). The main reasons for this focus on diffractive OVD's are, that their iridescence can be easily observed by the naked eye and that their fraud-resistance is considered excellent. However, it has been argued on an earlier occasion[1] that some non-diffractive optical security elements, e.g. intaglio and watermark, which we called optically invariable devices (OID's), actually show the same favorable properties. Upon further consideration, reversible photosensitive phenomena, viz. luminescence and photochroism, may be considered optically variable phenomena as well, although not of a diffractive nature. And, being copy-resistant, such phenomena are therefore also interesting from a security point of view. In this paper attention will be focused on optically variable phenomena like luminescence and photochroism which may be employed in non-diffractive OVD's.

2. SECURIDAT - A DATABASE ON DOCUMENT SECURITY

In order to get a survey of the apparently very extensive field of document security, the contents of a number of public domain databases were searched on this subject: Derwent (patents), Paperchem (patents and journals), Rapra (patents and journals), Inspec (journals) and Datastar (journals). As may be expected, the journal literature on this topic is limited and rather general. Most of the more specific information is found in the patent literature. The main search-strategy consisted of a number of sets comprising coherent entries, all starting in 1980:

set1 Optical phenomena
entries: holography, interference, luminescence, etc.
set2 Security
entries: security-device, authentication, counterfeiting, etc.
set3 Documents
entries: passport, banknote, credit-card, etc.
set4 Copy-resistance
entries: copy-protection, copy-resistance, etc.

As some of these sets expectedly contain an insurmountable number of records, mostly with a too low percentage of relevance, the search was narrowed by creating the following sets which were all completely downloaded:

set5 set1 and set2
set6 set1 and set3 not set5
set7 set2 and set3 not (set5 or set6)
set8 set3 and set4 not (set5 or set6 or set7)

The result is compiled in the library SECURIDAT, comprising nearly one thousand relevant records containing titles, sources and abstracts on the subject of document security. Periodically the library is updated applying the above search-strategy.

To the purpose of gaining more insight in possible security applications of reversible photosensitivity for non-diffractive OVD's, SECURIDAT was searched with entries like luminescence, fluorescence, phosphorescence, photochroism, etc. This research resulted in about 90 relevant records on the topic. A study of these records resulted in the further selection of a number of patents for scrutiny. It is the purpose of this paper to report on a few rather exotic security applications of luminescence and photochroism disclosed in these patents.

3. LUMINESCENCE

Luminescence is a collective noun for the emission of light by substances that are relatively cool ('cold light'). It comprises phenomena like the aurora borealis, fluorescence, phosphorescence ('afterglow'), chemo- and bioluminescence (firefly, glowworm). The practical value of luminescence is, that energy, e.g. invisible radiation like ultraviolet can be converted into visible light or infra-red.

Fluorescent inks, fibres and planchettes based on organic fluorescent substances are very frequently used to create security elements on documents. Such elements are invisible in white light but emit visible light (or infra-red) on excitation with ultraviolet or other actinic radiation or -when mixed with absorbing inks- change color on actinic irradiation. Fluorescent emission of organic molecules is generally comprises a broad waveband and ceases immediately (within about 10^{-8}s) once the excitation is interrupted. A general drawback of these organic compounds is that they can be easily commercially obtained or may be synthesized using common optical brighteners and therefore do not create significant problems to counterfeiters. A method to overcome this drawback is to apply luminescent materials that have a proprietary composition and require high technology for their production. On the other hand the expense of such rare compositions may prohibit their application.

3.1. Dual fluorescence with longwave remanence by TICT

An interesting invention of Arjomari-Prioux[8)] is the application in security papers of a family of tertiary amine derivates of benzene, naphthalene, anthracene and other polycyclic substances, e.g. para N,N-dimethyl amino benzonitrile (DMABN) and N,N-dimethyl amino-1 cyano-4 naphthalene (DMACN). Such amines, when embedded in certain solid matrices e.g. polyvinyl alcohol (PVA) or a polyamide, show an unusual double fluorescent emission, which is patented by CNRS[9)]. The longer waveband emission is remanent after the exciting illumination (ultraviolet) has ceased. The phenomenon is explained by a rotation of the aminogroup with respect to the aromatic ring, an excited state generally referred to as twisted intramolecular charge transfer (TICT).

TICT-fluorescence of such substances depends on the hydrogen bond forming capability of their polymer matrix. Figure 1a for instance shows the absorption spectrum and the emission spectrum of DMABN doped PVA. The absorption spectrum peaks around 300nm while the fluorescent emission (figure 1b) peaks around 370nm (ultraviolet) and 450nm (blue); the strong blue peak is remanent for several seconds. Figure 1c and d on the other hand show the absorption spectrum and the emission spectrum of DMABN doped polyvinylchloride (PVC). The absorption spectrum peaks around 300nm while the emission spectrum shows only normal single fluorescence around 370nm in a PVC matrix. Another example is DMACN doped PVA, given in figure 2. The emission spectrum -on irradiance between 360nm and 380nm- shows normal fluorescence around 425nm (blue) as well as TICT-fluorescence around 560nm (yellowgreen), remanent for several seconds. The remanent emission curve was separately obtained by means of a phosphoroscope. In general the shortwave emission peak of TICT-fluorescent benzene derivatives is in the ultraviolet while TICT-fluorescent derivatives of naphthalene or anthracene have both emission peaks in the visible spectrum[9)].

It has been shown possible to include TICT-fluorescent threads in the mass of security paper, to prepare a TICT-fluorescent printing ink or to uniformly render a security paper TICT-fluorescence[8]. The peculiar characteristics of TICT-fluorescence comprise a distinct fluorescence under ultraviolet radiation, a defined color change of the fluorescent emission after the ultraviolet radiation is interrupted and a specific decay of the remanent emission within seconds. Such phenomena should be easily verifiable by the general public having the disposal of simple ultraviolet sources and are suited for machine detection as well.

In its patent Arjomari states that the commercial availability of such doped polymers is restricted and that they are otherwise difficult to synthesize from commercial products. TICT-fluorescent security elements therefore would be expected to make counterfeiting extremely difficult. This may be true for a graphic artist but not for an organic chemist. It may be further noted that, although DMACN is not, DMABN is a regular commercial product and the production of DMABN doped polymers therefore may not be expected to create unsurmountable problems for the counterfeiter.

3.2. Thermochroism by TAET

A curious discovery is that of Petrel SARL, published in 1988[10], which comprises the security application of a thermotropic color change in the fluorescent emission of mixtures of certain lanthanide chelates preferably synthesized with beta-diketon type ligands, e.g. thenoyltrifluoroacetone, benzoylaceton. Separately such chelates e.g. of europium (Eu) and terbium (Tb) fluoresce red and green respectively, independent of temperature. A mixture of chelates of Tb and Eu however, yields a red fluorescence typical for Eu at room temperature while the green Tb fluorescence is completely absent. But, when cooled with liquid nitrogen (77°K) the red Eu fluorescence vanishes and the mixture only yields green Tb fluorescence.

The inventor explains this thermochroism as 'thermally assisted energy transfer' (TAET). The ultraviolet radiation (365nm) is absorbed by the ligand of the chelate, which energy is effectively transferred to the rare earth, thus activating its emission of fluorescent radiation. The energy levels of the rare earths, though not coincident, are near enough to each other to allow the transfer of energy via a cascade of energy levels from Tb to Eu at room temperature. With decreasing temperature however the transfer distance between the energy levels diminishes and the energy transfer is progressively blocked. This causes the excitation energy to be increasingly passed to Tb.

Further examples are:
A mixture of Eu and neodymium (Nd) chelates changes its fluorescence from red (Eu) to infrared (Nd) when cooled to 77°K. A mixture of lanthane (La) and Tb chelates does not fluoresce at room temperature but shows a strong green fluorescence at 77°K. Security fibers, threads and varnishes are prepared with such chelates to create security documents and papers. Another possibility mentioned is the preparation of a printing varnish made of thermochromic chelate mixtures (e.g. of Gd, Eu and Tb) as well as a non-thermochromic varnish solely containing e.g. a Eu chelate. Patterns printed alternately with both varnishes show a uniform red fluorescence at room temperature but, at liquid nitrogen temperature, show the printed pattern in an alternate red and green fluorescence.

The temperatures needed to produce this thermochroism would seem to be extremely low. But an example is also given of the application of an offset ink, mixed with chelates of gadolinium (Gd), Tb and Eu, on a credit card, yielding red fluorescence at room temperature but green fluorescence at -30°C. In fact the relative proportions of the rare earths determine the temperature at which TAET is blocked. For instance a mixture of chelates with Tb and Eu in a 99:1 proportion emits green fluorescence already at 0°C. In general, the lower the concentration of one chelate, the sooner the fluorescence of the other chelate will appear while lowering the temperature. In between, the emission will tend to either one of both fluorescent colors and is an additive mixture of them.

An apparatus is proposed by the inventor to detect the presence of TAET on security documents. The document is illuminated with ultraviolet and will emit the fluorescence of one rare earth. Subsequently the document is fed through a reservoir containing a liquid gas and will, still being illuminated with ultraviolet, emit the fluorescence of a second rare earth. The effect of thermochromic fluorescence may either be visually verified or detected by photosensors. It is the opinion of this author that, although such an apparatus will certainly function, it is far too unpractical for wide application. It would therefore seem worthwhile to investigate the applicability of a thermoelectric device which may cool the relevant part of the document considerably below 0°C. And after all, verification would not require a complete thermotropic color transition: a small but well defined change in the wavelength distribution of the emission would already suffice as a verification of the presence of TAET. Nevertheless its relative complexity will prohibit the use of this phenomenon as a verification tool by the general public and will confine it to banking and forensic environments. Finally it may be noted that, although the application of TAET chelates in security elements may raise a considerable barrier for counterfeiters, the various compounds, necessary for their laboratory synthesis, are commercially available and eventual misuse therefore cannot be precluded.

3.3. Excitation and stimulation of mixed inorganic phosphors

Common phosphors when excited absorb energy and emit this energy, according to Stoke's law, at longer, less energetic wavelengths. Such phosphors may be called 'down converters'. On the other hand 'up converter' phosphors are capable of multiphoton absorption and will emit their stored energy as wavelengths of a higher energy level ('anti-Stokes' radiation). An intricate security application of phosphorescence, claimed to be "immune to counterfeiting", was disclosed by R.J. Blach in 1983[11]: excitation and stimulation of mixed inorganic phosphors preferably of the so called intermediate converter type. Such intermediate converters are capable of absorbing and storing the excitation energy for a prolonged period and will
- discharge only part of this energy spontaneously as lower energy phosphorescence, while
- simultaneous or later stimulation of the phosphor with intense infrared radiation will eliminate its phosphorescent emission and may further cause a luminescent discharge of the stored energy in a visible spectrum different from the common phosphorescent spectrum.

A further property of these mixed phosphors is their capability of electroluminescence: the stored energy may be discharged by applying a strong electric field (typically 1 to 10kV/cm) over the phosphor.

Suitable mixed phosphors of this type may consist either of:
- two different phosphor cations, e.g. Zn/Cd or

- two different phosphor anions, e.g. O/S or S/Se, or
- two different metal activator ions, e.g. Pb/Cu or Eu/Sm.

Examples of these three alternative mixed phosphors are ZnS/CdS(Cu), SrO/SrS(Eu/Sm) and SrSe(Eu/Sm), where the traces of the activator ions embedded in the phosphor crystal lattice are given between parentheses. These phosphors are then incorporated in a protective polymer matrix which is subsequently used to impregnate security fibres or to manufacture a printing ink.

An example is given of a strontium sulfide lattice, activated with traces of europium and samarium: SrS(Eu/Sm). Such a mixed phosphor shows a greatly increased energy storage and a markedly depressed phosphorescent discharge to the favor of its infrared and electro stimulation capability. Figure 3 shows the absorption (excitation) spectrum of SrS(Eu/Sm) around 480nm, its infrared stimulation spectrum around 1000nm and its emission spectrum[12]. Authentication of this phosphor would comprise the following steps:

1. Excitation of the 480nm absorption band of this mixed phosphor, causing the energy to be stored for a certain period of time.
2. Termination of the excitation and observation of the decay of the spontaneous phosphorescence to a low level of luminescence within a few seconds.
3. Stimulation of the mixed phosphor by intense infrared radiation at its 1000nm stimulation band, some time after excitation has ceased, and observation of the eventual suppression of existing phosphorescence to the favor of the appearance of stimulated emission of a different spectral composition, in this case an orange emission typical of Eu.
4. During or after step 3, electroluminescence is induced by applying an electric field over the phosphor. Depending on the composition, an orange (Eu), yellow (Sm) or orange-yellow (Eu & Sm) emission will result.

Highly efficient mixed phosphors can only be manufactured by first preparing them to the highest possible purity before heating them together with the exact amount of activator traces in the right proportion. As the mixed phosphors described are not commercially available, require high technology for their manufacture, and cannot be faked with commonly available phosphors, their application would indeed raise a formidable barrier for the potential counterfeiter. Supplies of such stimulatable mixed phosphors can be well controlled and may be reserved by their manufacturers for security applications. The changes in luminescence, described in the above authentication steps, are all visible to the naked eye. The inventor therefore states that this verification process constitutes an unambiguous, easy test which can be performed in retail stores, squad cars and other non-laboratory settings. However, the test apparatus required would be rather more complicated than the simple ultraviolet source now frequently applied in retail stores and at counters and may therefore hardly be expected to rejoice wide circulation. Confinement to banking and forensic environments seems a more realistic option. On the other hand, fast machine readability, at least comprising the first three steps of the authentication process described seems well feasible.

4. PHOTOCHROISM

Photochromic compounds reversibly change color when irradiated with actinic light, e.g. ultraviolet or sunlight (heliochromic). The time required for complete photocoloration depends on the level of exposure and may take small fractions of a second, when laserirradiation is applied, to seconds or even minutes under exposure with ordinary sources of actinic radiation. In the absence of actinic radiation photochromes gradually fade to their original state, which is generally pale or colorless. This color reversal to the bleached state generally takes seconds to minutes but may be accelerated by exposure to visible light or by gently warming the compound. Such compounds are used for sunglasses and optical data storage (holography) but may also be used in security OVD's. An important drawback of many photochromic compounds however, is their high reactivity and resultant liability to thermal and photochemical degradation. This reduces the number of possible photochromic conversions, which has severely limited their usefulness for security purposes in the past. However various types of photochromes have since been developed that show a good resistance to fatigue, good photosensitivity and a high color conversion speed. In particular certain fulgides (Aberchromes) have been reported to withstand over 8000 color conversion cycles without appreciable fatigue effects[13)]. Most photochromic compounds are not commercially available and cannot be easily synthesized from common commercial products.

Two important classes of photochromes are 1) certain spirocompounds and 2) fulgides and fulgimides:

1) Spirocompounds contain a system of two molecular rings, having a single atom in common, resulting in a figure-eight arrangement of both rings. The position of the common atom is called the spiro location. Well known examples of spirotype photochromes are pyrans, e.g. benzopyran or naphtopyran, which are substituted in their 2-position with heterocyclic groups like indolyl. The photochromic effect of these spirocompounds is brought about by a reversible opening of the pyran ring at the spiro location to form an ionic structure consisting of an oxygen anion and a nitrogen cation (figure 4a). Such a dipolar state however is liable to fatigue through oxidative degradation and such spiropyrans have to be protected against atmospheric oxygen and other reactive compounds. This type of spirocompounds is heliochromic, turning to red or blue. If the substituent in the 2-position of the pyran is an adamantylidene group (tricyclodecane), stable heliochromic compounds result, turning to yellow/orange or to orange/-red[14)] as shown in figure 5.
2) Fulgides are derivatives of the anhydride of fulgenic acid or 3,4-dimethyl succinic anhydride in current nomenclature. Fulgides and fulgimides are defined as derivatives of succinic anhydride and succinic imide respectively. In its 3-position the succinic ring is generally substituted with an alkyl (e.g. ethylidene) substituted benzene-, 3-furyl-, 3-pyrryl- or 3-thienyl ring or with some heterocyclic group (e.g. benzofuranyl, indolyl, benzothienyl). In its 4-position the succinic ring is generally substituted with an alkyl group like isopropylidene or adamantylidene. These compounds derive their photochromic properties from so called photocyclisation, i.e. a reversible ring closure between both substituents in the 3 and 4-position of the succinic group. As an example figure 4b and c show the photocyclisation of two related fulgides, Aberchrome 540 which turns red, and Aberchrome 850 which turns dark blue on irradiation with ultraviolet (366nm). Figure 6 shows the absorption spectra of both Aberchromes prior to as well as after irradiation[13)].

A number of recent patent applications discloses ways to apply photochromes to security devices. Plessey[15)] has disclosed various methods to apply photochromic screen print varnishes to aluminum adhesive backed labels and credit cards. A protective polymer film covers the photochromic print as a protection against oxygen and water vapor. Sicpa[16)] has surprisingly discovered that, under certain conditions, photochromes can be directly introduced to printing ink vehicles, which after drying or curing act as a sufficient protection against detrimental chemical alterations. A large number of methods to compose stable photochromic printing inks is described for the production of security documents, e.g. heliographic, letterpress, intaglio, offset and silk screen inks. Although sufficiently stable photochromic OVD's may presently be manufactured, they still appear sensitive to degradation by massive overexposure. This follows from a disclosure by Courtaulds17) describing how to make use of this phenomenon by imagewise ultraviolet overexposure of films sensitized with photochromic compounds. Contrary to printed photochromic images, which presence can generally be distinguished even if the ink itself is colorless, such images are completely inconspicuous. Writing the images with ultraviolet laserbeams creates characteristic images that will be more difficult to counterfeit. Apparently, the photochromic effect of certain compounds may be destroyed by frequent or prolonged exposure to ultraviolet from sunlight. As a countermeasure Traqson18) has configured a photochromic security element with a controlled sunlight protection layer, containing a saturable ultraviolet absorber, e.g. a laser dye like triazinyl stilbene. The protection layer is transparent in the visible part of the spectrum but at normal sunlight intensities it has a high ultraviolet absorption. Above a certain intensity threshold however, the absorption process is saturated and the layer becomes highly transparent for the ultraviolet radiation required for authentication.

From the foregoing it appears that highly secure photochromic OVD's may be realized, that can be authenticated relatively easy with the use of an ultraviolet source or even in sunlight. They may also offer fast machine readability if photochromic color conversion is established with high energy sources, e.g. uv lasers or flash guns.

5. DISCUSSION

OVD's must not only be considered to comprise diffractive structures e.g. holograms, kinegrams, pearl lustre and thin-film devices, but also non-diffractive devices based on reversible photosensitivity, e.g. luminescence and photochroism. As these photosensitive compounds can be made into printing inks, as such they become well integrated within the document. Non-destructive dissociation from their carriers and subsequent transfer to counterfeit documents is then virtually impossible. Such integration is not always realized with embossed diffractive structures1). Moreover, certain photosensitive OVD's may throw up a considerable barrier for the would-be counterfeiter as they are generally not readily available and are difficult to synthesize. An advantage of diffractive OVD's is, that their authentication is readily accomplished with available light, while the non-diffractive OVD's described in this paper require ultraviolet excitation or sunlight. Inexpensive ultraviolet sources are available as pocket-devices however. It may therefore be worthwhile to consider a wider security application of reversible photosensitive OVD's other than those based on common fluorescence. The health or environmental hazards of certain compounds have to be assessed.

6. ACKNOWLEDGEMENT

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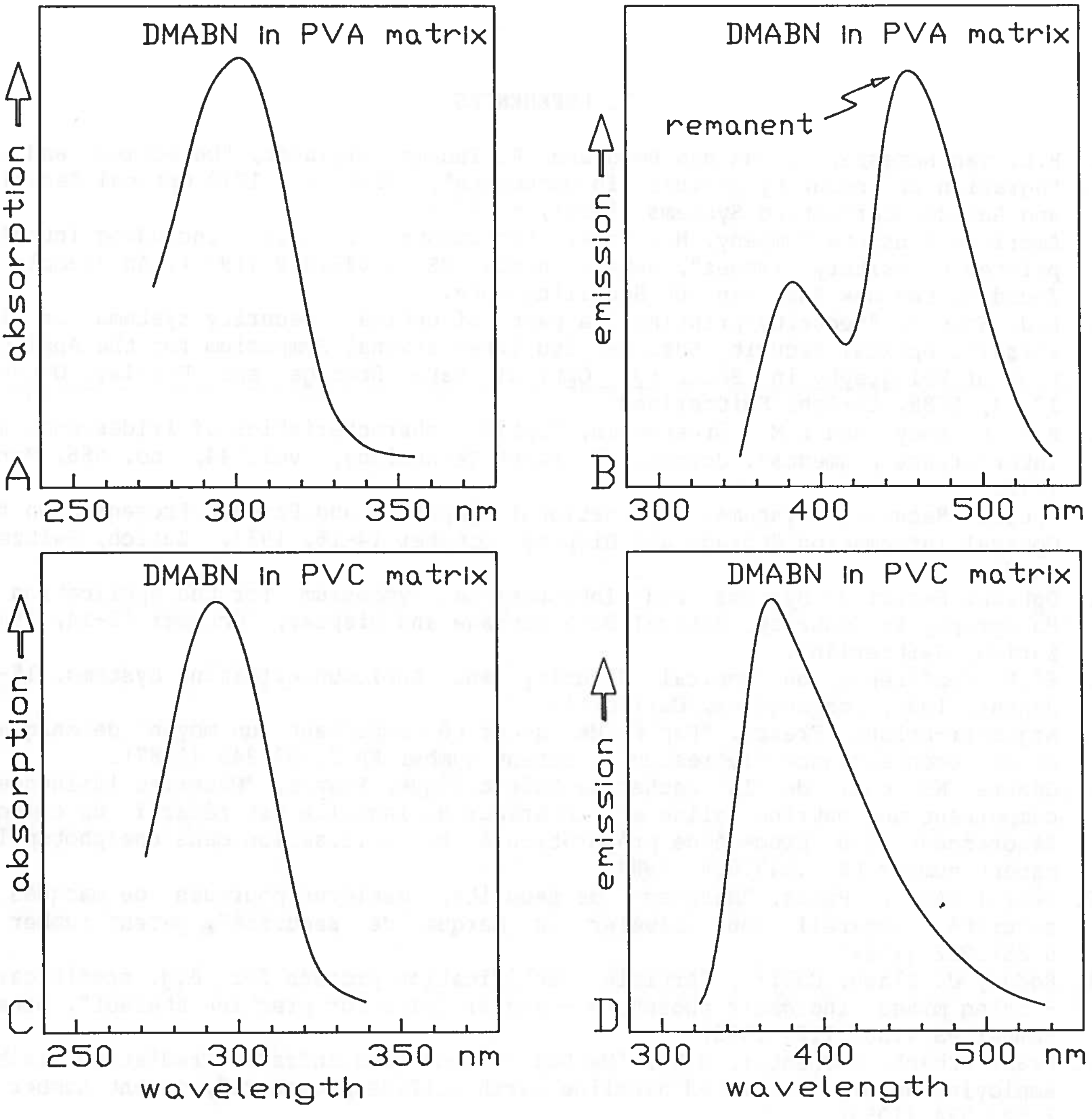


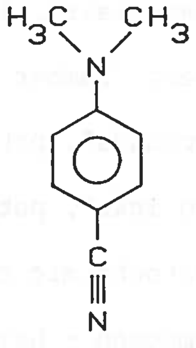


Fig. 1 TICT-fluorescence

absorption spectra and emission spectra of para N,N-dimethylamino benzonitrile (DMABN) in two different matrices (PVA and PVC).[9]

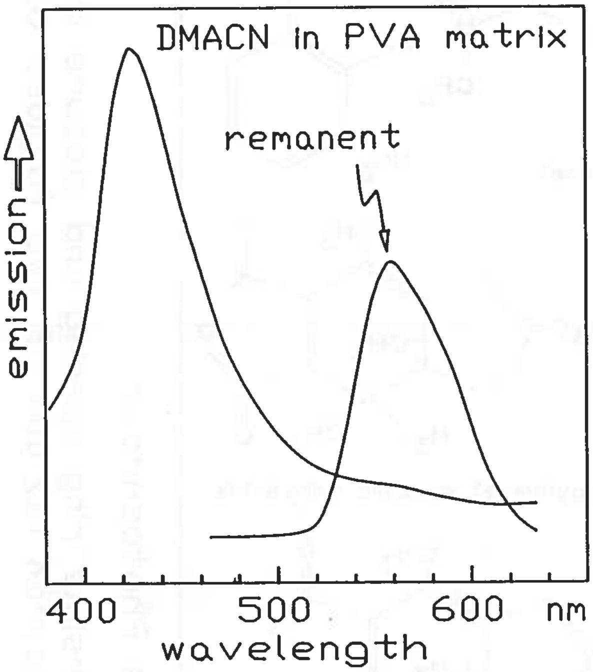
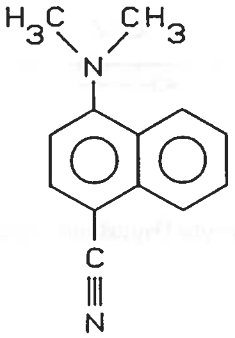


Fig. 2 TICT-fluorescence emission spectra of normal and TICT-fluorescence of N,N-dimethylamino-1 cyano-4 naphthalene (DMACN) in a PVA-matrix.9)



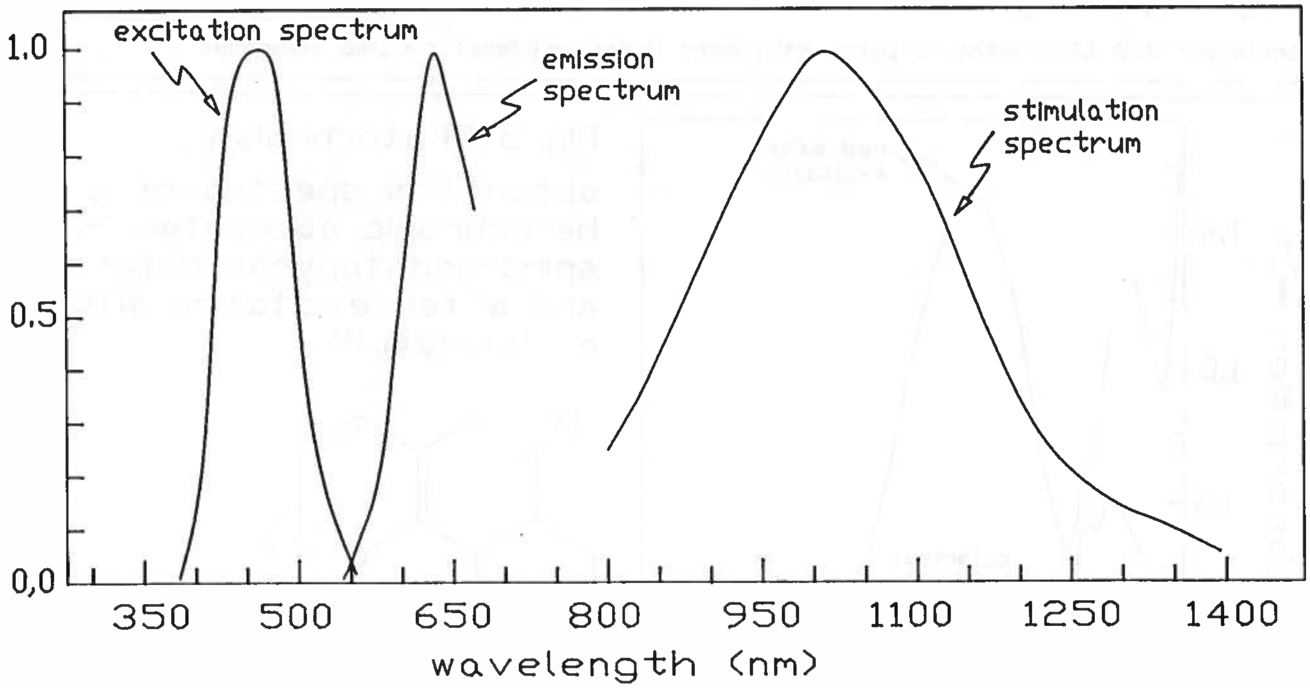


Fig. 3 Mixed inorganic phosphors
Normalized excitation, stimulation and emission spectra for SrS(Eu/Sm).12)

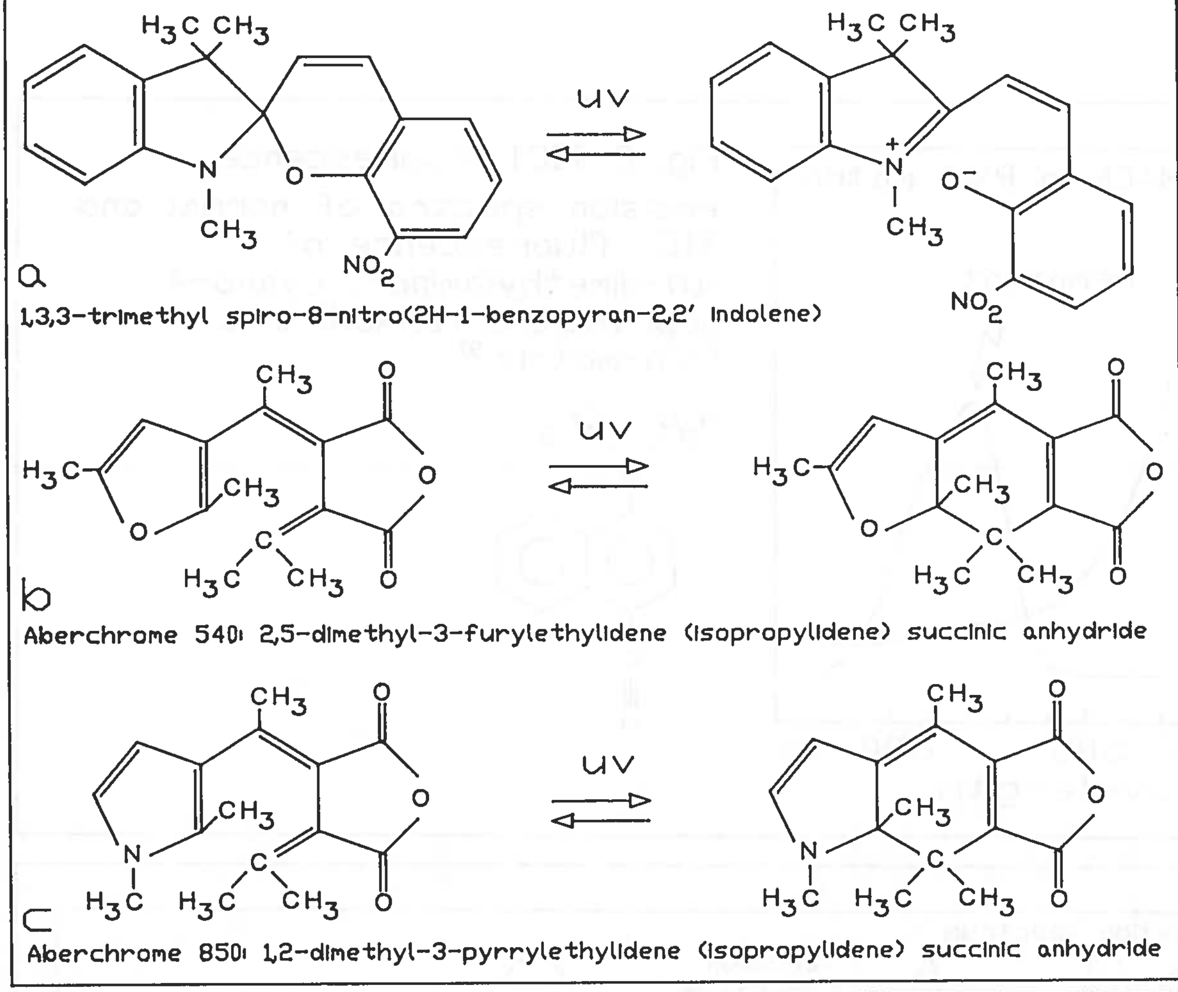


Fig. 4 Photochroism reversible ring opening and closure of a spiropyran (a) and of two fulgides (b, c).

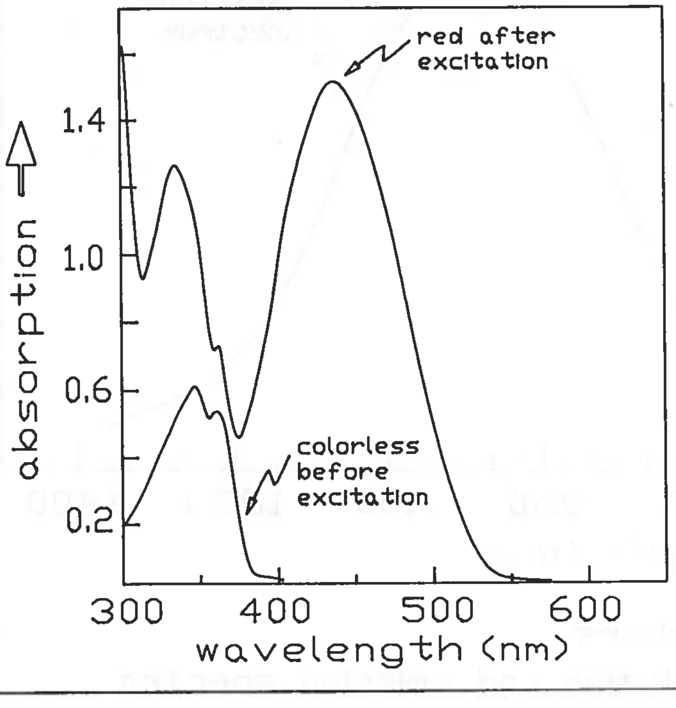
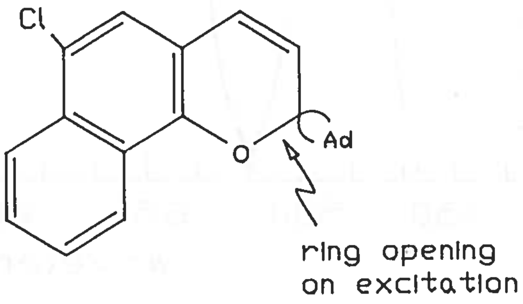


Fig. 5 Photochroism absorption spectra of a heliochromic adamantane -2-spiro-naphtopyran before and after excitation with a flashgun.[14]



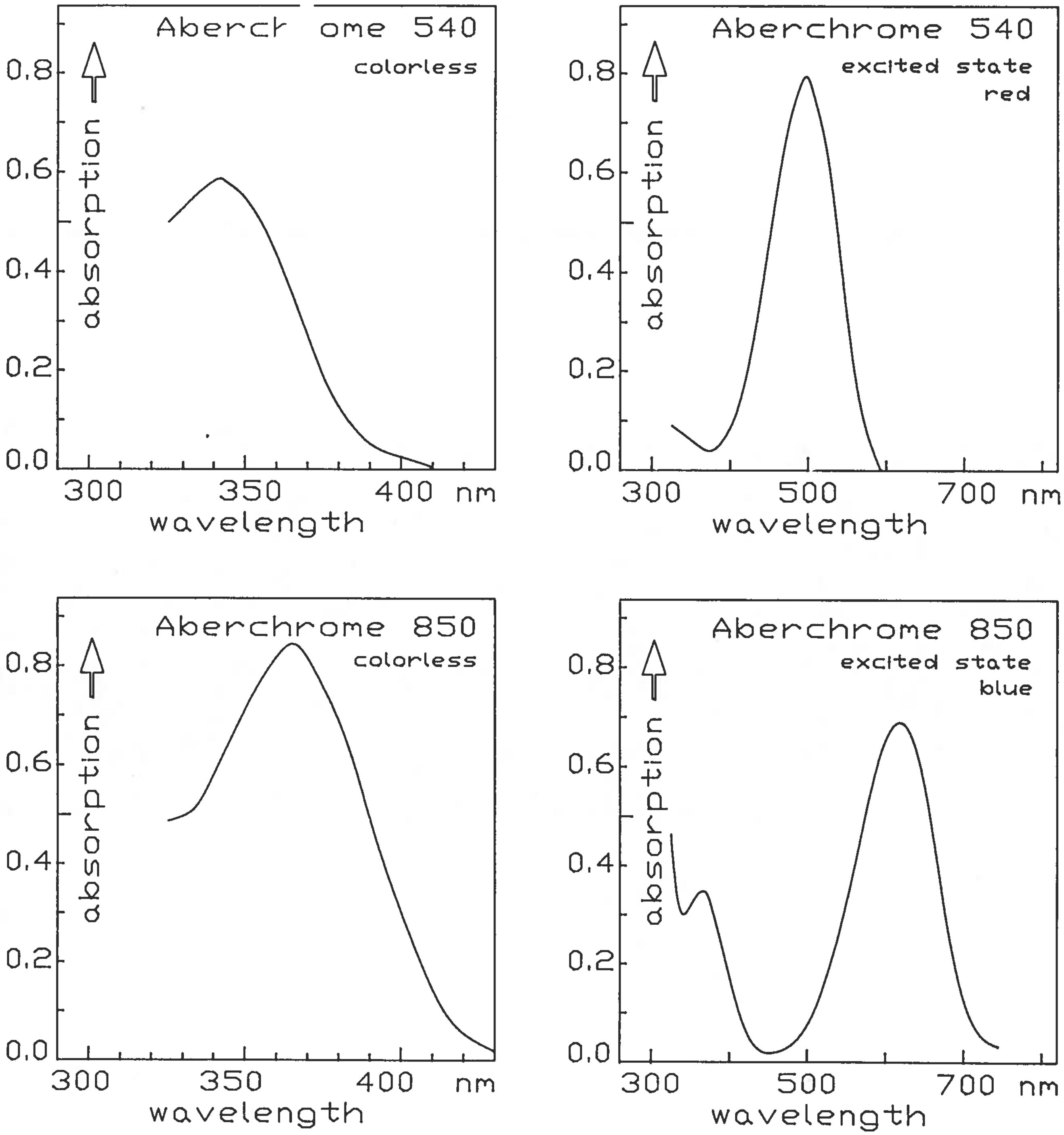


Fig. 6 Photochroism

absorption spectra of two related photochromic fulgides before and after ultraviolet excitation.[13)]