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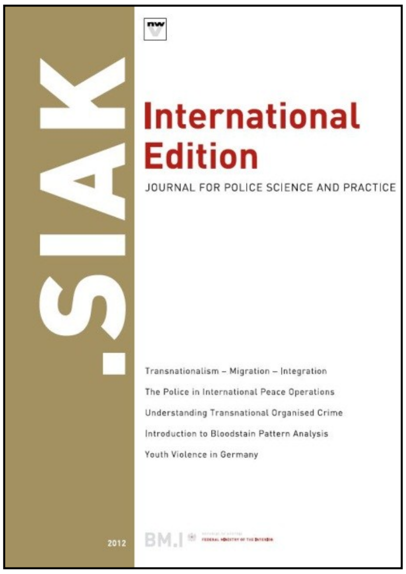

Findeisen, Anna Maria/Aigner, Stephan (2013):

Rare Earths and their Use in High Security Printing. Security pigments out of rare earths and the anti-Stokes luminescence with rare earths in high-security printing at OeSD

SIAK-Journal − Journal for Police Science and Practice (International Edition Vol. 3), 74-83.

doi: 10.7396/IE_2013_G

Please cite this articel as follows:

Findeisen, Anna Maria/Aigner, Stephan (2013). Rare Earths and their Use in High Security Printing. Security pigments out of rare earths and the anti-Stokes luminescence with rare earths in high-security printing at OeSD, SIAK-Journal − Journal for Police Science and Practice (International Edition Vol. 3), 74-83, Online: http://dx.doi.org/10.7396/IE_2013_G.

Note: A hard copy of the article is available through the printed version of the SIAK-Journal published by NWV (http://nwv.at).

published online: 8/2013

Rare Earths and their Use in High Security Printing

Security pigments out of rare earths and the anti-Stokes luminescence with rare earths in high-security printing at OeSD

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Security and identity are catchwords associated with the printing company, Österreichische Staatsdruckerei (OeSD), for more than 200 years. Since as far back as the days of the Dual Monarchy products of the security printing field of the printing industry have been an important ingredient for the functioning of our society. Österreichische Staatsdruckerei products – such as passports, visas, residence permits, driving licences, ownership titles, paper money, and postage stamps – often also serve as proof of the identity of the current owner as well as having a material value. For this reason it is necessary to protect such products in particular against forgers. With built-in security features, however, the longer they are in use, the greater the likelihood of forgery and criminal abuse. In order to minimise this effect and thus also the risk of falsifications, it is essential that the high-security printing industry maintain the security features used at the cutting edge of technology through continuous research, improvements, and further development, and that the latest innovations be incorporated into the various products. This is why in 2010 OeSD established a new Research and Quality Centre that enables state-of-the-art production and guarantees the high quality of the secured products and will rise to the challenge posed by the innovation pressure facing security printing companies.

The development of a new security feature for various printed products was the result of one of the innovative projects carried out last year. OeSD in collaboration with Aerospace & Advanced Composites GmbH (AAC) developed and patented a security pigment which is based on rare earths and which displays anti-Stokes luminescence.[1] By virtue of its very high security integrity, and because of the specific conformation of the fingerprint band of the compound, use of the newly developed pigment not only ensures a high degree of security against forgery, but also – via an appropriate validating process – allows an exact determination of such product-specific parameters as production batch number and origin. Good processibilty of the rare-earth pigment in printing applications, high stability, and a quick, uncomplicated detection and verification of the authenticity of documents having the new security element round off the list of the excellent practical properties of the OeSD security pigment. This opens up a broad application spectrum in the high-security printing sector for various printed products and enables OeSD to continue maintaining the high security of its products at the cutting edge of the technology.

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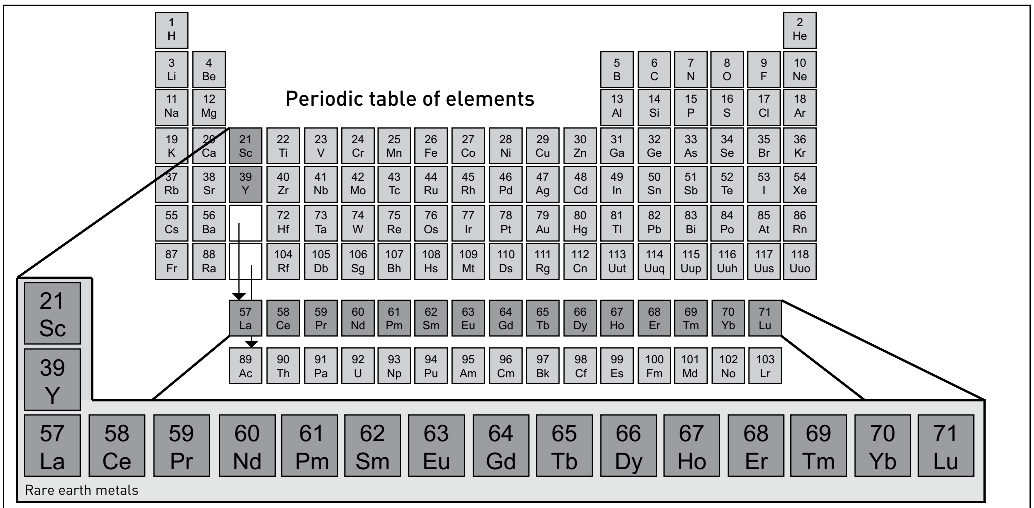

Rare earth metals include 17 elements from the periodic table. These are the lanthanides plus scandium and yttrium.

Figure 1: The Rare earths in the Periodic System

RARE EARTHS AND ANTI-STOKES LUMINESCENCE

The rare earths are metals in the 3rd group of the periodic system and lanthanide series (see Figure 1). In all there are 17 elements in this series which includes yttrium (Atomic Number Z: 39), lanthanum (Z: 57), cerium (Z: 58), and erbium (Z: 68) (Holleman/Wiberg 2007). Uses for these elements in engineering and industry range from semiconductor and electrical engineering through to entertainment electronics, (e.g. in plasma, LCD and LED television sets) and on to luminous colorants which are also used as fluorescent colorants in printing technology. Particularly through the use of rare earths in entertainment electronics and mobile telephony, the demand for and the mining of them increased rapidly in recent decades (c.f. Waltritsch 2010). In particular their good properties when used for the doping of materials are exploited. Meanwhile, through the ever more intensive reliance on mobile appliances – such as cell phones, tablet PCs and the like – the use of rare earths in the necessary accumulators and microchips has accorded a still greater role to rare earths in modern society. In the high-security printing industry rare earths are used in special printing inks. Already when in pure crystal form the metallic elements of rare earths display a strong tendency to fluoresce, i.e. to emit light when exposed to excitation by UV light. By deliberately exchanging lattice atoms in solid bodies, and thus changing the stoichiometric order of different atoms in the lattice structure it is possible to change the properties of the material in question so that exposure to infrared (IR) light will also lead to a special, spontaneous light emission.

Such luminescence phenomena on the part of molecules are by no means the norm in natural chemistry since they can only occur under strictly defined conditions. Luminescence is the term used to describe that effect by which a detectable optical radiation of light is emitted during the transition from an excited state to the ground state. In an initial stage the electrons are excited to a higher energetic state. This means that the energy balance of the system is increased. This absorption of energy can occur by different means, the absorption of a photon or the result of a chemical reaction. At the second stage the system now reverts to its energetically lower basic state. In doing so the system must release or convert the absorbed energy (law of conservation of energy). This release of energy can take place as a result of the molecules colliding with ambient molecules, heat release, or through visible or invisible light emission. In the case of the latter we speak of luminescence. The nature of the luminescence is classified according to the particular method by which the electrons in the molecule are excited – e.g. by means of a chemical reaction, electrical potential (electroluminescence) or through photons (photoluminescence).

In the case of photoluminescence the excitation of the electrons is caused by the absorption of photons from a suitable energising light source. This could be a UV lamp or a laser, for example. Depending on the relevant energy and wavelength (λ) of this energising light source the electrons will be varyingly strongly excited. After a molecule-specific dwell time in the excited state the electron reverts to the lower energy ground state. As this is happening a light is emitted in the case of photoluminescence (see Figure 2). The lifetime of these conditions can vary between 10^{-9} and 10^{-6} s (fluorescence) up to a matter of some seconds or up to a number of hours (phosphorescence). Thus the occurrence of luminescence is only measurable or visible during direct active radiation from the energising source or for a very short time span afterwards. By contrast, phosphorescence remains even after the excitation has ended. In both these instances the radiating emission light – due to molecular collisions and heat loss – is lower in energy than the radiation used for excitation purposes. This circumstance is in keeping with the law of conservation of energy and thus also with Stokes' Law. The latter law states that the energy level of the emitted radiation is the same as or lower than the radiation used for excitation. Since the wavelength is indirectly proportional to the energy here, this means that the lower the energy the longer the wavelength. Consequently, with regard to the spectrum, the following rule applies: the spectrum of the emission light in relation to the excitation light is always shifted to higher wavelengths. The resultant distance between the spectra is known as the Stokes shift (Otto 2006).

However, it is also possible that an already excited electron may absorb the energy

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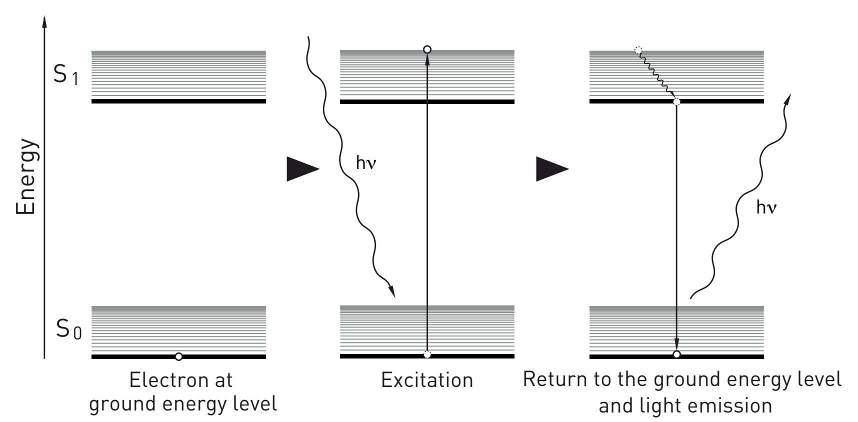


Following the absorption of a photon, an electron at ground energy level is excited to a higher energy level. Light emission occurs through the return of the electrons to the ground energy level.

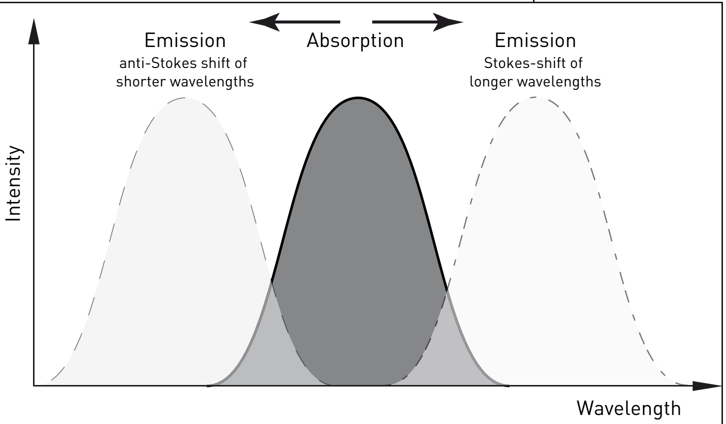
Figure 2: Photoluminescence

of yet another photon and become additionally excited. Once this electron reverts to the ground state and emits radiation, this radiation may display a higher energy level – namely that of the two photons which excited it minus the lost collision and heat energy – and thus also have a shorter wavelength. This phenomenon is known as upconversion or as anti-Stokes luminescence. In this case the spectrum of the emitted light – in contrast to the above mentioned Stokes shift – on fluorescence is shifted to a shorter wavelength range (see Figure 3). But if the energising photon comes from an infrared light source, and thus in a wavelength range invisible to the human eye, this light, with the help of the upconversion fluorescence and due to the anti-Stokes shift, will be shifted into the visible range (Atkins/de Paula 2006). This happens with the OeSD rare-earth pigment whereby an "invisible" light (infrared light) impinging on the pigment "generates" a red emission light visible to the naked eye.

THE ROAD FROM RARE EARTH PIGMENT TO SECURITY ELEMENT

OeSD developed a pigment produced on the basis of a stoichiometric mixture of several different rare earths as the key component of a newly developed security element. The synthesis of this rare-earth pigment involved a multi-stage manufacturing process in the laboratories of ACC. In the process the different elements of the rare earths were integrated into the crystal lattice of the pigment structure as oxides. Through the use of oxides – i.e. atoms with firmly bound oxygen – good stability and inert behaviour in the presence of other compounds and chemicals can be assured. As a result of this complex synthesis a crystalline powder is obtained. Due to the strict configuration of the different elements in the crystal lattice, and the fact that they are in the exact proportions to one another, this crystalline powder displays anti-Stokes luminescence. Knowledge of the exact composition and distribution of the rare earths, the additional elements in the crystal structure of the rare-earth pigment, and the exact directions needed to synthesise the crystalline powder is decisive the further use as the security feature and for security against forgery. Following excitation by means of an "invisible" infrared laser beam, counter-radiation visible to the human eye is generated. In the process the excitation spectrum of the infrared light at a wavelength of 980 nm generating emission light in the range of 750 nm is shifted to 600 nm whereby a red emission light visible to the naked eye can be observed. Yet this is not the only characterising property because the pigment, rather like humans with their biometric data, has its own distinct fingerprint in its unique emission spectrum. When the entire spectrum is recorded each wavelength is assigned an exact intensity. With a resolution in the

Source: Findeisen/Aigner



The spectrum (here shown schematically as a single peak) is shifted to a longer wavelength during the emission radiation of the "normal" luminescence Stokes-shift. By contrast, in the case of the OeSD security pigment an "upconversion" takes place, i.e. the spectrum of the emission light in comparison to the absorption spectrum is shifted into a shorter wavelength. This phenomenon is also known as an anti-Stokes shift.

Figure 3: Displacements of the spectrum following photoluminescence

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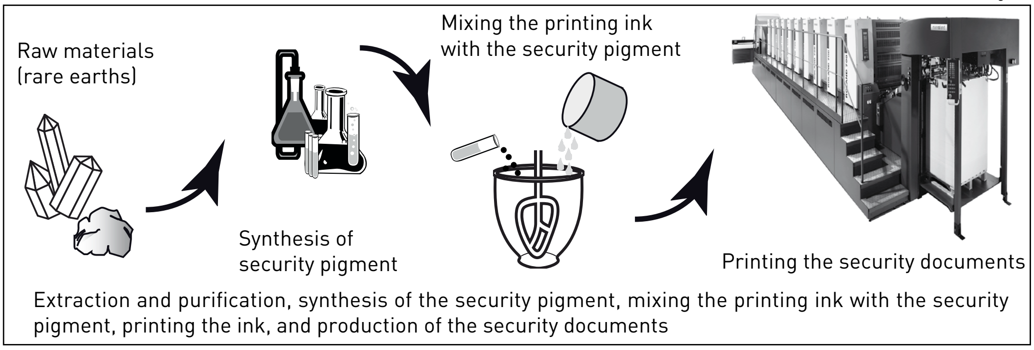

Figure 4: Processes on the way from a rare earth metal through to a security document

range of 1 nm up to 600 information pairs are used across the range of 300 to 900 nm to describe the spectrum. This information represents a unique fingerprint of the rare-earth pigment. The fingerprint itself can be changed by modifications at the synthesising stage either by varying the proportional distribution of the rare earths to one another or by incorporating other elements into the crystal lattice. In this way it is possible to incorporate and link information regarding production data such as date of production or production batch numbers.

However, in order to introduce the rare-earth pigment actually into a secured document the pigment must first be mixed into a printing ink or lacquer system. Only after this has been done can the pigment be processed in a high-security printing application. Important here is not only the miscibility but also the size of the pigment particles. These should not be too fine, but not too coarse either, otherwise the pigment will either not be printable (e.g. by offset printing) or will display poor detection. But at the same time is necessary to be able to print and detect even fine structures with the new security ink. Only once it can be successfully printed under such conditions can the rare-earth pigment be used as a security element for printed products.

The embedding in the design of a printed product is effected in such a way that the best possible detection of the pigment is possible, the most important information is protected by the pigment, and the aesthetic aspect of the print image as a whole is not spoilt. In order to take these considerations into account, a modern test design for the most well-established identity documents (passports and visas etc.) was designed at OeSD and made available in the form of a printing plate for the following printing trials.

PRINTING TRIALS AND APPLICATIONS

In order to test the patented rare-earth pigment for its suitability as a security element and its ability to satisfy the above described requirements, OeSD carried out a series of printing trials. These involved testing not only use of the rare-earth pigment at different concentrations in different printing ink and lacquer systems, but also the use of different substrates.

The printing trials at OeSD were performed using the wet offset printing technique. In particular with this indirect planographic printing process the interaction between hydrophilic and hydrophobic behaviour is decisive, i.e. on printing a variety of physical and chemical interfacial activities occur and thus there is a complex interaction involving the printing cylinder, the printing plate, the inks, the dampening solution, and the substrate (Kipphan 2000). In an offset printing machine the printing areas of the printing plate are hydrophobic in design, i.e. they are water-repellent, whilst the non-printing parts of the printing plate are hydrophilic, i.e. they display a high affinity for water. On to these hydrophilic areas the machine's dampening unit applies a thin film of dampening solution (water with additives, e.g. to regulate the surface tension) and thus prevent them from accepting ink. By contrast, the hydrophobic areas absorb printing ink from the inking unit and become inked. This matrix of ink and dampening solution is now transferred to a rubber cylinder which then impresses it onto the substrate to leave behind the print image (those inked areas) as shown schematically in Figure 5. Also to be noted here is that this transfer of ink and dampening solution involves more than just an uptake of ink but rather also always a separation of the liquid films in contact with one another. This has a major influence regarding the quality and composition of the inks used in offset printing and thus also on the composition of the printing ink systems used in the trials with the security pigment. Accordingly, the printing ink must be so prepared that, despite the presence of a water film, it can be applied to the image surface and so that it can displace the water at the time of inking the printing plate cylinder and on transfer to the rubber blanket cylinder. For this reason it is essential that the pigment be incorporated into an ink system which complies with the above printability requirements and also keeps the pigment particles in suspension and very well dispersed.

The ink systems used for the printing of the security pigment are high-viscosity mixtures comprising a binder, carrier substances, and additives. The role of the binder is to bind and fix the pigment (colorant) onto the substrate. It also affords protection against mechanical abrasion in that it forms a protective film around the pigment particles. Mineral oils or vegetable oils can be admixed with the ink as carrier substances to perform the transport function and act as a lubricant for the ink. Further additives may be used in order to minimise printing difficulties or also to afford the ink special properties. These properties might include the viscosity, which, in the case of the rare-earth pigment, plays a key role with regard to stability of the suspension of the pigment particles in the ink system. Accordingly, it is essential that the incorporation of additives in the test ink be optimised. Depending on the desired colour, organic or inorganic pigment colorants may be incorporated to determine the shade of the printing ink. However, no use was made of these here because of the requirement to develop an "invisible" security feature. Instead, the rare-earth pigment was added.

The prepared ink was transferred to the inking unit of the OeSD offset printing machine and applied to various substrates using the design developed for this test. In view of the broad application spectrum of the newly developed rare-earth pigment a

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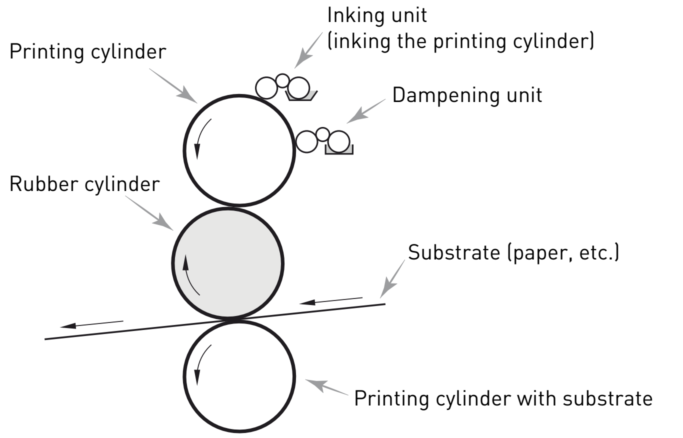

The wetting agent and the ink are applied to the printing plate sleeve on the printing cylinder whereby here an interaction takes place between hydrophilic and hydrophobic forces. The applied ink is transferred to the rubber cylinder, which then prints it onto the substrate, e.g. paper. The impression cylinder presses the substrate against the rubber cylinder.

Figure 5: Schematic presentation of a printing unit of an offset machine

wide variety of paper qualities was used in the trials. Voucher papers as well as passport and visa quality papers were printed using the ink mixed with the security pigment. The possibility of using the pigment in different design elements such as solid areas or halftone structures was taken into account when creating the image and implemented when producing the printing plates and during the printing trials. Such features can also be assessed at the subsequent detection stage and thus the universal suitability of the rare-earth pigment in high security printing can be guaranteed.

After they had been printed the different printed products were moved on to the final fabrication stage where they were fashioned into their respective customary formats, i.e. in the case of passports this would mean booklets, while visas are fashioned into individual visa stickers, and other documentary papers into an A4-format.The inclusion of this additional production process was necessary in order to ensure that any possible influencing of the pigment, e.g. as a result of exposure to heat in places (during a laminating process) or through contact with the adhesives or solvents used during the further processing, was recognised, and thus that the printed pigment remains suitable for industrial printing use. Also at this final stage documents were personalised with sample data records and the detection and characterisation of the new security element tested by different methods.

DETECTION OF THE NEW SECURITY ELEMENT

In the finished products the newly developed OeSD rare-earth pigment can be detected in different ways. One such way is through the recognition of certain structure patterns in the design which could result from mixing the rare-earth pigment into a printing ink system which contains pigment colorants. If so desired, the sites where the security pigment is present can immediately be recognised with the naked eye by conducting a visual check. By means of a laser having the suitable wavelength (980 nm) the rare earth pigment in the ink can be excited and through its red light emission becomes detectable to the naked eye. Further enhanced security is obtained if the rare earth pigment is first mixed into gloss white and thus becomes "invisibly" hidden in the design. Only through excitation by means of IR-laser radiation is it possible to check for the presence of the rare-earth pigment in the right place. Visually checking the emitted light serves two purposes in that it enables an on-the-spot verification of the originality of the document on the basis of the presence of the light-emitting pigment on the defined position in the document whilst also allowing an appraisal of the originality of the pigment on the basis of the colour of the emitted light (see Figure 6 a, page 81).

However, for an exact identification of the rare–earth pigment on the document a measurement of the spectral composition of the emitted light must be carried out. For this purpose it is necessary to plot the exact emission spectrum (see Figure 6 c). The shape of the spectrum, i.e. the intensity at the respective wavelength, can be influenced and determined by the stoichiometric distribution of the rare earths at the time of manufacturing the pigment. If the thus obtained measured spectrum is compared with a reference spectrum of the starting compound, a definitive statement can be made with regard to the rare-earth pigment, its origin and its genuineness.

In addition to having a distinct spectrum, the emitted light also has a specific decay time, which in turn can also be used as a parameter to characterise the rare-earth pigment. The decay time of the light emission is just as unique as the emission spectrum and a material-specific parameter. Accordingly, the decay behaviour of the anti-Stokes luminescence can also be used to characterise the rare-earth pigment. For this purpose the duration and the intensity of the luminescent light are measured. With these two parameters it is possible to determine a distinct decay curve for any emission light of a given luminescing compound. The actual measuring involves pulsed excitation of the rare-earth pigment on the printed product by means of a 980 nm IR laser (laser diode) which, depending on the preselected pulse duration, continues until either the emission light has decayed completely, or until the expiration of a predefined time since the initial excitation. Within this timespan the emitted light is recorded by means of a CCD sensor and the intensity of the light determined (see Figure 6 b).

On the basis of the different detection and characterisation methods mentioned above, the rare-earth pigment is suitable as a security element in travel documents and other identity documents. For fast visual checking purposes only a hand-held laser is needed i.e. in the form of a laser pointer which mobile security officials can take with them on patrol. A cigarette-packet-sized portable measuring appliance is used to measure the decay curve and then compare the curve shape with a previously fed in reference curve in order to give a yes-no response regarding the authenticity of the pigment. The measurements to be taken for an exact forensic examination are more complex and necessitate the availability of a suitable spectroscopic testing instrument. Nevertheless, such floor-mounted appliances can be installed at checkpoints or government agencies and in suspicious cases can be used to deliver a precise appraisal of the authenticity. With these forensic measuring appliances it is also possible to read out data embedded across the fingerprint band of the emission spectrum and thus gain access to other information in addition to verifying the authenticity of the document and the pigment.

A further major advantage when checking the security pigment is its quick signal response to the excitation. Since the luminescence starts directly upon exposure to IR light irradiation and requires no reaction time, the necessary information (such as emission light colour) can be read off. In this way both the determination of the decay curve and the presence of the emission light can be automatised – with the result that it will now be possible to check

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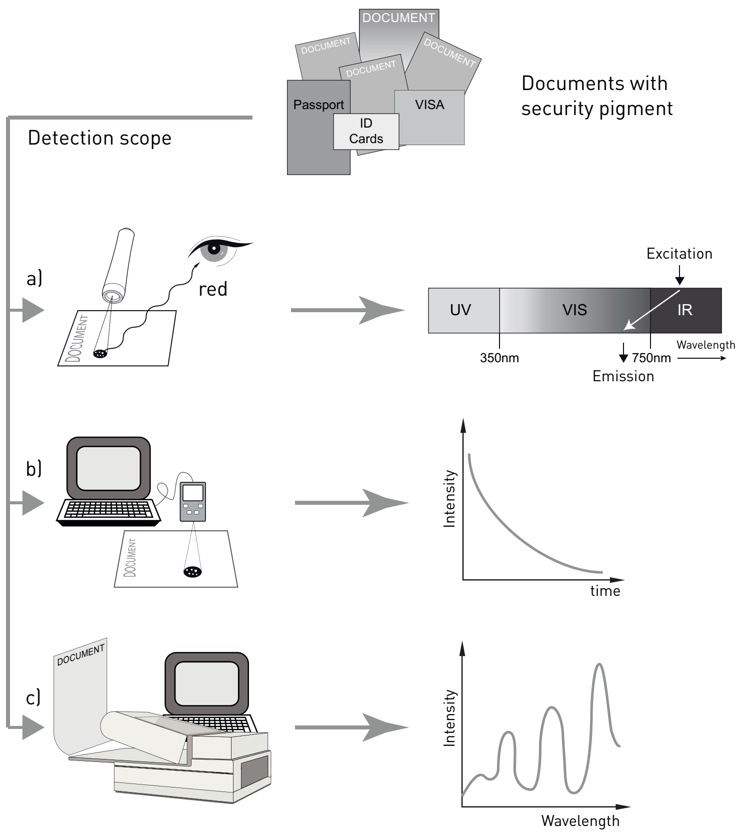

The new security element with the rare-earth pigment can be detected in different ways: a) Fast detection using an IR laser (such as a hand-held laser pointer): In this case a red emission light must become visible at the clearly defined place on the document. b) Measurement by means of a hand-held instrument (operable with or without a computer): in this case the pigment can be characterised on the basis of the luminescence decay curve. c) With the use of forensic and analytical appliances the entire spectrum can be displayed and the originality of the pigment verified via the fingerprint.

Figure 6: Detection scope in the case of documents with embedded security pigment

the rare-earth pigment at highly busy locations such as airports and railway stations.

STABILITY OF THE SECURITY PIGMENT

Since identity documents are in use throughout the world, the embedded security features must be highly resistant to a wide range of climatic influences and processing conditions. The climatic conditions for the normal use of the finished products range from temperatures of -40°C through to +60°C at an air humidity equivalent to between 10 % and 90 % relative humidity. However, during further processing the printed product may be briefly exposed to temperatures of up to 200°C, as happens in the case of documents subjected to a laminating process for example. In the climatic as well as in the processing tests conducted the rare-earth pigment developed by OeSD and AAC demonstrated that – despite the fact that the tests were conducted across the whole bandwidth of test conditions – it remained displayable throughout, and that it could be verified by the test methods used (980nm-IR-Laser and hand-held sensor instrument to determine the decay curve). Similarly, the individual emission spectrum could be identified in all the stability tests conducted. Thus the good stability and high resistance of the rare earth pigment in the security element of the various products is given.

RESULTS

The purpose of the tests conducted at OeSD was to process the newly developed rare earth pigment – together with its characteristic anti-Stokes luminescence – in offset printing applications and to embed this pigment as a new security element in OeSD products such as passports, visas, and identity cards. Taking into account the complex interaction between the printing ink system, the substrate, and the rare-earth pigment, the limits of the printability were tested, as was the detectability of the embedded pigment. The thus ascertained parameters guarantee not only processing in the printing and after-processing machines, but also problem-free detection of the anti-Stokes luminescence. By virtue of the inimitability of the emission light, and thus also of the related fingerprint band of the emission spectrum, it is possible to characterise the rare earth pigment and verify its originality on the basis of spectrophotometric analyses. Since this is only possible with the use of special measuring appliances, the feasibility of using hand-held testers was also investigated. Use of the latter enables, on the one hand, an immediate statement with regard to the authenticity of the document to be tested, whilst on the other hand, and on the basis of the decay behaviour of the luminescence, with regard to an identification of the rare-earth pigment used. The findings ascertained on

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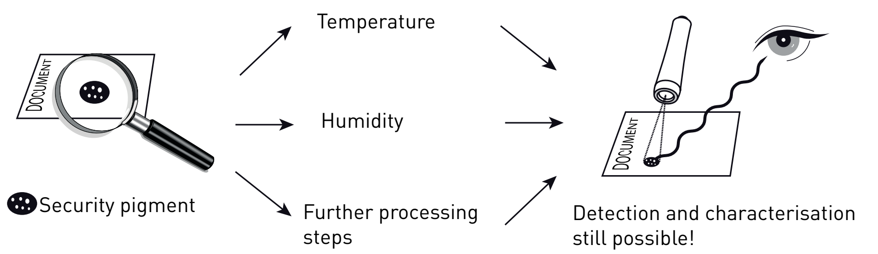

The security pigment was exposed to various influencing factors whereby its stability was verified. Accordingly, it was found that even after a wide range of climatic tests (temperature and air humidity), as well as after various further processing conditions the pigment remained displayable and verifiable.

Figure 7: Stability of the security pigment

completion of the entire test and development series confirm that the pigment tested is suitable for application in high-security printing and can be used in OeSD products in future. Accordingly, a further innovative step has been taken towards securer products and the ability of OeSD to assure customers of even greater security against the risk of document forgery. This project was promoted within the framework of the promotion programme "Innovation (Secure Identification Documents through Anti-Stokes Luminescence)" by ZIT – Die Technologieagentur der Stadt Wien GmbH.

1 *Patent AT 505007 (B1) and Patent AT 508253 (B1).*

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