Anticounterfeiting Technology – A Luminescent Path: Short Review

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Abstract

In the recent years, there are number of problems related to counterfeit in drug industry, banking industry, insurance sector and range of products including fake university degrees, documents etc. There are number of products, which can be easily duplicated by simple processes and the product seems original that nobody doubts. Even the counterfeit of currency is also a main problem in world’s economy. So there are number of anti-counterfeiting technologies including electronic combat mechanism are available in the market to prevent these antisocial activities. Printing ink is very useful as per the security purpose to write down confidential documents or sign. Fluorescent material-based inks can be difficult to counterfeit and relatively easier to handle. This ink has diverse properties in different options so that it can be a very good option to frame an anticounterfeiting system. This paper explains about the brief overview of anticounterfeiting technology and different methods of it. It also explains the applications of fluorescent based security ink to prevent the counterfeiting of the products and documents. This can be a reliable source for the security purpose to make the confidential documents secure. The review article also describes the concept of luminescence and its applicability for further development in various sectors.

1. Introduction

Counterfeiting is as old as the human desire to create objects of value in an alternative cheaper method. For example, historians have identified counterfeit coins even in Neolithic period. Archaeological findings have identified examples of counterfeit coins from 500 B.C. [1,2]. Counterfeit is also a problem of security. Other type of improper products can be considered threats to security even if it is not thought of as a challenge to incorruptibility. Product that is for example, diverted from its proper distribution channel, or sold after it is out of date, or tampered with by being laced with poison or by alteration of the package are also related to the problem of counterfeiting. Trademark-infringing products may include correct ingredients in incorrect quantities or may be a re-combinatorial formula. Products can furthermore contain non-active or even toxic ingredients. Ailments which could be remedied by genuine products may prove ineffective or worsen the symptoms; in some cases this may lead to death. Most purchasers/customers who buy counterfeit products may prove ineffective or worsen the symptoms; in some cases this may lead to death. Most purchasers/customers who buy counterfeit products are unaware of the fact that they have been victimized by counterfeiting [3,4]. Counterfeiting is on the rise and intrude every product category, from consumer goods to medicines and spare parts. Quantitative assessments on the impact of counterfeiting have been carried out by international organizations and business associations. The Organisation for Economic Cooperation and Development (OECD), for instance, estimates that trafficking in counterfeit products accounted for USD 250 billion in 2007, approximately 1.9% of international trade. According to the International Chamber of Commerce, in 2011 counterfeiting was a USD 600 billion business, amounting to 5% - 7% of world trade. Building upon the work of the OECD, a 2011 study by Frontier Economist estimated that the value of trade counterfeited and pirated products in 2015 reached up to USD 960 billion [3-5]. An ideal anti-counterfeiting technology should possess a high level of security (non-clonable), varied product application, easy authentication, counterfeit technology should possess a high level of security (non-clonable), varied product application, easy authentication, and packaging companies sell components outside of contract with the design house (component’s intellectual property (IP) owner). Note that this category does not include overproduced goods, which have identical components and design of the valid goods. In this case, this is considered a contract policing issue. This category is related to overproduced goods, which have different components or materials (often of lower quality).

2. Classification of Anti-Counterfeiting Technology

2.1 Cloned

Cloning can be done by reverse engineering and by obtaining intellectual property (IP) illegally (also called IP theft).

2.2 Overproduced

Due to globalization of markets, design houses outsource their designs for fabrication and packaging to companies all around the world, mainly to reduce the manufacturing cost. Overproduction occurs when bundies and packaging companies sell components outside of contract with the design house (component’s intellectual property (IP) owner). Note that this category does not include overproduced goods, which have identical components and design of the valid goods. In this case, this is considered a contract policing issue. This category is related to overproduced goods, which have different components or materials (often of lower quality).

2.3 Out-of-Spec/Defective

A part is considered defective if it produces an incorrect response to post-manufacturing tests. These parts should be destroyed, downgraded, or otherwise properly disposed-off. However, if they are sold on the open markets, either knowingly by an untrusted entity or by a third party who
has stolen them, there will be an unknown increase in risk of failure which may even cause life threat.

2.4 Recycled
It refers to an electronic component that is reclaimed/recovered from a system and then modified to be misrepresented as a new component of the proper manufacturer. Recycled components can be declared counterfeit if they are not declared as such and they are instead sold as genuine/new components.

2.5 Remarkable
Most legitimate components contain markings on their packages that indicate manufacturer, trademark, part number, grade, lot code, etc. If a company is remarked to indicate another model or category, it can be considered counterfeit.

2.6 Tampered
Components that are tampered can have dangerous consequences for the systems that incorporate them for security and safety. In this case, goods can be considered counterfeit when it has been tampered to replace internal components.

3. Types of Anti-Counterfeiting Technology

Multiple anti-counterfeit technologies with distinct advantages and drawbacks exist today [11,12]. Primarily, these can be used in three different ways.

3.1 Tamper-Evident/ Tamper-Resistant Packaging
Packaging having an indicator or barrier to entry which, if breached or missing, should provide visible or audible evidence to consumers that tampering has occurred [13]. E.g. Film wrappers, shrinkable seals and bands, breakable caps, tape seals, blister packs, etc.

3.2 Holograms for Anti-Counterfeiting
Holograms can combine three layered security features and become a most powerful weapon against counterfeiting. In such solutions, holograms can provide first line authentication while covert features such as binary encrypted holograms, light diffraction, and thermal monitoring [15,16].

3.3 Track and Trace Technology
This is the process of assigning a unique identity to each stock unit during manufacture which then remains with it through the supply chain until its consumption, and is called the track and trace system. Information is attached in the form of a unique pack coding, enabling access to the same information on a secure database [17].

3.4 Mass Serialization
Serialization includes the processes of generating, encoding, and verifying the unique identity of individual physical items [18]. Without mass serialization, the authenticity and validity of the product relates only to the lot number consisting of thousands of bottles. However, a specific bottle of a particular drug cannot be authenticated [19]. When combined with track and trace technology, serialization facilitates the tracking of a product through the supply chain and allows for targeted identification of products for recall [18]. Global Standards one (GS1) is a not-for-profit organization that develops global standards for the identification of goods and services. GS1 standards are used for the identification of pharmaceutical products in 60 countries around the world [20].

3.5 Multi-Level Approach
Anti-counterfeiting technological approaches are interdependent for their effectiveness, and integrating them yields a more robust system. In this respect, a combination of overt and covert measures may provide optimal security because they help prevent counterfeiting and reassure end-users [21]. For example, using drug product serialization in combination with electronic pedigree greatly increased the level of security by the ability to verify both the product and the transaction integrity [22]. Some organizations such as Authentix and Nosco have made initiatives to combine the respective limitations and the potential of both Data Matrix and RFID, such that cases and pallets can be tracked with RFID tags, while medicines can be tracked with Data Matrix [23]. However, a multi-level approach may also result in additional costs as the technologies become more sophisticated and should be implemented based on the risk analysis of the drug to be counterfeited [22].

4. Applications of Luminescent Materials

4.1 Fluorescence
Luminescence is the emission of light from any substance and occurs from electronically excited states. Luminescence is formally divided into two categories, fluorescence and phosphorescence, depending on the nature of the excited state. In excited singlet states, the electron in the excited orbital is paired (of opposite spin) to the second electron in the ground state orbital. Consequently, return to the ground state is spin-allowed and occurs rapidly by emission of a photon. The emission rates of fluorescence are typically 10^4-5 s^-1, so that a typical fluorescence lifetime is near 10 ns (10 X 10^-8 s). The lifetime (τ) of a fluorophore is the average time between its excitation and its return to the ground state. It is valuable to consider an I-ns lifetime within the context of the speed of light. Light travels 30 cm or about one foot in one nanosecond. Many fluorophores display subnanosecond lifetimes. Because of the short timescale of fluorescence, measurement of the time-resolved emission requires sophisticated optics and electronics. In spite of the experimental difficulties, time-resolved fluorescence is widely practiced because of the increased information available from the data, as compared with stationary or steady-state measurements. Phosphorescence is emission of light from triplet excited states, in which the electron in the excited orbital has the same spin orientation as the ground state electron. Transitions to the ground state are forbidden and the emission rates are slow (10^-7-10^-8 s^-1), so that phosphorescence lifetimes are typically milliseconds to seconds. Even longer lifetimes are possible, as is seen from "glow-in-the-dark" toys: following exposures to light, the phosphorescent substances glow for several minutes while the excited phosphors slowly return to the ground state. Phosphorescence is usually not seen in fluid solutions at room temperature [24,25].

This is because there exist many deactivation processes which compete with emission, such as nonradiative decay and quenching processes. It should be noted that the distinction between fluorescence and phosphorescence is not visibly clear. Transition-metal-ligand complexes (MLCs), which contain a metal and one or more organic ligands, display mixed singlet-triplet states. These MLCs display intermediate lifetimes of 400 ns to several microseconds [26]. Fluorescence spectral data are generally presented as emission spectra. A fluorescence emission spectrum is a plot of the fluorescence intensity versus wavelength (nm) or wavenumber (cm^-1). Two typical fluorescence emission spectra are shown in Fig. 1. Emission spectra vary widely and are dependent upon the chemical structure of the fluorophore and the solvent in which it is dissolved. Some compounds such as perylene shows significant structure due to the individual vibrational energy levels of the ground state and excited states. Other compounds show spectra which are devoid of vibrational structure [27,28].
The processes which occur between the absorption and emission of light are usually illustrated by a Jablonski diagram. Jablonski diagrams are often used as the starting point for discussing light absorption and emission. They exist in a variety of forms, to illustrate various molecular processes which can occur in excited states. These diagrams are named after Professor Alexander Jablonski, who is regarded as the father of fluorescence spectroscopy because of his many accomplishments, including his descriptions of concentration depolarization and his definition of the term “anisotropy” to describe the polarized emission from the solution [25,26].

4.2 Jablonski Diagram

The processes which occur between the absorption and emission of light are generally decay to the lowest vibrational level of $S_i$. Furthermore, fluorophores generally decay to the lowest vibrational levels of $S_0$ (Figure 2), resulting in further loss of excitation energy by thermalization of the excess vibrational energy. In addition to these effects, fluorophores can display further Stokes’ shifts due to solvent effects, excited-state reactions, complex formation, and/or energy transfer [29,32].

4.4 Fluorescence Lifetime and Quantum Yields

The fluorescence lifetime and quantum yield are perhaps the most important characteristics of a fluorophore. The quantum yield is the number of emitted photons relative to the number of absorbed photons. Substances with the largest quantum yields, approaching unity, such as rhodamines, display the brightest emission. The lifetime is also important, as the lifetime determines the time available for the fluorophore to interact with or diffuse in its environment, and hence the information available from its emission. The meaning of the quantum yield and lifetime is best represented by a simplified Jablonski diagram. In this diagram we do not explicitly illustrate the individual relaxation processes leading to the relaxed $S_i$ state. Instead, we focus attention on those processes responsible for return to the ground state. In particular, we are interested in the emissive rate of the fluorophore ($r$) and its rate of nonradiative decay to $k_{nr}$. The fluorescence quantum yield is the ratio of the number of photons emitted to the number absorbed. The processes governed by the rate constants $r$ and $k_{nr}$ both depopulate the excited state. The fraction of fluorophores which decay through emission, and hence the quantum yield is given by: $[24,27]$

$$Q = \frac{r}{r + k_{nr}} \quad (1)$$

The quantum yield can be close to unity if the radiationless decay rate is much smaller than the rate of radiative decay, that is, $k_{nr} < r$. We note that the energy yield of fluorescence is always less than unity because of factors which affect either of the rate constants ($r$ or $k_{nr}$). For convenience, we have grouped all possible nonradiative decay processes with the single rate constant $k_{nr}$. The lifetime of the excited state is defined by the average time the molecule spends in the excited state prior to return to the ground state. Generally, fluorescence lifetimes are near 10 ns (Figure 3).

4.3 Stokes’ Shift

Examination of the Jablonski diagram (Fig. 2) reveals that the energy of the emission is typically less than that of absorption. Hence, fluorescence typically occurs at lower energies or longer wavelengths. This phenomenon was first observed by Sir G. G. Stokes in 1852 in Cambridge. These early experiments used relatively simple instrumentation. The source of UV excitation was provided by sunlight and a blue glass filter, which was part of a stained glass window. This filter selectively transmitted light below 400 nm, which was absorbed by quinine. The exciting light was prevented from reaching the detector (eye) by a yellow glass (of wine) filter. Quinine fluorescence occurs near 450 nm and is therefore easily visible.

Careful reading of this paragraph reveals several important characteristics of fluorescent solutions. The quinine solution is colourless because it absorbs in the UV, which we cannot see. The blue colour comes only from a region near the surface [24]. This is because the quinine solution was relatively concentrated and absorbed all of the UV in the first several millimeters. Hence, Stokes observed the inner filter effect. After passing through the solution, the light was “enfeebled” and no longer capable of causing the blue glow. This occurred because the UV was removed and the “enfeebled” light could no longer excite quinine. However, had Stokes used a second solution of fluorescein, rather than quinine, it would have still been excited because of the longer absorption wavelength of fluorescein. Energy losses between excitation and emission are observed universally for fluorescent molecules in solution. One common cause of the Stokes’ shift is the rapid decay to the lowest vibrational level of $S_i$. Furthermore, fluorophores generally decay to higher vibrational levels of $S_0$ (Figure 2), resulting in further loss of excitation energy by thermalization of the excess vibrational energy. In addition to these effects, fluorophores can display further Stokes’ shifts due to solvent effects, excited-state reactions, complex formation, and/or energy transfer [29,32].

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Single transition is forbidden by symmetry, and the rates of spontaneous emission are about 10^{-5} or smaller. Since k_{\text{R}} values are near 10^{-3}, quantum yields of phosphorescence are small at room temperature [32].

5. Security Ink: A Major Role in Anticounterfeiting

Invisible ink, also known as security ink, is a substance used for writing which is invisible either on application or soon thereafter, and which later on can be made visible by some means. These are majorly used in steganography, anti-counterfeiting features to documents and currency, authenticity indicators on packaging, brand protection and in classified communications. There is a wise variety of security printing inks. Based on the use of pigment, the inks can be classified as follows. The security feature may differ and is only known to the designer of the same. Based on the requirement the security ink may be visible or invisible under normal light conditions. Below diagram explains how visible and invisible inks work. Basically in visible inks, the pigments suspended homogeneously in ink vehicle reflect and scatter incident white light making it visible to naked eyes. In contrast, invisible inks carry either white pigments or not at all allowing the substrate do the reflection and scattering of incident light. Hence ink appearing invisible to naked eyes [33].

5.1 Pigments/Fillers

The function of pigments in a graphic printing ink is to provide color. For color inks there are some chemistries and parameters involved in using pigments. However as discussed before, pigments in conductive inks are replaced by micron or nano sized metal particles or precursors of metal particles. The main parameters in selecting the type of metal always depend on the conductive properties desired by the end product. Other parameters in selecting these metallic particles are application based, process used for deposition and method of curing of the conductive inks. For this study, conductive carbon and Graphene is selected as a primary pigment for the formulation of the ink [34].

5.2 Resin

The primary function of resins in ink formulation is to provide adhesion of filler material to the substrate along with cohesive adhesion of filler material. Resins can be a naturally occurring substances or man-made materials produced in non-crystalline solid or liquid form. Along with adhesion, the resins also provide crucial properties such as hardness and flexibility of ink film. Resins can be classified by various ways by source, solubility or by molecular weight. Source resins can be classified as natural or synthetic resins. Synthetic resins are prepared by polymerization of a single monomer or a combination of two or more monomers such as epoxies, acrylic, polyamides and vinyls. Based on the solubility, resins can be classified as water-based or solvent-based. Solvent-based resins are soluble in solvents such as alcohol or acetates. Water-based resins, as the name indicates, are soluble in water. Usually, in water based ink formulation, solution and emulsion resins have its own function and both should be present in the finished ink. Solution resins are low molecular weight acrylic resins, which are good for dispersing the pigments, while grinding on a three-roll mill or a bead mill. These solution resins are not very good film formers but they do provide hardness to the ink film; hence they are only used for grinding purpose. Emulsion resins are high molecular weight resins, which have very good film forming properties, are typically added to the ink formulation after the grinding stage. Depending on the application and end-user requirements, various combinations of these resins can be used. In graphic inks, all the properties except color depend upon the properties of the resin mixture. Commonly used resins are acrylics, alkyds, cellulose derivatives, rubber resins, ketones, maleics, formaldehydes, phenolics, epoxies, fumarics, hydrocarbons, isocyanate free polyurethanes, poly vinyl butyral, polyamides and shellac. Choice of resin for conductive ink is a very critical as is its compatibility with the solvent, fillers, and substrate should be taken into consideration [35,36].

5.3 Solvents

Solvents form the major part of the ink and are responsible for controlling the rheological properties of the ink, such as viscosity, flow and leveling properties and evaporation rate of solvents from the inks. The basic function of the solvents is to keep the ink in liquid form when applied to the image carrier until transferred to the substrate. Solvents are classified as volatile solvents or slow drying solvents depending on the speed of evaporation. The selection of the solvent depends upon various factors such as the printing process, press speed, absorptivity of the substrate, compatibility of other raw materials used in the process, toxicity, resin solubility and end use properties. Gravure and flexography printing processes run at high speed and the primary drying method is evaporation; hence require very highly volatile solvents such as ethyl acetate, isopropyl, or N-propyl acetate. On the other hand, offset and screen printing requires a high boiling point solvent such as hydrocarbons, which should be viscous and hydrophobic [37,38].

5.4 Additives

Additives are the minor components (up to 5% by weight) of ink, but greatly alter the physical properties of the ink. Plasticizers, wetting compounds, anti-setoff compounds, waxes, shortening agents, anti-skinning agents, and anti-pin holing compounds are some of the few additives used in the ink formulations. Additives, when used correctly, can greatly benefit the runnability and functionality of ink. Waxes are used to improve the rub resistance, plasticizers make the ink softer and improve its flexibility, adhesion and, to some extent, gloss. Wetting agents are used to decrease the surface tension of the vehicle and increase the wettability of pigments. Dispersing agents are beneficial for dispersing the pigment in the vehicle to avoid agglomeration. Additives can vary depending upon the process; shorting compounds are used in paste inks for lithography and screen printing to minimize print defects such as misting of the ink. Defoamers are used in aqueous liquid inks to reduce foam. Driers are a special kind of additive used in sheet-fed offset inks to increase their drying speed by oxidative polymerization. Some commonly used drying agents are manganese and cobalt. For conductive inks it is not advisable to use very many additives since they can affect the final conductivity of the ink. However, depending on the printing conditions and formulation, plasticizers can be used to improve the flexibility and adhesion of inks. Wetting agents could be useful since they decrease the surface tension of the vehicle and increase wettability of the pigments/fillers. Dispersing agents can be beneficial in conductive inks, since they avoid agglomeration and metal particles being heavy can settle and agglomerate [39,40].

5.5 Substrates

Substrate is an important component in Printed Electronics. Different properties of the substrates are critical and hence important for various applications of PEIs. Mechanical properties along with the surface properties of the substrate can affect the print quality and printability. Paper being a biodegradable product, has attracted a lot of attention of researchers and investors over the years. Paper, depending on gram mage, is used mostly for manufacturing bags, labels, cartons, or rigid packaging boards in graphic printing of packaging applications, while polymer films are widely used for manufacturing labels and flexible packaging, which require high barrier properties. Thus, paper is used where structural stability, absorbency and stiffness is desired while flexible substrates are used where high mechanical stability, smoothness and really good barrier properties are necessary. Compared to polymeric substrates paper is thermally more stable and more economical to use. Also, with the application of coatings, paper surface can be modified in terms of the surface wetting properties of the paper and its smoothness and porosity [41,42].

6. Recent Findings

It was reported that Cd-fluorescent inks have identical steady state emission properties, but they have distinctive and well separated emission lifetime which allows the authentication of security tags using exclusively fluorescent lifetime imaging. This can be applicable to variety of security protecting purposes and it can be extended to integrate fluorescent lifetime encoded CDs in multichannel bioimaging, high throughput flow cytometry and optical data storage [43]. A phosphorescent supramolecular polymer material was constructed and found that it facilitate fluorescence resonance energy transfer process via two component co-assembly strategy. On this basis, dual mode anticounterfeiting patterns have been successfully fabricated by Zhao Gao et al. via inkjet printing techniques [44]. Suresh et al. synthesised a novel and highly effective red emitting phosphor Pd^{2+} doped (1-11 mol %) lanthanum oxyfluoride (LaOF) nanoparticles as part of solid state light emitting diodes by a low temperature solution combustion method using Centella asiatica leaf extract as a reducing agent and identified that it could be used for visualization of latent fingerprints and anticounterfeiting applications [45]. Feiliang Chen and his co-workers prepared oxide QDs, which provides a low-cost way to prepare the unclonable fluorescent anticounterfeiting labels for versatile security primitive [46]. Shuyu Tian et al. doped CaAlSi3O8:Eu^{3+}/Eu^{2+} ions as a multiple emission centers for a three-path authenticating model [47].
7. Conclusion

Innovative techniques are pursued for the detection and avoidance of counterfeit in this modern society of electronic era. Recent reports say that Carbon dots are the most promising luminescent materials for anti-counterfeiting technology because of their high fluorescent quantum yield and nontoxicity. Cooperative supramolecular polymerization of photochromic fluorescent molecule represents an effective approach towards anticounterfeiting materials with enhanced security reliability, fast response and easy operation. Raising demand for security and explosion of creative counterfeiting methods posed a big challenge on humanity which need to be addressed with at most interest. Our society should move towards inventing higher level of security system and methodology to combat counterfeiting industry protect the society from emergence of counterfeiting in any kind of documents and products is mandatory in order to stay one step ahead of criminals. Future trends in Security Printing are getting on the way with the new nanoprint technologies, printed electronics and revolutionary inventions in digital printing. These techniques and many more are yet to grow as a new security printing features in order to protect the public from illegal activities and bring in more safety and secure feature for printed documents too.

References

[38] M.L. Allen, Nanoparticle sintering methods and applications for printed electronics, Aalto University, Canada, 2011.