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Perspectives

# Particles with an identity: Tracking and tracing in commodity products

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ABSTRACT

Identity is value. Knowledge of the origin, processing and supply chain of a product determines its market price. As particles can be used to carry very unique information (size/shape/optical/electronic/chemical), and at the same time be of extremely small dimensions and invisible, powders are an ideal choice to be used as a taggant — as an information carrying entity that is added to another product to identify it. Recent advantages in synthesizing and analyzing unique features of particles address the growing need of identifying products in the product life cycle. This is illustrated by particulate tracers, which are of non-toxic composition and can be uniquely analyzed at part per billion (ppb) concentration ranges in fully automated procedures. It is envisioned that these technological advances in powder technology will help to build a global materials identification system, guaranteeing product value and increasing manufacturer responsibility and liability.



## 1. Unique identifiable particles

Counterfeits, alterations and unlawful additives in products challenge all kinds of industries ranging from automobiles, luxury goods to pharmaceutical industries. The global market value of counterfeit goods is estimated to around 500–600 billion USD [1]. Tremendous possibilities of counterfeiting are given by the increasing complexity and dynamics of the global market. Products pass through a large and intransparent supply chain. In order to distinguish genuine products from false ones a direct assigned product identity is needed. While every human being has a genuine fingerprint, enabling direct and near to unforgeable identification, common product identifications currently consist of visible, printed authentication systems (e.g. barcodes, holograms, watermarks) or Radio-Frequency Identification (RFID) chips. These systems are presently only located on the final product or even only on the outside product packaging, which neglects the requirement of material identification from the raw material to intermediates to the final product along the material life cycle. Furthermore, the implementation of identification in a broad range of materials is not trivial. For instance, how can a bulk polymer be labeled? A direct and individual barcoding of polymers with barcoded particles would facilitate to track and trace each single product processing step in a supply chain spreading the global market (Fig. 1). As this research field is under fast scientific development, and at the same time is being transferred to commercial application, this perspective article gives a combination of scientific strategies and product fabrication challenges (i.e. IP literature). It also has to be noted, that some of the described approaches have already been implemented into the market (e.g. Polysecure GmbH, GenuineID, SICPA Holding SA, 3S Simons Security Systems GmbH).

## 2. Strategies to give particles an identity — the barcode

In a classic implementation a barcode consists of a sequence of space and vertical lines (= bars) varying in their widths, which represent a unique code. Unlimited numbers of codes can be generated by modifying the combination of space, bars and widths. The same concept can be transferred to particles carrying a unique identity using coding elements. Methods to encode particles have been investigated extensively in the area of life sciences in order to simultaneously carry out a very large number of bioassays in gene expression, drug screening and clinical diagnostics [2]. In these assays multiple independent reactions take place at the same time in the same solution. Each unique identifiable particle acts as an individual chemistry lab that independently identifies and tracks the potential compounds by reading out the corresponding code. The gained knowledge of particle-based encoding methods can also be translated for the use as product identification measure. Compared to purely molecular approaches, the use of particles brings several main advantages: Particles can be utilized to host the encoding (molecular) elements making these more resilient; a tracer particle may be considered as a self consistent unit within which various encoding elements can be simultaneously introduced; and the concentration of a molecular element within a tracer particle can be kept high, facilitating read-out, still keeping the overall concentration of the (expensive) molecular element in the final product low. The currently available particle based barcoding techniques can be divided into

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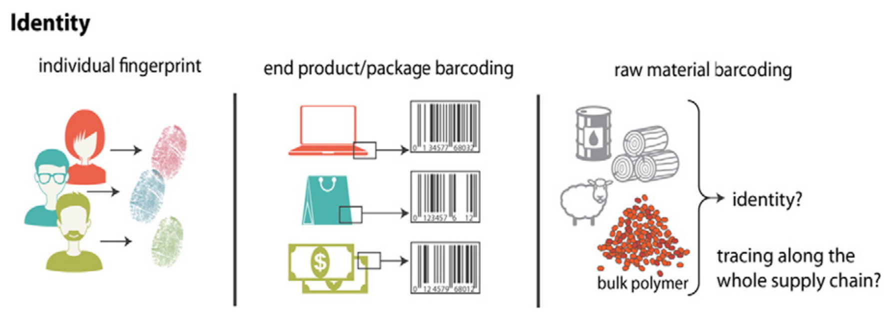


**Fig. 1.** Illustration of identity giving systems. Human beings carry their unique identity in their fingerprint and their DNA within each single cell. Products are commonly only labeled on their package with a barcode to give their identity, which provides no identification of raw materials or individual parts.

three main strategies: (a) utilizing the pattern or shape of the encoded particles (= graphical encoding), (b) making use of unique properties [2,3] (optical, spectrometric or electronic) of molecules or nanoparticles, which are attached or incorporated into the carrier particle and (c) applying unique chemical tags.

## 3. Graphical encoding strategies

The usual supermarket barcode is an example of graphical encoding. Translated to particles, the individual codes are deciphered by the pattern or shape of the particles themselves. The coding elements can be modulated by various techniques ranging from simple arrangements of colored polymer layers [4], striped metal nanowires [5] to selective photobleaching [6]. 3S Simons Security Systems GmbH has developed color-coded microparticles based on stringing together melamine alkyd polymer layers of up to ten different color coatings (Fig. 2a). The variation of the color arrangement in the 8–100 μm sized particles allows the formation of 4.35 billion different codes [7]. For the identification of the codes a pen microscope is sufficient. A second method writes the barcode on nanowires based on sequential electrochemical deposition of metal ions (e.g. $Ag^+$, $Au^+$) into mesoporous alumina membranes, followed by particle release (see Fig. 2b) [3,5,8]. The discriminability of specific optical reflectivity results in metal striped wires/rods, where the stripes are modifiable in thickness, order and number as well as the type of metal and the overall length of the rods. By varying these parameters a nearly unlimited number of individual codes can be generated. The read-out of the codes is accomplished by light-microscopy and recognition software. For reliable optical detection a minimal stripe length of ~500 nm is needed, whereas the overall particle length is 1–50 μm. For example, a 5 μm particle containing two metals with ten stripes yields 528 individual codes. An alternative to this approach is the use of selective photobleaching. Here, the pattern is written onto homogeneous, fluorescently dyed microspheres by a photo-induced process, which leads to a local loss of the fluorescent properties (Fig. 2c) [3]. With this method any geometry or symbol can be generated with different bleaching levels by using adapted confocal scanning laser microscope (CSLM) as described by Braeckmans et al. [6] and identified by standard confocal microscopy.

## 4. Optical encoding strategies

Most of the encoding methods described in literature utilize molecules with unique optical properties as coding elements. Particles act as carriers and the molecules are either loaded into or onto the particles for increased stability and simplified identification [2]. By far the most commonly used coding elements are fluorescent organic dyes, which are easily produced and abundantly present in many laboratories [9]. The intensity of each dye is detected by a simple spectrometer and/or flow cytometer to quantify the corresponding intensity ratio in order to reveal the barcode. A prominent example of fluorescent encoding was developed by Luminex Corp (Austin, TX), where two dyes are incorporated at ten different concentrations to obtain 100 unique encoded particles.

With the development of quantum dots (QDs) several problems related with fluorescent molecules have been overcome [10,11]. Quantum dots are semiconducting inorganic nanocrystallites with unique photoluminescent properties, which were successfully incorporated into polystyrene particles for optical encoding [12,13]. Their narrow and symmetric emission spectrum (spanning from UV to near-infrared) can be easily tuned by changing the particle size. The detection is conducted by flow cytometry and/or photo spectrometry. A realistic system consists of five to six colors with six intensity levels to obtain 10,000–40,000 unique codes [14]. In contrast to fluorescent organic dyes, QDs have a broad absorption providing simultaneous excitation of various QDs. They are also brighter and less prone to photobleaching. Limitations to the widespread application of QDs is their relatively low chemical stability [15] and the cytotoxicity of the most commonly used materials (e.g. CdS, CdSe, CdTe).

Alternatively, the unique optical properties of rare-earth ions can be used for particle encoding. In a potential implementation, oxide nanoparticles or glass rods are doped with rare-earth ions to generate unique barcodes [16–18]. The use of rare-earth elements has significant advantages, they are generally considered nontoxic, highly photo-stable and are excited by infrared or ultraviolet photons. In order to overcome the limitation of code generation from overlapping spectra, Dejneka et al. developed tags containing patterns of different rare-earth elements (see Fig. 2f) in ribbons [19]. This approach can generate $>10^6$ unique codes that are identified using a UV illumination system and an optical microscope.

The fluorescent lifetime is a further optical property, which can be used to create optical codes embedded into particles. This temporal code can be built around the tunable lifetime of lanthanide ions or rare-earth doped nanocrystals ranging from micro to milliseconds [20]. The identification the luminescence decay can be measured by orthogonal scanning automated microscopy (OSAM) systems. Utilizing a combination of color, intensity and lifetime Lu et al. recently generated 10,000 distinguishable codes [21].

## 5. Chemical sequence encoding strategies

Besides unique photo-luminescent properties, molecules can have additional features, which make them suitable for coding. In the field of chemical encoding, chemical tags are used to build up the code [22]. The detection of these coding elements is based on identifying the structure or sequence of the molecules. A variety of molecular tags are commonly used for combinatorial libraries, such as haloaryls [23], peptides [24] and oligonucleotides [25]. The use of DNA as molecular tag has tremendous advantages as nearly an unlimited number of codes can be generated and detected at high precision.

DNA is the natural way to store information (= genetic constitution) of all known life forms. This polymeric biomolecule consists of four nucleobases (adenine (A), cytosine (C), guanine (G) and thymine (T)).