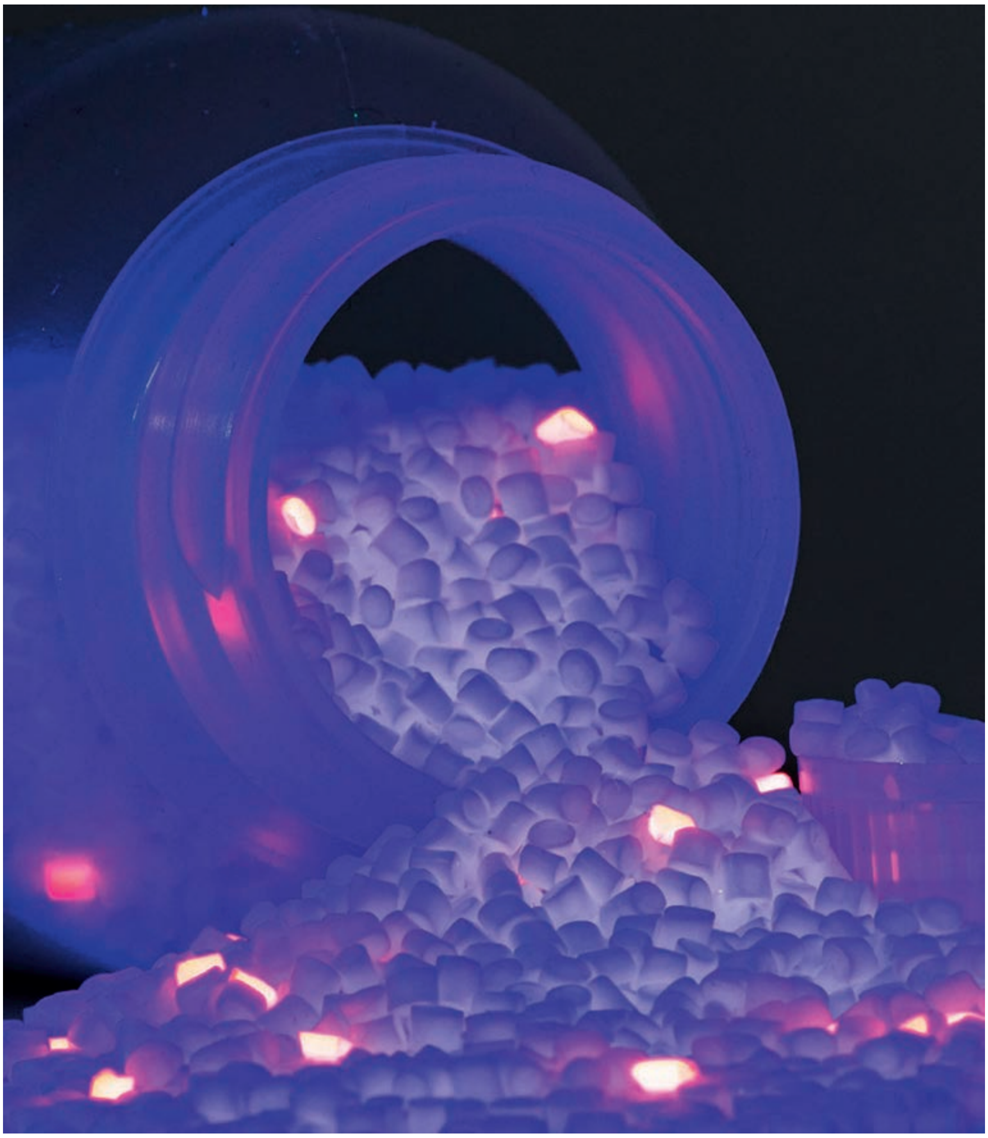
Improved Sorting of Plastic Waste with Luminescent Pigments

Luminous Markers instead of Holy Grail

The HolyGrail 2.0 Initiative aims to improve the sorting of plastic waste. For this purpose, digital watermarks containing information on packaging type, material, and usage will be applied on products. However, the method also has certain drawbacks. Here, luminescent pigments provide an alternative that is permanent and can withstand several processing cycles.



Marker masterbatches enable different information to be embedded in plastics. This can be used to improve the recycling circle. © Leuchtstoffwerk Breitungen

Meanwhile, the use of near-infrared sensors to separate plastic waste according to color and material works quite well. Additional image processing systems coupled with corresponding AI detect the shape of an object to provide additional information for classification of the respective plastic packaging. Further improvements in sorting are expected from the HolyGrail 2.0 Initiative. Hereby, a method was developed for applying so-called digital watermarks all over the object's surface, in which information on plastic type as well as usage (for example food or non-food). Subsequently, the watermarks can be detected by means of suitable camera systems.

Two methods are distinguished: print film-based (2D microdots) process and mold-based (3D microspikes) process. Created in this way, the microdots/microspikes are applied with a coded separating distance and cover an »

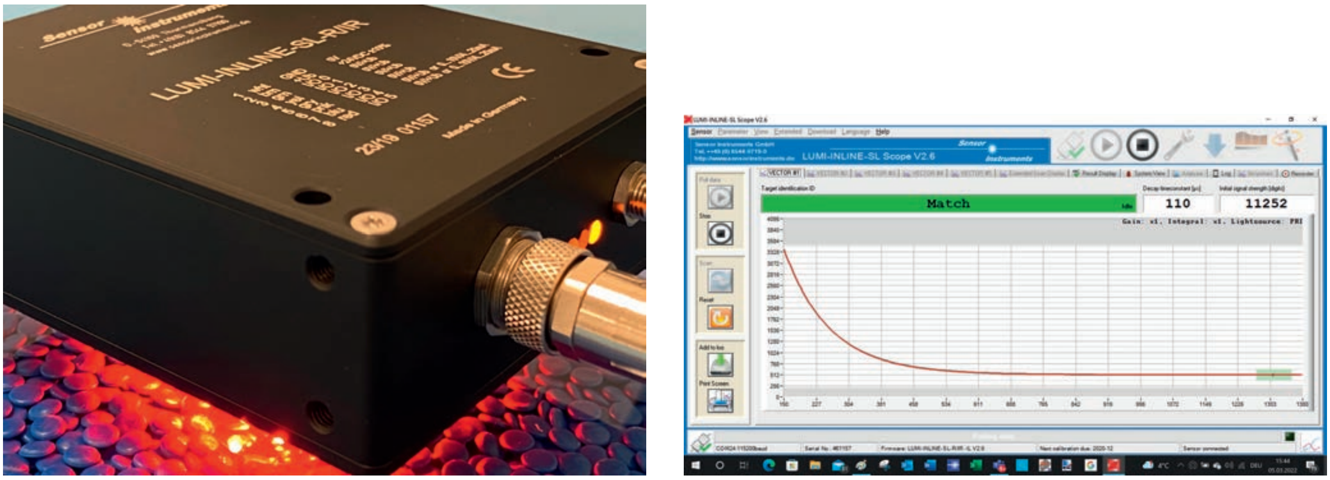


Fig. 1. The luminescent pigments are stimulated by light, and their emissions measured. Evaluation software is used to visualize the results.

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area of 22 x 22 mm on the respective object, thereby forming the digital watermark. The watermark is then repeated over the object's entire surface.

Difficulties of HolyGrail 2.0

However, with such a contrast-based optical approach, light-colored plastics in particular are likely to represent a coding legibility problem for the vision systems. Moreover, deformed and also soiled material – which moves past the cameras at about 3 m/s and a distance of a few hundredths of a millimeter – must be expected in the sorting operation. In addition, code detection will presumably be impossible after the objects have been shreddered. During extrusion at the latest, the digital code will melt, and the information stored on the object is inevitably lost. As a result, differentiation between food and non-food will then no longer be possible.

Furthermore, due to manufacturing processes and component geometries, the application of digital watermarks is likely to be difficult on many plastic products. The complexity of some components as well as their surface structure, e.g. fabric in flexible packaging, foams or textiles, will make it almost impossible to apply a 2D or 3D watermark. Therefore, complete monitoring of the plastic circuit by means of digital watermarks is unlikely.

Processing-Resistant Permanent Markers

In order to monitor the recycling process section immediately before or after extrusion of the recyclate, a permanent, processing and temperature-resistant marking or coding must be embedded into the plastic matrix. This permits the gap in material monitoring to be closed, in particular regarding identity, origin, and quality. Typically, the marking consists of phosphorescent inorganic microparticles. Because of their inert properties and size, their introduction in practically all plastic parts will be possible, including polyamide (PA) fibers as well as plastic wires and tapes with a thickness of a few hundredths of a millimeter.

Advantageous hereby is that the marker can be integrated in the plastic material without intervening in the established production processes. Therefore, it is advisable to fall back on established processes in plastic production. As a result, marker-based masterbatches (**Title figure**) were developed by Gabriel Chemie in recent years under the trade name TagTec (Taggant Technology). They ensure integration of the information into the plastic matrix by means of the marker. The markers are precisely matched to the respective application and have no influence on other properties of the final product.

Robust Luminescent Pigments

TagTec markers are based on inorganic luminescent pigments developed and produced by Leuchtstoffwerk Breitungen. Thanks to their inorganic nature, the pigments are very stable and insensitive to chemical and physical influences. This means that plastic products can be identified and recycled even after a long service life with contamination and heavy loads.

With a particle size between 2 and 8 µm, the markers are invisible for the human eye, and due to their small size do not change the product's properties.

Another advantage of markings based on these luminescent pigments is their toxicological safety in numerous materials. Some of them even have food contact approval and meet the high requirements of the ÖkoTex standard. Via masterbatches, the pigments can be integrated into every plastic product without problems, where they are firmly embedded in the matrix. They were developed specifically for high efficiency in combination with good resistance plus easy processability. For efficient marking, highly luminous markers must be used because – for economic reasons – their concentration must be very low for widespread use in plastic recycling. The markers can be produced in large quantities and always in the same quality. Therefore, the spectral answer of TagTec pigments, e.g. for the food industry, is always the same and can be distinguished permanently and safely from other TagTec markings.

Fluorescence or Phosphorescence

Apart from the markers' efficiency, economic use of the system is influenced decisively by detection performance. Therefore, the marker-detecting sensors from Sensor Instruments were optimized accordingly. Detection of inorganic luminescent pigments is based on two material properties: fluorescence and phosphorescence.

With fluorescent pigments, the material is stimulated with light of a particular wavelength, e.g. in the UVA range, and subsequently the optical emission of the particles is measured. Normally, it lies in the higher wavelength regions, about in the visible range. After switching off the stimulating light, pigments with phosphorescent behavior exhibit an exponential decrease of the so-called secondary light (**Fig. 1**). One characteristic value for this is time constant Tau. If the fluorescence of a marker in a certain wavelength range is measured simultaneously with the stimulation, optical filters are required to separate stimulation and emission. But apart from the emission intensity in a spectral range, the random distribution of marker particles in a surface area can also be used as information.

If the surface of a plastic part is illuminated with a marker-specific stimulating light, and the fluorescent image is viewed with a suitable camera, the marker particles appear like a starry sky, as shown in **Figure 2.** The distribution of luminous points detected in this way can be coded mathematically, stored in a data cloud, and used for the authentification of individual products. Hereby, the counterfeit protection does not result from the marker's luminous intensity or emission characteristic, but from the random distribution of the selected luminous points. Sensor Instruments uses this method under the trade name Lumi-Star.

The use of phosphorescent markers is advantageous for material identification of plastics, because it requires no database. In fact, more relevant for detection is that the markers used do not influence each other optically. With all phosphorescent markers, stimulation is carried out with a very short but intense and narrow-banded flash of light. This pulse of light creates an afterglow of the phosphorescent marker type that is receptive for this wavelength. The intensity (Int) of the afterglow informs about the quantity of markers in the respective product, while the decay time (Tau) is an indication of the corresponding marker within a marker family. Defined by the time constant (optical echo), the decay duration is marker-dependent and lies somewhere in the range between 100 and 1000 µs. Markers can be determined both in the packaging, after the flakes have been shreddered, and also in the pellets after extrusion. For this purpose, Sensor Instruments offers Tau detectors from the Lumi-Tau family.

Four Application Areas for the Batches

Developed specially for the TagTec system, the marker masterbatches are to ensure a specified detectability combined with cost-optimized implementation. Principally, the TagTec systems can be divided into the following areas:

The **product authentification area** encompasses the application areas of product identification and product safety. This permits simple to complex tasks to be implemented – from low to very high safety levels as well as information transfer by means of marker wordings. In accordance with the required safety and function levels, these customer-specific marker wordings permit tailored solutions to be represented. They can be used in different processes, including recycling and circular economy applications.

The **material detection area** (Tau process) describes all marker wordings that are used specifically for the procedure described above. They can »

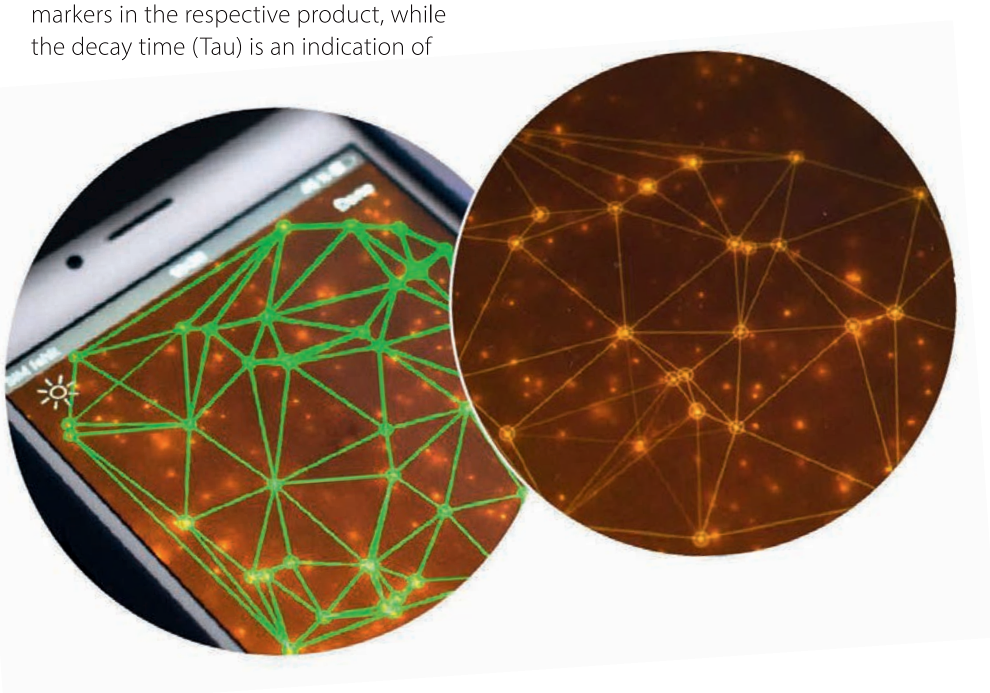

Fig. 2. By selecting certain marker points (marker set), an individual product marking can be defined. The set is stored, and can later be used for identification.

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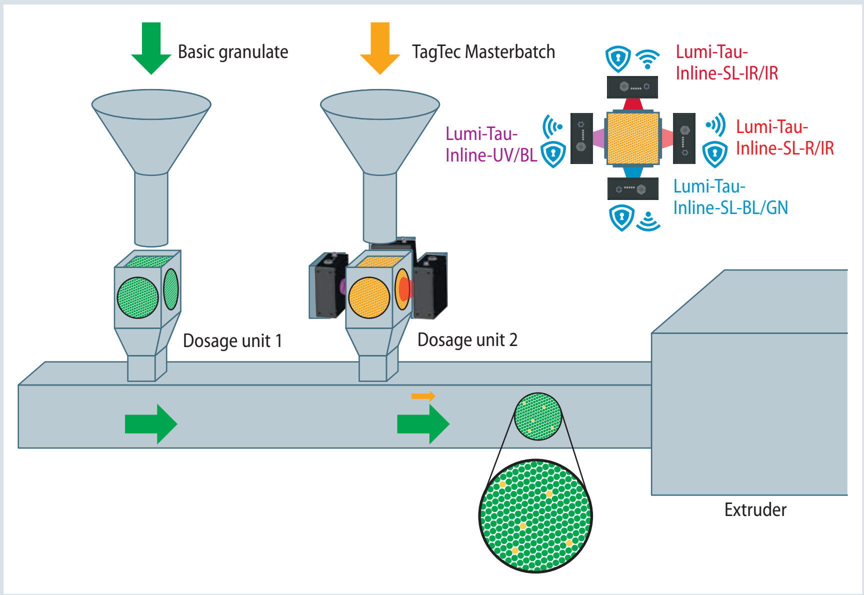

Fig. 3. The masterbatches are added during the extrusion process as usual. Hereby, sensors ensure that the correct marker and the right quantity are involved. Source: Sensor Instruments; graphic: © Hanser

be used for closed material detection, independent of location and shape, and also for determining the amount of recycling material in a plastic product.

The **individual detection area** (Star process) encompasses all application-specific marker wordings that have been optimized in different wavelength ranges for the Star code sensors.

Moreover, by means of the TagTec technology it is possible to implement various additional **functional aspects**. These include e.g. the measurement of stretch or material wear, dosing monitoring in correlation with special additivation of a plastic, and the design of different measurement, control, and assembly applications. Also a deposit system can be implemented in different ways.

The TagTec masterbatches also permit individual functions or a combination of different functions to be realized. This is possible, because different marker systems can be combined. They do not influence each other negatively.

All of the marker versions used are invisible for the human eye, are tasteless and odorless, consist of inert inorganic particles, are high-temperature, shear, and UV-resistant, and do not influence the quality and mechanics of a component. Consequently, there is no reason why they should not be used widely in the plastics processing industry.

TagTec masterbatches can also be produced as combination masterbatches with colorants and additives. In many cases, and in particular for plastics recycling, this offers a significant added value, because colorants and additives are introduced at the latest during the subsequent compounding process. Apart from material type and recyclate amount contained in a product produced in the second loop, in future this will also enable e.g. the amount of stabilizer added during material preparation to be detected. Particularly in terms of material quality in future recycling circles, this is an important aspect.

Basically, use of a masterbatch is as follows: the first life cycle of a plastic packaging starts e.g. with a virgin polymer plus a corresponding TagTec masterbatch, which has been selected to suit the respective application area. By means of the dosing units, it is now possible to determine the marker concentration in the packaging. Corresponding sensors check whether the marker is correct and has the right concentration (**Fig. 3**). Following the subsequent extrusion operation, the marker particles are present in random positions in the plastic matrix. By means of the Star camera system, an individual code is detected for every plastic packaging. An area of 10 x 10 mm in a previously defined position on the packaging is then illuminated with light of the matching stimulation wavelength, causing the marker particles to fluoresce, whereby they exhibit an individual „star pattern". The system then stores the constellation of the luminous particles for every packaging type in coded form (**Fig. 4**).

Supply Chain Monitoring with Blockchain

The Tau technology permits a check of whether the correct marker in the matching concentration for the respective product group has been used. The data can be transferred to the supply chain monitoring software in coded form. If necessary, blockchain technology can be used to track the product group over its entire life cycle. As a result, monitoring by means of inline or mobile equipment is possible at different points in the supply chain. Hereby, the Tau units can be used to monitor the group code, while the Star devices determine the matching individual code of the respective object.

After its first use, the plastic packaging usually reaches the recycling plant in a deformed state. Here, the product stream is pre-sorted with the help of color and NIR cameras. Subsequently, Tau detectors search for objects with

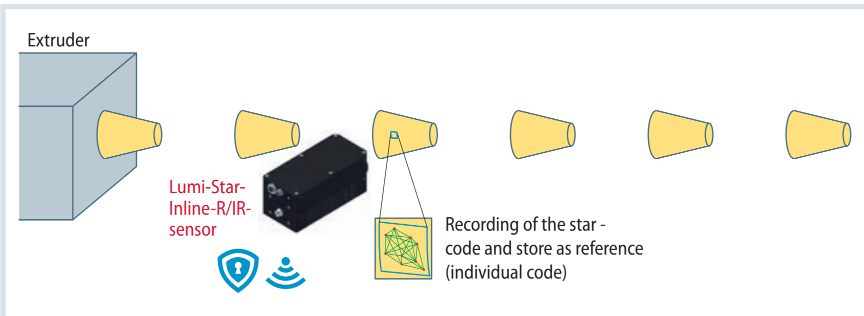

Fig. 4. The stored star pattern is specific for every packaging. Source: Sensor Instruments; graphic: © Hanser

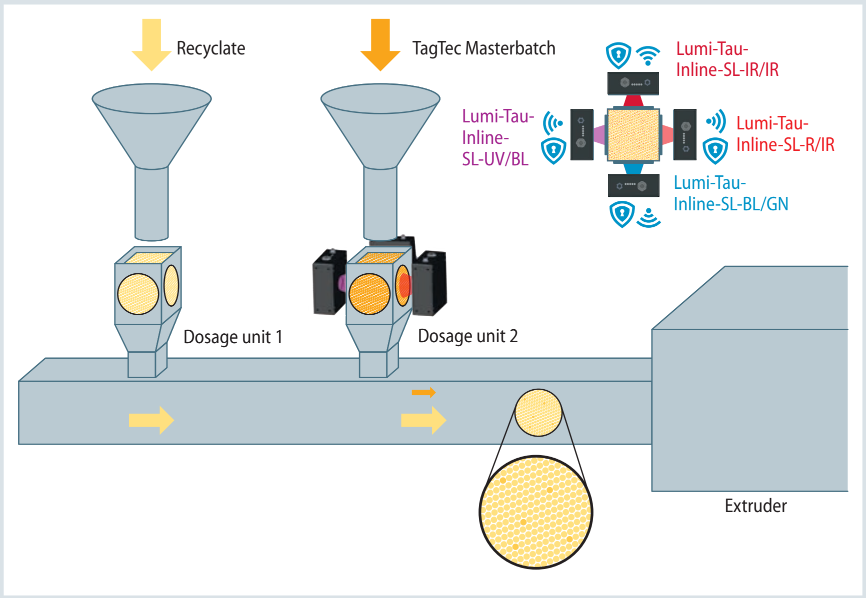

Fig. 5. When using recyclates, the masterbatch quantity is adapted to the concentration of TagTec markers contained in the recyclate, thereby ensuring that this is matched precisely to the manufactured product. Source: Sensor Instruments; graphic: © Hanser

TagTec markers. Depending on the detected marker type, the corresponding objects are sorted or removed from the remaining product stream. After shreddering and also after extrusion, the amount of the respective TagTec material can be checked with the Tau reader. Subsequently, a second production process can start, but with recyclate instead of virgin material (**Fig. 5**). With the help of the two dosing units, the marker quantities are then proportioned accordingly.

TagTec masterbatches and the corresponding Tau sensors enable the use of the respective plastic to be monitored in all sections of the product's life cycle. The technology is also suitable for small objects such as plastic wires, tapes, and tubes, as well as complex component geometries, textiles, and foamed materials. The use of Star sensors permits further definition of every individual object. However, this requires the creation of a reference code on the corresponding object, with subsequent transfer of the coded data to the cloud.

Combining Marker and HolyGrail

Use of digital watermarks from the HolyGrail 2.0 Initiative requires rework of the injection mold or printing roller used to produce the respective objects. Usually, the injection molds are reworked using a laser texturing process to engrave a corresponding code. Hereby, it is an individual code regarding the mold, but not regarding the respective object. This outlay is not required if markers are used. Due to the different application and embedding procedures as well as the different detection methods, the TagTec marker method can also be combined with digital watermarks. As no mutual negative influences are to be expected, the plastics' life cycle can be tracked even more precisely. ■

Info

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