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Sealing Technology –
Challenges accepted!

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Enhancing sealing element security: Quantum dot marking Solutions of NBR and TPU sealing elements

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This study addresses the rising need for product security against counterfeiting by utilizing luminescent labels with nanoparticles for marking. Integrating quantum dot (QD) marking solutions into NBR and TPU used in hydraulic and pneumatic sealing elements enhances product safety, traceability, and sustainability while reducing costs. The research examines the optical and mechanical properties of QD-infused elastomers, both post-abrasion and aging. Special sensors and smart algorithms convert optical readings into electronic signals for verification against reference data, ensuring authenticity. The study demonstrates the effectiveness of QD marking in enhancing the security of sealing elements and combating counterfeiting in critical industrial systems.

1 INTRODUCTION

Quantum dots (QDs) are semiconductor crystals with a nanocrystalline structure, a diameter of approximately 2–10 nm, and good optical properties, such as easy wavelength control based on the controllable size and narrow full width at half maximum (FWMH) of the emission wavelength. The optoelectronic properties of QDs are determined by the size of the crystal, which is described as the quantum confinement effect. In bulk semiconductors, the energy levels overlap because of the countless adjacent atoms, thereby forming an almost continuous energy band. Owing to the overlaps, the continuous energy band decreases gradually, and the bandgap increases with decreasing size of the semiconductor material. Therefore, a discrete energy level occurs when the size of the semiconductor material becomes smaller than the exciton Bohr radius, and the electrons inside the semiconductor are confined to this energy level. As a result, the energy gap of QDs and the wavelength of the light emitted can be controlled by changing the particle size [1].

With the increasing development of global commerce, the dangers of counterfeit goods cannot be underestimated. In particular, counterfeit medicines pose a significant threat to patient safety and public health, and counterfeit high-tech products cause significant economic losses. The urgent anticounterfeiting demands in the global economy and human health push people to develop reliable anti-counterfeiting technologies. Currently, the graphical anti-counterfeiting labels that combine easy detection and rich anti-counterfeiting features are one of the best answers to the problems [2].

Counterfeiting and forgery is a global problem that causes significant financial damage and poses security threats to individuals, companies, and society as a whole. Over the past decades, counterfeit products have spread from daily consumer goods to medicines and high-tech products. Although majority of the products are protected by an anti-counterfeiting technique, the global economic loss of counterfeiting has been increasing annually and estimated to reach 1.7 trillion US dollars in 2015 [3].

Quantum dot technology has been widely used in our daily life, including energy, solar cells, displays, biomedical and biological applications.

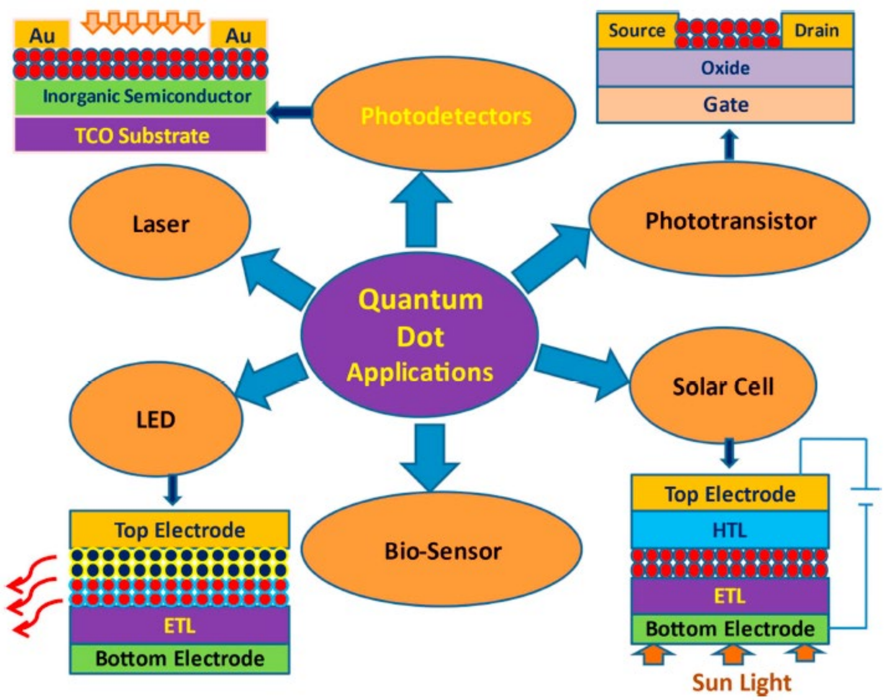

Figure 1.1: Device applications of quantum dots in photodetectors, LED, solar cell, phototransistor, laser and biosensor

Kastaş, integrated product security in mind, has aimed to adopt the Quantum nanodot marking solution to its products through an innovative approach. To ensure end-to-end product tracking and secure product authenticity, a series of R&D studies have been conducted. This work is expected to enable real-time verification of products through previously unseen technology applications, smart sensor systems, and intelligent algorithms, preventing revenue losses caused by counterfeiting. Fundamentally, this study will guarantee product authenticity against potential problems in the field.

To summarize QDots technology: Quantum Labels are produced using different types of QDots, either together or separately. These quantum labels generate a series of codes by utilizing the optical properties of the quantum dots, which are read and converted into signals by specially manufactured sensors and intelligent algorithms. This signal is compared with reference data for verification. In the continuation of the study, the mixing ratios of raw materials with nanoparticles and the comparison of sensor values with reference values will be conducted.

2 MATERIAL AND METHOD

2.1 Application of Qdots on Kastaş Raw Materials

In this study, Qdots applications and measurements were performed on elastomer rubber and thermoplastic raw materials from Kastaş. Experiments were conducted using five different raw materials with water-based, xylene-based, ethylbenzene-based, and benzyl alcohol-based Qdots. Based on the measurement results from these experiments, various studies were conducted concerning the amount of marker used. Mechanical tests were performed on the raw materials at the concentrations where the marker was detected. It was demonstrated that the addition of Qdots to the raw materials did not affect their mechanical properties.

2.2 Labeling Studies

Labeling studies were conducted with markers on rubber elastomer samples, including FKM, NBR, HNBR, VMQ, and thermoplastic polyurethane, which were prepared using Kastas's compound mixtures.

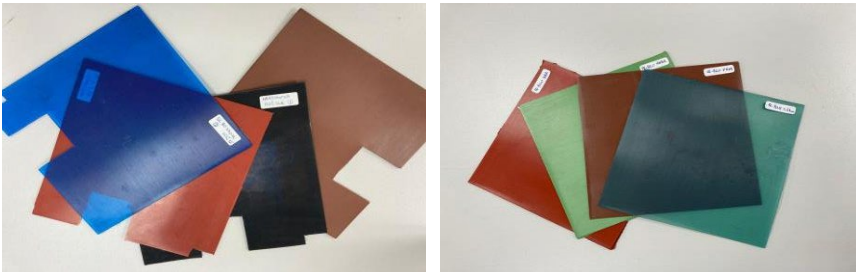

Figure 2.1 : Samples of Raw Materials with Qdots (as plates)

Figure 2.2: Products with Qdots

Classification of Sealing Element Raw Materials and Added Qdots:

- Water-based QDots 1: 150000 ppm
- Water-based Qdots 2: 250,000 ppm

Pu

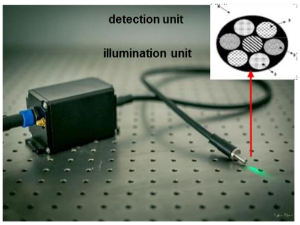

Figure 2.3 Qdots Reading Device

- Xylene-based QDots: 500 ppm
- Ethylbenzene-based QDots: 500 ppm
- Xylene-based QDots: 6450 ppm
- Ethylbenzene-based QDots: 12000 ppm
- Benzyl alcohol-based QDots: 28000 ppm

NBR
HNBR
FKM
VMQ

2.3 Measurement Methods

After preparing the mixture, it is necessary to determine the measurement method.

	Surface Measurements	Liquid (Extraction) Measurements
Advantage	Quick check capability, portable device for fast and on-site measurement	More precise measurement capability with lower doping amounts, independent of sample geometry, contamination, and deformation
Disadvantage	Low measurement sensitivity: • Sample geometry and operator effect • Influence of surface contamination and physical changes (deformation) • High marker concentration requirement due to small area reading Sample holder requirement specific to the product	Additional processing, infrastructure, and time requirements: The product with the customer complaint must be sent to the laboratory for liquid measurements

Based on the above table, the appropriate measurement method for both the thermoplastic product PU and the elastomer group products (FKM, NBR, HNBR, VMQ) has been determined as follows:

- For the PU product, it was decided to use surface measurement.
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- For the elastomer product group, due to surface and color parameters, effective reading with an optical reader was not possible. Thus, it was decided to dissolve the samples with a suitable solvent before measurement.

2.4 Results of Studies with Water-Based Particles

- Using a special sensor for Qdots emitting in the blue region, surface measurements were performed on the plates.
- Initially, water-based Qdots 1 (150,000 ppm) were added to PU samples at a concentration of 2.5 ml per 1 kg of the compound.

- To minimize the amount of water introduced into the polymer and preserve material properties, a more concentrated product, water-based Qdots 2 (250,000 ppm), was used.
- Other particle concentrations used: 1 kg of material with 1.250 ml marker, 0.625 ml marker, 0.250 ml marker, and 0.125 ml marker.
- Initial quality control test results at Kastaş indicated that a concentration of 0.125 ml marker per 1 kg of material was suitable.
- In summary, it was found that water-based Qdots are appropriate for marking PU samples, and surface measurement methods are effective for their detection.

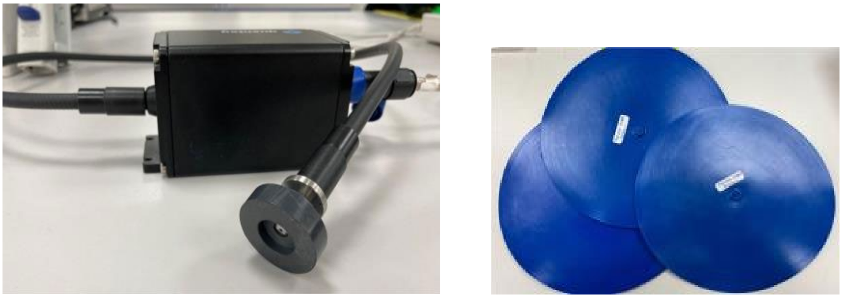

Figure 2.4 Qdots Reading Device and PU Qdots Plate

Due to low precision and high influence of other factors (sample geometry, contamination, etc.) in surface measurements, the labeled product must be at least 2 times the unlabeled reference product.

Thus: $S_{product} \geq 2 \times S_{ref}$

1 kg Material - 0,125 ml Marker Trial
S_{PU}/S_{ref} : 4.7 → Marked Product ✓

2.5 Results of Studies with Solvent-Based Particles

- Experiments were conducted with xylene-based QDots and ethylbenzene-based QDots on four different rubbers (FKM (Brown), NBR (Black), NBR (Brick), VMQ (Blue)). The doping ratio was 2.5 ml per 1 kg of compound. However, due to the active marker concentration in the sample being 500 ppm, readings could not be taken with either method.
- Dosing studies were conducted with benzyl alcohol-based QDots at a ratio of 2.5 ml Marker per 1 kg of compound.
- Surface measurements of samples prepared with solvent-based markers at a ratio of 2.5 ml Marker per 1 kg of compound did not yield reliable results.

- Subsequent liquid measurements with an appropriate solvent showed that the samples were labeled and successfully distinguished from the reference.

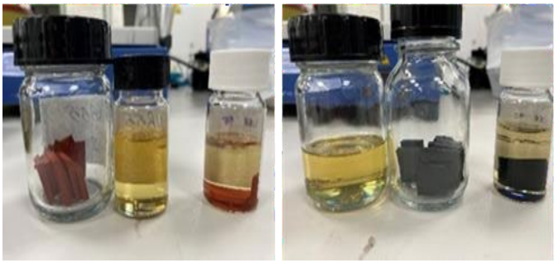

Figure 2.5 NBR 55 (Nitril Butadiene Rubber) and NBR 90 (Nitril Butadiene Rubber)

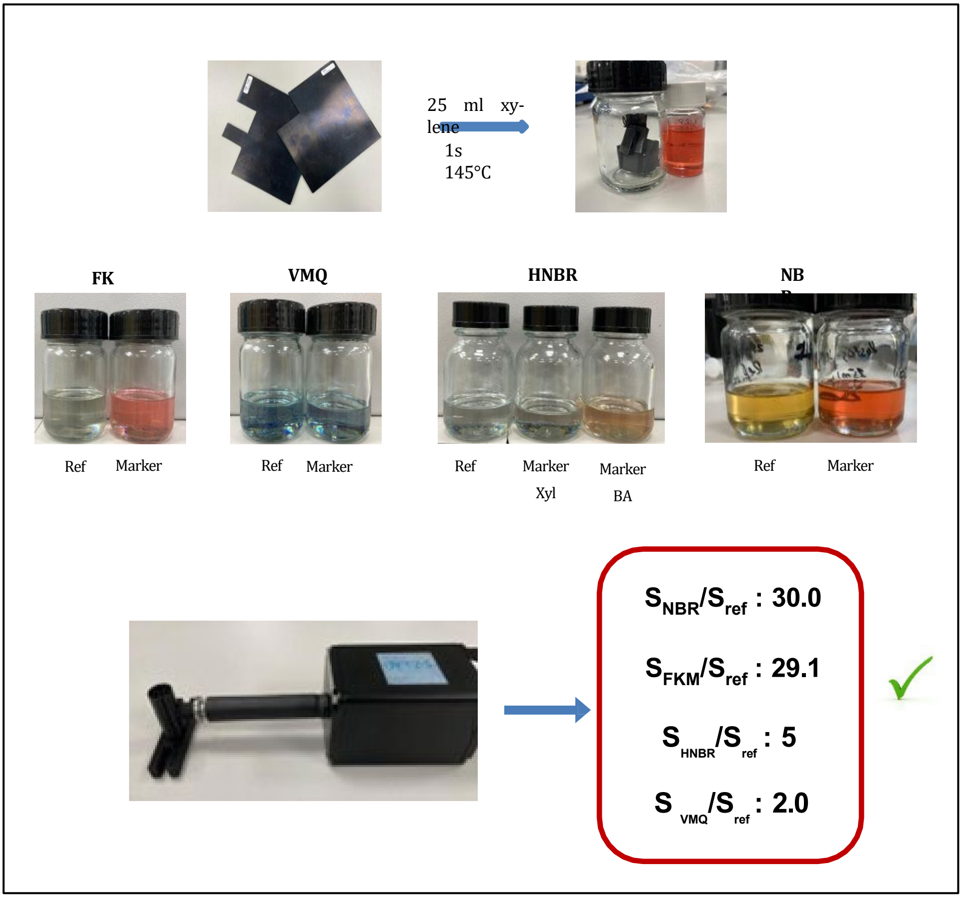

Figure 2.6 Detail of Solvent-Based Particles

3 CONCLUSION

- Quantum Labeling is technically applicable for PU, NBR, FKM, VMQ and HNBR rubber structures.
- Marker concentrations that do not affect the rubber's critical characteristics but are still detectable need to be determined.
- The proof of concept is successful.

After applying QDots to thermoplastic and elastomer raw materials, mechanical tests were carried out to determine whether there was any deterioration in their mechanical properties. Both the previous and next values of the test results are shared in the table.

Table 3.1 PU6006 Test Results

Property	**Before QDots Application PU6006**	**After QDots Application PU6006**
Hardness (Shore D)	63.3	62.09
Tensile Strength (MPa)	48.6	48.11
Elongation at Break (%)	440	439.12
Compression Set % (22 hours at 100°C)	28.53	28.21

Table 3.2 NB9001 Test Results

Property	**Before QDots Application NB9001**	**After QDots Application NB9001**
Hardness (Shore A)	88.13	88.02
Tensile Strength (MPa)	20.8	21
Elongation at Break (%)	166	165.74
Compression Set % (22 hours at 100°C)	19.53	19.03

3.1 Future Work

- Optimization studies specific to product and color should be conducted, and standard methods for each product should be established.
- Used and aged products should also be studied. The effects of deformation, contamination, etc., particularly on surface readings, should be evaluated on used samples.

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