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ILLUMINATING TIMES

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Enhanced lightfastness and migration properties in daylight fluorescent pigments. By Rami Ismael, Aralon Color.

The lightfastness of fluorescent pigments [1–4] has been improved in recent years. Recently developed daylight fluorescent pigments are formaldehyde-free and stand out due to their excellent migration fastness in defined paints and coatings, in PUR artificial leather and in PVC.

Hardly any other performance criterion of daylight fluorescent pigments is discussed more frequently than their comparatively low lightfastness (UV stability). Lack of lightfastness is the main argument advanced for discriminating against daylight fluorescent pigments in many outdoor applications involving permanent exposure to sunlight. The UV stability of fluorescent pigmented systems depends on various factors, such as colour, type and chemistry of the pigment and binder, pigment concentration, as well as the layer thickness and layer structure in the final application. While fluorescence can remain stable for several years indoors, it decreases very quickly in direct sunlight and outdoors.

LIGHTFASTNESS

Lightfastness is usually measured on the Blue Wool (BW) scale, in which each increase in value corresponds to roughly double the lightfastness of the previous level. Fluorescent systems typically score between 1 and 7. A value of “2” indicates double the lightfastness of “1”, a “3” represents 4 times, a “5” corresponds to 16 times and “6” equals 32 times the lightfastness of “1”.

SHADES AND BINDER DIFFER IN PERFORMANCE

Fluorescent shades usually differ in their lightfastness performance, which decreases in the order: blue, green, lemon, UV blue, orange, magenta. “Strong” shades in general have less lightfastness than their standard shades. High pigment concentrations, thick layers and transparent formulations, on the other hand, increase lightfastness. The binder also influences the lightfastness of the system. Binder performance decreases in the following order:

- PVC carrier
- transparent cPP
- PC or ABS
- aliphatic PUR
- acrylics
- olefins
- alkyds
- aromatic PUR

The best results can be achieved in multi-layer systems, such as a white primer followed by a transparent, fluorescent layer and a topcoat filled with UV absorber.

MORE LIGHTFASTNESS, LESS WEIGHT

In Araqua-30 (“AQ-30”) fluorescent pigments, we have been able both to develop and crosslink specific hybrid polymers that, in stabilised paint systems, have 10 times the lightfastness of conventional daylight

RESULTS AT A GLANCE

→ In technical textiles, the new fluorescent effect pigments have up to 7 times the lightfastness of legacy pigments.

→ A reduction in total weight of technical textiles with improved lightfastness is possible.

→ Migration in PVC or PUR artificial leather applications can be reduced to zero.

→ In highly stabilised paints, lightfastness up to 10 times that of legacy pigment technologies is possible.

→ Fluorescent paints based on the new pigments (ΔE < 2.5 after 2,000 hours of light exposure) are increasingly penetrating areas that were previously exclusive to the mass colouring of plastics.

→ New fluorescent effect pigments are available both as daylight fluorescent pigments and as invisible UV-fluorescent pigments.

Figure 1: Fluorescent-yellow technical textiles / fluorescent-yellow safety coat.

fluorescent pigment series and to combine this improvement with excellent migration fastness in PVC and PUR formulations.
As a result, typical safety colours, such as fluorescent yellow and fluorescent orange, in technical PVC textiles can be made far more lightfast within the colour gamut (the range of all acceptable colours) specified in EN ISO 20471. At the same time, the weight of the technical PVC textile can be reduced from 400 g/m² to 350 g/m². The new technology has much better lightfastness than its formaldehyde-containing counterparts. Recent lightfastness tests conducted with the new technology show a clear advantage over previous technologies.
The new results apply equally to all types of coatings and paints. In particular, performance can be significantly improved in multi-layer paint systems (ΔE < 2.5 after 2,000 xenon test hours).

PROTECTING THE WEARER

EN ISO 20471 defines requirements for high-visibility clothing (*Figures 1 and 2*). The bright orange, yellow or red in this clothing is referred to as fluorescent background material. This increases the visibility of the wearer during the day [5].
Technical safety textiles are produced by coating a paste-like plastisol dispersion consisting of PVC, fluorescent pigment, plasticiser and a few additives onto skin-friendly textiles and crosslinking at 150 to 190 °C. This coating should have, and retain, a colour value within the range of standard colour reference values, even after standardised exposure to sunlight of specified intensity and duration. These values differ for the safety colours fluorescent yellow, fluorescent orange-red and fluorescent red [6, 7].
Current legislation aimed at protecting consumer health requires that coatings be free of harmful substances. All fluorescent pigments discussed here are free of both formaldehyde and other harmful substances, particularly of raw materials such as formaldehyde, styrene, acrylonitrile, bisphenol-A and nitrosamines.

Figure 2: Fluorescent-orange technical textiles / fluorescent-orange safety coat.

Figure 3: Fluorescent-yellow technical textiles: measured as per EN ISO 20471. White: new technology. Red: legacy technology.

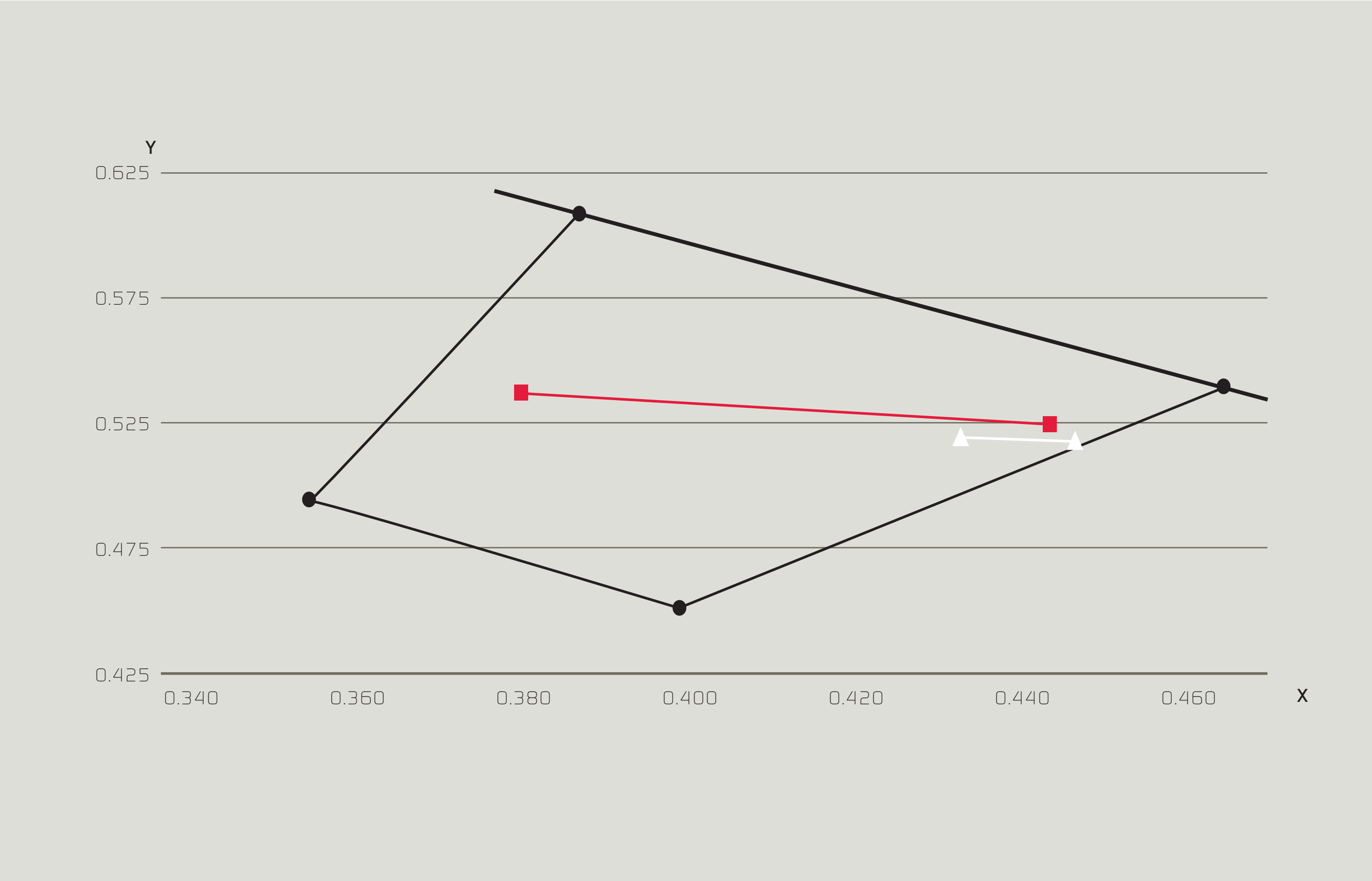
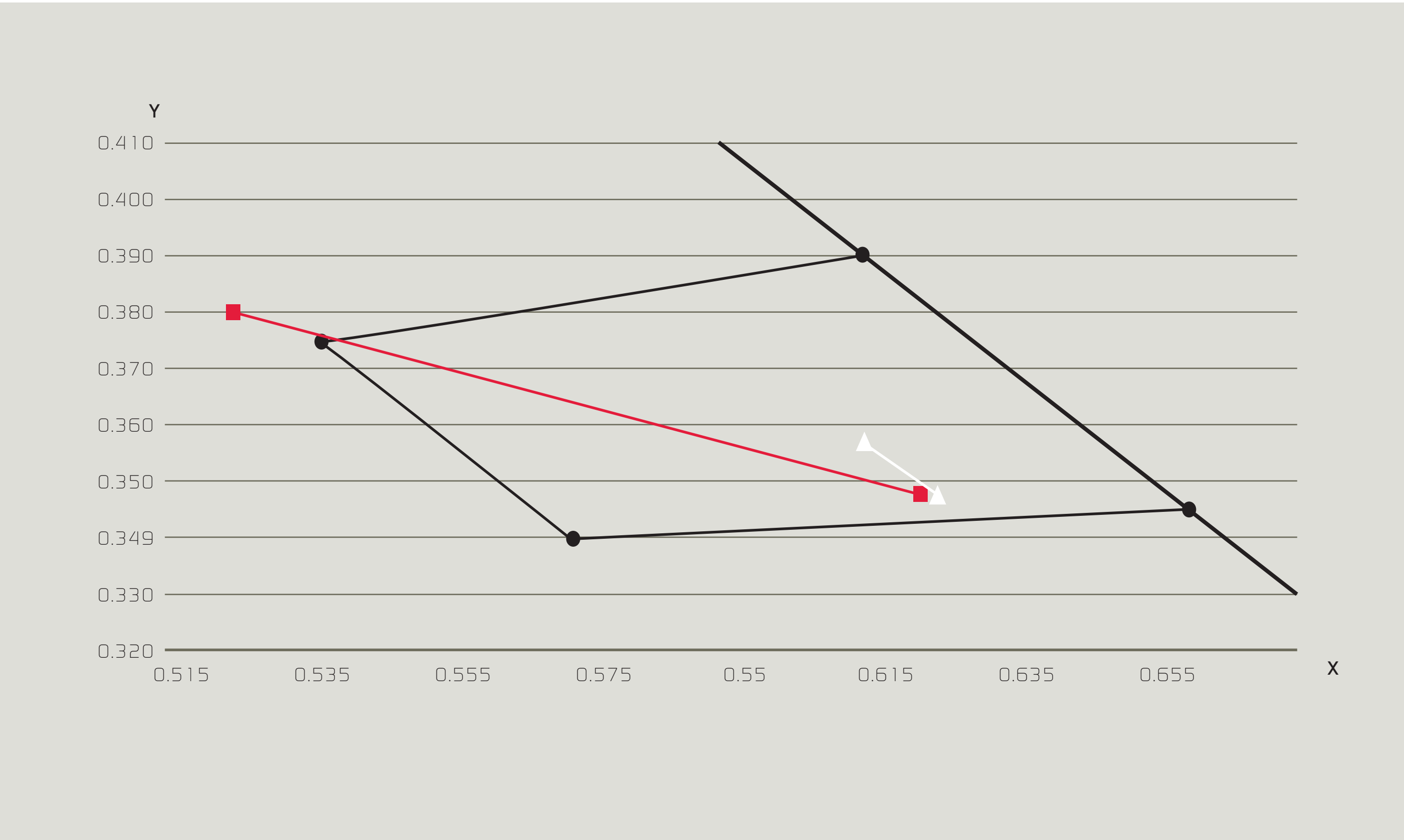


Figure 4: Orange-red technical textiles: measured as per ISO 20471. White: new technology. Red: legacy technology.



MORE COMFORT, LOWER COSTS

Another objective is to improve wearing comfort and reduce the weight of technical textiles for cost reasons. To meet this challenge, the following formulation was used for the coating: fluorescent layer: 180 g/m² with 10.8 % fluorescent pigment or 25 parts fluorescent pigment per 100 parts PVC, 1 part UV absorber 1 and 1 part UV absorber 2. This made it possible to reduce total weight of the fluorescent layer and underlying white vinyl acrylic layer from 400 g/m² to 350 g/m².

Tests show that a high total weight of 400 g/m² cannot prevent the colour values of the legacy pigment technology from moving through almost the entire colour gamut and reaching, just after illumination, a colour space outside the relevant quadrilateral in EN ISO 20471. In contrast, the same safety colour based on the new pigment technology has 5 times the lightfastness, even at a reduced total weight of 350 g/m².

The same formulation was used for the fluorescent orange-red colour as for the fluorescent yellow, the only difference being that the fluorescent yellow pigment was replaced by a fluorescent orange-red pigment. Here too, it was possible to reduce the total weight of the fluorescent layer plus underlying white vinyl acrylic layer from 400 g/m² to 350 g/m² while increasing the lightfastness.

In this test, the legacy pigment technology benefits from a higher total weight of 400 g/m². However, the colour values move outside the colour gamut range, meaning that the colour does not meet EN ISO 20471. The safety colour based on the new pigment technology, on the other hand, has 7 to 8 times the lightfastness in this application, despite the reduced total weight of 350 g/m², and remains very robust, changing only minimally within the quadrilateral of the standard.

In both colours – fluorescent yellow and fluorescent orange – the new technology offers significantly higher lightfastness combined with improved wearing comfort of the technical textiles by reducing the overall weight and optimising the cost. This also applies to the results for fluorescent red, which are not presented here.

In this context, it is important to point out that the starting colours (before exposure) should always be set such that the measured colour coordinates are in the lower right corner of the standard's quadrilateral. Experience shows that colours move from bottom to top and from right to left within the quadrilateral during exposure (*Figures 3 and 4*). This means that, with each exposure, the length of the path increases within the standard's quadrilateral before the set colour no longer meets the standard.

NO COLOUR TRANSFER

A textile coated with fluorescent PVC and a fluorescent-coated PUR synthetic leather were tested for their migration fastness as follows. Both preparations were clamped between two white PVC layers in a press fitted with two heatable metal plates and subjected to a pressure of 690 bar at 94 °C for 15 h.

After the metal plates were removed, the fluorescent coated preparations were separated from the white PVC layers on both sides. The results showed no colour transfer of the new generation of fluorescent pigments to the white PVC layers.

While limitations of previous generations of daylight fluorescent pigments in terms of light stability, migration fastness and chemical stability restricted these pigment classes to a very narrow range of applications, the new fluorescent pigment qualities can now be used in more sophisticated design products (*Figure 5*).

Thanks to these new pigment technologies, fluorescent swim and underwear applications are no longer out of reach. High migration fastness and colour fastness to repeated washing cycles have become enabling performance attributes, in addition to the crucial freedom from formaldehyde. AQ-20 fluorescent pigments are especially designed for such washable textiles.

In theory, increasing the migration fastness in the production of fluorescent pigments should be a simple undertaking. Increasing the polymer crosslinking of the embedding polymer in daylight fluorescent pigments will always help improve migration fastness, but that alone does not explain the very good test results. The understanding gained of the differences in how the pigments are used in various applications and the role of polarity have led to further improvements in migration fastness through diversification of the fluorescent pigments into specific applications. AQ-30 fluorescent pigments now offer the best migration fastness in aqueous PUR artificial leather formulations and in PVC colouring. A different polarity setting for the AQ-20 pigments, however, ensures better migration fastness in normal textiles. Since formulations often differ significantly even within the same application, it is not always easy to decide in advance, which of the AQ pigment technologies (AQ-10 for standard fluorescent pigments, AQ-20 or AQ-30) should be recommended without testing all three variants.

USE IN FLUORESCENT PAINTS

The aforementioned advantages over legacy generations of fluorescent pigments can be further exploited in paints and coatings. While the AG pigments are limited to use in solvent-borne paints and coatings, the AQ pigments are recommended for aqueous, plasticizer-based or 100 % solids formulations.

The advantages of the new fluorescent pigments diminish as the stabilisation of the paint system decreases. Conversely, as the paint system becomes more stabilised, the benefits of these pigments become increasingly evident.

The following paint structure achieves a level of lightfastness more than 10 times that of paints made with legacy fluorescent pigment technologies:

1. base coat (conventional red or white)
2. fluorescent paint layer with 20 % fluorescent pigment, 4 % UV absorbers and 80 µm layer thickness, aliphatic PUR binder
3. topcoat with 4 % UV absorber mixture that blocks all UVA and UVB light
4. aliphatic PUR binder

Figure 5: New fluorescent pigment grades for sophisticated design products.

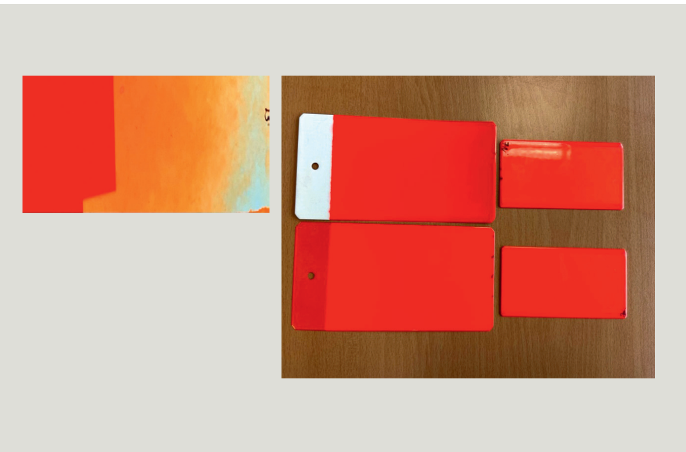
With this paint structure, a $\Delta E < 2.5$ is achieved, even after 2,000 hours of xenon light exposure (0.51 W/m^2), while the legacy fluorescent pigments end up with a $\Delta E > 35$ (*Figure 6*).

Stabilisation of the system is critically important for capturing the maximum benefit of the new pigment technologies. A summary of the lightfastness (shown as ΔE as a function of exposure time) of different coating systems made with the new technology (here AG-105 RED) in comparison with the legacy technology (described as "state of the art") is shown in *Figure 7*. The coating systems differ in the use of UV absorbers and a topcoat or without UV absorbers/topcoat.

Three variants of paint systems were examined:

- paint systems without UV absorbers,
- paint systems without UV absorbers, but with a topcoat,
- paint systems with UV absorbers and with a UV stabilised topcoat.

Figure 6: Left: Legacy technology before (left) and after (right) with a $\Delta E > 35$ after 2,000 h in the xenon test. Right: New technology before (left) and after (right) with a $\Delta E < 2.5$ after 2,000 h in the xenon test.



The much greater lightfastness of this class of effect pigments opens up previously unthinkable outdoor applications, such as paints for racing cars and racing boats, for bicycles/motorcycles and helmets, forklifts and construction machinery featuring enhanced safety through improved visibility or a customised appearance.

INVISIBLE UV-FLUORESCENT PIGMENTS

It is worth mentioning that the new pigments are available not only as daylight fluorescent pigments, but also as pure UV-fluorescent pigments. These appear colourless or slightly whitish under daylight. However, when activated under UV light (at wavelengths from 356 to 365 nm), they glow in yellow, green, red, purple or blue. More shades can be created by mixing. For example, UV-yellow mixed with UV-red yields a bright UV-orange. Typical areas of application are markings, automation, product authentication and document security (*Figure 8*).

Such pigments and the corresponding aqueous dispersions offer a wide range of applications, with many advantages:

- marking of products against product piracy
- document security
- authentication
- labelling
- branding
- automation of production steps, e. g. by marking adhesives of production intermediates. Different parts (like shoe sole and shoe upper leather) are assembled first after automatic control under UV light of the homogeneous coverage of one part with adhesive.
- contrast liquids that glow under UV light for effective detecting and locating of leaks, e. g. in flat roofs and pipes, dye-free (no dye migration into undesirable areas in the masonry).

ON THE TRAIL OF WATER – REVERSIBLE FLUORESCENT PIGMENTS

The formaldehyde-free AQ/AG technology has led to the development of a new type of UV pigment technology for visualising water and, conversely, visualising markings through the addition of water.

"Aramoist-101" UV green ("101") is almost colourless and, when dry, is visible neither in daylight nor under UV light. However, once these pigments come into contact with water, they begin to glow intensely green under UV light. The optimal activation wavelength of the UV light used is 356 nm. The resulting emission wavelength is between 510 and 520 nm, the exact figure depending on the application.
The functionality of 101 is also reversible. Once the pigment dries in its medium (paint, adhesive, etc.), no glow or fluorescence is visible. While electrical or electromagnetic sensors [11] indicate moisture in the gaseous state (atmospheric humidity), 101 only reacts, with a colour change, when water particles are present in the liquid state. This qualitative and reversible indication of the presence of water particles enables the detection of leaks in pipes or containers or even of moisture in cellar walls.
In laboratory tests, 1 % 101 was added to commercial white emulsion paint. The 16 µm dry-paint layer is virtually colourless. When water particles come into contact with the paint, an intense green fluorescence appears in the affected areas under UV light, whereas the dry areas remain colourless. This dry-wet-dry process can be repeated multiple times.

The UV pigments presented here remain colourless when dry, wet or in humid atmospheres. Only when in contact with water will they glow under UV light. This was tested by placing the pigments in a humidity chamber at different humidity levels and temperatures. Even at 100 % humidity and 50 °C, they remain invisible. Fluorescence under UV light is only activated by physical water particles. This property also makes 101 an ideal additive for detecting water in basement walls, seals and insulation or painted probes. The drying progress of certain adhesives or sealants, paints or polymer surfaces can also be visualised with the aid of 101.
Further examples of applications are:

- creation of real, water-sensitive watermarks in paper or textile printing
- marking of proprietary products against product piracy
- security printing inks, especially for screen or gravure printing
- colouring or marking of any permeable coatings, such as UV coatings for plastic nail polishes or other decorative applications
- combating mould indoors
- leak testing of insulation material through visualisation of condensation

Figure 7: Exposure table for AG-105 RED compared with the legacy technology.

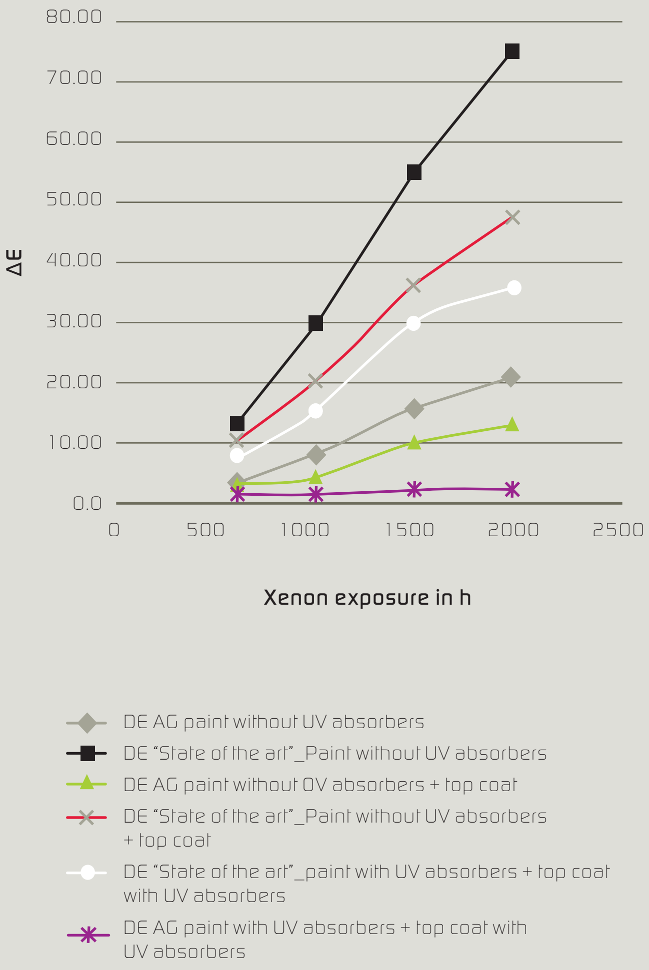


Figure 8: UV-fluorescent pigments, invisible under daylight and glowing vividly under UV light, in both paint applications and plastics colouring.


Under daylight in acrylic paint, 15 µm layer thickness


Under UV light (356 – 365 nm) in acrylic paint, 15 µm layer thickness


Under daylight @ 1 % in LDPE


Under UV light (356, 365 nm) at 1 % in LDPE

- identification of leaks in pipes and containers (colour additive)
- coating of immersion probes for identifying water on the bottom of heavy-oil reservoirs
- indication of corrosion protection, e. g. of steel structures. 101 can be added to the primer. If a glow is visible under UV light, the water permeability of the top layer is proven.
- monitoring the curing process of polymers, resins, glues and adhesives (provided drying takes place at approximately the same time as the curing in these applications)

SUMMARY

An increase in lightfastness from 200 to 1,500 % or from 1 to 3.5 steps on the BW scale was demonstrated in comparison with conventional fluorescent pigments made with melamine-toluenesulfonamide-formaldehyde resins. The increase was even greater compared with their benzoguanamine-formaldehyde counterparts. Thanks to their superior lightfastness, these pigments have been adopted across a wide range of outdoor applications, including paints for bicycles, racing cars, fire engines, police cars, forklifts and agricultural equipment. Apart from architectural paints and conventional automotive paints, the latest formaldehyde-free fluorescent effect pigments are suitable for technical textiles and advanced paints where lightfastness is a determining factor.
High chemical stability, even at pH values up to 13 and temperatures up to 220 °C, along with the absence of harmful substances and high migration fastness, crucial for enabling applications that were once exclusive to non-fluorescent pigments [8–10].

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