



A BRILLIANT FUTURE

Daylight fluorescent pigments (DLFP) for enhanced performance and colour intensity.
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Fluorescent pigments require brilliance as well as function. Traditionally, they have been based on the carcinogen formaldehyde, which needs to be replaced without compromising pigment performance. Using formaldehyde-free daylight fluorescent pigments and enhancing their functional properties has produced promising pigments that offer improved stability in both water-borne and solvent-based formulations.

For about a decade, fluorescent colours have been an integral part in marketing sports goods. Whether wetsuits, buoyancy aids, skis, bicycle helmets, all kinds of balls, sports shoes or goalkeeper gloves, all are available in luminous colours. Whilst appearance is important, function is also criti-

cal. Every sports article has its own critical properties. This will be briefly discussed using the example of goalkeeper gloves.

Goalkeeper gloves (*Figure 1*) are a technical masterpiece [1], [2]. There are now special goalkeeper gloves for almost every surface and even for different weather conditions. For a team to win the UEFA Champions League or the FIFA World Cup also depends on the goalkeeper's ability to catch the ball safely. Here, latex foam is a key contributing factor [1], [2].

The production of latex adhesive foam is a very critical application in which high temperatures, water and ammonia (both base and solvent at the same time) could attack the pigment particles. The neutrality (inertness) of the new fluorescent pigments with regard to the functionality in the described

application promises far-reaching neutrality and stability in other coating systems and lacquers with demanding process parameters.

DLFP HELPS TO INCREASE COLOUR INTENSITY AND AVOID FORMALDEHYDE

Fluorescent pigments are usually based on formaldehyde. Since January 1, 2016, formaldehyde has been classified as a carcinogen by the European Union (decision dating back to June 2014). As a consequence, new formaldehyde-free technologies are replacing those that used formaldehyde. Success and speed of adoption will depend on critical functional characteristics such as pigment luminosity or brilliance, migration, light stability and in our case, the ad-

RESULTS AT A GLANCE

- New polymer and resin developments take us a big step closer to our vision of formaldehyde-free fluorescent pigments
- These new technologies beat their formaldehyde-based precursors in key attributes but particularly in terms of light and storage stability. It is possible to replace formaldehyde without compromising performance in both solvent and aqueous formulations
- A formaldehyde-free hybrid polymer technology obtains the best results in aqueous formulations though it can also be used for oil, naphtha and UV resin-based formulations. Less crosslinking enables finer grinding resulting in higher colour strength.
- The inertness of the new luminescent pigments against extreme conditions (high process, thermal and chemical impact) guarantees far-reaching neutrality and stability in other coating systems and lacquers with demanding process parameters.

Figure 1: Goalkeeper gloves.



hesion properties of the goalkeeper gloves to the ball. The latest technologies do not compromise on performance, but rather show improvements over previous technologies. Product safety shall not come at the expense of grip and brilliance. Instead, the transition to formaldehyde-free formulations should exploit the potential of new technologies to improve products. This was achieved with two series of newly developed formaldehyde-free daylighting pigments for solvent-based and aqueous formulations. It is not only the new European champion that has held the ball with fluorescent goalkeeper gloves, coloured with those pigments. The glowing gloves of the Portuguese champions, goalkeeper Rui Patrício, could not be missed in the final against France [2b].

The advantage of daylight fluorescent pigments (DLFP) for aqueous applications is that they perform well with less hardening and less crosslinking compared with DLFP for solvent applications. This enables finer grinding to increase the colour intensity. Previous formaldehyde-free technology uses polyester-based chemistry, which has shown significant stability deficiencies during storage in aqueous formulations. Not only is the new technology stable in aqueous systems, it also offers other substantial improvements, for example light stability increased by 70-100% compared with conventional fluorescent pigments based on melamine-toluenesulfonamide-formaldehyde resins and even up to 350-500% compared with their benzoguanamine-formaldehyde counterparts.

EXPLOITING KEY PROPERTIES OF DLFP TO OBTAIN BETTER FLUORESCENT PIGMENTS

Fluorescent pigments are typically solid solutions (encapsulations) of fluorescent dyes in resins and polymers (carriers). The dyes are usually physically, and partially chemically bound to the carrier. The development of naphthalimide and xanthene fluorescent dyes in Germany and England in the late 19th and early 20th century marked the beginning of this class of effect pigments. Advances in polymer chemistry opened the door to new solid solutions of known dyes and other, subsequent dyes, which has led to the development and growing commercialisation of fluorescent pigments [3]. In addition to replacing formaldehyde, re-

search and development continues to focus on improving important functional pigment parameters such as light stability, heat stability, colour strength, brilliance, opacity or transparency, migration, efflorescence, solvent and water fastness, type and amount of (residual) monomers. In particular, the replacement of formaldehyde in the formulations is currently a major target. Below is an attempt to shed light on which parameters influence and limit the functional properties of fluorescent pigments based on melamine formaldehyde technology. Finally, the latest research results and progress into obtaining better fluorescent pigments is presented.

FINER PIGMENT GRINDING FOR BRILLIANCE & COLOUR STRENGTH

DLFP give a reflectance (brilliance) that is up to 3 times higher than conventional, non-fluorescent pigments.

It is scientifically proven that fluorescent items are detected 3 times earlier in their environment compared with conventionally coloured objects [8], [9], [10]. Children select fluorescent toys three times more often than conventionally coloured toys. Advertising and security requirements make use of this early recognition property to attract and direct attention.

Finer grinding of pigment particles, or a higher dosage of pigment particles in the application, generally leads to higher fluorescence and colour intensity. However, increasing the concentration of dyes used in DLFP is only beneficial to a certain extent. This level of concentration is system dependent. Saturation and so-called concentration quenching lead to an inflection point, beyond which we see negative returns in fluorescence and colour intensity. Finer grinding of pigments initially increases colour strength, but eventually reduces luminosity (pastel colour). As long as pigment particles are larger than 8-12 microns, colour strength and brilliance increase simultaneously with decreasing particle size. Between 8 and 6-3 microns (depending on chemistry) colour strength increases, but reduces particle stability. Especially with polyester pigments, the greater surface area provides more space for nucleophilic attack on the carboxyl groups.

More polyamide components and finer grinding of pigment particles result in higher swelling in waterborne formulations. Increasing pigment surface in this pigment class leads to improved colour strength, but causes a rapid decline in stability. At a particle size below 3 microns the whiteness increases, resulting in reduced luminosity. This does not apply to in-situ synthesis pro-

Figure 2: Polymer structure of DLFP based on melamine-formaldehyde resins.

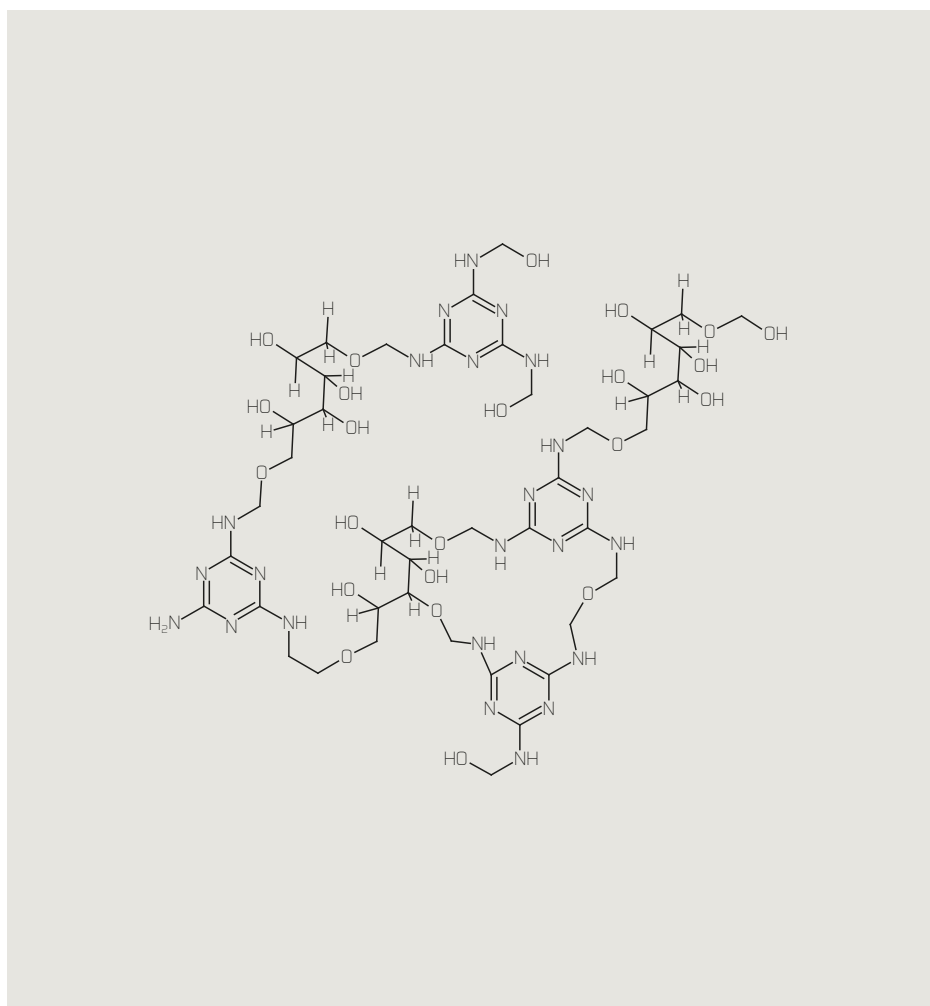
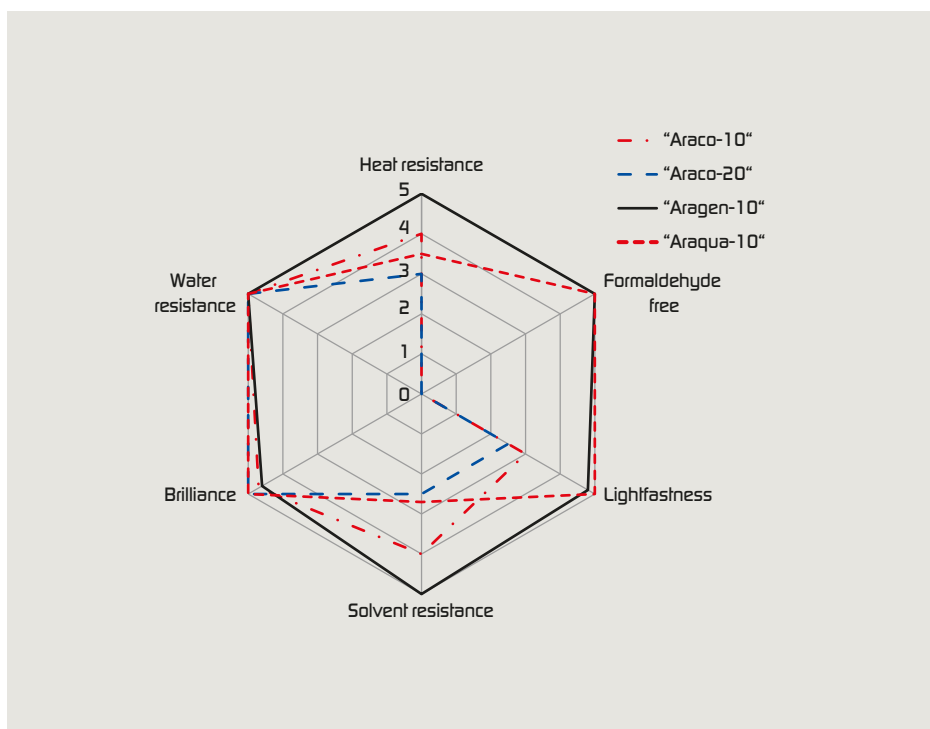


Figure 3: Stability properties of formaldehyde-free series "AG-10" and "AQ-10" compared with formaldehyde-containing series ("AC-10" and "AC-20").



cesses (suspension, emulsion) generating very small pigment particles [3]. However, the light stability of such fine particles leaves much to be desired. Finer particle size and distribution usually leads to increased migration and reduced solvent resistance. These effects are more pronounced for DLFP, which are produced based on older polyester/polyamide technologies.

NEW TECHNOLOGIES IMPROVE COLOUR STRENGTH AND BRILLIANCE

To improve the solvent resistance of formaldehyde-containing DLFP requires greater crosslinking of the hydroxymethylene (CH₂-OH) terminal groups under elimination of water. At constant chemical parameters this normally requires a longer curing time, resulting in darkening of the colour and lower luminance. Another way of improving solvent resistance is to increase the relative share of paraformaldehyde in the reaction. At elevated temperatures this leads to eliminating some paraformaldehyde chains and formaldehyde degassing.

Higher solvent resistance is unnecessary when using DLFP in aqueous media. Thus, more brilliant colours with higher colour intensity can be achieved. On the other hand, as shown in Figure 2, a lower cure rate is associated with less crosslinking and a higher content of terminal hydroxyl-methylene (CH₂-OH) groups. This is accompanied by intramolecular paraformaldehyde groups that – particularly at higher temperatures – results in formaldehyde degassing. However, this increases the disadvantages of conventional, non-hardened formaldehyde-containing pigments in aqueous formulations. Higher crosslinking via longer curing reduces the problem, but does not solve it.

Lower colour strength is partially compensated for by increasing the dye concentration in the DLFP resin. However, this causes lower light fastness, higher bleeding and lower fluorescence due to concentration quenching. Typically, improvements of certain properties will compromise the performance of other properties – that no longer applies to the latest DLFP technologies.

Due to higher formaldehyde content and high solubility of formaldehyde in water, the substitution of formaldehyde-containing polymers and resins is more compelling in aqueous formulations than in solvent-based formulations.

The formaldehyde-free "Aragen-10 (AG-10)" DLFP for PVC, PU, latex and solvent

formulations as well as their Araqua-10 (AQ-10)" DLFP counterparts for aqueous emulsions, were developed on the basis of a new hybrid technology [4], [5].

Precursors to the new hybrid technology were modifications based on polyester resin, which is the basis for the "Araco-60 (AC-60)" DLFP pigments showing low solvent resistance. Modifying polyester resins by adding amide units resulted in good fluorescence, but in lower solvent resistance.

Conversely, an increase in multi-functional components (pentaerythritol) in the polyester resin improved the solvent resistance, but reduced fluorescence.

Similar results are obtained by increasing the multifunctional parts in polyamide and polyurethane resins. To date, traditional formaldehyde-containing amine resins have been far superior to alternative resins.

The new developed pigments utilise a formaldehyde-free hybrid polymer technology [4], [5]. Compared to the "AG-10" DLFP, the polarity of the particle surface was increased, which made it ideal for aqueous formulations. Less crosslinking also permits finer grinding which results in higher colour strength. The best results are therefore obtained in aqueous formulations, though UV resin, oil or naphtha formulations are also possible.



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Table 1: Storage stability of different technologies DLFP.

Grey: high storage stability.

Green: viscosity increase.

Red: formulation thickening.

¹⁾ aqueous dispersion of a terpolymer of vinyl acetate, ethylene and vinyl chloride,

Wacker Chemie AG

²⁾ water-borne glycol pigment dispersions, Aralon Color

"AQ-103 Orange"				
Storage hours at 40 °C	24 h	48 h	96 h	148 h
10% TLP in EtOH/H ₂ O (2:8)				
10% TLP in "Vinnapas LL 3031"				
5% TLP in "Aradis -W10"				
"AG-103 Orange"				
10% TLP in EtOH/H ₂ O (2:8)				
10% TLP in "Vinnapas LL 3031" ¹⁾				
5% TLP in "Aradis -W10" ²⁾				
"AC-213 Orange"				
10% TLP in EtOH/H ₂ O (2:8)				
10% TLP in "Vinnapas LL 3031"				
5% TLP in "Aradis -W10"				
"AC-603 Orange"				
10% TLP in EtOH/H ₂ O (2:8)				
10% TLP in "Vinnapas LL 3031"				
5% TLP in "Aradis -W10"				
"G-13 Orange"				
10% TLP in EtOH/H ₂ O (2:8)				
10% TLP in "Vinnapas LL 3031"				
5% TLP in Aradis -W10				



Figure 3 compares the characteristics of the formaldehyde-free DLFP pigments and the DLFP pigments containing formaldehyde.

Table 1 compares the storage stability of the two new formaldehyde-free DLFP grades with the older formaldehyde-free grades based on modified polyester technologies in defined aqueous formulations. The superiority of the new products is evident.

IMPROVEMENTS IN LIGHT FASTNESS AND HEAT STABILITY

The light fastness of the new formaldehyde-free DLFP is higher than the types that contain formaldehyde. This has been previously demonstrated and reviewed in the literature [4], [5].

Compared with solvent-resistant "AG-10" DLFP formulations, properties have been further improved that make the "AQ-10" DLFP ideal for aqueous formulations. In defined patented systems, a light fastness of greater than 6 on BWS (Blue Wool Scale) for "AQ 100 Lemon" was achieved with one such formulation. This is the highest light stability in the given series.

"AQ-10" DLFP begin to melt at about 120 °C. They are therefore limited to application processes at lower temperature or to applications in which melting pigments do not interact with the basic medium. For applications such as polyoxymethylene (POM), injection moulding PU or PVC, the solvent resistant "AG-10" pigments remain the better choice, also in terms of migration and bleeding.

There are some applications in which the melting of the DLFP is beneficial during processing. Luminosity and intensity remain stable in applications of up to 280 °C, although not recommended at above 200 °C. Here again, we refer to the more appropriate solvent-resistant "AG-10" DLFP. The most compelling applications for the formaldehyde-free "AQ-10" DLFP are aqueous coatings, aqueous artist paints and aqueous gravure, transfer and screen printing inks.

EFFECTIVE FORMALDEHYDE MEASUREMENTS

Standard formaldehyde measuring methods are typically based on UV-vis absorption measurement of synthesised dyes, which are generated by the use of derivatisation reagents with formaldehyde for its photometric determination. Such reagents include 2,4-dinitrophenylhydrazine, chromotropic acid, phenylhydrazine or acetylacetone. However, these methods are not suitable for measuring formaldehyde in fluorescent pigments because aqueous extractions of DLFP always show a certain absorption in the visible light spectrum, which inevitably





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“Melting the pigments increases their migration tendency while the colour strength increases.”

3 questions to Rami Ismael

What needs to be considered besides the temperature during formulation? In typical aqueous lacquer binders, it is possible to disperse the pigments without using any dispersing additives and without grinding the pigments. In addition to the reduced particle size, which is advantageous for very thin-layer printing processes, milling does not offer any other advantages.

What are examples of applications where melting of the pigments is an advantage during application? Melting the pigments increases their migration tendency while the colour strength increases. However, molten AQ-10 fluorescent pigments are not soluble in LDPE (generally in olefins). Thus, after melting the pigment particles, it is possible to benefit from a higher colour strength without suffering migration. A further example of application in which it is advantageous to melt pigments during application is the coloration of bright PVC-plastisol / PVC organosol coatings. These are often applied in three or more layers. A first white covering base layer assists the luminosity of the subsequent fluorescent pigment-containing layer. The right choice of a migration-inhibiting top coat with UV absorbers enables a very high colour strength while maintaining good migration stability.

Is it also possible to use the pigments in printing inks without problems? The use of “Araqua” daylighting pigments is readily possible in screen and gravure printing processes, both in aqueous and in UV formulations. When using in more thin-layered offset or flexographic printing processes, it is advisable to grind to the desired particle size.



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➤ lead to distorted results. This is unsurprising, considering that daylight-fluorescent pigments are solid solutions of fluorescent dyes in encapsulation resins. These dyes always show certain absorption in the visible light spectrum.

Today, HPLC methods without downstream absorptiometry of long-wave derivatives offer far more appropriate methods for measuring formaldehyde in fluorescent pigments. For example, derivatisation to very shortwave absorbing derivatives such as 3,5-diacetyl-1,4-dihydrolutidine [6] are far more suitable methods for measuring formaldehyde in DLFP since the light absorption of the encapsulated dye in DLFP is mostly not disruptive in this range.

A further recommended detection method is FIA. Air is drawn through a tube that contains a smaller, concentric tube made of Nafion (semi permeable) through which water flows in the opposite direction and serves to trap formaldehyde; addition of 1,3-cyclohexanedione, in acidified ammonium acetate to form dihydropyridine derivative in flow injection analysis system (FIA) [7]. It is advisable to prepare samples with acetone instead of water. This achieves higher

wetting of the pigment particles and certain pigment technologies are better penetrated. Furthermore, using acetone instead of water does not cause slow replacement by water. Combined slow outgassing of CO₂, N₂, and O₂ from the surface of the pigment particles during measurement gives questionable results. ➤

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