# Digging for iron and hitting on gold!

*Daylight fluorescent pigments & moisture sensible UV fluorescent pigments for paints, printing inks, adhesives, resins and plastics.*

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## Introduction

We could not imagine 8 years ago, once we approved the final plans for our major strategic long term R&D project moving away from formaldehyde based fluorescent pigments, we are going to find, what forms the pillars of our technical advancement today. The new fluorescent - or better said - functional pigment technologies have proven themselves in the last 4 – 5 years in the applications of our customers being by far the top technology regarding light fastness, chemical stability and comprehensive fastness properties. This has paved the way to enter with those fluorescent shades wider and easier into the high demanding “Non direct food contact”, textile and artificial leather applications and glass coating while taking care for related legal compliance at renowned brand names.

Fluorescent pigments are usually based on formaldehyde. Since the 1st of January 2016, formaldehyde has been classified as carcinogen by the European Union (decision dating back to June 2014). As a consequence, new, formaldehyde-free technologies are replacing former, formaldehyde containing technologies. Thorough success and high speed adoption is ongoing due to outstanding critical functional characteristics like pigment luminosity or brilliance, migration fastness, light stability. Translated into some consumer goods products, this means e.g. the performant adhesion properties of the goalkeeper gloves to the ball (Fig. 5), good “non-direct Food” performance in the Coca Cola glasses (Fig. 1), high safety performance in artificial leather (Fig. 2) and underwear clothes (Fig. 6) and high light stability of the bicycle (Fig. 3 & 4) and forklift paints. Latest available technologies do not compromise on performance, but show improvements over preceding technologies instead. Product safety shall not come at the expense of performance and brilliance. Instead, the transition to formaldehyde-free formulations has been used to exploit the potential of the new technologies for product improvement. This was achieved with two series of latest generations of lately developed formaldehyde-free daylighting pigments, the ARAGEN technology for solvent based and the ARAQUA technology for waterborne formulations.

Figure 1: ARAQUA-100 LEMON and ARAQUA-106 PINK coloring the Coca Cola glasses at the McDonalds promotions of 2017.

Today fluorescent colors have been integral part in marketing sports goods, designer bags and designer shoes and clothes. Whether wetsuits, buoyancy aids, skis, bicycle helmets, balls of all kinds, sports shoes or goalkeeper gloves, whether Nike, Adidas, Coca Cola or Chanel, all have succumbed to the spell, all are available in fluorescent colors.


Figure 2: Fluorescent artificial leather at top brand names.

Freedom of formaldehyde without compromises was the main target [4a], [4b], [5a], [5b]. The new technology shows much better light stability compared to its formaldehyde containing pendants. Latest light stability tests of the new technology shows a solid step ahead of the old technology. Looking on Fig 3, while the Δa for the right side remains below 2,5, after 2000 hours in the Xenon test (0,51 w/qm), a huge stability deficit indicates a Δa above 35 for the left side.

The right side was made utilizing ARAGEN-105 RED. Once above white base coat and once above red conventional base coat with high light stability for architecture coatings. The left side was made with the older pigment quality.

Both paints in Fig 3, right and left, have utilized:

1. Base coat, conventional red or white.
2. Fluorescent coat with 20% pigment, UV absorbers and 80 µm thickness. Aliphatic PU binder.
3. Top Coat with 4% UV absorber mix blocking all UVA and UVB light. Aliphatic PU binder.

Figure 3: Left: Old technology before (upper side) and after (lower side) the Xenon test.
Right: New ARAGEN technology before (upper side) and after (lower side) the xenon test.

We can document a light stability increase by 200-1500% or from 1 till 3,5 steps on the BWS when compared with conventional fluorescent pigments based on melamine-toluenesulfonamide-formaldehyde resins (for example our ARACO technology) and even much more when compared to their benzoguanamine-formaldehyde counterparts. Thanks to the higher light stability those pigments has been in the meantime established in a variety of outdoor applications utilizing paints for bicycles (Fig. 4), racing cars, fireguard cars, police cars, forklift and agriculture instruments. Still the light stability is not enough for normal car paints or architecture paints.


Figure 4: Fluorescent bicycle, a STANDARD outdoor application thanks to ARAGEN-10 pigments.

Every application and consumer good has its own critical properties. Pigments have to provide safety and perform well through the complete production process followed by the final use. This will be briefly discussed using the example of goalkeeper gloves (Fig. 5) and the fluorescent coating of the Coca Cola glasses (Fig. 1).

Goalkeeper gloves are a technical masterpiece [1], [2]. In the meantime there are 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]. Not only the 2016 soccer European champion has held the ball with fluorescent goalkeeper gloves, colored with those pigments, the glowing gloves from the Portuguese European champion, goalkeeper Rui Patrício, could not be overlooked in the final against France [2b].

Figure 5: Goalkeeper gloves, a technical masterpiece.

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.

Same robustness is requested for the waterborne aliphatic PU coating for the Coca Color glasses. The aliphatic waterborne PU coating is kept soluble through high alkaline ammonia concentration, which helps through its chemical aggressiveness towards the glass surface to create the targeted high adhesion. Final glasses withstand 70 dish-washer cycles without showing any recognizable migration, any fading or performance changes (Fig. 1).

Figure 6: Fluorescent underwear. No go domain for the old formaldehyde-containing technology.

Fluorescent underwear was a no go domain for the old technologies. Nowadays, the “underwear” sector is offering as part of its Standard color range, also fluorescent underwear. High migration fastness, robust color shades through repeated wash cycles are additional attributes of the new technologies in addition to the crucial freedom of formaldehyde.

**Critical properties of DLFP**

Fluorescent pigments are typically solid solutions (encapsulations) of fluorescent dyes in resins and polymers (carrier). 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, later available dyes, which has led to the development and growing commercialization of fluorescent pigments [3].

In addition to replacing formaldehyde and reaching breakthrough results for light stability, research and development continues to focus on improving important functional pigment parameters to integrate those new technologies in the majority of the consumer goods. In particular, the elimination of formaldehyde in consumer products while prolonging at the same time their life time are the main gains, making the new pigments a solid step ahead towards desired higher products safety and sustainability.

Below is an attempt to shed light into which parameters influence and limit the functional properties of fluorescent pigments based on melamine formaldehyde technology.

Above, we have shown the latest results regarding the improved light fastness of the new technologies and shall close later down with an update on latest research for moisture sensitive functional pigments.

**Brilliance & color strength**

DLFP show up to 3-times higher reflectance (brilliance) compared to conventional, non-fluorescent pigments.

It is scientifically proven that fluorescent items are detected 3 times earlier in their environment compared to conventionally colored objects [6], [7], [8]. Children select fluorescent toys three times more often than conventionally colored toys. Advertising and security requirements make use of this early recognition property to attract and guide attention.

Finer grinding of pigment particles, respectively a higher dosage of pigment particles in the application, generally leads to higher fluorescence and color intensity. However, increasing the concentration of dyes used in DLFP is only of benefit up to a certain level. 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 color intensity. Finer grinding of pigments initially increases color strength, but eventually leads to a reduction of luminous ability (pastel color). As long as pigment particles are larger than 8-12 microns, both color strength and brilliance increase simultaneously with decreasing particle size. Between 8 and 6 - 3 microns (depending on chemistry) color strength increases, but particle stability declines. 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 an improvement in color strength, but causes a rapid decline in stability. At a particle size below 3 microns the whiteness increases resulting in a reduction of luminosity. This does not apply to in-situ synthesis processes (suspension, emulsion) generating very small pigment particles [3]. However, light stability of such fine particles leaves much to be desired. Finer particle size and distribution usually leads to increased migration and reduction of solvent resistance. These effects are more pronounced for DLFP which are produced on the basis of older polyester / polyamide technologies.

**solvent resistance vs. color strength and brilliance**

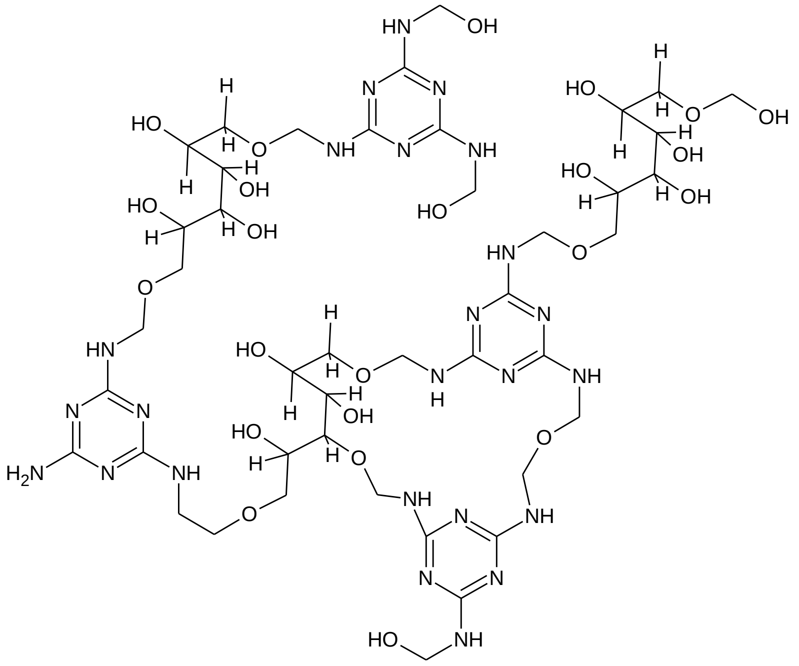


Figure 7: Polymer structure of DLFP based on melamine-formaldehyde resins.

In order to improve solvent resistance of formaldehyde-containing DLFP a higher crosslinking of the hydroxymethylene (CH2-OH) terminal groups under elimination of water is necessary. At constant chemical parameters this normally requires longer curing time resulting in darkening of the color and lower luminance. Another method of improving solvent resistance is to increase the relative share of paraformaldehyde in the reaction. In applications, where pigments are processed at elevated temperatures, this leads to cleaving some paraformaldehyde chains and formaldehyde degassing.

Higher solvent resistance is not necessary for the use of DLFP in aqueous media. Thus, more brilliant colors with higher color intensity can be achieved.

On the other hand, as shown in in Fig. 7, a lower cure rate is associated with less crosslinking and the presence of higher content of terminal hydroxyl-methylene (CH2-OH) groups. This is accompanied by intramolecular bound paraformaldehyde groups that – particularly at higher temperatures – results in higher formaldehyde degassing. That, however, increases the disadvantages of conventional, non-hardened formaldehyde containing pigments in aqueous formulations. A higher crosslinking via longer curing reduces the problem, but does not solve it and it reduces brilliancy too.

A lower color strength is partially compensated by increasing the dye concentration in the DLFP resin. However, this leads to a 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 fully to the latest developed 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-DLFP for injection molding PVC, hard PU, silicone, EVA and solvent based formulations (paints, coatings) as well as their ARAQUA-DLFP counterparts for aqueous emulsions or 100% solids (UV, epoxy) or plasticizers PVC formulations, were developed on the basis of a new hybrid technology [4a], [4b], [5a], [5b].

Precursors to the new hybrid technology were modifications based on polyester resin, which is the basis for the ARACO-70 pigments showing low solvent resistance. Modifying polyester resins by adding amide units resulted in good fluorescence, but in lower solvent resistance and higher swelling of the pigment particles in water. Conversely, an increase of multi-functional components (pentaerythritol) in the polyester resin improved the solvent resistance, but reduced fluorescence. Similar results are found by increasing the multifunctional parts in polyamide and polyurethane resins.

Insofar traditional formaldehyde-containing amine resins have been far superior to alternative, resins before the new developed ARAGEN and ARAQUA DLFP technologies. For ARAQUA DLFP the polarity of the ARAGEN particle surface has been increased, which make the ARAQUA DLFP the best choice for integration into aqueous formulations. Less crosslinking also permits finer grinding resulting in higher color strength (Fig. 8). Thus best results are obtained in aqueous formulations, while UV or epoxy resins, latex, foamed latex, playdough, crayon, plastisol, oil or naphtha formulations are also optimally suitable.

A comparison of characteristics between the formaldehyde-free ARAGEN-10 and ARAQUA-10 DLFP and the formaldehyde-containing AARACO-10 and ARACO-30 DLFP are shown in Fig. 8.

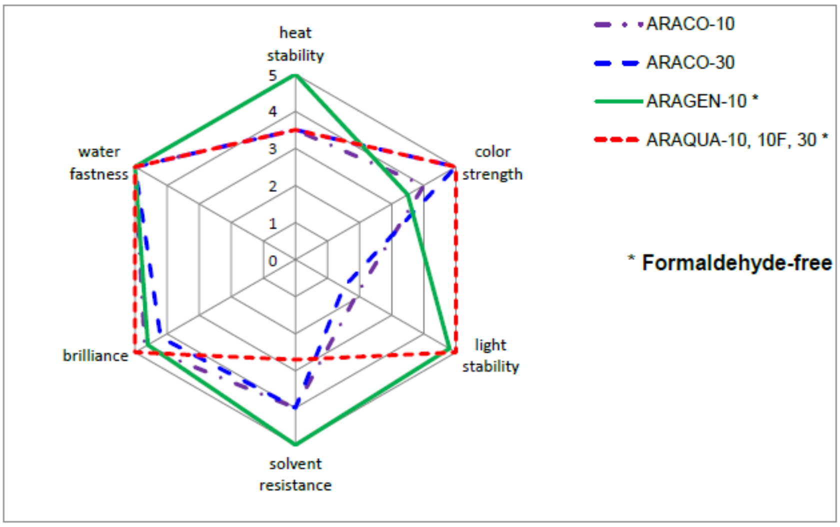


**Figure 8:** Stability and other properties of formaldehyde-free ARAGEN and ARAQUA daylight fluorescent pigments compared to formaldehyde-containing series (ARACO-10 and ARACO-30).

**On the trail of water – ARAMOIST Reversible Fluorescent Pigments - Latest functional pigments development**

The formaldehyde-free ARAQUA / ARAGEN technology [4a], [4b], [5a], [5b] has been utilized to create a novel UV pigment technology allowing the visualization of water and, conversely, the visualization of marks through addition of water.

ARAMOIST-101 UV GREEN - pigments are almost colorless and when dry neither visible under daylight nor under UV light. However, if these specially developed luminescent pigments come into contact with water, they begin to glow intensively green under UV light. The optimal activation wavelength of utilized UV light is 356 nm. The resulting emission wavelength is between 510 and 520 nm, depending on the application.

ARAMOIST-101 UV GREEN is also reversible in its functionality. If the pigment dries in its medium (lacquer, glue, etc.), no glow or fluorescence could be detected anymore.

While electrical or electromagnetic sensors [9] indicate moisture in a gaseous state (air humidity), ARAMOIRT-101 UV GREEN only reacts by changing color in the presence of water particles in the fluid phase. This qualitative and reversible indication of water particles allows e.g. the detection of leaks in pipes or containers filled with water.

In laboratory tests, 1% ARAMOIST-101 UV GREEN was added to commercially available white emulsion paint. The 16 µm dry colored layer appears colorless. Upon contact with water particles, intense green fluorescence is generated in the respective contact areas under UV light, while the dry areas remain colorless (Fig. 9). This process can be repeated several times.

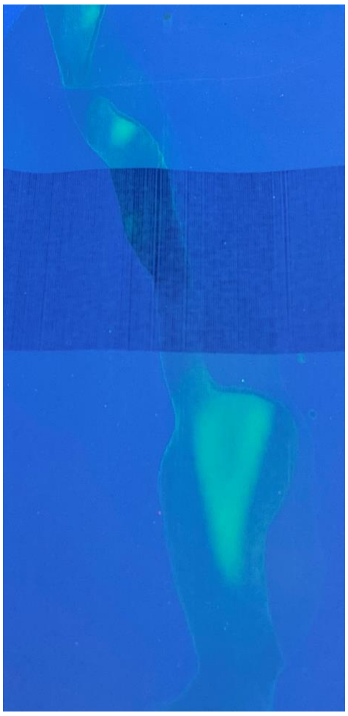

Figure 9: ARAMOIST-101-UV GREEN at 1% in white emulsion paint, colorless or intense green glowing under UV light (356 nm) after contact with water.

The UV pigments presented here are colorless not only under dry, but also under wet conditions, they remain colorless under humid conditions, only contact with water brings the pigments to glow solely under UV light. For this purpose, the pigments were tested in a humidity chamber at different humidity levels and temperatures. Even with a humidity of 100% and a temperature of 50 °C, the pigments remain invisible. It needs physical water particles to activate fluorescence under UV light. This property also makes ARAMOIST-101 UV GREEN an ideal additive for identifying water in cellar (basement) walls, seals and insulation. The drying process of certain adhesives or sealants, varnishes or polymer surfaces can also be made visible with ARAMOIST-101 UV GREEN.

Other interesting application examples of ARAMOIST:

- Generation of real, water-sensitive watermarks in paper or textile printing.
- Marking of own products against product piracy.
- Security printing inks, especially for screen or gravure printing.
- Coloring or marking any permeable coatings, like UV coatings for plastic nail varnishes or other decorative applications.
- Fight against mold indoors.

- Leak tests of building´s insulations by visualizing condensation water.
- Identification of leaks in pipes and containers (paint additive).
- Display of the corrosion protection e.g. of steel structures. ARAMOIST-101 UV GREEN can be added to the primer. If a glow is visible under UV light, the top coating is proven to becoming permeable to water.
- Indicator in the curing process of polymers, resins, glues and adhesives, provided that drying is fully or partially simultaneous with the curing of such applications.

**Results at a Glance**

ARAGEN and ARAQUA new polymer and resin developments take us a big step closer to our vision of formaldehyde-free production and application of fluorescent pigments. These new technologies beat their formaldehyde-containing precursors in all important attributes, but particularly in terms of light and storage stability. Substitution of formaldehyde is possible without the need to compromise, both in solvent and in aqueous formulations.
The neutrality (inertness) of the new luminescent pigments against extreme conditions (high process, thermal and chemical impact) stands as a guarantee for far-reaching neutrality and stability in other coating systems and lacquers with demanding process parameters.

Latest ARAMOIST novel pigment technology has been discussed that allows water contamination to be made visible through fluorescence. This technology also allows product markings to be made visible through water. The pigments described here are reversible several times in their functionality. They light up when they come into contact with water and the glow stops when they dry. ARAMOIST-101 UV GREEN expediently complements the range of functional additives for industrial applications [4a], [4b], [5a], [5b].

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