Glowing with promise

Daylight fluorescent pigments for paints, PVC and PU open up new applications in packaging

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Daylight fluorescent pigments (DFPs) have found wide use in warning and safety applications, while, more recently, the packaging industry has turned to daylight fluorescent pigments, as brands look for new ways to make their products stand out on the shelf. However, solvent-resistant, strongly fluorescent pigments have been so far only available based on formaldehyde containing polymers.

Daylight fluorescent pigments are colourants that absorb energy upon illumination with daylight. The invisible UV part of the daylight is transferred into visible light. Additionally, a variable shortwave part of the visible light is transferred into the fluorescence colour. The light yield is enhanced at a distinct wavelength of the perceived colour so they appear more brilliant and look more intense compared with conventional colours and also show a strong luminosity under black light (UV light), while conventional colours appear dull.

Applications of flourescent pigments

Daylight fluorescent pigments have found wide use in warning and safety applications, as well as marking and danger identification. Typical applications are paints for rescue vehicles or safety vests in luminous orange and yellow. Their use in advertising and in consumer brands has also been rising in recent years. Neon colours are used for eye-catching fashion designs and accessories, while magazines and advertising posters count on the impact of luminous signal colours.
The packaging industry has become increasingly interested in daylight fluorescent pigments, as more and more brands present their products in a striking manner, to stand out from the competition.
The vast majority – some 99 % – of DFPs are organic fluorescent dyes, which are bound to a carrier resin or polymer and available as stir-in pigments, where no grinding is needed and the compatibility with other resins is optimal. Stability and resistance properties of the pigments depend mainly on the polymer technology deployed.

Solvent-resistant, strongly fluorescent pigments have been so far only available based on formaldehyde containing polymers. Among these, melamine-toluenesulfonamide-formaldehyde resins, as well as benzoguanamine-formaldehyde resins with lower light stability [1] can be identified. High fluorescent formaldehyde-free pigments are partially available on the market [1] and are characterised by low solvent-resistance compared with their formaldehyde-containing counterparts. These are based on modified polyester resins and are suitable for applications, which do not require solvent stability like waterborne paints, crayons, paper and target coatings.

Optimising solvent resistance

Solvent resistance of fluorescent (and all other) pigments can be easily tested. The pigment needs to be grinded to a median particle size of 3–10 µm. Then 1 g of the pigment is mixed with 10 ml of solvent in a test tube and left to stand 40 minutes in a water bath at 37 °C.
Solvent-resistant pigments should float in the tube upon gentle shaking and should not show any tendency towards gel formation. Depending on the degree of gel formation the pigments are evaluated between 5 (no gel formation, the best) and 1 (complete gel formation, the worst). Common solvents are mixture of methyl-ethyl-ketone with xylene (50:50), acetone, methanol, ethanol, propanol, ethyl acetate, xylene and their mixtures.
The formaldehyde containing (< 0,1 %) "Araco-10" (AC-10) series with its pigments "AC-100 Lemon" to "AC-107 Magenta" is compared with the formaldehyde-free pigments of the "Aragen-10" (AG-10) series ("AG-100 Lemon" to "AG-107 Magenta").
Precursors of AG-10 series are modifications based on polyester resins. The polyester resins are the basis for the "Araco-60" (AC-60) pigments, which have a low solvent resistance. Modifications of the polyester resins by the addition of amide units have led to good reflection, accompanied by a low resistance to solvents.

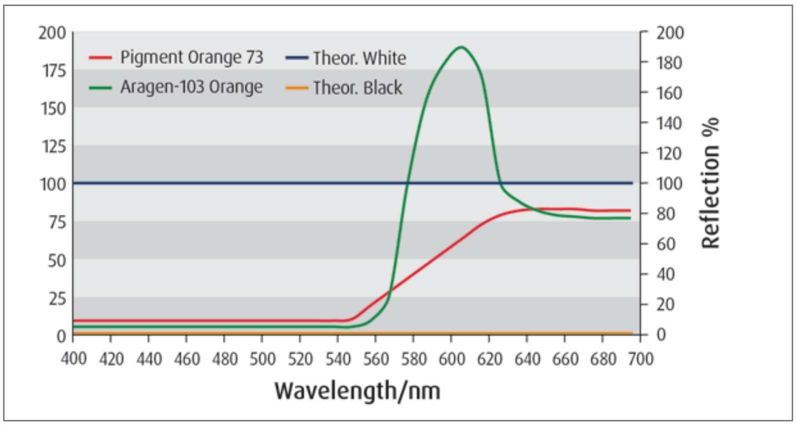

Figure 1: Reflection of "AG-103 Orange" vs. Pigment Orange 73 (same concentration, same titanium oxide parts)

Increasing the multifunctional parts in the polyester resin (pentaerythritol) led to improvement in the solvent resistance, but to the cost of the reflection.
Similar results have been found by increasing the multifunctional parts in polyamide or polyurethane resins. The traditional formaldehyde-containing amine resins have been superior to other resins.
The AG-10 technology uses a hybrid polymer of the mentioned formaldehyde-free technologies. The solvent resistance is given in *Table 1*. *Table 2* compares the reflec-

Solvent	"AC-103 orange"	"Ag-103 orange"
MEK: Xylene (50:50)	5	5
Methanol	5	5
Ethanol	5	5
Propanol	5	5
Ethyl acetate	4	5
Xylene	5	5
Acetone	3	5
Methyl-ethyl-ketone (MEK)	4	5
Cyclohexanone	3	5
3 % NaOH solution	5	5
Water + Ethanol	5	5

Table 1: Solvent resistance of AC-103 Orange (melamine-formaldehyde-toluenesulfonamide resin) compared with AG-103 Orange (hybrid resin)

Table 2: Comparison of the reflection maximums and the $L^*a^*b^*$-values between AC-10 (formaldehyde containing) and AG-10 series (formaldehyde-free) in Acryl resin

Product	Colour	max. refl.	WL/nm	L*	a*	b*
"Araco-100"	Lemon	190	520	109	-43	115
"Aragen-100"	Lemon	195	520	110	-50	116
"Araco-103"	Orange	235	610	82	85	92
"Aragen-103"	Orange	233	600	86	74	89
"Araco-104"	Orange-red	226	610	87	87	72
"Aragen-104"	Orange-red	213	610	84	84	79
"Araco-105"	Red	223	610	72	92	56
"Aragen-105"	Red	212	610	74	87	54
"Araco-106"	Pink	218	610	75	94	10
"Aragen-106"	Pink	212	610	77	91	18
"Araco-107"	Magenta	190	620	71	91	6
"Aragen-107"	Magenta	182	620	72	88	3

WL = Wave length. Max. refl. = Maximum reflection

Results at a glance

- ››› With the new technologies, the possibility of formaldehyde-free production of fluorescent pigments is realistic.
- ››› Eliminating formaldehyde in daylight fluorescent pigments is no longer combined with compromises.
- ››› The new technologies discussed in the paper excel in all their attributes compared with their formaldehyde-containing predecessors.
- ››› A similar technology will soon allow the use of fluorescent pigments in cosmetic products. These hybrid resins will be combined with cosmetic dyes such as D&C Yellow 8, D&C Red 28, D&C Red 21, D&C Violet 2, FD&C Blue1, FD&C Red 5 and all available Lake-versions of these dyes.

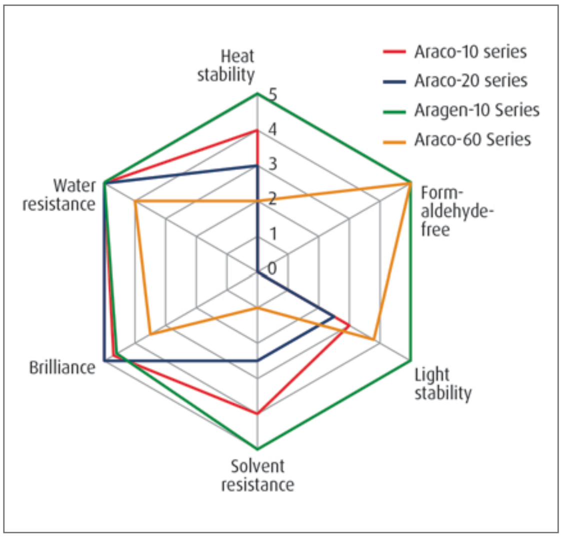

Figure 2 (left): Test of "AG-100 Lemon", 5 % in PVC at 175 °C

Figure 3 (right): Stability properties of the formaldehyde-free series AG-10 and AC-60 as compared with the formaldehyde-containing series (AC-10 and AC-20)

tion and the L*a*b* values that identify the saturation, brightness and chromaticity differences between the AC-10 (formaldehyde containing) and the AG-10 pigments (formaldehyde-free).

A closer look at luminosity

To compare the fluorescence and thus the luminosity intensity, pigments are mixed into acrylic paint. The typical reflection curve of "AG-103 Orange" compared with conventional pigments (here Pigment Orange 73) is shown in *Figure 1*. Similar comparisons can be created for all the bright colours of the AG-10 series with conventional pigments. The reflection of all colours is 2-3 times higher than with conventional pigments. "AG-103 Orange" achieves in white pigment-free formulations, a reflection of 233 % or more, as shown in *Table 2*.

Light fastness and heat resistance

In addition to the solvent resistance of daylight fluorescent pigments, light fastness and heat resistance are important application criteria. The new formaldehyde-free pigments exceed, even in these properties, their formaldehyde-containing counterparts. On the Blue Wool Scale (BWS) "Araco-103" shows in orange acrylic paint (30 %), at a layer thickness of 16 microns, a light fastness of 3, while "Aragen-103 Orange" shows a light fastness of 4 on the BWS under the same conditions. Experience shows that it is possible to use selected UV-absorbers, a thickness of 100 microns and a pigment concentration of 30 % to achieve light fastness of 6 in PVC. A topcoat with UV absorbers helps to achieve a better light fastness.

Thanks to the good solvent resistance; light fastness and to the good reflection the door is open for the AG-10 series in luminous paints and spray cans.

For applications on the PVC calendar or in injection and blow moulding a good or heigh level of heat resistance is required.

Mixtures of "AG-100 Lemon" respectively "AG-103 Orange" were tested in soft PVC formulations at 165 °C and 175 °C over a period of 20 minutes. The pigment concentration was increased from 5 to 10 %. The typical pigment concentration of 30 % was omitted in order to better assess the effect of heat stress on the colour development. In all tests, the colour development was uniform, and the fluorescence of the PVC films consistently high. Through the influence of heat, there were no odours or sticking of the mass on the roll, as shown in *Figure 2*.

To evaluate the heat resistance at higher temperatures, HDPE was coloured with 1 % pigment and tested at various temperatures in an injection moulding machine. Injection moulded in olefins "AG-100 Lemon" remains stable up to 240 °C and loses only on colour strength and brilliance to 280 °C. "AC-100 Lemon" loses stability above 220 °C and at 260 °C begins to show black combustion traces associated with an unpleasant odour. However, plastic parts that were coloured with "AG-100 Lemon" have been heated up to 280 °C without the generation of odours and showed no traces of burning and up to 240 °C with the colour remaining stable.

Figure 3 provides a summary comparison of the main properties of the traditional technologies of daylight fluorescent pigments with the properties of the new AG-10 series. The results of the tests show that daylight fluorescent pigments of the AG-10 series have multivalent uses. They are equally suitable for the colouring of aqueous and solvent-containing concentrates, inks, paints and

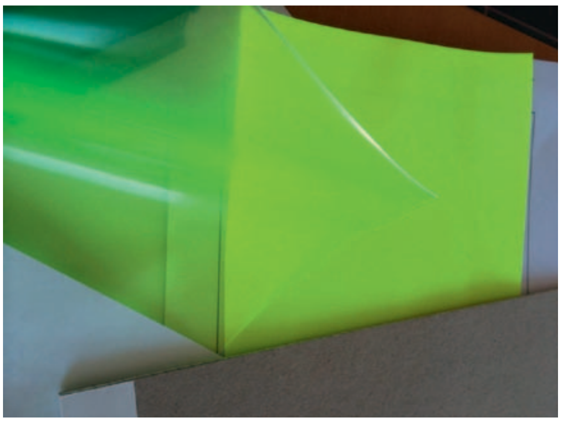

Figure 4: Left: LDPE film with 1.35 % "AP-100 Lemon and a layer thickness of 150 microns. Right: LDPE film with 1.35 % AP-100 Lemon and a layer thickness of 100 microns mounted on a white layer of 100 microns

coatings. Moreover, they are suitable for the colouration of plastics such as PVC, PU, olefins and some engineering plastics. The higher light resistance also allows for a greater range of outdoor applications, but not sufficient for use in car or construction paints.

Other formaldehyde-free technologies for daylight fluorescent pigments

In addition to the pigment series which retain their particle form in the application, there are pigments which melt at a certain temperature in the application, without being soluble in it. This leads to high migration fastness and improved colour strength. Melting daylight fluorescent pigments (MDFP) use such a technology. Both series "Araplast-10" (AP-10) and "Araplast-20" (AP-20) are formaldehyde-free polyester amide resins, coloured with fluorescent dyes.

The colouring of solventbased paints or coatings is not possible with MDFP technology, this fails in such media due to the poorer solvent resistance.

AP-10 & AP-20 pigments already begin to melt at 100 °C and are completely melted at 140 °C. For this reason, and because they are partially soluble in PVC and PU, MDFP pigments are not suitable for the colouration of these polymers. On the other hand a high migration fastness makes the use of AP-10 & AP-20 pigments suitable for the colouring of TPU and olefins (LLDPE, LDPE, HDPE, PP and cPP), while the applications in polystyrene, polycarbonate and PET are limited.

The following properties are important for the colouring of thermoplastics:

» No sticking on the extruder screws during the master batch production
» No, or very low, plate-out on the tools of injection moulding machines
» High heat resistance and acceptable to good light fastness
» Low odour
» Low level of residual monomers for low migration (efflorescence) and for enabling blow moulding of thin layers or sheets
» Good fixation of the dyes to improve the migration properties of the dyes
» High compatibility of the polymers, in order to prevent subsequent efflorescence or bleed. High polymer compatibility is also important for the production of thin layers, or films, by blow moulding or rolling.

Daylight fluorescent pigments in plastic packaging are used mainly for household cleaning products. Other methods, such as the blowing of thin luminous PE films or bottles with fluorescent outer layer and white inner barrier layer, have failed at production scale due to high residual monomer content and plate-out of daylight fluorescent pigments and their limited compatibility with olefins. In this context, the AP-10 & 20 technology should be evaluated.

A 45 % master batch was made with AP-100 Lemon in LDPE. In the final product, the master batch was reduced with LDPE to a final concentration of 1.35 % "Araplast-100 Lemon" in LDPE (corresponding to 3 % master batch).

First, a PE film was produced at 100 microns thickness and was then mounted on a white sheet having a thickness of 100 microns. Another film was produced with a layer thickness of 150 microns. The higher layer thickness is necessary because the fluorescence effect without the opaque, white background appears weaker. Film production went smoothly and the resulting films were homogeneous and without shortcomings, as shown in *Figure 4*.

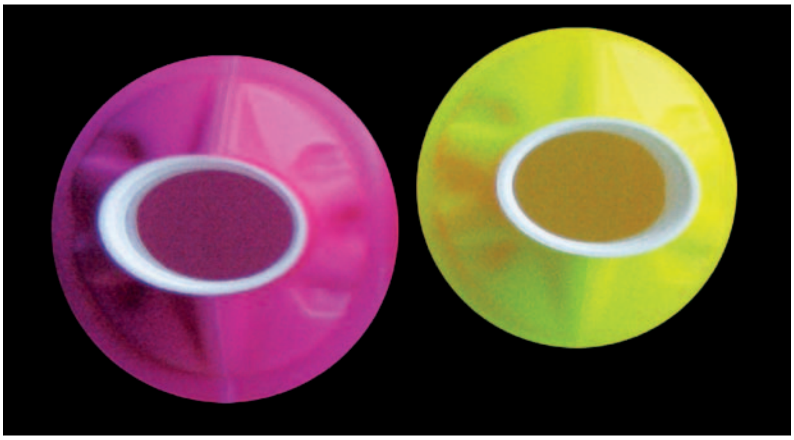

Figure 5: In extrusion blow molding process produced HDPE bottles with a fluorescent outer skin layer and a white barrier inside layer

The high compatibility of the AP pigments with olefins, the very low plate-out and the very low content of residual monomers have enabled the preparation of thin, fluorescent LDPE films. Previously, thin fluorescent plastic films were only available with PVC or PU as a carrier polymer or by coating procedures.

In another test, the melting pigments were tested in extrusion blow moulding (EBM) process. Two extruders have produced two hoses, which were combined in the injection tool to a two-layer bottle with fluorescent, thin outer skin layer of 250 microns and a white inner barrier layer of 500 microns, as shown in *Figure 5*.

In the course of the entire test, over 4000 bottles were produced. The combination of outer fluorescent skin layer and the opaque white inner layer resulted in higher fluorescence visibility. This technique allows the use of daylight fluorescent pigments for new applications in packaging. The white barrier layer prevents any migration of colour towards the content and supports simultaneously the fluorescence and brilliance.

LITERATURE

[1] *Ismael R.*, *Schwander H.*, and *Hendrix P.*, 2013 Fluorescent Dyes and Pigments. Ullmann's Encyclopedia of Industrial Chemistry. 1–22.