secret sensations

Novel functionalities triggered by light - Part II: Photolatent fragrances.

Karin Powell, Johannes Benkhoff, Walter Fischer, Katharina Fritzschke.

UV technology is attractive in the coatings, inks and adhesives industry essentially because of the photolatency of photoinitiators. Photolatent effects can also be found in other areas. In the second article on this subject, the properties and uses of photolatent fragrances are examined.

The concept of photolatency is well-known in the context of photoinitiators for UV-curing technology. This photolatency brings many advantages, such as the ability to produce storage-stable one-pack systems, triggering of reactions on demand, fast achievement of effects and a wide choice of photoinitiators to match irradiation conditions ranging from short wavelength UV to daylight activation. The energy sources require little space and are easy to handle. Photolatency can be maintained simply by the exclusion of light.

Some recent research activities have focused on creating new photolatent effects perceptible with the senses for use in coatings and inks. Photolatent colours, which were described in the last issue (ECJ 7-8/2006, p. 34), allow in-depth images to be created by masking of laser or the colouration of larger surface areas from a colourless precursor. Photolatent fragrances, discussed below, allow production and curing at elevated temperatures and yet retain an extended fragrance-release period.

What smells good, seems good

Olfactory perception has a strong influence on our decisions and actions. Whether we like or dislike another person is strongly related to the subconscious influence of that person's body odours, even if we do not consciously notice them. Fragrances are the ingredients that give food and drink their distinctive taste. For example a high-quality red wine contains a variety of fragrances, which make the experience of drinking it pleasant, and the spices used in Indian cooking give the food its typical taste.

Our instincts keep us away from the source of malodours, as they could be poisonous, whilst pleasant fragrances can help us to feel content. In our industrial environment, with its wide range of artificially manufactured products, the scents released by products can affect the value we give to them. Products with a pleasant smell will always be rated more highly than those omitting smells associated with industrial processes. This applies to body care products, which express our personality, just as it does to wall paint or carpets. In short, fragrances affect our decisions.

Enhanced stability adds value to fragrances

Most fragrances are by nature highly volatile. Their use in products or substrates that are processed at elevated temperatures is very limited, as the fragrant effect will diminish during manufacture and the olfactory effect will be of short duration. Several chemical delivery systems have been developed to extend the duration of perception and increase the stability of fragrant compounds. Most systems are based on the cleavage, including thermal and photo-induced cleavage, of a precursor (pre-fragrance) upon stimulation. Alternatively, encapsulation techniques can be used to achieve higher stability and prolong the effect.

State-of-the-art pre-fragrances are mainly used for home and personal care products, such as detergents, moisturisers and hair care. Several concepts recently reviewed by Herman et al. [1] are relevant to this topic. However, these applications only require a relatively short life-cycle, ranging from a few hours to several days.

Coatings make great demands on fragrance stability

In coatings, the pre-fragrance has to be compatible with the system, thermally stable at even higher temperatures, and also, once activated with light, should have no effect on coating properties or appearance. Further, a single release mechanism for a whole series of fragrances would be preferable, as it would allow the release of predefined scents comprising a blend of components.

New systems currently being designed for application in coatings are stable during coating manufacture, application and curing, and have prolonged, slow fragrance release. Figure 1 shows the concept of photo induced release of vanilla from a temperature-stable vanilla pre-fragrance incorporated in a coating film.

This novel photolatent precursor is able to release a wide variety of natural or synthetic fragrances, so that scents ranging from floral fruity sweet, fresh citrus and minty to spicy herbal or even wine-like or woody can be created.

The benefits of a fragrant product are clear, as fragrances are perceived as pleasantly aesthetic and strongly associated with well-being and security, or can serve as a marker, even to providing unique product branding. Photolatent fragrances are not restricted to simply scenting a coated surface; they can conveniently be used to conceal the malodours of newly manufactured products.

Some odours emitted by new products, even if their concentrations are low and non-toxic, create an unfavourable impression, whereas a pleasant fragrance perceived when opening the packaging can definitely add value. In this application, irradiation is the last step before packaging, or if light transparency is sufficient, fragrance release can be triggered at any point by irradiation through the packaging material.

Another application is in products that imitate natural materials, such as synthetic leather and veneers. Appearance and tactile properties of these products can largely be imitated today. Using photolatent fragrances to add a typical scent to artificial products will bring the synthetic product even closer to its natural counterpart.

Comparing photolatent and natural fragrances

The following photolatent fragrances have been developed, using a novel chromophore:

- Photolatent Vanilla (denoted as PLV)
- Photolatent Lemon (PLL)
- Photolatent Floral (PLF)
- Photolatent Mint (PLM)

Experiments were carried out to compare photolatent fragrances with natural ones. In addition, properties of a state-of-the-art photolatent vanilla based on o-nitrobenzyl (designated NBV), as shown in Figure 2, were compared with those of the novel photolatent vanilla (PLV).

Absorption spectra of vanilla pre-fragrances were measured at 0.05% in acetonitrile using quartz cells in a “Perkin Elmer Lambda Bio 40”. To ensure an equal amount of pre-fragrance or natural fragrance was present within the coatings formulation, all concentrations were calculated to equimolar ratios (0.075 mol/kg) on solids. Fragrances were tested in two conventional thermally cured alkyd-melamine formulations:
As TiO₂ absorbs in the UV range, the vanilla derivatives used to trigger fragrance release. Sources, but also daylight, which contains UV A, can thus be of PLV to be about 380 nm. Various artificial UV-light at a longer wavelength). The enlargement of the wavelength more bathochromic than PLV (that is, its peak absorption is show strong absorption in the UV-A range. NBV is slightly As can be seen in Figure 3, both types of photolatent vanilla TiO₂ does not inhibit fragrance release perceptible at very low concentrations.) Dark storage stability of fragrances is confirmed Samples prepared using the white formulation containing PLV were stored under light exclusion but good ventilation for six months. One sample was stored immediately after curing; the other was irradiated once under UV and then stored. Even though the irradiated sample was markedly fragrant after irradiation, the vanilla scent disappeared during the storage period so that both samples were olfactorily neutral after three months. After irradiation, vanilla was clearly released from both samples. This experiment shows that the pre-fragrance is stable within a film for long periods, provided it is not exposed to light. It also shows that sufficient pre-fragrance remains in a pre-irradiated film for a further release. Durability is tested under daylight irradiation To evaluate the duration and perceived strength of fragrance release under more natural light conditions, samples of the white pigmented film containing PLV were placed under artificial daylight lamps. Fragrance strength was assessed at regular intervals. The samples were permanently irradiated during working days and kept in the dark with good ventilation during the weekends. As can be seen in Figure 4, vanilla release is perceptible for about four weeks. As there were no dark periods except at the weekends, it can be assumed that release would be even longer in a night and day cycle. Superior lightfastness of new photolatent vanilla The light stability of the photolatent vanilla derivatives was tested in both formulations. Colour was measured at regular intervals. Figure 5 shows the colour difference \( \Delta E \) after irradiation for 1000 hours. The graph on the right shows the measurements in the white stabilised formulation. A significant colour change is observed only with NBV, while both PLV and the coating itself are lightfast. In both pigmented and clear systems, discolouration of NBV decreases with exposure time. A complete recovery from such discolouration is, however, unlikely. Comparing these results, it is clear that the HALS stabilisation and the pigmentation have a positive effect on durability. The extent of colour change is significantly lower in the stabilised white than in the clear, which starts to discolour even after 500 hours exposure. NBV causes a substantial colour change in the clear formulation, which appears bright orange over a white background. The clear sample (Figure 5, left) containing PLV showed stronger discolouration than the clear reference or natural vanilla. The remaining concentration of natural or pre-fragrance in the film was not measured. However, it can be assumed that the concentration of natural vanilla was already lower at the beginning of the irradiation than the concentration of the photolatent vanilla. The concentration of natural vanilla will decrease during curing (at 120°C), and it will quickly vanish at the elevated temperatures present in the irradiation chamber. This may

- A white pigmented (25% TiO₂) formulation containing 1% HALS type light stabiliser. Samples were prepared by stirring photolatent or natural fragrances into the formulations and dissolving them at 50°C. Coatings were applied at ambient temperature by wire-wound bar on 5 x 10 cm white pre-coated aluminium panels and cured at 120°C for 30 min. Cured samples were irradiated with "Geo" UV-curing equipment from Aetek International, using 2 mercury bulbs at 80 W/cm at a line speed of 10 m/min, while artificial daylight lamps as described in DIN 6173 were used for continuous irradiation. The scent released by the coating was evaluated olfactorily by at least two persons and ranked from 0 to 2 (0 = no perception, 1 = slight perception, 2 = strong perception). It should be borne in mind that the sense of smell is a subjective perception and the human sensation does not represent the actual concentration. To test the possibility of fragrance release or renewal of the effect after storage, samples were kept in the dark for 6 months at room temperature. The samples were then irradiated with UV curing equipment as described above. The duration of fragrance release was tested under permanent irradiation with artificial daylight lamps during workdays (interrupted at weekends). Samples were evaluated olfactorily at regular intervals. In both cases the white formulation was used. Light stability was tested in both formulations in a Xenon WOM as described in DIN 53387/E EN ISO 11341/C. Colour was measured at regular intervals on a "Minolta 3600 d" with total colour difference DE used as the measure of discolouration. Photolatent fragrances are little affected by heating All products were tested in the clear formulation, and the vanilla derivatives were also tested in the white pigmented formulation. One irradiation pass was performed on UV-curing equipment. Table 1 shows the strength of fragrance perception before and after irradiation in the clear alkyd-melamine film. All photolatent fragrances showed a clear fragrance release after UV irradiation; yellow discolouration was observed with NBV. The natural lemon and floral fragrances were no longer perceptible after thermal curing. Both products are highly volatile and vanish at the elevated temperatures required for curing. Natural mint fragrance remained in the freshly prepared film with low perceptibility; natural vanilla was strongly perceptible, which shows that the substance has the lowest volatility of all the fragrances tested. (Additionally, vanilla is perceptible at very low concentrations.) TiO₂ does not inhibit fragrance release As can be seen in Figure 3, both types of photolatent vanilla show strong absorption in the UV-A range. NBV is slightly more bathochromic than PLV (that is, its peak absorption is at a longer wavelength). The enlargement of the wavelength range between 300 and 450 nm shows the absorption peak of PLV to be about 380 nm. Various artificial UV-light sources, but also daylight, which contains UV A, can thus be used to trigger fragrance release. As TiO₂ absorbs in the UV range, the vanilla derivatives were also tested in a white pigmented formulation in order to determine whether the pigment reduces or even inhibits photo-cleavage and hence the release of fragrance. In both cases, the odours were not detectable before irradiation but were quite strong after UV irradiation. It is therefore clear that TiO₂ does not inhibit fragrance release; light penetration is sufficient to release a clearly perceptible amount of vanilla. Pigmentation of formulations containing photolatent fragrances should thus be possible so long as the pigment does not quench the cleavage of the pre-fragrance. NBV showed very good fragrance release properties. However, both clear and pigmented samples showed significant discolouration after irradiation. In addition, a sharp, unpleasant secondary smell was noticed. The lightfastness of this product is therefore expected to be relatively poor.
explain the high lightfastness of the natural product. Comparing the photolatent vanilla derivatives, it is clear that PLV is much more suitable for coatings applications than the existing NBV product.

**Range of photolatent fragrances will be extended**

The novel photolatent system has thus been shown to exhibit various benefits compared to a state-of-the-art photolatent product and natural fragrances. Experiments demonstrate that it is indeed suitable for coatings, as it is highly compatible with the widely used alkyd-melamine coatings, allows long-lasting fragrance release and is highly durable. Development work will continue, focusing on a wider variety of fragrances especially those suitable for products that imitate nature, such as veneers or leather. A fragrance imitating wood will give the missing typical wood fragrance to a synthetic product with the appearance and feel of wood. Other developments will focus on concealing malodours.

**REFERENCE**


**Results at a glance**

- Since odours affect our perceptions of the quality of goods, synthetic fragrances can add value to many products.
- A range of four photolatent fragrances that are odourless until exposed to UV light has been developed and tested.
- These products are compatible with conventional coatings and remain in the film after thermal curing, while natural fragrances volatilise during cure.
- In both clear and opaque films, fragrance release can be triggered by a short UV exposure. Under daylight irradiation, the fragrance remains perceptible for a long period.
- It was shown that one product (photolatent vanilla) causes significantly less discoloration than an existing product, and that it can be stabilised by HALS addition.

**The authors:**

- Karin Powell received her degree in chemical engineering from the University of Applied Sciences in Esslingen, Germany in 2003. After completing her diploma thesis she joined Ciba Specialty Chemicals in 2003, working in the Technology Centre, Business Line Coatings (Coating Effects Segment) as an application specialist.
- Johannes Benkhoff received his Diploma degree in chemistry from the University of Bochum, Germany, in 1991. After obtaining his PhD at the University of Essen, he continued academic research at Harvard University, U.S.A. He joined Ciba Specialty Chemicals in 1998. Recently he was appointed Head, Technology Centre of Business Line Coatings, Coating Effects Segment.
- Walter Fischer received his Diploma degree in chemistry from the University of Basel, Switzerland in 1972. After completing his PhD he continued academic research at the University of Basel and the University of Arizona, Tucson, (USA). He joined Ciba-Geigy AG, Basel, in 1978 and is currently head of Research Group Product Design CH, Plastic Additives Segment.
- Katharina Fritzschke received her Diploma degree in chemistry from the University of Freiburg, Germany, in 1983. After completing her PhD thesis in 1987, she continued her academic research at the University of Massachusetts, Amherst, USA. In 1989 she joined the former dyestuff research department of Ciba-Geigy AG, Basel. She is now a synthetic chemist in the research group of the Plastic Additives Segment.
Figure 1: General mechanism of light-induced fragrance release of vanilla
Figure 2: Structure of nitrobenzyl vanilla (NBV)
Figure 3: Absorption spectra of vanilla pre-fragrances with magnification of selected wavelength band on right.

Figure 4: Duration of vanilla fragrance release under irradiation with artificial daylight.
Figure 5: Colour change during irradiation in Xenon WOM of vanilla pre-fragrances and natural fragrance (left: clear formulation, right: white pigmented formulation)
Table 1: Fragrance strength of natural and photolatent fragrances in clear formulation before and after irradiation

<table>
<thead>
<tr>
<th>Timing/Fragrance</th>
<th>Photolatent</th>
<th></th>
<th>Natural</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Vanilla</td>
<td>neutral</td>
<td>strong</td>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>Lemon</td>
<td>neutral</td>
<td>strong</td>
<td>neutral</td>
<td>neutral</td>
</tr>
<tr>
<td>Floral</td>
<td>neutral</td>
<td>slight</td>
<td>neutral</td>
<td>neutral</td>
</tr>
<tr>
<td>Mint</td>
<td>neutral</td>
<td>strong</td>
<td>slight</td>
<td>slight</td>
</tr>
<tr>
<td>Nitrobenzyl Vanilla</td>
<td>neutral</td>
<td>strong</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>