

Photoinitiators

For cationic curing

 **Deuteron**[®]
ADDITIVES TO YOUR SUCCESS



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Cationic photoinitiators by Deuteron

Radiation-curing systems are becoming more important because of their low emissions. They are solvent-free and thus environmentally friendly. They dry immediately after curing and are quickly ready for further processing, which enables a fast and cost-effective production. Radiation-curing systems consist of reactive resins (oligomers or prepolymers) and reactive thinners (monomers). The „thinner“ is firmly integrated into the polymer matrix by the same chemical reaction as the resins and contributes to the film formation and its subsequent properties. UV-curing systems require additional photosensitizers/initiators because the energy density of the UV rays alone is not sufficient to start the chain reaction.

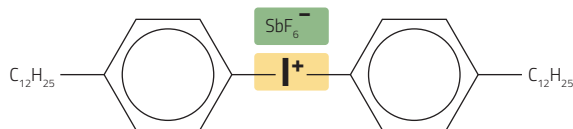
There are two fundamentally different UV-curing systems:

During **radical polymerization** a free radical is transferred from monomer to monomer of the unsaturated compounds.

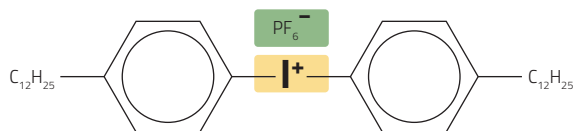
During **cationic polymerisation** a charge is transferred from monomer to monomer.

Specific properties of cationic curing

- Insensitive to oxygen, thereby eliminating the need for cost-intensive inertisation.
- Volume shrinkage occurs comparatively less, as the cationic reaction's chain-extending opening of the oxiran group barely influences the density. In radical systems the intermolecular distance between neighboring monomers is slightly reduced. The lower density increase, leads to less shrinkage and therefore less tensions in the finished coating.
- Our photoinitiators do not release benzene and are less odorous than initiators based on sulphonium salts. The odour of the liquid coating, as well as of the cured layer is usually lower and more fleeting compared to radical systems.
- Significantly lower hazard potential, than radical systems.
- Sensitive to moisture relative humidity should remain below 70 %.
- Contamination with alkaline materials (for example from amines alkaline additives, pigments and fillers) can impair or even completely prevent curing.



Deuteron UV 1240 / 1242



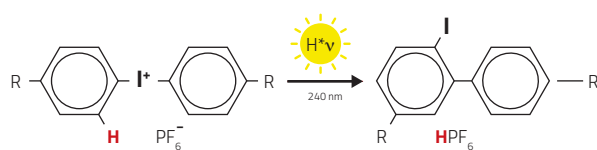
Deuteron UV 3100

Formulation

The resins used are mainly epoxy resins. Vinyl ethers and oxetanes can also be used. The selection of the optimum binder depends on the application. Cycloaliphatic epoxides are more reactive than aliphatic epoxides. Less reactive types include epoxidized vegetable oils, such as epoxidized linseed oil. Combining epoxides with polyols enables the film properties to be adjusted from hard/tough to flexible in order to meet various specific requirements. Polyols can be used as reactive thinners and/or modifiers; for example, to counteract embrittlement. They act as monomers and are crosslinked in the epoxy network. While the selection of cycloaliphatic epoxides is limited, many different polyols are available, from di- and tri-functional glycols to high-functional polyols, to adjust the desired properties. Curing speed can be further improved by using small amounts of alcohols with their good chain transfer properties.

Blocked Lewis or Brønsted acids are used as cationic initiators, which, upon absorption of UV radiation, convert the initiator molecules into strong acids, either Lewis or Brønsted acids.

The **cationic** part of the photoinitiator molecule absorbs the UV radiation. The **anionic** part of the molecule is broken down into the strong acid.



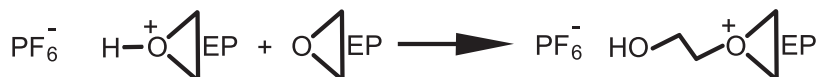
Simplified illustration of the reaction mechanism to produce a strong acid from a diaryl iodonium salt.

The acid's proton causes an opening of the epoxy ring and starts the polymerization with continuous chain growth.

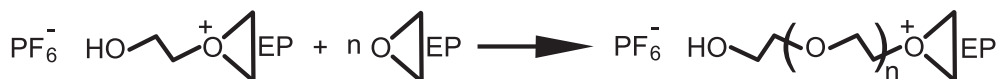
1. Protonation of an epoxy group from the photogenerated acid.



2. Opening of the protonated epoxy group and charge transfer to another epoxy group.



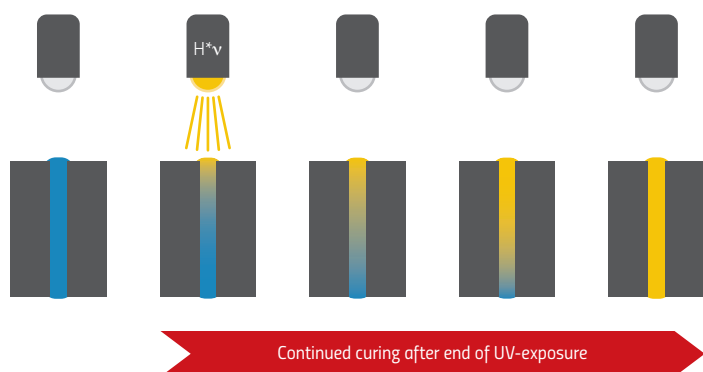
3. Chain growth ends when all monomers are consumed or charge is transferred to another chain.



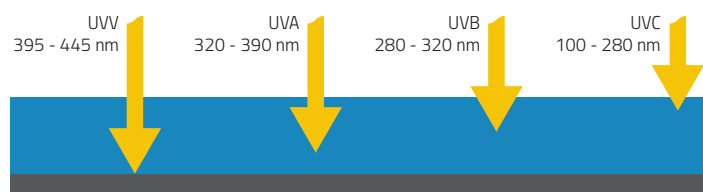
Dark curing

Compared to the very short lifetimes of free radicals, the photoinitiator's acids are extremely long-lived during the cationic chain reaction. **The reaction continues after exposure without requiring further light energy.** The polymerization can remain active for up to several days.

Initially, curing occurs mainly at the surface and then progresses gradually. The active acid can diffuse through the still liquid layer, curing areas that were not directly exposed. This curing process continues even in the dark, and has the advantage that opaque and pigmented systems and complex geometries can be completely cured. This effect is called "dark curing" and is an essential characteristic of cationic photopolymerization.

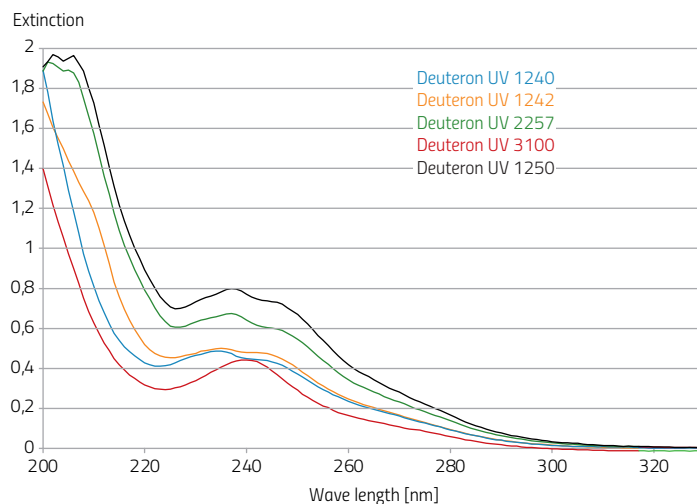


Relative penetration depth for UV sources. The shorter the wavelength, the lower the penetration depth of the UV light into the liquid coating matrix.



Absorption range

Like different radical photoinitiators, cationic photoinitiators, which in our case are based on different molecular configurations around the iodine atom, have different absorption spectra. Our initiators have their absorption maximum at about 240 nm. Since the optimal wavelength ranges for initiation are therefore more in the short-wave range, Iron-doped Mercury vapor lamps, are suitable as UVC light sources. However, standard Mercury vapor lamps also emit a high proportion in the short-wave range.



Dosage

The amount of initiator molecules is relevant for the number of starting points for the chain reaction. The more starting points, the faster the reaction – however the chain length is correspondingly shorter, which directly influences the properties of the resulting polymer network.

Experience shows that the dosage should range from 1 % to 4 %. Adding more than 5 % of initiator is unnecessary.

Co-catalysts and Sensitizer

Co-catalysts can be used to increase the utilisation of the available UV light or to adjust the disproportion between the initiator's absorption maximum and the emission range of the UV source. This is becoming increasingly important, especially with LED technology, as their emission spectra are narrower than gas-discharge lamps and therefore less IR radiation occurs.

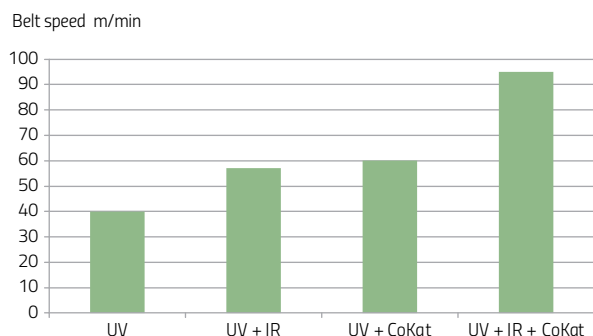
The catalysts and sensitizer absorb some of the long-wave light and the radical reaction in turn supports the formation of the superacid from the cationic initiator. The starter compound for a radical chain reaction is degraded by long-wave UV light and forms a free radical, which in turn supports the protonation or formation of the superacid. In principle, all starter compounds are suitable as photochemical reduction agents if the free radical has sufficient reduction potential.

Examples of starter compounds for radical chain reactions are hydroxyketones and hydroxyketals, hydroxyethers and acylphosphine oxides. The optimum ratio of iodonium compound to co-catalyst must be adapted to the application. Significant acceleration effects are achieved with an amount of 5 % to 30 % co-catalyst, based on the used amount of cationic initiators.

Type	CAS-Nummer
Hydroxyketone	106797-53-9
Bis-Acylphosphin oxide	162881-26-7
Benzylidimethyl ketal	24650-42-8

In many applications, the efficiency of cationic initiators can be increased by adding photosensitizers. The light yield and speed of the initiator's photolysis can thus be increased. Long wave UV light of up to 390 nm can also be used to initiate the reaction in deeper layers. This results in improved depth hardening. Typical sensitizers that can be used are thioxanthenes such as CPTX, DETX and ITX. They are, however, not suitable for all areas of application.

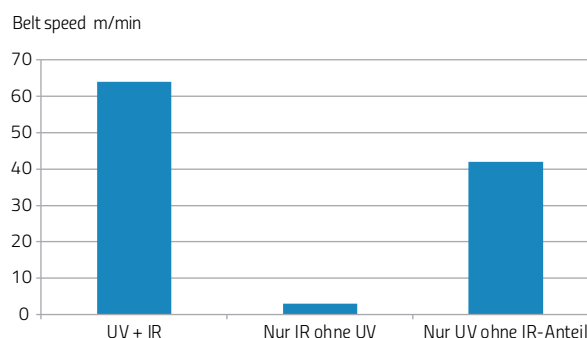
The use of small amounts of polyhydric alcohols (PEG, PPG) also improves the curing speed and reaction time, as they have good chain transfer properties.



Example of the effect of co-catalysts and heat on the curing of cycloaliphatic epoxies.

Thermal and photochemical initiation

With cationic photoinitiators, epoxy resins can be cured thermally via catalysis with thermal activators (e.g. copper compounds: Cu(2) naphthenate or copper(2+) neodecanoate) and co-catalysts (e.g. benzyl dimethyl ketal) in combination with polyols. The activator is an unstable compound that becomes a reduction agent when subjected to thermal stress. The formed Cu(I) salt decomposes the initiator and starts the polymerization. 0.1 g to 0.3 g of co-catalyst can be added to the system in order to increase the initiator's efficiency of the initiator as a photochemical promoter. Benzyl dimethyl ketal itself also acts as a thermal activator.



IR-radiation and temperature

The actual initiation is very fast. Accelerating measures therefore have no influence on the formation of the superacids. However, the reaction speed of the cationic chain reaction benefits from increasing the temperature through heat. Post-curing is also accelerated, for example by utilising IR dryers.

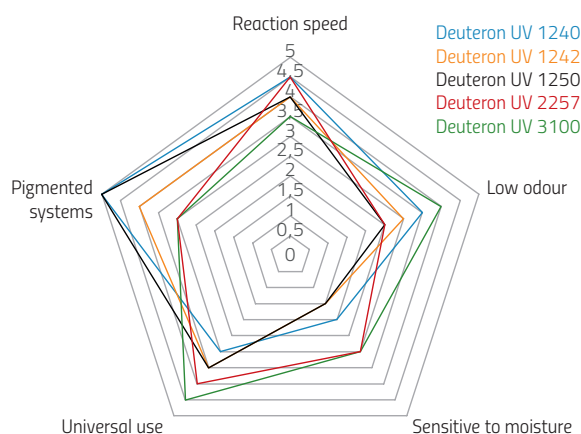
Electron beam curing

Cationic systems can also be initiated with electron radiation. Unlike radical systems, cationic systems still require the use of photoinitiators. Instead of UV light, higher energy electrons split the initiator salt into the required super-acid. The electron's relatively large penetration leads to the activation of initiator molecules, even in deeper layers. This can significantly increase the efficiency of the curing process. There is no limitation as to special required wavelength ranges from the initiators' unsuitable absorption maxima.

Differences of curing mechanisms

	Cationic	Radical
Reaction speed	medium	very high
Post-crosslinking	yes	no
Shrinkage	3-5 %	5-15 %
Inhibition by atmospheric oxygen / inerting necessary	no	yes
Sensitive to humidity.	yes	no
Sensitive to alkaline contamination.	yes	no
Adhesion properties on plastics, metal and glas	good to very good	moderate
Mechanical resistance	very high	moderate
Gloss and hardness	very high	moderate
Range of raw materials	limited	high
Cost level	Initiator high	moderat
Outdoor weathering capability	limited	good
Sensibilisation potential	low	partially
Migration potential	low	partly high
Odor intensity	low	high
Elektron beam crosslinkable	with initiator	without Initiator

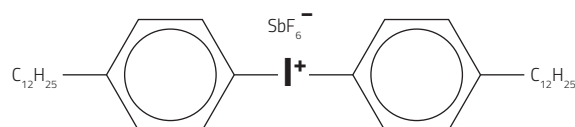
Application properties



	UV 1240	UV 1242	UV 1250	UV 2257	UV 3100
Overprint varnishes	X	X	X	X	X
UV screen printing	X	X	X	X	X
UV flexo printing	X	X	X	X	X
UC Laminating adhesives	X	X	X	X	
Metal Coatings	X	X	X	X	X
Plastic coatings	X	X	X	X	X
UV/EB release coatings		X			
Food Packaging			X	X	X

Our cationic photoinitiators are iodonium salts as antimonate or phosphate:

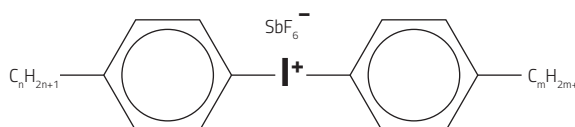
Deuteron UV 1240 / 1242



Bis-(4-dodecylphenyl) iodonium hexafluoro antimonate

Linear, good depth hardening, especially suitable for coloured coatings, good price-performance ratio.

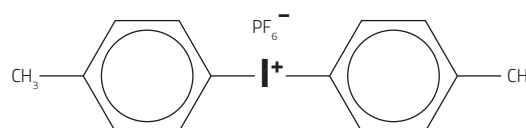
Deuteron UV 1250



Bis-(4-(C10-C13) alkylphenyl) iodonium hexafluoro antimonate

Branched, low migration, especially for highly-filled pigmented systems and indirect food contact.

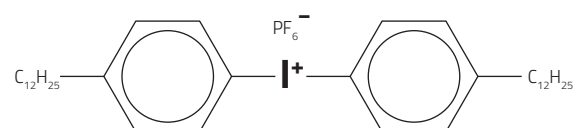
Deuteron UV 2257



Bis-(4-methylphenyl) iodonium hexafluoro phosphate

Free from Antimony, faster than UV 3100

Deuteron UV 3100



Bis-(4-dodecylphenyl) iodonium hexafluoro phosphate

Free from Antimony, less odorous than UV 2257

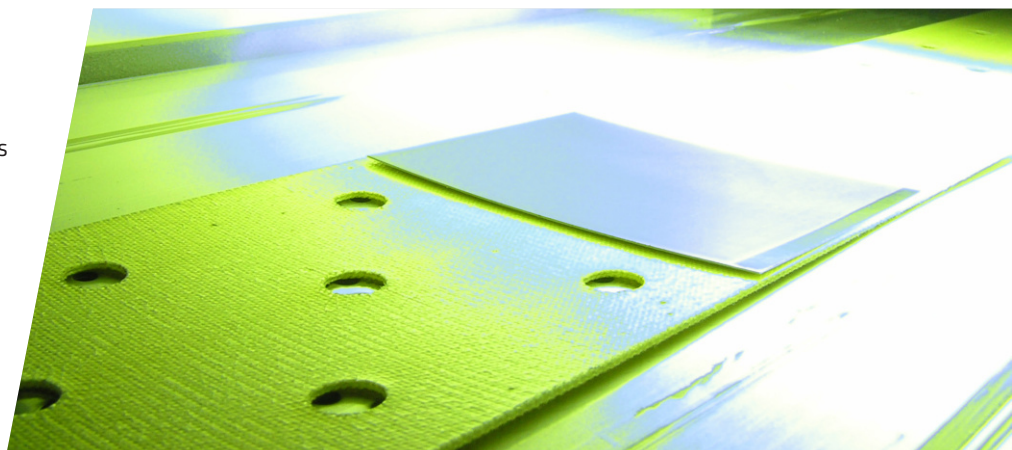


Photoinitiators

For cationic curing

Properties at a glance

- Living polymerization
- Good adhesion to glass, plastic, metal or ceramics
- No oxygen inhibition
- Sensitive to moisture and amines
- Low shrinkage
- Extreme toughness and flexibility
- Less odorous than sulphonium salts
- No release of benzene
- Excellent flexibility
- High gloss



Technical data

	Anion	Solvent	Active content %	Density kg/L	Flash point °C	Sensitive wavelength range nm	Absorption maximum nm	Benzene-free	Appearance
DEUTERON UV 1240	Antimonate	Propylen-carbonate	50	1.25	>135	220-250	240	Yes	Reddish, viscous oil
DEUTERON UV 1242		C12/C14 Glycidether		1.1	>100				Brownish, viscous liquide
DEUTERON UV 1250									
DEUTERON UV 2257	Phosphate	Propylen-carbonate	40	1.4	>135				Yellowish, liquid of low viscosity
DEUTERON UV 3100		C12/C14 Glycidether		1.1	>100				Reddish, viscous liquid

Research and Development:

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Visit us on the Internet

Our documents such as product datasheets, safety datasheets, regulatory information and brochures are available in the download area of our website without registration.

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