

Applications: Free Radical Initiators

Photoinitiators: Classification

A photoinitiator is a compound especially added to a formulation to convert absorbed light energy, UV or visible light, into chemical energy in the form of initiating species, viz., free radicals or cations. Based on the mechanism by which initiating radicals are formed, photoinitiators are generally divided into two classes:

- Type I photoinitiators undergo a unimolecular bond cleavage upon irradiation to yield free radicals.

- Type II photoinitiators undergo a bimolecular reaction where the excited state of the photoinitiator interacts with a second molecule (a coinitiator) to generate free radicals.

UV photoinitiators of both Type I and Type II are available. However, visible light photoinitiators belong almost exclusively to the Type II class of photoinitiators. Table I summarizes the various classes of available Type I and Type II photoinitiators and their common applications.

Table I: Common Applications for Different Classes of Photoinitiators

Photoinitiator Class Application	UV-Photoinitiators								Visible Photoinitiators Titanocenes
	Type I Photoinitiators						Type II		
	Benzoin ethers	Benzil ketals	α -Dialkoxy-acetophenones	α -Hydroxy-alkyl-phenones	α -Amino-alkyl-phenones	Acyl-phosphine oxides	Benzo-phenones/ amines	Thio-xanthenes/ amines	
Wood coatings (polyester)	X	X	X			X			
Paper coatings				X			X		
Clear coatings (on metal, wood, plastic)		X	X	X	X ²				
Printing plates		X			X	X			X
Offset inks				X ¹	X		X	X	
Screen inks					X ³		X	X	
Pigmented coatings					X			X	
White lacquers					X ⁴	X			
Photo resists					X ³			X	X

(1) In combination with benzophenone. (2) Only systems of high reactivity. (3) Partially in combination with thioxanthenes. (4) Thin layers only.

This chart is reprinted with permission from SITA Technology Ltd.

Applications: Free Radical Initiators

Photoinitiators: UV Absorption Spectra

For photoinitiation to proceed efficiently, the absorption bands of the photoinitiator must overlap with the emission spectrum of the source and there must be minimal competing absorption by the components of the formulation at the wavelengths corresponding to photoinitiator excitation. For the initial selection of a photoinitiator in your application, viz., one with excitation wavelengths that lie in the emission spectrum of your UV source, as well as in the absorption window of your formulation, information about the photoinitiator absorption spectrum is essential.

To aid in this initial selection, UV absorption spectra of 47 commonly used radical and cationic photoinitiators (see Table I) are displayed in this section. Approximately 100

additional substituted acetophenones and benzophenones that are potential photoinitiators are available from Aldrich; search our product database at www.sigma-aldrich.com.

Spectra were recorded on a Perkin Elmer UV/Vis Lambda 2 spectrophotometer using Perkin Elmer Computerized Spectroscopy Software 4.01. Concentrations are expressed as % weight of solute in volume of solvent. The solvent used was A.C.S. spectrophotometric grade methyl alcohol. For comparison purposes, the emission spectrum of a medium pressure mercury lamp, the most widely used energy source, is shown as the [last figure](#).

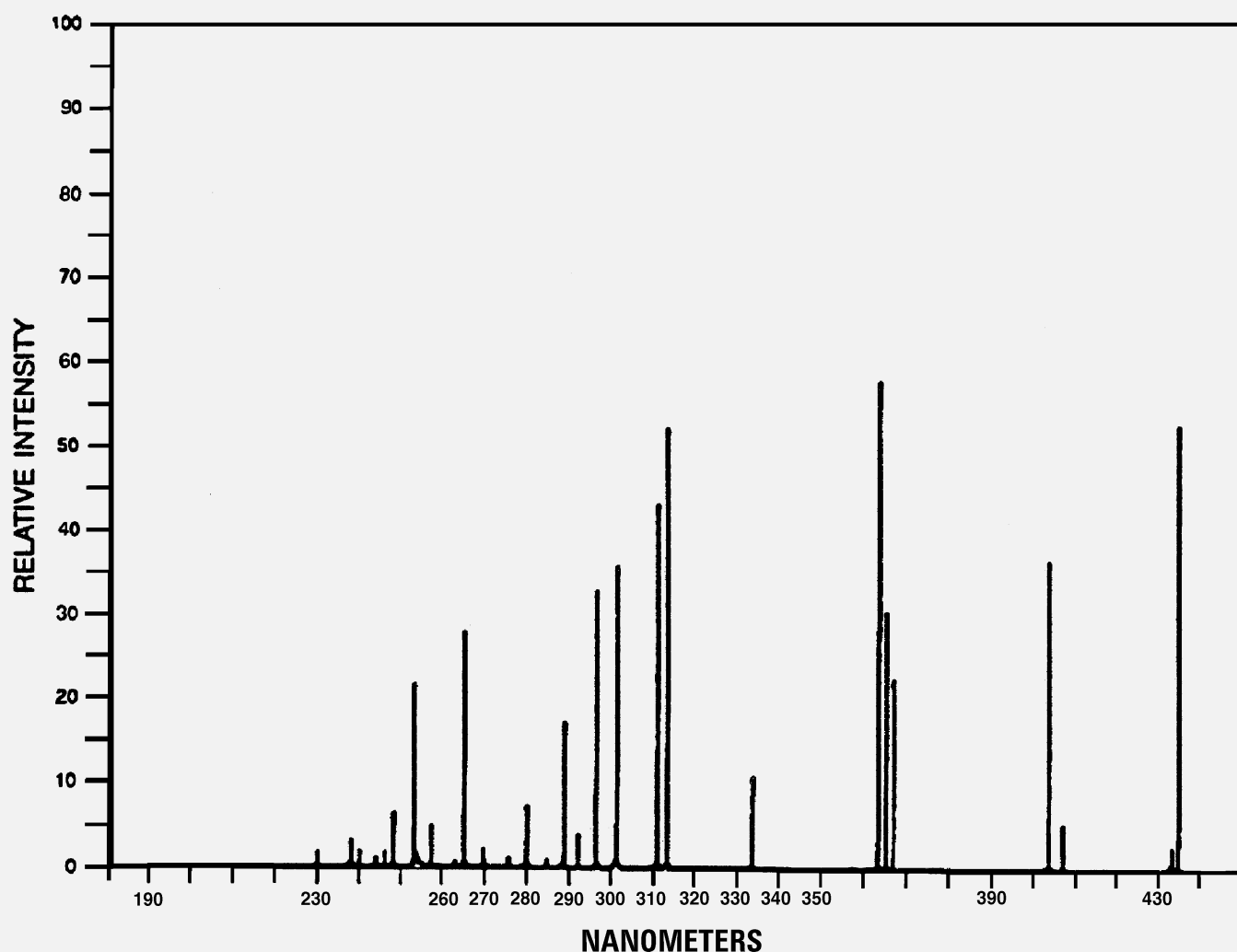
Table I: Commonly Used Radical and Cationic Photoinitiators whose UV Absorption Spectra are Displayed in this Section. (Click on the photoinitiator name coded red to view the UV spectrum. Click on the product number coded blue to link to the product document sheet on the Sigma-Aldrich Web site.)

Cat. No.	Photoinitiator	Cat. No.	Photoinitiator
A1,070-1	Acetophenone, 99%	19,611-8	2,2-Dimethoxy-2-phenylacetophenone, 99%
A8,840-9	Anisoin, 95%	14,934-9	4-(Dimethylamino)benzophenone, 98%
A9,000-4	Anthraquinone, 97%	14,670-6	4,4'-Dimethylbenzil, 97%
12,324-2	Anthraquinone-2-sulfonic acid, sodium salt monohydrate, 97%	D14,966-7	2,5-Dimethylbenzophenone, tech., 95%
11,931-8	(Benzene) tricarbonylchromium, 98%	D14,967-5	3,4-Dimethylbenzophenone, 99%
B515-1	Benzil, 98%	40,566-3	Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide/2-Hydroxy-2-methylpropiophenone, 50/50 blend
39,939-6	Benzoin, sublimed, 99.5+%	27,571-9	4'-Ethoxyacetophenone, 98%
17,200-6	Benzoin ethyl ether, 99%	E1,220-6	2-Ethylanthraquinone, 97+%
19,578-2	Benzoin isobutyl ether, tech., 90%	F40-8	Ferrocene, 98%
B870-3	Benzoin methyl ether, 96%	32,810-3	3'-Hydroxyacetophenone, 99+%
B930-0	Benzophenone, 99%	27,856-4	4'-Hydroxyacetophenone, 99%
40,562-0	Benzophenone/1-Hydroxycyclohexyl phenyl ketone, 50/50 blend	22,043-4	3-Hydroxybenzophenone, 99%
26,246-3	3,3',4,4'-Benzophenonetetracarboxylic dianhydride, sublimed, 98%	H2,020-2	4-Hydroxybenzophenone, 98%
B1,260-1	4-Benzoylbiphenyl, 99%	40,561-2	1-Hydroxycyclohexyl phenyl ketone, 99%
40,564-7	2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone, 97%	40,565-5	2-Hydroxy-2-methylpropiophenone, 97%
16,032-6	4,4'-Bis(diethylamino)benzophenone, 99+%	15,753-8	2-Methylbenzophenone, 98%
14,783-4	4,4'-Bis(dimethylamino)benzophenone, 98%	19,805-6	3-Methylbenzophenone, 99%
12,489-3	Camphorquinone, 98%	M3,050-7	Methylbenzoylformate, 98%
C7,240-4	2-Chlorothioxanthen-9-one, 98%	40563-9	2-Methyl-4'-(methylthio)-2-morpholinopropiophenone, 98%
40,807-7	(Cumene)cyclopentadienyliron(II) hexafluorophosphate, 98%	15,650-7	Phenanthrenequinone, 99+%
D3,173-7	Dibenzosuberone, 97%	29,074-2	4'-Phenoxyacetophenone, 98%
22,710-2	2,2-Diethoxyacetophenone, 95%	T3,400-2	Thioxanthen-9-one, 98%
D11,050-7	4,4'-Dihydroxybenzophenone, 99%	40,722-4	Triarylsulfonium hexafluoroantimonate salts, mixed, 50% in propylene carbonate
		40,721-6	Triarylsulfonium hexafluorophosphate salts, mixed, 50% in propylene carbonate

Applications: Free Radical Initiators

Photoinitiators: UV Absorption Spectra (continued)

Emission spectrum of a medium pressure mercury arc lamp



SPECTROPHOTOMETRIC GRADE SOLVENTS



- Excellent for applications requiring
 - High purity
 - UV transparency
 - Low residue on evaporation
- Rigorously analyzed during and after production, and during packaging to ensure high purity
- Once packaged, leakage and breathing problems are eliminated because we use the Sealed for Quality system
 - 4-Liter sizes come in standard amber glass bottles. These bottles have a PVC shrink band around the neck to provide additional closure integrity and tamper evidence.