Photocuring Activity of Several Commercial, Near UV Activated Photoinitiators in Clear and Pigmented Systems

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Some of the most important commercial near UV photoinitiators have been analyzed by UV spectroscopy to evaluate the type of electronic transitions occurring upon absorption of light. Photocuring studies have been undertaken by real time infrared spectroscopy (RTIR) in clear and pigmented (black, magenta, cyan, and yellow) systems with UV and visible light at different photoinitiator concentrations in the presence of air. Generally, the Type I photofragmenting photoinitiators appear to operate more effectively under UV excitation when compared with the Type II thioxanthones, especially in pigmented systems. There is a reasonable correlation between the UV and visible absorption properties of the respective initiators and their overlap with the excitation source.

INTRODUCTION

The photocuring of coatings and inks by ultraviolet or visible light has become established technology for many industrial applications.[1-5] One notable area is in the development of inks where the reactivity of photoinitiators and their absorption spectra play a complex and intricate role. In this regard, several types of photoinitiators have been developed to induce the photopolymerization or photocrosslinking of acrylated systems for inks.

There are two basic categories of photoinitiators that meet these requirements. The first group involves Type I photoinitiators which undergo a direct photofragmentation process (α or less common β cleavage) upon absorption of light and formation of initiating radicals capable of inducing polymerization. These photoinitiators do not normally operate through an excited state, but undergo direct photofragmentation on optical excitation.[5]

The second group, known as Type II photoinitiators, undergo a primary process of hydrogen atom abstraction from the environment, which may be the compound itself or a solvent, but usually a tertiary amine co-synergist is used for enhanced efficiency. The reaction usually occurs from the lowest excited triplet state of the ketone and depends on the intersystem crossing (ISC) rate, the configuration of the triplet state (n,π^* or π,π^*), and its corresponding energy. Here, the excited triplet state of the ketone forms an intermediate excited electron transfer complex (exciplex) with the tertiary amine. Electron transfer occurs with the subsequent formation of radicals, the amino radical is then believed to be the main initiating radical.

The UV curing industry commonly uses combinations of Type I and Type II photoinitiators to overcome oxygen inhibition and design cost effective photoinitiator blends. Oxygen can quench the lowest excited state of many aromatic ketones. Additionally, the initiating and propagating radicals are also quenched especially on the surface of thin films. The selection of a photoinitiator is of prime importance in the design of UV curing systems, since the polymerization and/or crosslinking rate depends on the photoinitiator package, and the physical properties of inks and coatings such as flexibility, hardness, scratch, rub and chemical resistance properties are dependent on the degree of cure of the system. One of the major directions in this field is the development of efficient, cost-effective, near UV/visible light activated photoinitiators for curing pigmented systems with UV/visible light.[6-12]

TYPE I PHOTOINITIATORS

α-Cleavage Photoinitiators

The most important Type I photoinitiators due to their high reactivity and thermal stability are α-cleavage photo-

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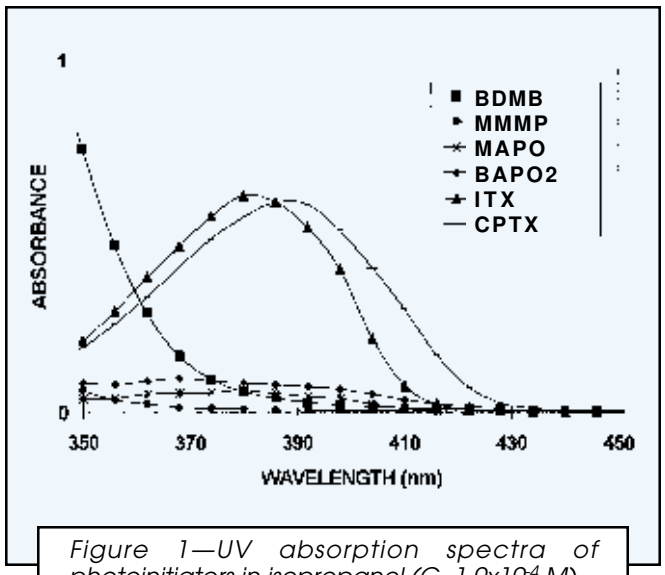

Figure 1—UV absorption spectra of photoinitiators in isopropanol (C=1.0x10^{-4} M).

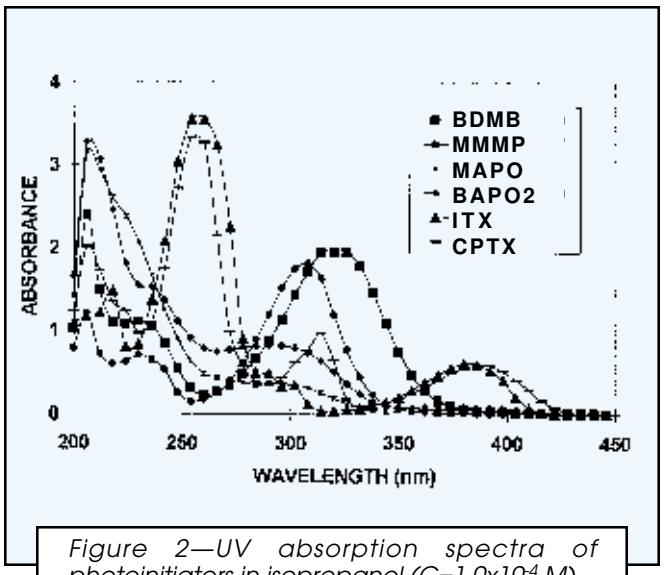

Figure 2—UV absorption spectra of photoinitiators in isopropanol (C=1.0x10^{-4} M).

initiators. Some of the applications in which α-cleavage photoinitiators are used are clear coatings, printing inks, printing plates, and white lacquers. The most important families are:

α-Aminoalkylphenones

A relatively new kind of Type I photoinitiator (PI) are α-aminoalkylphenones. They are of particular use in pigmented systems due to their absorption in the near ultraviolet region, in applications such as printing inks. Different attempts have been made to elucidate their curing behavior in pigmented systems.[13] Two α-aminoacetophenone PIs are currently available: 2-methyl-1-4-(methylthio)phenyl)-2-morpholino-propan-2-one (MMMP/Irgacure™ 907) and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (BDMB/Irgacure™ 369). BDMB is more extensively used due to its lower odor characteristics in comparison to MMMP. MMMP has been replaced in some applications such as printing inks due to its odor. It has been shown by 1H-NMR-CIDNP[14] experiments that BDMB in solution undergoes predominantly α-cleavage from its triplet state and minor β-cleavage.[15]

Acylphosphine Oxides

Acylphosphine oxides were introduced some years ago as a new class of α-cleavage photoinitiators. They are derived from diethoxyacetophenone (DEAP) by replacing C-H by P=O and alkoxy by aryl groups. Relatively high oxygen inhibition may decrease their reactivity in the curing of thin films.[16] Mono-acylphosphine (MAPO e.g., Lucirin™ TPO) and bis-acylphosphine oxides such as BAPO1 (Irgacure 1700 and 1800) and BAPO 2 (Irgacure™ 819) have absorption bands in the near UV/Visible region, and so are specially indicated in pigmented systems,[17] additionally acylphosphineoxides bleach upon irradiation. Hence there is a decrease of absorptivity in the near UV Visible range and radiation can penetrate into deeper layers. Acylphosphine oxides produce little yellowing immediately after curing and on long-term exposure; therefore they have been used in applications where low yellowing requirements are required as with white and pale inks. Acylphosphine oxides possess short-lived excited states and present low quenching characteristics; hence they are suitable in styrene-based formulations for the furniture manufacturing industry.

Table 1—$\pi \rightarrow \pi^*$ Transitions of Photoinitiators in Different Solvents

	Methylcyclohexane		Acetonitrile		Isopropanol	
Photoinitiator	λ max	log ε	λ max	log ε	λ max	log ε
BDMB	311.7	4.36	315.0	4.23	317.5	4.31
MMMP	300.4	4.31	302.8	4.27	307.1	4.25
MAPO	282.0	3.75	288.2	3.62	294.7	3.57
BAPO2	291.0	3.96	291.0	3.90	292.7	3.91
ITX	255.4	4.58	257.3	4.56	257.0	4.55
CPTX	255.4	4.58	257.3	4.51	256.8	4.59

Table 2—n $\rightarrow \pi^*$ Transitions of Photoinitiators in Different Solvents

	Methylcyclohexane		Acetonitrile		Isopropanol	
Photoinitiator	λ max	log ε	λ max	log ε	λ max	log ε
BDMB	—	—	—	—	—	—
MMMP	—	—	—	—	—	—
MAPO	381.8	2.61	380.4	2.72	379.9	2.76
BAPO2	371.4	2.93	368.7	2.97	367.9	2.98
ITX	380.7	3.85	381.8	3.84	382.3	3.79
CPTX	385.0	3.81	385.0	3.75	388.0	3.78

TYPE II PHOTOINITIATORS

Thioxanthones

Thioxanthones are used in printing inks due to their interesting absorption characteristics exhibiting absorption in the near UV/Visible range of the spectrum. The photochemical and photophysical properties of a range of thioxanthone[18,19] photoinitiators have been extensively studied and reviewed[20] in the literature. Modification of the structure of conventional photoinitiator chromophores for improved property requirements is a subject of much interest and activity. In this context, structures based on the thioxanthone chromophore have attracted intensive academic and industrial interest. Consequently, several thioxanthone derivatives are currently used in the UV curing industry in various applications. In this study the kinetic characteristics of the two most important thioxanthone derivatives on the market Quantacure™ ITX (2- and 4-isopropylthioxanthone isomers) and Quantacure™ CPTX (1-chloro-4-propoxythioxanthone) have been compared and related to their photophysical and photochemical characteristics. The basis of this study is to determine and compare the photocuring activities of a range of Type I and Type II photoinitiators in both clear and pigmented coatings used in the manufacture of inks. From this data one can ascertain the most important structural and spectral requirements for effect cure under both UV and visible excitation and how this efficiency relates to the output of the excitation source.

EXPERIMENTAL

Materials

Irgacure™ 369 (BDMB) (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), Irgacure™ 907 (MMMP) (2-methyl-1-(4-(methylthio)phenyl)-2-morpholino propan-1-one), and Irgacure™ 819 (BAPO2) (bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide) were supplied by Ciba-Geigy Corp., Switzerland. Lucirin™ TPO (MAPO) (2,4,6-trimethyl benzoyldiphenyl phosphine oxide) was supplied by BASF. Quantacure™ ITX (2- and 4-isopropylthioxanthone isomers) and Quantacure™ CPTX (1-chloro-4-propoxythioxanthone) were supplied by Great Lakes Ltd., Cheshire, UK. The solvents methylcyclohexane, acetonitrile, and isopropanol used in this work to obtain the UV spectra were of HPLC grade quality. The reactive diluent glyceryl propoxylated triacrylate (GPTA) (Actilane™ 432) was supplied by Akcros and the oligomer Ebecryl™ 870 (modified polyester hexafunctional acrylate oligomer) was supplied by UCB. Four commercial color process offset lithograpic inks containing no photoinitiators were supplied by Swale Process, Manchester.

UV Spectroscopy

The study of the absorption shifts of photoinitiators with solvents of varying polarities can help identify the nature of the different absorption transitions occurring on absorption of light. The solvent polarity effect on the absorption characteristics can be explained by the different relative polarity of the ground and the excited state. The high stabilization of non-bonding n orbitals observed with polar solvents is due to its polar nature, similarly π^* orbitals are more stabilized than are π orbitals since π^* orbitals are more polar.

Such solvent shifts are due to differences in the relative capabilities of solvents to solvate the ground state of a molecule as compared with their ability to solvate the

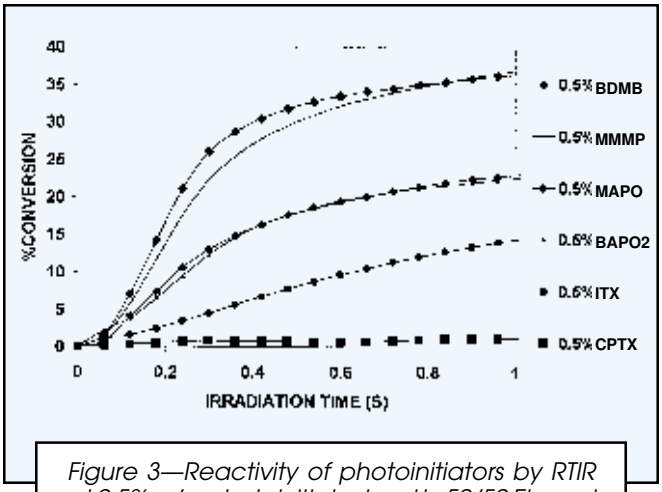

Figure 3—Reactivity of photoinitiators by RTIR at 0.5% w/w photoinitiator level in 50/50 Ebecryl 870/GPTA cured with UV (Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

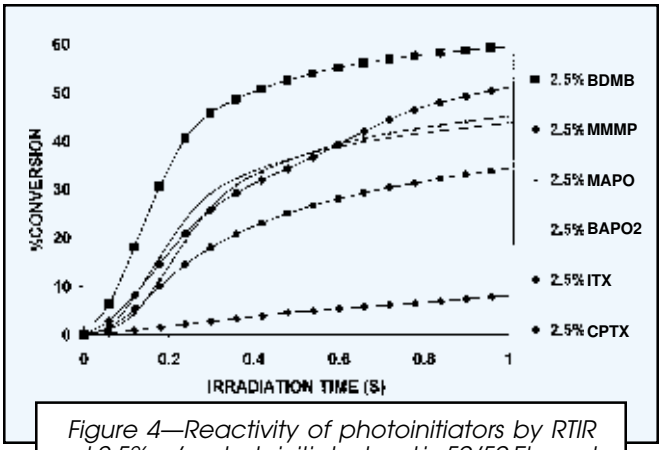

Figure 4—Reactivity of photoinitiators by RTIR at 2.5% w/w photoinitiator level in 50/50 Ebecryl 870/GPTA cured with UV light (Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

Table 3—Extinction Coefficients ε (l/mol.cm) of Different Photoinitiators in Isopropanol at the Most Important Emission Wavelengths of the Medium Pressure Mercury Lamp

Photoinitiator	253 nm	303 nm	313 nm	365 nm	404 nm
BDMB	3.53	4.16	4.29	3.34	1.90
MMMP	3.09	4.24	4.22	2.06	—
MAPO	3.80	3.52	3.39	2.70	2.33
BAPO2	3.97	3.89	3.81	2.97	2.71
ITX	4.60	3.51	2.57	3.63	3.32
CPTX	4.55	3.82	3.99	3.57	3.62

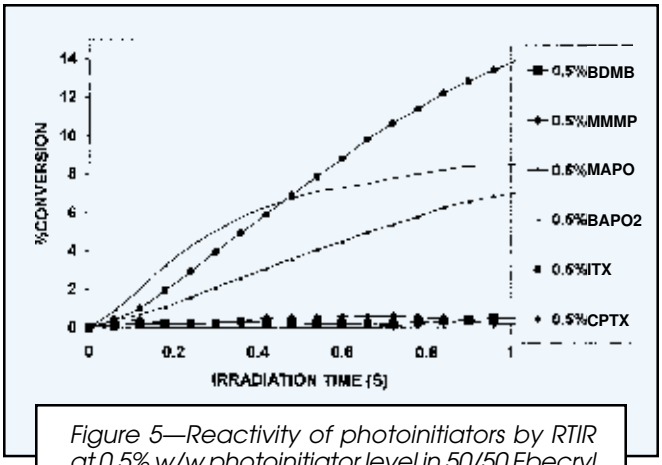

Figure 5—Reactivity of photoinitiators by RTIR at 0.5% w/w photoinitiator level in 50/50 Ebecryl 870/GPTA cured with visible light (Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

excited states. Polar solvents cannot form hydrogen bonds as readily with excited states as with ground states of polar molecules; hence the energies of electronic transitions can be increased. Transitions of the $n \rightarrow \pi^*$ type are shifted to shorter wavelengths by polar solvents, since the ground state is more polar than the excited state. In particular, hydrogen bonding solvents interact more strongly with unshared electron pairs in the ground state than they do in the excited state. As a result, an $n \rightarrow \pi^*$ transition has its absorption maximum shifted to shorter wavelength (hypsochromic shift) as the hydrogen bonding ability (polarity) of the solvent increases. On the other hand, $\pi \rightarrow \pi^*$ transitions are shifted to longer wavelengths by polar solvents, since the excited state may form stronger hydrogen bonds than the corresponding ground states due to its polar character, which is stabilized more strongly with the excited state than with the ground state. Consequently, the transition is shifted to longer wavelengths (bathochromic shift).

Absorption spectra were obtained using a Perkin-Elmer Lambda 7 absorption spectrometer on solutions of photoinitiators in three solvents of different polarity to study the effect of solvent polarity on the absorption properties of photoinitiators such as hyperchromic and hypochromic effects and hypsochomic and bathochromic shifts. Methylcyclohexane, acetonitrile, and isopropanol were the chosen solvents. The solutions were analyzed by UV spectroscopy at different concentrations to obtain the best correlation by regression analysis. From the slope of the linear regression lines, the photoinitiator extinction coefficients were calculated in the previously mentioned solvents.

UV spectroscopic studies were conducted using quartz cells with a path length of 1 cm. The sample in the cell was subjected to ultraviolet light between 200 nm to 500 nm, and the extinction coefficients were calculated using Beer-Lambert's Law.

Real Time Infrared Spectroscopy RTIR

Real time infrared spectroscopy[19,20] (RTIR) is based on the decrease in the vinyl absorbance at 812 cm^{-1} during the polymerization reaction. The sample is polymerized with UV radiation while the infrared beam measures the decrease of absorbance.

The irradiation source used was a Xenon lamp ILC 302UV(Laser Lines Ltd.) connected to a dispersive infrared spectrophotometer. The photoinitiators were dissolved at 0.5% w/w and 2.5% w/w in 50/50 w/w Ebecryl 870/GPTA in formulations that simulated clear overprint varnishes. The samples were applied with calibrated wire bars (No. 1) on sodium chloride plates to give a film thickness

Table 4—Reactivity of Photoinitiators by RTIR at 0.5% w/w Photoinitiator Level in 50/50 Ebecryl 870/GPTA Cured at 6 Microns with UV and Visible Light (Xenon Lamp with a Cut Off at 390 nm) in the Presence of Air

	0.5% Photoinitiator Light			0.5% Photoinitiator Visible Light		
Photoinitiator	Rp Maximum (mol L s^{-1}) ± SD	% Conversion (15 s) ± SD	No. of Runs	Rp Maximum (mol L s^{-1}) ± SD	% Conversion (15 s) ± SD	No. of Runs
BDMB	1.224 ± 0.020	41.9 ± 0.7	2	0.002 ± 0.001	1.6 ± 0.2	2
MMMP	1.064 ± 0.007	47.6 ± 2.1	3	0.000 ± 0.000	1.3 ± 0.2	2
MAPO	0.641 ± 0.085	31.6 ± 0.9	2	0.193 ± 0.023	14.3 ± 0.2	2
BAPO2	0.539 ± 0.073	29.0 ± 0.2	2	0.206 ± 0.012	11.8 ± 0.1	2
ITX	0.191 ± 0.024	29.8 ± 0.7	2	0.171 ± 0.021	29.3 ± 0.2	2
CPTX	0.007 ± 0.000	2.0 ± 0.0	2	0.002 ± 0.001	1.6 ±0.2	2

Table 5—Reactivity of Photoinitiators by RTIR at 2.5%w/w Photoinitiator Level in 50/50 Ebecryl™ 870/GPTA Cured with UV and Visible Light (Xenon Lamp with a Cut Off at 390 nm) at 6 Microns in the Presence of Air

	2.5% Photoinitiator Light			2.5% Photoinitiator Visible Light		
Photoinitiator	Rp Maximum (mol L s^{-1}) ± SD	% Conversion (15 s) ± SD	No. of Runs	Rp Maximum (mol L s^{-1}) ± SD	% Conversion (15 s) ± SD	No. of Runs
BDMB	2.164 ± 0.182	71.1 ± 0.6	2	0.473 ± 0.030	39.2 ± 0.7	2
MMMP	1.508 ± 0.148	71.2 ± 1.7	3	0.002 ± 0.001	3.1 ± 0.9	3
MAPO	1.374 ± 0.117	60.6 ± 1.0	3	0.958 ± 0.046	42.6 ± 2.2	3
BAPO2	1.386 ± 0.043	57.7 ± 0.2	3	1.177 ± 0.146	53.0 ± 0.3	3
ITX	0.797 ± 0.112	52.6 ± 1.9	2	0.762 ± 0.001	49.6 ± 0.0	2
CPTX	0.139 ± 0.022	18.0 ± 0.3	2	0.140 ± 0.005	18.8 ± 0.4	2

of 6 microns and were positioned uncovered in the sample holder. The reactivity of the photoinitiators in four-color process, offset-lithographic inks was determined at 4.5% w/w photoinitiator with UV light in a vehicle system consisting in 90/10 w/w GPTA/ink at 6 microns in the presence of air.

Plots of conversion percentage and polymerization rate versus irradiation time were obtained. The polymerization rates were calculated from the slope of conversion versus time plots at short irradiation times. For each sample replication was done to have an estimation of the pure errors and to prevent gross errors. The results were expressed as the mean values, and the standard deviations gave an indication of the spread of the results. The reactivity plots shown in the figures were averaged.

RESULTS AND DISCUSSION

UV Spectroscopic Results

The most important UV transitions of the photoinitiators studied in isopropanol, acetonitrile, and methylcyclohexane are shown in *Tables* 1 and 2 for the short and long wavelength bands, respectively. These absorption bands correspond to the π,π^* and n,π^* transitions of the initiators. The UV spectra of several near UV photoinitiators are shown in *Figures* 1 and 2. The extinction coefficients of the respective photoinitiators corresponding to the emission output lines of the spectral emission source are also shown in *Table* 3 for activation comparisons.

UV curing is associated with the n, π^* or π,π^* transitions (or a combination of these) that occur between 250 to 400 nm. The π,π^* transitions are shifted to longer wavelengths by an increase of the extension of the conjugation and by an increase in solvent polarity. The π,π^* transitions are also more intense than n,π^* transitions, the latter being shifted to shorter wavelengths by an increase in solvent polarity.

The majority of the photoinitiators exhibit π,π^* transitions below 300 nm (*Table* 1). The α-aminoalkylphenone derivative type photoinitiators BDMB and MMMP exhibit a bathochromic effect showing absorptions (π,π^* transitions) over 300 nm. This is mainly due to substitution at the para position by electron donating groups such as morpholino and alkylthio respectively within the aromatic ring of the benzoyl group.

Acylphosphineoxides MAPO and BAPO2 also have red shifted absorptions (n,π^* transitions) over 360 nm tailing into the visible, mainly due to extension of aromatic conjugation. These red shifted transitions are particularly interesting in pigmented systems since some pigments present absorption windows in the near UV/Visible region.

The thioxanthone derivatives ITX and CPTX have extended absorption up to 420 nm, depending upon the type of substitution. Solvent shift data indicate a transition with a mixed $n\pi^*/\pi\pi^*$ character with little change in extinction coefficient values. In the case of thioxanthones, there is a variable red/blue shift in the absorption maxima with increasing solvent polarity, indicative of a strongly mixed

Table 6—Reactivity of Photoinitiators in a Black Ink (2% w/w Pigment Black 7) Cured with UV Light at 6 Microns in the Presence of Air

	4.5% Photoinitiator in a Black Ink		
Photoinitiator	Rp Maximum (mol L s^{-1}) ± SD	%Conversion (15 s) ± SD	No. of Runs
BDMB	1.978 ± 0.077	70.2 ± 0.03	2
MMMP	0.580 ± 0.003	54.3 ± 0.7	2
MAPO	0.381 ± 0.002	20.8 ± 0.6	2
BAPO2	0.584 ± 0.005	31.0 ± 1.2	2
ITX	0.006 ± 0.003	4.4 ± 1.0	2
CPTX	0.019 ± 0.000	7.4 ± 0.4	2

Table 7—Reactivity of Photoinitiators in a Cyan Ink (2% w/w pigment blue 15:3) Cured with UV Light at 6 Microns in the Presence of Air

	4.5% Photoinitiator in a Cyan Ink		
Photoinitiator	Rp Maximum (mol L s^{-1}) ± SD	%Conversion (15 s) ± SD	No. of Runs
BDMB	2.129 ± 0.375	75.6 ± 2.1	2
MMMP	1.163 ± 0.064	66.5 ± 1.8	2
MAPO	0.993 ± 0.015	38.2 ± 0.8	2
BAPO2	1.181 ± 0.073	48.1 ± 1.6	2
ITX	0.107 ± 0.017	22.3 ± 0.7	2
CPTX	0.012 ± 0.002	6.3 ± 0.07	2

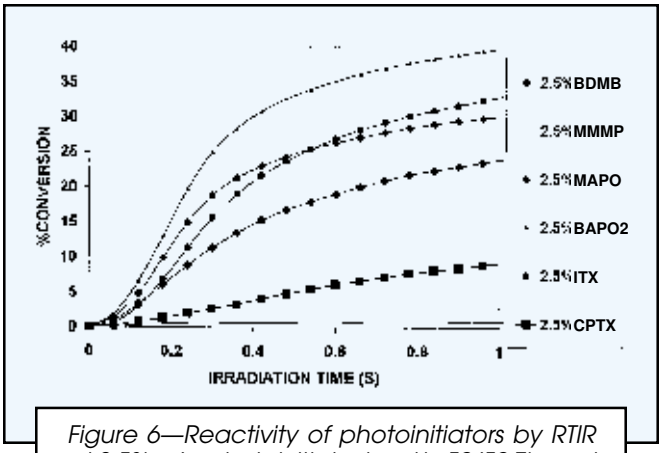

Figure 6—Reactivity of photoinitiators by RTIR at 2.5% w/w photoinitiator level in 50/50 Ebecryl 870/GPTA cured with visible light (Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

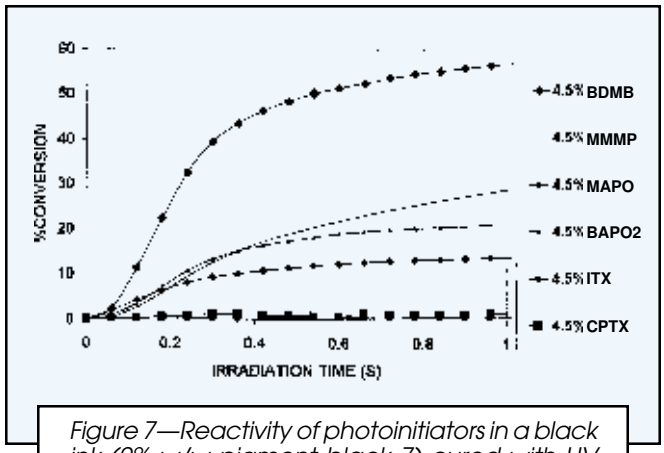

Figure 7—Reactivity of photoinitiators in a black ink (2% w/w pigment black 7) cured with UV light at 6 microns in the presence of air.

Table 8—Reactivity of Photoinitiators in a Magenta Ink (2% pigment red 57:1) Cured with UV Light at 6 Microns in the Presence of Air

	4.5% Photoinitiator in a Magenta Ink		
Photoinitiator	Rp Maximum (mol L s^{-1}) ± SD	% Conversion (15 s) ± SD	No. of Runs
BDMB	1.837 ± 0.104	80.9 ± 0.5	2
MMMP	1.455 ± 0.001	72.2 ± 0.7	2
MAPO	1.296 ± 0.169	49.5 ± 0.7	2
BAPO2	1.498 ± 0.137	54.8 ± 1.1	2
ITX	0.235 ± 0.013	28.7 ± 0.8	2
CPTX	0.022 ± 0.001	7.2 ± 0.5	2

Table 9—Reactivity of Photoinitiators in a Yellow Ink (2% w/w pigment yellow 13) Cured with UV Light at 6 Microns in the Presence of Air

	4.5% Photoinitiator in a Yellow Ink		
Photoinitiator	Rp maximum (mol L s^{-1}) ± SD	% Conversion (15 s) ± SD	No. of Runs
BDMB	2.53 ± 0.009	76.9 ± 0.1	2
MMMP	1.328 ± 0.241	70.4 ± 1.6	2
MAPO	1.334 ± 0.100	51.7 ± 2.4	2
BAPO2	1.687 ± 0.046	59.0 ± 0.4	2
ITX	0.188 ± 0.046	26.7 ± 5.9	2
CPTX	0.022 ± 0.001	7.7 ± 1.1	2

$n\pi^*/\pi\pi^*$ state. CPTX shows a more pronounced red shifted maximum than ITX that may be due to an inductive effect by the chlorine atom substituted in the 1-position and of resonance by the propoxy substituent in the para position.

Photopolymerization Results

Reactivity of Photoinitiators in Clear Films with UV Light: The reactivity of several near UV photoinitiator systems cured with UV light are compared in *Tables* 4 and 5 showing Rp and conversion values at 0.5 and 2.5% w/w of the initiators. *Figures* 3 and 4 show the corresponding rate curves from the actual RTIR experiments. BDMB displayed the highest photoinitiation activity (polymerization rate and conversion) in the presence of air at two different photoinitiator concentrations. MMMP showed higher reactivity than MAPO and BAPO2 possibly due to the higher degree of oxygen inhibition typically found in phosphine oxide radicals at low film thickness in the presence of air. BAPO2 exhibited a similar polymerization rate and conversion to MAPO. BDMB exhibits a very strong near UV transition with a broad weak tail extending beyond 400 nm. As can be seen from the extinction coefficients in *Table* 3 for the source emission lines the BDMB exhibits the highest values followed by the MMMP. The MAPO and BAPO2 exhibit lower extinction coefficients and comparable activities in the near UV.

The thioxanthone photointiators had much less activity in this system with ITX exhibiting higher reactivity than CPTX in the absence of a tertiary amine. Although the thioxanthones exhibit higher extinction coefficients, they are less active in the absence of a tertiary amine.

Reactivity of Photoinitiators in Clear Films with Visible Light: The reactivity of several near UV photoinitiator systems cured with visible light have also been compared in *Tables* 3 and 4 showing the Rp and % conversion values. *Figures* 5 and 6 show the corresponding rate curves form the RTIR plots. Generally, the conversions were all very low under visible light irradiation. However, BAPO2 displayed the highest photoinitiation activity (polymerization rate and conversion) in the presence of air at two different photoinitiator concentrations. Above 400 nm the BAPO2 exhibits the strongest extinction coefficients of the photofragmenting initiators as seen by the data in *Table* 3. MAPO showed a higher polymerization rate than ITX. On the other hand, at long irradiation times ITX gave higher conversion than TPO. ITX exhibited a higher polymerization rate than both BDMB and MMMP due to the low absorptivity of these photoinitiators in the visible region. Obviously, both the thioxanthones exhibit some degree of hydrogen atom abstraction ability under visible light irradiation.

Reactivity of Photoinitiators in Pigmented Films with UV Light: The reactivity of several near UV photoinitiator systems cured with UV light has been compared in *Tables* 6 through 9 for black, cyan, magenta, and yellow pigmented inks. These tables show both Rp and % conversion values. *Figures* 7 through 10 show the corresponding rate curves from the RTIR plots. There was no observable cure under visible light exposure.

BDMB displayed the highest photoinitiation activity (polymerization rate and conversion) in the presence of air in the four color process inks studied. MMMP showed higher conversion at long irradiation times than MAPO and BAPO2 possibly due to the higher degree of oxygen inhibition typically found in phosphine oxide radicals at low film thickness in the presence of air. On the other hand, BAPO2 exhibited a higher maximum polymerization rate than both MMMP and MAPO. These data, as for clear films, correspond with the absorption and extinction coefficients of the initiators in the near UV region of the spectrum up to 400 nm.

The thioxanthones showed the lowest reactivity among the photoinitiators studied. ITX showed higher reactivity than CPTX in the absence of a tertiary amine in the cyan, magenta, and yellow inks. Both ITX and CPTX showed very poor reactivity in the black ink, which is reflected by its low conversion below 10% after 15 sec of irradiation time.

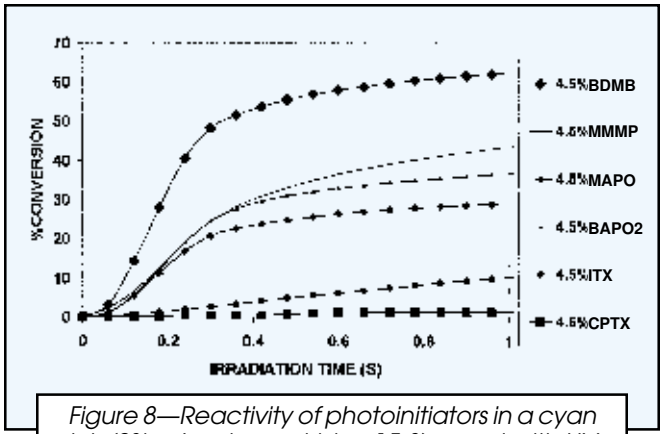

Figure 8—Reactivity of photoinitiators in a cyan ink (2% w/w pigment blue 15:3) cured with UV light at 6 microns in the presence of air.

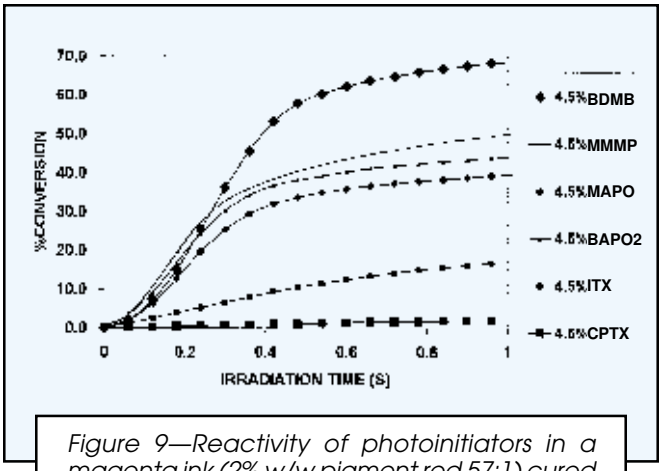

Figure 9—Reactivity of photoinitiators in a magenta ink (2% w/w pigment red 57:1) cured with UV light at 6 microns in the presence of air.

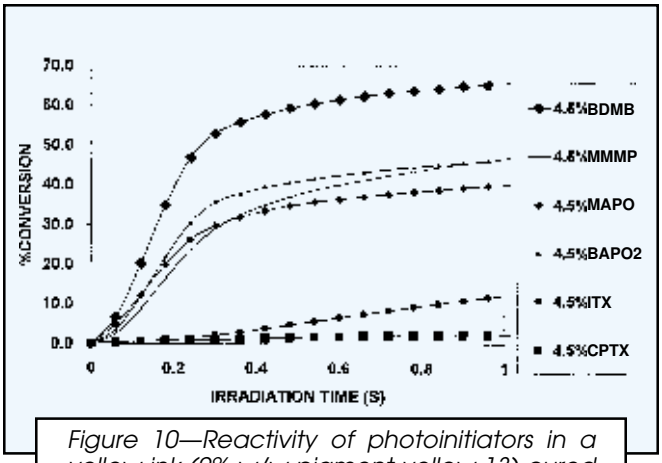

Figure 10—Reactivity of photoinitiators in a yellow ink (2% w/w pigment yellow 13) cured with UV light at 6 microns in the presence of air.

CONCLUSIONS

The photopolymerization activities of the important, commercial, near UV photoinitiators are highly dependent on the degree of substitution of the chromophore, which controls the degree of charge transfer content and the energy of the lowest lying triplet states. The photoinitiation activity of Type I initiators corresponds closely to their extinction coefficients at the maximum output of the emission lines of the source lamp.

In clear films α-aminoalkylphenone type photoinitiators such as BDMB and MMMP exhibit higher initiation efficiency than acylphosphine oxide type photoinitiators such as BAPO2 and MAPO in films cured with UV light. Thioxanthone derivative photoinitiators such as ITX and CPTX showed lower reactivity than their Type I counterparts due to their lower efficiency bimolecular reaction mechanism.

On the other hand, BAPO2 displayed the highest initiation efficiency in films cured with visible light. BAPO2 showed higher polymerization rate than MAPO and ITX. Even in the absence of amine, ITX exhibited a similar (slightly lower) reactivity than MAPO, which makes possible the design of cost effective photoinitiation systems. BDMB and MMMP showed the lowest reactivity due to their low absorptivity in the visible region.

In pigmented films cured with UV light the α-aminoalkylphenone type photoinitiator BDMB exhibited the highest reactivity among all the photoinitiators studied. BAPO2 showed slightly higher polymerization rate than MMMP while it gave lower conversion at long irradiation times. BAPO2 is also more reactive than MAPO and ITX in all the pigmented ink systems studied.

Thioxanthone derivative photoinitiators such as ITX and CPTX showed lower reactivity than their Type I counterparts due to their lower efficiency bimolecular reaction mechanism. In contrast, with other results obtained in the presence of amine, ITX showed a higher photoreactivity (polymerization rate) than CPTX in the absence of an efficient electron/proton donor, such as a tertiary amine, possibly due to the higher degree of charge transfer observed in CPTX, which induces a decrease of its lowest lying triplet estate energy. Consequently, the direct hydrogen atom abstraction ability might decrease and justify its lower reactivity in the absence of an efficient electron/proton donor.

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