

**PHOTOCHEMICAL CHARACTERISTICS AND
DESIGN OF SYNERGISTIC PHOTOINITIATOR
COMBINATIONS FOR UV CURABLE INKS AND
COATINGS**

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**PHOTOCHEMICAL CHARACTERISTICS AND DESIGN OF
SYNERGISTIC PHOTOINITIATOR COMBINATIONS FOR UV
CURABLE INKS AND COATINGS**

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LIST OF ABBREVIATIONS

A	Absorbance
A_{λ}	Absorbance of the solution at wavelength λ .
A_0	Absorbance before the flash.
A_R	Absorbance at the excitation wavelength of the reference solution.
Area _R	Integrated area under the corrected emission spectrum.
Area _X	Integrated area under the corrected emission spectrum.
A_t	Absorbance at time t.
A_X	Absorbance at the excitation wavelength of the sample solution.
B	Fraction of light absorbed by the sample.
BDK	Benzyl dimethyl ketal BDK or 2,2-dimethoxy-2-phenylacetophenone.
BDMB	2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one.
BP	Benzophenone.
C	Molar concentration of solute (M).
CIDNP	Chemically induced dynamic nuclear polarisation
CIE	Commission Internationale de l'Eclairage.
CMC	Colour Measurement Committee.
CPTX	1-Chloro-4-propoxythioxanthone.
DBAP	2,2-Di-sec-butoxyacetophenone.
DBMP	Dimethyl aminobenzylmorpholinophenylbutanone.
DEAP	α - α Diethoxy-acetophenone.
DGEBA	Bisphenol A diglycidyl ether.
DITMPTA	Ditrimethylolpropane tetracrylate.
DMPA	Benzyl dimethyl ketal BDK or 2,2-dimethoxy-2-phenylacetophenone.
DOE	Design of Experiments.
DPGDA	Dipropylene glycol diacrylate.
Ft/min	Feet per minute.
GPTA	Glyceryl propoxylated triacrylate.
H ₁₂ MDI	Dicyclohexylmethane diisocyanate.
HCPK	(Irgacure 184) 1-Hydroxy-cyclohexylphenylketone.
HEA	Hydroxyethyl acrylate.
HEMA	Hydroxymethyl methacrylate.
HLB	Hydrophilic-Lipophilic Balance.
HMDI	Hexamethylene diisocyanate.
HMMP	2-Hydroxy-2-methyl-1-phenyl-propan-1-one.

HOMO	Highest occupied bonding molecular orbital.
HPLC	High Performance Liquid Chromatography.
I	Intensity of the light leaving the sample cell.
I_0	Intensity of the incident light upon the sample cell.
I_0	Phosphorescence intensity at time zero.
ICI	Imperial Chemical Industries.
IPDI	Isophorone diisocyanate.
I_R	Intensity of the light at the excitation wavelength λ for the reference.
ISC	Intersystem crossing.
I_t	Phosphorescence intensity at time t.
ITX	Isopropyl thioxanthone.
I_x	Intensity of the light at the excitation wavelength λ for the sample.
k	Kinetic rate constant.
K_1	First order rate constant.
K_2	Second order rate constant.
L	Length of sample cell (cm) or pathlength.
LUMO	Lowest Unoccupied antibonding molecular orbital.
MAPO	2,4,6-Trimethyl benzoyl diphenyl phosphine oxide (Lucirin TPO).
MDI	Diphenylmethane diisocyanate.
MMMP	2-Methyl-1-4-(methylthio)phenyl)-2-morpholino-propan-2-one.
Mw	Molecular weight.
PI	Photoinitiator.
PVC	Poly vinylchloride.
Q	Thermal Energy (Heat).
R_1	Regression analysis for a unimolecular mechanism.
R_2	Regression analysis for a bimolecular mechanism.
R_p maximum	Maximum polymerisation rate.
rpm	Revolutions per minute.
RTIR	Real Time infrared Spectroscopy.
S	Multiplicity.
S	Singlet state.
s	Total spin angular momentum quantum number.
T	Triplet state.
TDI	Tolylene diisocyanate.
TMPTA	Trimethylolpropane triacrylate

TMXDI	Tetramethylxylene diisocyanate.
TPGDA	Tripropylene glycol diacrylate.
Type I	Unimolecular type photoinitiators.
Type II	Bimolecular type photoinitiators.
UV	Ultraviolet.
VOC	Volatile Organic Compound.
XDI	Xylene diisocyanate.

Symbols

ϵ	Molar extinction coefficient.
η_x	Refractive index of the solvents used in the sample.
η_R	Refractive index of the solvents used in the reference.
$\phi_{\text{phosphorescence}}$	Phosphorescence quantum yields.
ΔL	Lightness difference.
ΔH	Hue difference.
ΔE	Total colour difference.
ΔC	Chroma or colour difference. The Chroma can be expressed by $C=(a^2 + b^2)^{0.5}$ where a and b represent colour axes.
τ	Triplet lifetime. τ can be defined as the time required to the intensity to decrease to a value $I_\tau=1/e I_0$
χ	Oscilloscope deflection value.
ϵ	Molar extinction coefficient at wavelength λ .
λ	Excitation wavelength.

Statistical terms

ADJ R-SQR	Adjusted R-squared.
ANOVA	Analysis of Variance.
DF	Degrees of freedom.
DOE	Design Of Experiments
F value	F ratio is calculated by dividing the means square of the model by the mean squares of the residual error.
MS	Mean Square or variance corresponds to the sum of squares divided by the number of degrees of freedom.
n_e	Degrees of freedom of pure error SS.

n_{lof}	"lack of fit" SS is obtained by subtraction $n_r - n_e$.
n_r	Degrees of freedom of residuals.
PRE R-SQR	Predicted R-squared.
PRESS	PRESS statistic or Predicted Residual Sum of Squares.
prob > F	Probability that all the variation in the results are due to random error.
Root MSE	Square root of the residual Mean Square Error.
R-SQR R	Squared or the multiple correlation coefficient.
SD	Standard Deviation.
SS	Pure error or Sum of Squares.

ABSTRACT

The aim of this project was to design near eutectic liquid photoinitiators (PI) blends of outstanding reactivity and stability in bulk for curing UV printing inks and coatings.

The curing performance and kinetics of several UV resins (or UV prepolymers) commonly used in UV offset lithographic and UV flexographic printing inks were investigated by Real Time Infrared Spectroscopy RTIR. The maximum polymerisation rates and final conversion were measured for the different resins. Their reactivity was related to their mechanical properties by pendulum hardness at different thickness. The rheological properties of the resins were also measured and related to their polymerisation kinetics. The structure and functionality of the resin play an important role in controlling its tack and rheological properties and these, in turn, have an important influence on their rate of photocuring.

The reactivity and mechanical properties of several low viscosity acrylates (monomers or UV reactive diluents) were analysed and correlated with their chemical composition such as chemical backbone and functionality. The rheological properties of several acrylates, such as viscosity and thixotropy were also measured, as well as their misting characteristics in a reference offset lithographic ink. The acrylate functionality appeared to play a crucial role in controlling the cure rate and final film properties associated with the crosslink density.

An overall representation of the most important commercial free radical photoinitiators in the market were analysed by various spectroscopic techniques to evaluate the relationship between their photophysical properties and photoinitiation activity for photocuring of commercial acrylated systems. The types of electronic transitions occurring upon absorption of light were established via UV spectroscopy. Phosphorescence spectroscopy was used to study their triplet energies, lifetimes, and phosphorescence quantum yields. Microsecond flash photolysis was undertaken to determine the nature of the free radical intermediates. The free radical intermediate decay kinetics of the different photoinitiators were determined, as well as the first and second order rate constants, the transient radical absorption and radical lifetimes. Photopolymerisation studies were undertaken by Real Time Infrared Spectroscopy RTIR, at different photoinitiator concentrations in the presence and absence of oxygen using commercial UV reactive diluents and resins. Pendulum hardness measurements were also carried out to correlate the film hardness properties with the kinetic results obtained with RTIR. Analysis of the data showed that, whilst PI activity is predominantly dependent upon the absorption maxima of the chromophore, structural influences play a major role in controlling the nature of the lowest excited triplet state and the formation of radical intermediates.

Photocuring studies were 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 near UV Type I photofragmenting photoinitiators appeared to operate more effectively under UV excitation when compared with the Type II thioxanthenes, 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.

The discoloration and yellowing of acrylated coating films after photocuring with a broad range of photoinitiators were measured by colorimetry. The yellowing of the photoinitiators was evaluated and related to the chemical structure of the photoinitiator fragments and to the unreacted photoinitiator itself. The total colour difference was related to the type of chromophoric substituent in the basic structure of the photoinitiator.

Several synergistic near eutectic photoinitiator blends containing unimolecular (Type I) and bimolecular (Type II) photoinitiators were designed for curing pigmented systems by Design of Experiments DOE-Mixture Design. Mixture Designs were used to improve the reactivity of photoinitiator blends in order to design cost effective, synergistic, near eutectic photoinitiator blends for curing UV printing inks. Both the reactivity and bulk stability of photoinitiator blends were studied. The photoinitiator blends consisted of three commercial photoinitiators benzophenone (BP), isopropyl thioxanthone (ITX), which are Type II photoinitiators and benzil dimethyl ketal (BDK), a Type I photoinitiator. Ethyldimethylamino benzoate (EPD), a commercial aromatic tertiary amine, which is an efficient electron/proton donor was used to enhance the reactivity of the Type II photoinitiators.

The results highlighted that the EPD content plays a crucial role in the final reactivity of the photoinitiator blends. Relatively high proportions of EPD with respect to the overall centroid (25% each component) were required to design photoinitiator blends of enhanced reactivity. On the other hand, from the stability point of view, high proportions of EPD decreased the stability (near eutectic properties) of the photoinitiator blends. Benzophenone BP showed good solvating properties in the photoinitiator blends and had the highest influence on the stability of the photoinitiators studied. Relatively high proportions of BP enhanced the stability of photoinitiator blends. Multiple response optimisation for stability and reactivity resulted in photoinitiator blends that exhibited both enhanced reactivity and stability.

Two near eutectic liquid photoinitiator blends were designed by design of Experiments DOE-Mixture Design for curing both dark and light colour ultraviolet inks. These two blends possessed high absorbance in the short UV balanced with a relatively lower absorbance in the near UV. The two near eutectic liquid photoinitiators blends A and B had a high curing performance exhibiting higher reactivity than most commercial ink formulations. The first blend (blend A) based on isopropyl thioxanthone ITX (Type II) had lower reactivity for most of the pigments than the second blend (blend B), which was based on dimethyl aminobenzilmorpholino phenylbutanone, Irgacure 369 (Type I). These synergistic near eutectic photoinitiator blends are already being used in the manufacture of all the range of UV offset lithographic and UV flexographic inks of a printing ink manufacturing company.

CONTENTS

Acknowledgements

Abstract

Contents

CHAPTER I Radiation Curing	1
I.1 Introduction	1
I.2 Photoinitiator system	3
I.3 Oligomers, prepolymers and resins	3
I.4 Reactive diluents	9
I.5 Pigments	11
I.6 Curing of pigmented systems	12
I.6.1 Photoinitiator concentration effect	12
I.6.2 Film thickness effect	13
I.7 References	14
CHAPTER II Photochemistry	16
II.1 Introduction	16
II.2 Primary processes	16
II.2.1 Fluorescence	20
II.2.2 Internal conversion	21
II.2.3 Phosphorescence	21
II.3 Secondary processes	22
II.3.1 Unimolecular reactions	22
II.3.2 Bimolecular reactions	23
II.3.3 Energy transfer	26
II.4 References	27
CHAPTER III Photoinitiation of polymerisation	28
III.1 Introduction	28
III.2 Type I photoinitiators	28
III.2.1 α -cleavage photoinitiators	28
III.2.1.1 Benzoin ethers	28
III.2.1.2 Benzil ketals	29
III.2.1.3 α - α -dialkoxyacetophenones	30
III.2.1.4 α -hydroxyalkylphenones	31
III.2.1.5 α -aminoalkylphenones	32
III.2.1.6 Acylphosphine oxides	35
III.3 Type II photoinitiators	36
III.3.1 Benzophenones	36
III.3.2 Thioxanthenes	37
III.4 References	39
CHAPTER IV Experimental Design	41
IV.1 Introduction	41
IV.2 Mixture Design	41
IV.3 Design types	41

IV.4	Significance of the model	45
IV.5	References	47
CHAPTER V Instrumentation		48
V.1	Colour measurements	48
V.2	Ultraviolet absorption measurements	48
V.3	Luminescence measurements	49
V.4	Microsecond flash photolysis measurements	51
V.5	Photopolymerisation measurements	53
V.6	References	55
CHAPTER VI Experimental		56
VI.1	Materials	56
VI.2	Colour measurements	56
VI.3	Ultraviolet absorption measurements	56
VI.4	Luminescence measurements	57
VI.5	Microsecond flash photolysis measurements	58
VI.6	Real time infrared spectroscopy RTIR	58
VI.7	Hardness measurements	59
	VI.7.1 Pendulum hardness	59
	VI.7.2 Thumb twist resistance	60
VI.8	Rheological measurements	60
VI.9	Misting measurements	60
VI.10	Volatility measurements	61
VI.11	References	62
CHAPTER VII Photoyellowing and discoloration of UV cured clear coating systems: influence of photoinitiator type		63
VII.1	Introduction	63
VII.2	Results and discussion	63
VII.3	Conclusions	70
VII.4	References	71
CHAPTER VIII A comparative kinetic study of UV curable resins: structural and rheological inter-relationships		72
VIII.1	Introduction	72
VIII.2	Results and discussion	72
VIII.3	Conclusions	88
VIII.4	References	89
CHAPTER IX A comparative kinetic study of UV curable reactive diluent monomers: structural and rheological inter-relationships		90
IX.1	Introduction	90
IX.2	Results and discussion	90
IX.3	Conclusions	99
IX.4	References	100

**CHAPTER X Photochemistry and photopolymerisation activity of several
Type II commercial photoinitiators 101**

X.1	Introduction	101
X.2	Results and discussion	102
X.3	Conclusions	114
X.4	References	115

**CHAPTER XI Photochemistry and photopolymerisation activity of several
Type I commercial photoinitiators 117**

XI.1	Introduction	117
XI.2	Results and discussion	118
XI.3	Conclusions	127
XI.4	References	128

**CHAPTER XII Photochemistry and photopolymerisation activity of several
commercial near UV photoinitiators 129**

XII.1	Introduction	129
XII.2	Results and discussion	130
XII.3	Conclusions	146
XII.4	References	148

**CHAPTER XIII Design of synergistic near eutectic photoinitiator blends by
Mixture Design 149**

XIII.1	Introduction	149
XIII.2	Experimental	150
	XIII.2.1 Materials	150
	XIII.2.2 Preparation of photoinitiator blends	150
	XIII.2.3 Reactivity of photoinitiator blends	151
	XIII.2.4 Design of photoinitiator blends	152
	XIII.2.5 Stability	155
	XIII.2.6 Reactivity of photoinitiator blends	163
XIII.3	Results and discussion	169
	XIII.3.1 Stability	169
	XIII.3.2 Reactivity of photoinitiator blends	172
	XIII.3.3 Multiple response optimisation	175
XIII.4	Conclusions	178

**CHAPTER XIV Optimisation of the photopolymerisation performance of
commercial offset lithographic inks 180**

XIV.1	Introduction	180
	XIV.1.1 Curing performance of black inks	183
	XIV.1.1 Curing performance of cyan inks	185
	XIV.1.1 Curing performance of magenta inks	186
	XIV.1.1 Curing performance of yellow inks	187
XIV.2	Conclusions	188

APPENDIX

I. CHAPTER I RADIATION CURING

1.1 Introduction

The curing of coatings and inks by ultraviolet or visible light has become established technology for many industrial applications¹⁻⁵ including offset lithographic inks, flexographic inks, screen printing, metal decoration, basecoats for beverages cans⁶, wood coatings, pigmented coatings for textile applications⁷, coatings exhibiting an stereoscopic pattern⁸, pigmented primary⁹ and secondary optical fibre coatings¹⁰.

Over the years, several types of photoinitiators (PIs) have been developed to induce the photopolymerization or photocrosslinking of acrylated systems. Free radical photoinitiators induce a free radical chain process in which low molecular weight monomers and prepolymers are converted by the absorption of UV/Visible light into highly crosslinked films. Measurements of the rates of curing or crosslinking vary from the simplistic, such as the thumb screw test, pencil and pendulum hardness methods to the more scientific methodologies involving RTIR spectroscopy. The basic mechanism for any photocurable free radical system involves the formation of free radical species through the absorption of light by the photoinitiator. The active radical will then add to the monomer, inducing a chain growth polymerization and eventually termination. The photophysical and photochemical properties of the photoinitiators are extremely important in controlling the reactivity and they should possess the following properties:

- high absorbance in the region of activation,
- high quantum yield for free radical formation,
- solubility and solubility ease in resins,
- non yellowing,
- odourless,
- low volatility,
- non toxic,
- low migration and
- cost effective.

The selection of a photoinitiator is of prime importance in the design of UV curing systems, since the polymerisation 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. The selection of the PIs should be carefully considered in clear coatings and pale inks. Photoinitiators of the α -hydroxyalkylphenone type present very low yellowing properties and are the best choice for clear systems. Acylphosphine oxides are commonly used in white coatings due to their low yellowing and the fact that their absorption range is in the spectral window of titanium dioxide. Other important properties of PIs are solubility and ease of dissolution of the PIs in resins and acrylates.

Migration of photoinitiators and photoinitiator by-products has become one of the major concerns of the UV curing industry, specially for the graphic art industry in food contact inks. There is an intensive field of development of co-reactive and non-migratory polymeric PI systems¹¹ where the PI can react with the resin via acrylation of the PI moiety. Such acrylated PIs can either polymerise with the acrylate system or co-react with other acrylated PIs forming homopolymer oligomers, which are less extractable. Functionalised polystyrenes or polymethacrylates have been produced. Acrylated derivatives of thioxanthone¹², anthraquinone¹³, benzoin ethers¹⁴ and peresters¹⁵ are other examples reported in the literature.

A radiation curable formulation can be considered to consist of the following components:

- Photoinitiator system
- Oligomers or prepolymers
- Reactive diluents
- Pigments
- Additives

1.2 Photoinitiator system

Inherent in these technologies is the use of a photoinitiator system, which is capable of absorbing the incident UV and/or visible radiation wavelengths used for converting a monomer or prepolymer system into a crosslinked network. Important areas of interest include the development of photoinitiators with desirable properties such as improved reactivity and low migration¹⁶. UV curing technology often involves the use of co-synergistic mixtures of photoinitiators for cost-effective curing operations¹⁷.

1.3 Oligomers, prepolymers and resins

Acrylated resins are commonly used in the radiation curing industry as one of the main components of coatings and inks. Radiation curable resins are normally lower in molecular weight than conventional resins. Usually they are termed as oligomers or prepolymers consisting of reactive sites based typically on acrylate functionality. There are several types of prepolymers characterised by having different chemical backbone, epoxy acrylates, acrylated oils, urethane acrylates, polyester acrylates and polyether acrylates.

Epoxy acrylates are based on bisphenol A diglycidyl ether (DGEBA) reacted with acrylic acid (Figure I.1), they present high reactivity and hard film properties and usually they give chemically resistant films which makes them particularly suitable for use in wood finishing applications and varnishes for paper and board. They also provide adequate sanding properties in base coats for wood finishes.

Epoxy acrylates are used in different applications including clear coatings, overprint varnishes for paper, carton, wood and metal, pigmented systems in printing inks such as flexography and offset lithography, roller inks, silk screen inks for paper and board, coatings for electronic applications (printed circuit boards).

There are different grades of acrylated epoxy prepolymers, the range covers products presenting liquid form at room temperature for the lowest molecular weight grades to the solid ones for the higher molecular weight grades. Typically, they are highly viscous materials, which are commercialised as blends in low viscosity multifunctional acrylates such as glyceryl propoxylated triacrylate GPTA.

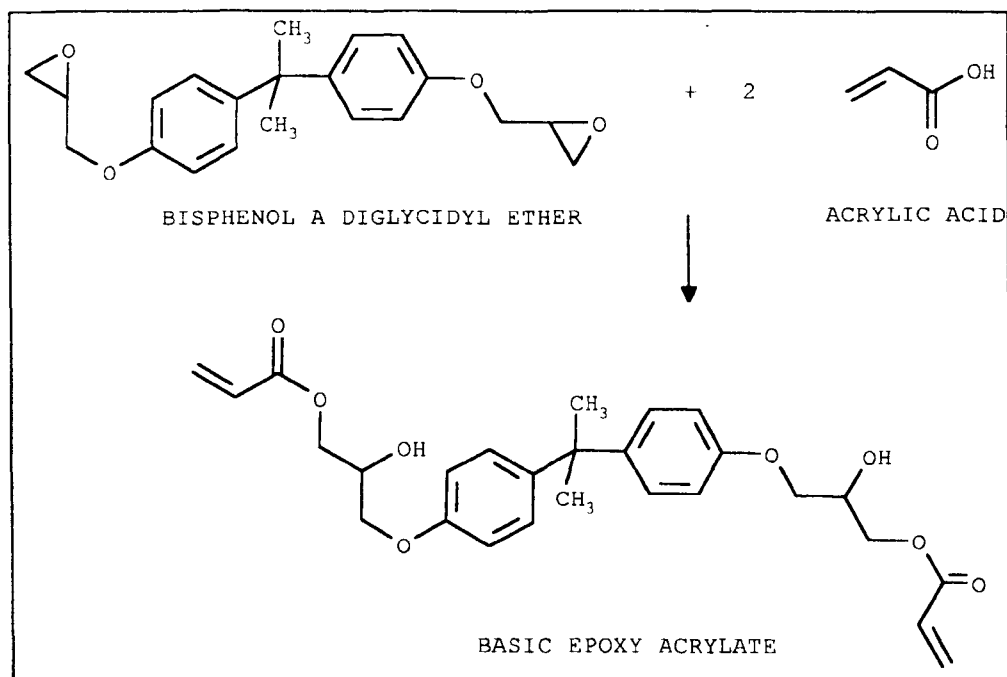


Figure I.1 Basic epoxy acrylate.

Acrylated oils are normally derived from natural products such as plants, trees and animals such as castor or fish oils, all of them are characterised by containing triglycerides oils (Figure I.2). Generally, acrylated oils present high flexibility or softness firstly due to its flexible acrylic aliphatic backbone and to their low level of acrylic unsaturation, and they present good pigment wetting characteristics, hence they are usually used as pigment wetters in printing inks.

Soya bean oil presents the highest consumption¹⁸ around 90% of the acrylated oils in the market due to its relatively low cost and availability and it consists of about 50% linoleic acid, 25% oleic acid, 10% palmitic and linolenic acids and around 5% stearic acid.

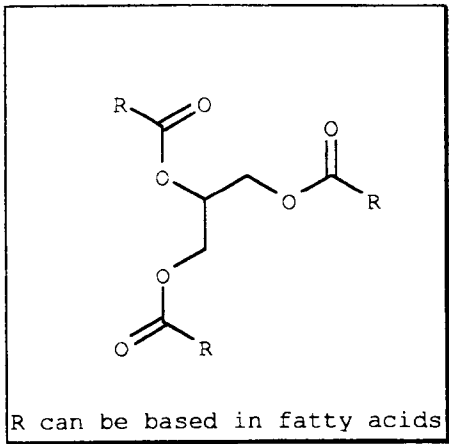


Figure I.2 Basic triglyceride oil.

These acids contain a relatively high level of unsaturation, which can be epoxidised by reaction with peracids¹⁹ and hydrogen peroxide²⁰. On the other hand, even though linseed oils present a lower market output than soya bean oils they are also extensively used due to their reasonable cost and relatively higher unsaturation level that reverts in a higher number of epoxy groups.

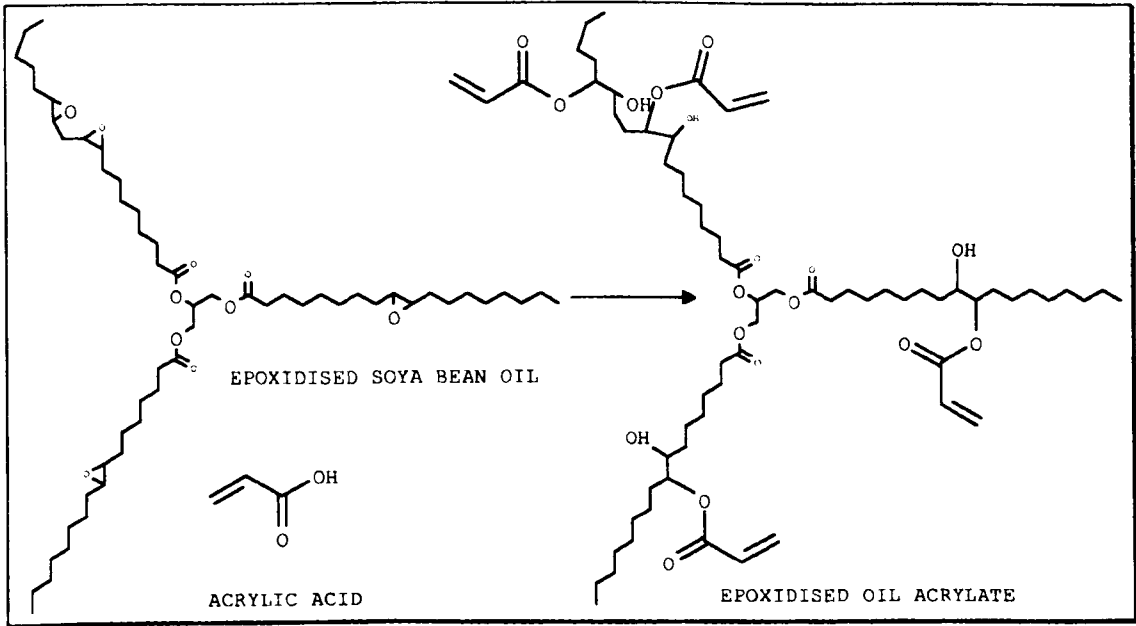


Figure I.3 Epoxidised oil acrylate.

Acrylation usually is performed with acrylic acid under similar conditions to epoxy acrylate manufacture (Figure I.3). The viscosity and unsaturation level of acrylated oils is lower than epoxy acrylates and consequently it is not necessary to use reactive diluents to decrease the viscosity.

Urethane acrylates are made by reacting diisocyanates with the hydroxyl groups of acrylic monomers such as hydroxyethyl acrylate HEA and hydroxyethyl methacrylate HEMA (Figure I.4). Urethane acrylates can be prepared from a broad range of diisocyanates of different chemical compositions, which contribute to the different properties encountered in this family of resins.

Urethane acrylates have excellent toughness, abrasion and chemical resistance and adhesion to difficult substrates. Depending on the backbone composition - chain length, aromatic-aliphatic nature and functionality- is possible to synthesise coatings of different properties.

Urethane acrylates are used in wood coatings, overprint varnishes, printing inks and adhesives. They are also used on flexible substrates such as PVC and polyester due to their good flexibility and adhesive properties.

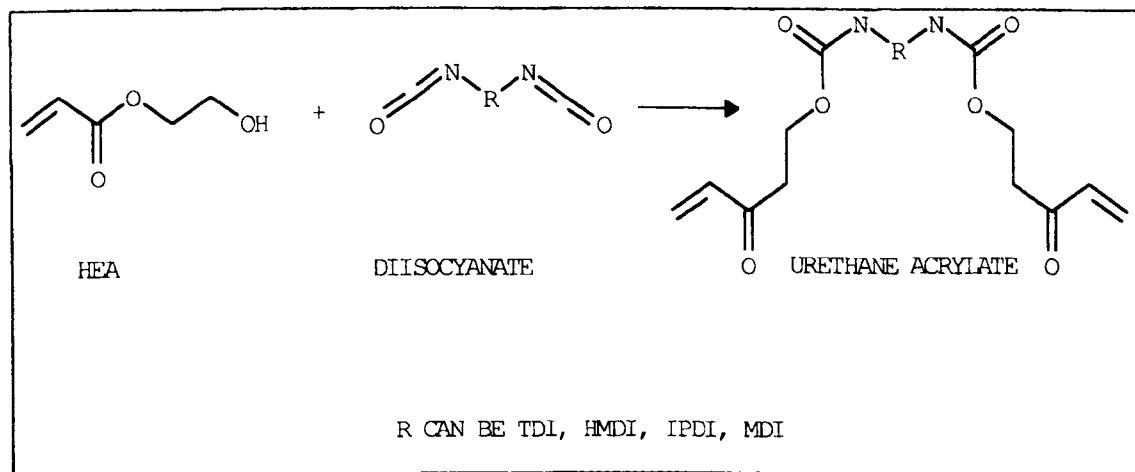


Figure I.4 Basic urethane acrylate.

Tolylene diisocyanate TDI and diphenylmethane diisocyanate MDI present aromatic structure, which can provide low flexibility of the chain and appreciable yellowing. Tetramethylxylene diisocyanate TMXDI and xylene diisocyanate XDI are aromatic diisocyanates, which contain an aromatic ring of certain backbone rigidity affecting the final mechanical properties such as hardness and flexibility.

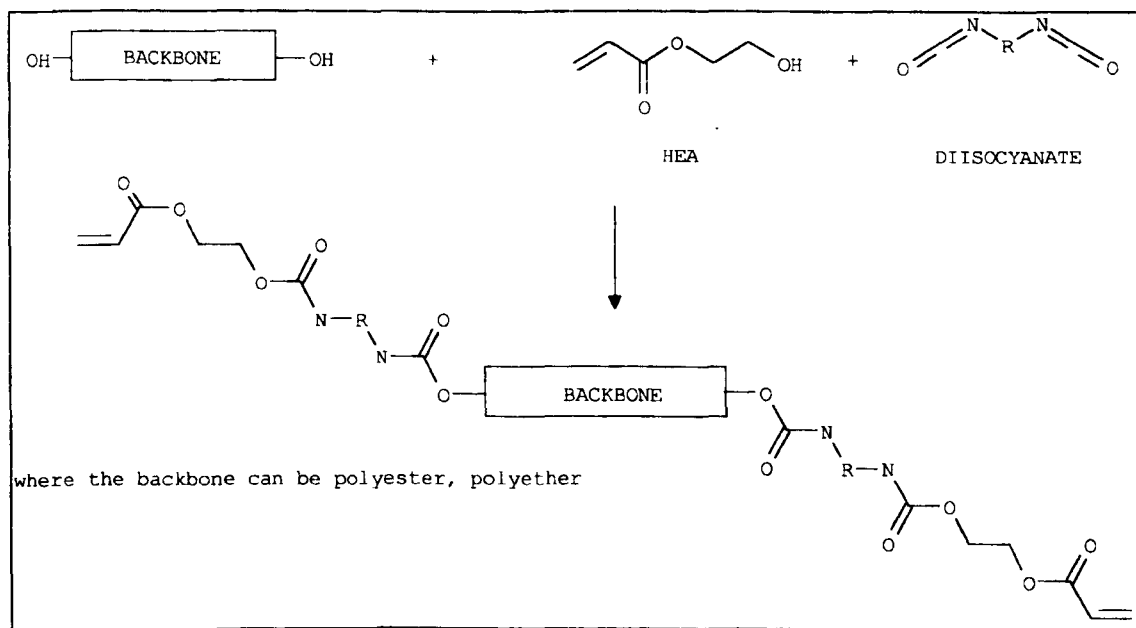


Figure I.5 Polyester and polyether urethane acrylates.

Aliphatic diisocyanates can be divided into linear and cyclic types. Isophorone diisocyanate IPDI and 4,4'-dicyclohexylmethane diisocyanate H₁₂MDI are the main representatives of the cyclic type and possess good colour stability in comparison to aromatic diisocyanates. Hexamethylene diisocyanate HMDI is an example of an aliphatic diisocyanate of high flexibility and low discolouration.

When polyester, polyether or polyols containing hydroxy groups are reacted with diisocyanates (Figure I.5), it is possible to make a wide range of different products characterised by having different chemical backbones (depending on the nature of the diisocyanate and hydroxy monomer or oligomer), viscosity, reactivity, functionality and molecular weight.

Hard urethane acrylates can be obtained either with tri or higher functional hydroxy polyester, polyether (or generally polyols resins or monomers) or with aromatic diisocyanates, which tend to give harder films than aliphatic diisocyanates. Normally these highly branched structures present high viscosity due to their rigid aromatic backbone, which will affect the final rheological properties as well as the mobility of the propagating radical during the polymerisation process.

Soft or flexible urethane acrylates can be obtained by using aliphatic chain polyols like 1,6 hexanediol, the longer the aliphatic chain the more flexible the resin becomes due to the flexible nature of unbranched aliphatic polyols and to the resulting lower crosslink density. This fact can be observed by comparison of 1,6 hexanediol and ethylene glycol, where 1,6 hexanediol provides more flexible films

than ethylene glycol. The use of aliphatic diisocyanates such as HMDI also contribute to the flexibility of the final resin.

Reactivity and good mechanical properties are one of the most important characteristics of resins, good flow characteristics and good pigment wetting are also important aspects to take into account specially in pigmented systems.

Polyester acrylates can be simply made by reacting acrylic acid with hydroxyl terminated polyesters. Some have good pigment wetting characteristics.

The following table highlights some of the properties which different classes of prepolymers can impart to the cured film (Table I.1):

Properties	Epoxy acrylates	Urethane acrylates	Polyester acrylates	Acrylated oils
Viscosity	High	High	Variable	Variable
Viscosity reduction	Good	Fair	Good	-
Pigment wetting	Fair	Low	Good	Excellent
Polymerisation rate	High	Variable	Variable	High
Cost	Low	High	Low	Low
Tensile strength	Low	Variable	Moderate	Low
Flexibility	Poor	Good	Variable	High
Hardness	High	Variable	Moderate	Low
Chemical resistance	High	Variable	Good	Moderate
Non-Yellowing	Moderate	Variable	Poor	-

Table I.1 General characteristics of prepolymers.

1.4 Reactive diluents

Reactive diluents or acrylate monomers are usually required to reduce the high viscosity of most UV curable oligomers or prepolymers and to facilitate the handling and application of formulations to the substrate.

Industrially, different ways have been used to decrease the viscosity of oligomers. The use of organic solvents in certain applications such as overprint varnishes has made a considerable contribution to volatile organic compounds VOC's emission. Water presents a more ecological alternative with interesting properties such as non toxicity, non flammability and low cost. Adversely, water presents low volatility resulting in a drawback in fast curing applications. Normally water based systems possess worse curing performance concerning chemical and mechanical properties than monomer based systems.

Monomer based systems still present good viscosity cutting properties whilst maintaining the advantages of radiation curing where the monomers or low viscosity acrylates are totally incorporated into the crosslinking of the film.

Monomers can be classified depending on their functionality or on the type of structure. Basically, there are three types of multifunctional monomers, namely polyester acrylates, polyol acrylates and polyether acrylates. Polyester acrylates are of higher viscosity than polyether acrylates due to their higher molecular weight. Polyether acrylates are an important class of monomers, which can be made by reaction of ethylene or propylene oxide with a polyol, in the presence of an acidic or basic catalyst, to produce a polyether polyol followed by transesterification with ethyl acrylate (Figure 1.6). An alternative method may be used by esterification of polyols with acrylic acid.

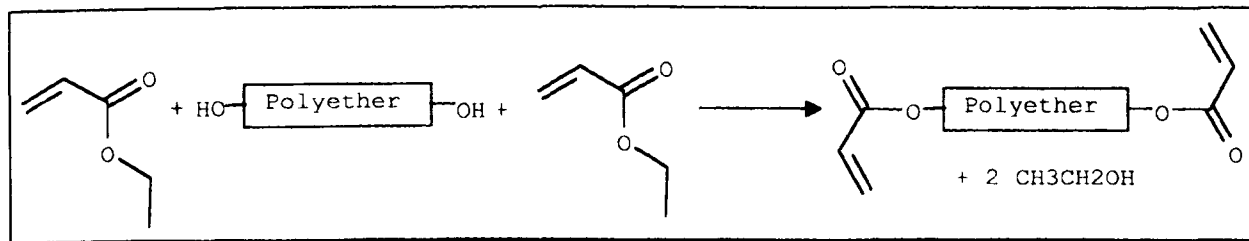


Figure 1.6 Transesterification of a polyether polyol with ethyl acrylate.

Polyol acrylates represent another important class of multifunctional acrylates such as trimethylolpropane triacrylate TMPTA and pentaerythritol triacrylate. The

reaction involves the acrylation of a polyol by esterification or transesterification (Figure I.7).

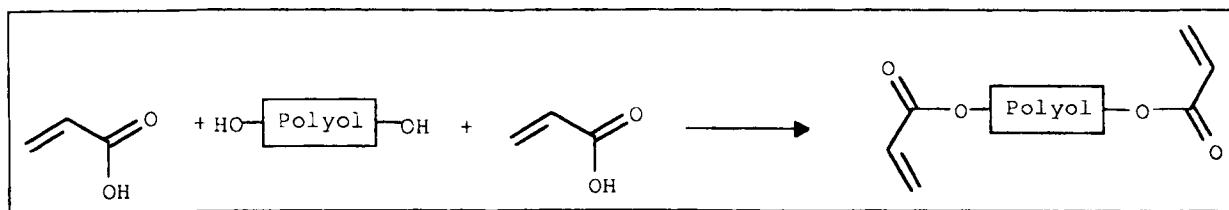


Figure I.7 Esterification of a polyol with acrylic acid.

Acrylates are required to exhibit low toxicity reflected in their Draize index²¹ especially in food contact inks and coatings (Figure I.8). Low volatility, low viscosity, high reactivity and outstanding mechanical properties are important requirements demanded by the radiation curing industry.

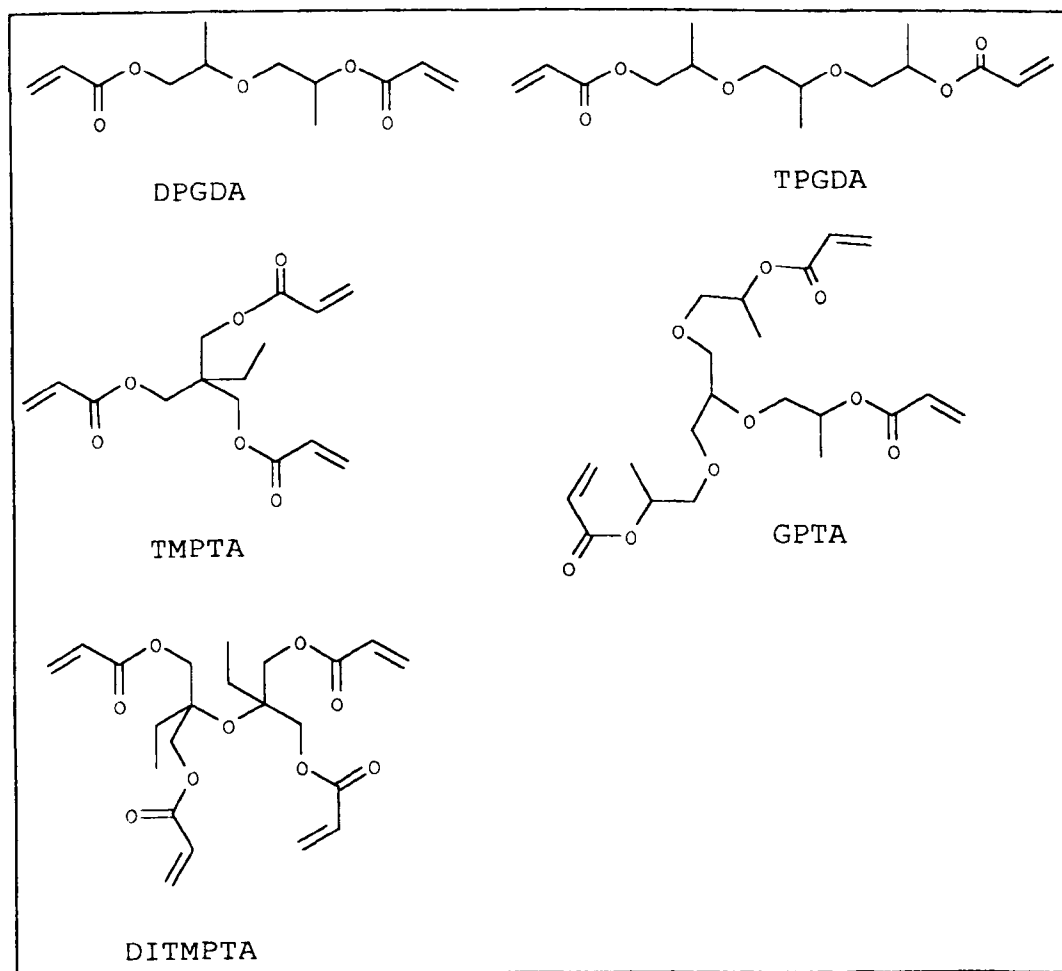


Figure I.8 Low viscosity acrylates.

Monofunctional acrylates are generally volatile and have high vapour pressure tending to be more hazardous due to flammability and health exposure. Their use has been restricted in most industrial applications.

Generally, multifunctional acrylates exhibit low volatility and consequently low odour. Their flammability risk is significantly reduced. Due to their higher molecular weight, they present higher viscosity than monofunctional acrylates.

1.5 Pigments

Pigments impart colour to any formulation containing them. Pigments are finely divided insoluble powders, which need to be dispersed, unlike dyes, which need to be dissolved. The dyes used in the ink industry compared to pigments have the following differences²²:

- higher transparency
- brighter and cleaner
- visually stronger
- more susceptible to attack by aqueous reagents
- poorer light fastness

Pigments are present as clusters or agglomerates, hence their particle size is obviously greater than that of a dyestuff. Organic pigments possess some aromatic character conjugated to further unsaturation, in order to produce a chromophore, which absorbs in the UV-visible region of the spectrum. The colour of the pigment can be tuned by using different substituents, such as hydroxyl, amino, carboxyl and nitro groups, on the aromatic rings. Hence, pigments absorb and/or scatter light of certain wavelengths affecting the curing process mainly by reducing the light accessible for the photoinitiator and/or by photochemical sensitisation or quenching of excited states. Some pigments can inhibit radical polymerisation or can be involved in chain termination reactions.

Pigments scatter light, increasing the fraction of light reflected at the air-coating interface and reduce the fraction of light, which penetrates into the formulation.

1.6 Curing of pigmented systems

Pigmented systems present an additional challenge in the development of UV curing systems. The effectiveness of curing depends to a large extent on the overlap of the output of the irradiation source (emission spectrum of the lamp) with the photoinitiator absorption spectrum.

Pigments absorb UV/Visible light, therefore there is competitive light absorption with photoinitiators, but most pigments possess sufficient transmission in certain parts of the UV/Visible spectrum to allow for competitive light absorption by the initiator. This range is termed the spectral window of the pigment.

1.6.1 Photoinitiator concentration effect

Photoinitiator concentration influences the light absorption characteristics throughout the film. According to Beer-Lambert's Law[#] the fraction of light absorbed by the photoinitiators is proportional to the photoinitiator extinction coefficient, its concentration and the pathlength. In UV curing systems there is an optimum photoinitiator concentration. In UV printing inks where thin films are used reactivity increases with increasing photoinitiator concentration until a maximum is reached²³. An excess of initiating radicals can increase the number of termination reactions decreasing the polymerisation rate and/or the crosslink density.

Molecular oxygen inhibits radical polymerisation reactions by quenching the photoinitiator triplet excited states²⁴, reacting with both the photoinitiator and the propagating radicals. The overall effect is more noticeable in thin films due to the high surface/volume ratio. Printing inks are normally printed at low film thickness (1-5 microns) and so, it is common to use high concentrations of photoinitiators (around 7-11% w/w) in order to increase the number of reactive sites in the top layers of the film. Deficient surface cure of a film is an undesirable outcome. Increasing the photoinitiator concentration and/or creating physical barriers, for example with waxes, the diffusion of oxygen to the bottom of the film can be reduced. The use of amine²⁵ co-initiators is indispensable for getting tack free films, specially tertiary amines which possess high oxidative properties and are used as oxygen scavengers. Also, amines act as a source of electrons and protons with Type II photoinitiators due to their low ionisation potential and proton labile character.

[#] The Beer-Lambert's Law is valid for dilute solutions of absorber and a parallel light beam

When photoinitiator systems consisting of more than one component are used, the relative concentration of the photoinitiators becomes important, since at an optimal photoinitiator/co-initiator/sensitizer ratio the best performance is obtained.

1.6.2 Film thickness effect

Photoinitiators at high concentrations or having high extinction coefficients are an advantage in thin films since there is competition with the pigment for the incident light and oxygen inhibition. In thinner pigmented films an increase of cure in comparison to clear systems can be observed due to higher fraction of light absorbed on the top layers of the film at certain pigment levels and at certain film thickness. Within the film, the light pathlength is increased-nearly doubled in high scattering pigmented systems²⁶ due to multiple scattering on the surface of pigment particles.

Thick pigmented films have an additional difficulty, firstly as for thin pigmented films a high concentration of photoinitiators is necessary to cure the top layers (surface cure), secondly enough radiation should reach the bottom layers in order to get through cure and adhesion of the film to the substrate²⁷.

At high film thickness a high photoinitiator concentration or a high extinction coefficient results in almost complete light absorption on the surface of the film. This effect is even more pronounced in pigmented systems due to their additional pigment absorbance.

Sufficient penetration of light into the bottom layers of the coating is essential for uniform through cure²⁸. Consequently, the fraction of light reaching the bottom of the film is reduced in thick pigmented systems.

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II. CHAPTER II PHOTOCHEMISTRY

II.1 Introduction

Ultraviolet and/or visible light induced reactions normally consist of chain reactions -such as radical, cationic and less commonly anionic polymerisation - initiated by light energy.

Radical polymerisation is the most extensively used method for curing UV/visible systems. Cationic polymerisation is also used in some industrial applications, for example cationic inks but it is not so commonly used as the radical type.

II.2 Primary processes

The first step of any photochemical reaction is the absorption of light ($h\nu$) by the photoinitiator molecule, in order to subsequently induce photopolymerisation or photocrosslinking of monomers. Through absorption of a photon by the PI an electron is promoted from its ground electronic state to an excited state¹ ($PI \rightarrow PI^*$), the process is referred as an electronic transition.

The selection rules dictate that for the transition to be allowed the position of the spin must remain unchanged, consequently the multiplicity¹ ($S=2s+1$ $s=1/2-1/2=0$ $S=1$) remains unchanged. This transition is referred to as a singlet-singlet transition $S_0 \rightarrow S_1$. The nature of the excited states depends on the specific type of molecule, especially its structure, and type of molecular orbitals.

In molecular orbital theory, a chemical bond is considered to consist of bonding, anti bonding and non-bonding orbitals with atoms possessing lone pair electrons. Sigma bonds are formed from the overlap of s atomic orbitals, which possess spherical symmetry. On the other hand π bonds are formed by the overlap of adjacent p atomic orbitals (at the same plane and symmetry) already possessing a sigma bond.

Photoinitiators possess carbonyl functional groups which present a ground state electronic configuration. If the number of occupied antibonding orbitals exceeds the number of occupied bonding orbitals the carbonyl can dissociate. This process occurs with high energetic sources beyond 180 nm in the far UV region of the spectrum.

The majority of UV photopolymerisation reactions occur in the region 250-400 nm, where the energy is not high enough to dissociate the carbonyl group.

The following diagram² represents the possible electronic transitions a PI can proceed (Figure II.1). These transitions occur at different wavelengths. The highest electronic transitions occur at lower wavelengths.

For the carbonyl group, the $n\text{-}\pi^*$ transition occurs in the UV region and it weakens the carbonyl bond, but not to the same extent as a $\pi\text{-}\pi^*$ transition.

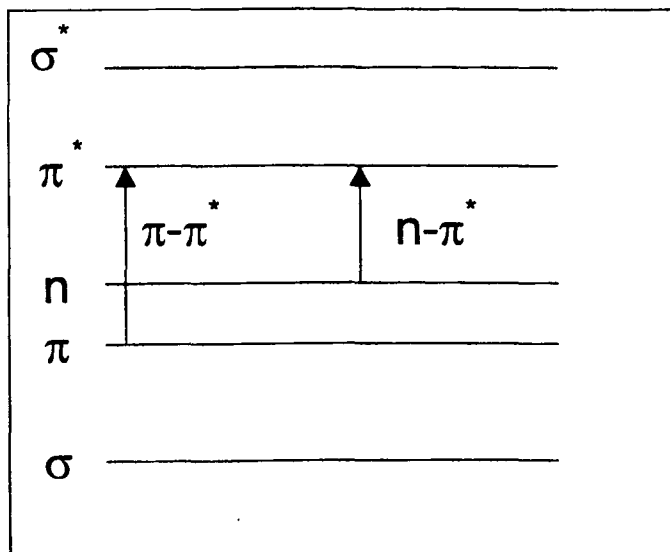


Figure II.1 Typical electronic transitions of photoinitiators

The allowedness of a $\pi\text{-}\pi^*$ transition is higher than the $n\text{-}\pi^*$ transition and complies with the selection rules, consequently the absorption is higher as is reflected by its higher extinction coefficient ϵ_{max} . On the other hand, $n\text{-}\pi^*$ transitions requires spin flipping (symmetry forbidden) and so present low absorptivity.

The nuclei of the different atoms play an important role in determining which wavelengths of radiation will be absorbed. The nuclei determine the strength with which the electrons are bound, and in this way influence the energy spacing between ground and excited states. Hence, the characteristic energy of a transition is a property of a group of atoms, rather than electrons themselves. The group of atoms exhibiting such absorption is called a chromophore. As structural changes are made, the intensity and energy of the absorption are expected to change accordingly.

Hence, attaching different chemical groups to chromophores may shift the absorption spectrum of the chromophore. This phenomenon enables the synthesis of PIs with extended absorption in the near UV.

Substituents, which increase the intensity of the absorption, and possibly the wavelength, are called auxochromes. Typical auxochromes might include methyl,

hydroxyl, alkoxy, halogen, and amino groups. Substitution may have the following effects on the absorption:

- Bathochromic shift (red shift): Shift to longer wavelengths or lower frequency
- Hypsochromic shift (blue shift): Shift to shorter wavelengths or higher frequency
- Hyperchromic effect: Increase of intensity
- Hypochromic effect: Decrease of intensity

One way to bring about a bathochromic shift is to extend the conjugation of a double bond system such as in conjugated polyene systems, since the electronic transition from the highest occupied bonding molecular orbitals (HOMO) to the lowest unoccupied antibonding molecular orbital (LUMO) has progressively lower energy. Additionally, conjugation attached to carbonyl groups shifts the absorption to longer wavelengths (red shift or bathochromic effect). Conjugation not only results in a bathochromic shift, but it can also increase the intensity of the absorption (hyperchromic effect). In a similar way, many auxochromes exert their bathochromic shifts by means of an extension of the length of the conjugated system. Such bathochromes possess a pair of unshared electrons on the atom attached to the double bond system. Resonance interaction of this lone pair with the double bond increases the length of the conjugated system.

Similarly, methyl groups also produce a bathochromic shift, by overlap of the electrons in a C-H bond with the π system. This type of interaction is called hyperconjugation.

As mentioned previously, carbonyl compounds have two principal UV transitions, the allowed $\pi \rightarrow \pi^*$ transition and the forbidden $n \rightarrow \pi^*$ transition. Substitution of the carbonyl group by an auxochrome with a lone pair of electrons gives a pronounced hypsochromic effect on the $n \rightarrow \pi^*$ transition and a lesser bathochromic effect on the $\pi \rightarrow \pi^*$ transition. This hypsochromic effect is due to the inductive effect of oxygen, nitrogen or halogen atoms. They withdraw electrons from the carbonyl carbon, causing the lone pair of electrons on oxygen to be held more firmly than would be the case in the absence of an inductive effect.

If the carbonyl group is part of a conjugated system of double bonds, both transitions are shifted to longer wavelengths. If the conjugated system becomes

long enough the $n \rightarrow \pi^*$ transition may be buried under the more intense $\pi \rightarrow \pi^*$ transition.

Aromatic ketone chromophores exhibit an interaction of the benzene ring electrons and the π electrons of the carbonyl group (Figure II.2). As a consequence, the resulting chromophore becomes electron deficient. Hence, the carbonyl group acts as an electron withdrawing substituent due to its capability of extending the π conjugation.

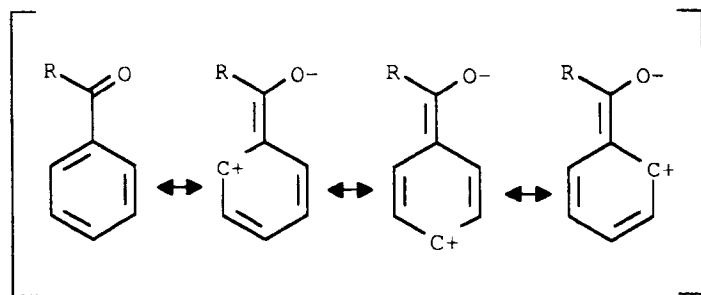


Figure II.2 Extension of π conjugation in aromatic ketones.

Substituents with unshared electrons on the benzoyl moiety can cause an increase of the length of the π system through resonance. The more available these n electrons are for interaction with the π system the greater the shift will be. In addition, the presence of n electrons gives the possibility of $n \rightarrow \pi^*$ transitions. If an n electron is excited into the extended π^* chromophore, the atom from which it was removed becomes electron deficient, while the π system acquires an extra electron. This causes a separation of charge, which is often called a charge transfer or an electron transfer excited state (Figure II.3).

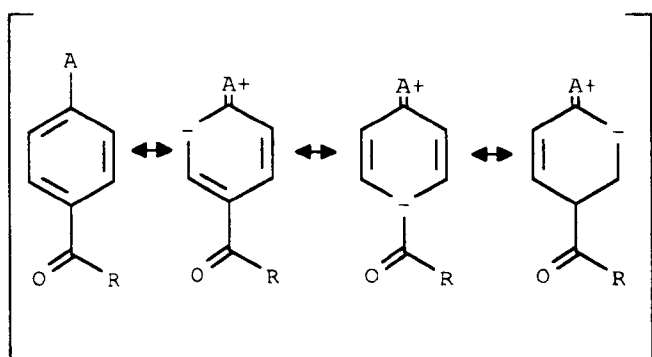


Figure II.3 Charge transfer or electron transfer excited states of molecules.

Effect of solvent polarity on the absorption characteristics

Solvents have the ability to shift the wavelength of ultraviolet light, which can be absorbed by a molecule. Such 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 excited states.

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 will have its absorption maximum shifted to shorter wavelength (hypsochromic shift) as the 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 stabilised more strongly with the excited state than with the ground state. As a result, the transition is shifted to longer wavelengths (bathochromic shift).

II.2.1 Fluorescence

From the lowest vibrational level S_1 can revert to the ground state S_0 by undergoing a radiative transition between states of the same multiplicity, this phenomenon is termed fluorescence.

II.2.2 Internal conversion

When S_1 or T_1 deactivates by non-radiative processes the phenomenon is termed internal conversion and it is characterised by occurring between states of the same multiplicity ($S_1 (S=1) \rightarrow S_0 (S=1)$ and $T_1 (S=3) \rightarrow T_0 (S=3)$).

II.2.3 Phosphorescence

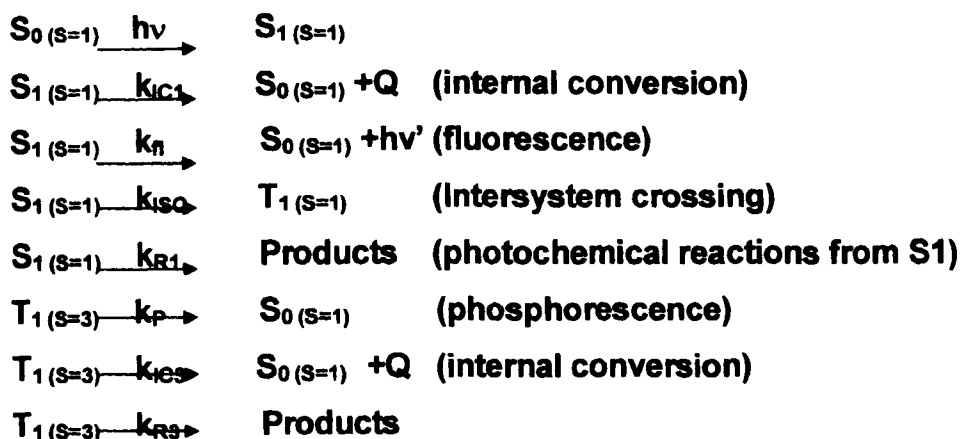
If the molecule undergoes a radiative transition from its lowest vibrational level of T_1 to the ground state the process is called phosphorescence. This process is characterised by the existence of a change of multiplicity ($T_1 (S=3) \rightarrow S_0 (S=1)$).

Phosphorescence emission is normally observed at low temperatures where quenching of excited triplet states is reduced due to the lower intermolecular collision rate typical of low temperature frozen matrices, in which rotational and vibrational modes are reduced.

The majority of the photochemical reactions are produced from the lowest triplet states of the molecule. The study of triplet states can be monitored by different techniques such as phosphorescence spectroscopy by measuring triplet state energies, phosphorescence quantum yield and flash photolysis by studying transient intermediate absorption spectra.

Quantum yield calculations provide information on the relative importance of the various pathways by which an excited molecule disposes of its energy. For any process a quantum yield can be defined as the number of molecules undergoing a particular process per number of photons absorbed by the system.

The following series of primary photochemical processes can help to understand the concept of quantum yields between different competitive processes.



The phosphorescence quantum yield can be determined by

$$\phi_P = \phi_{ISC} \frac{k_P}{(k_P + k_{IC3} + k_{R3})} \quad \text{where } \phi_{ISC} = \frac{k_{ISC}}{(k_F + k_{IC1} + k_{ISC} + k_{R1})}$$

A unimolecular reaction rate law characterised by an exponential decay governs emission of photons by fluorescence and phosphorescence. The mean radiative lifetime is defined as the time necessary to decrease the concentration of excited states to $1/e$ of their original concentration C_0 . The mean lifetime of a molecule is an important measurement in photochemistry since the quenching of an excited state is more probable for long-lived states. In addition, it should be taken into account that bimolecular photoinitiators need to interact physically by molecular orbital overlap, hence a relatively long lifetime is necessary in order to increase the reaction probability factor.

II.3 Secondary processes

Once the initiating species are formed the following reactions are termed secondary or dark reactions. These include:

- unimolecular reactions Type I, cleavage
- bimolecular reactions Type II, electron/proton transfer
- energy transfer.

II.3.1 Unimolecular reactions

Direct fragmentation or homolytic scission.

If the PI excited state possesses higher energy than the bond dissociation energy, then the PI can dissociate forming reactive species. PIs of this type are called Type I (Figure II.4).

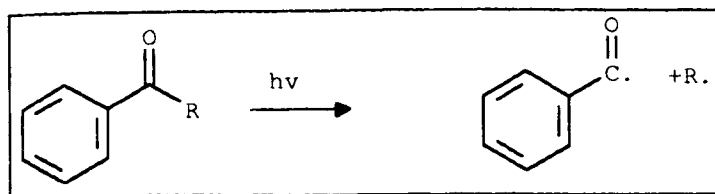


Figure II.4 Direct fragmentation reaction of a PI.

Norrish Reactions

There are two type of reactions considered by Norrish. Only the Type I can initiate polymerisation reactions. Norrish Type I reaction consists of homolytic cleavage of the bond between the carbonyl group and an adjacent α -carbon (Figure II.5).

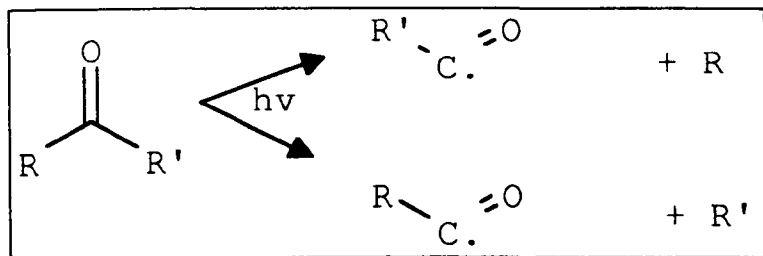


Figure II.5 Norrish Type I reaction.

Norrish Type II reaction is an intramolecular hydrogen abstraction process from the γ position to the carbonyl group, resulting in a 1,4-biradical as the primary product. Depending on the structure, this will either undergo a fragmentation reaction to give an enol and a vinyl entity or ring closure to give an oxetane (Figure II.6).

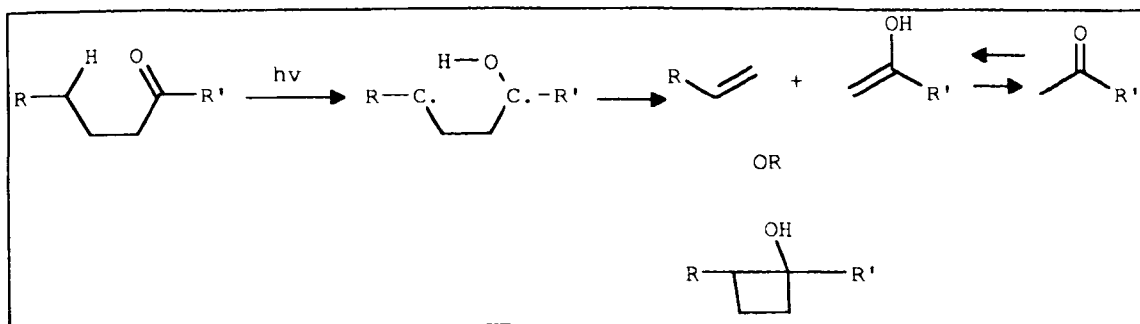
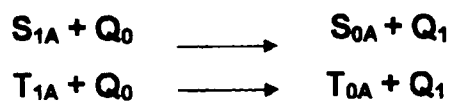


Figure II.6 Norrish Type II reaction.

II.3.2 Bimolecular reactions

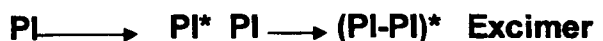
Type II PIs are characterised by undergoing bimolecular reactions. A molecule in its excited state can react with another molecule to create radicals capable of initiating polymerisation.

Certain compounds (quenchers) can deactivate the excited state of a molecule to the ground state.



This process is described as quenching. There are many types of quenching mechanisms and the majority occur as a result of collisions. This bimolecular process involves an encounter pair, excimer or exciplex.

An encounter complex is a species in which the two components are separated only by few Amstrongs, but have no special orientation, with the exception of having enough molecular orbital overlap. An excimer is one of more defined geometry between two molecules of the same type, while an exciplex³ is formed by two different type of molecules. Tertiary amines quench phosphorescence emissions of Type II PIs through formation of triplet exciplexes, where hydrogen transfer can take place.



The excited molecule is called the sensitiser and the second compound is referred to as the co-initiator. The initiating species (radicals) can be either the sensitiser and/or the coinitiator. It should be considered that a sensitiser once it is excited can activate the coinitiator via energy or electron transfer processes to initiating species. This process is commonly used in the UV curing pigmented systems in order to overcome competitive radiation absorption by pigments.

Another common process is electron/proton abstraction⁴ by addition of hydrogen donors such as tertiary amines (Figure II.7).

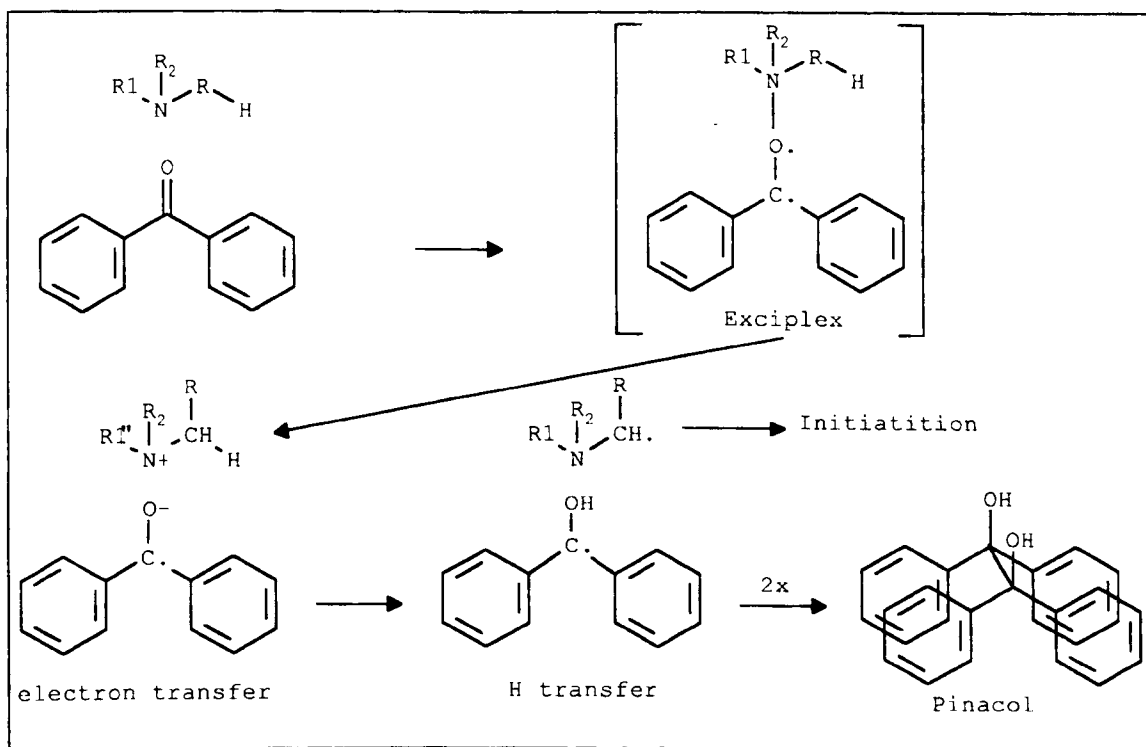


Figure II.7 Electron/proton abstraction process between benzophenone and an amine.

Tertiary amines in the α -aminoalkyl radical form can also scavenge oxygen by formation of peroxy radicals which subsequently can react cyclically with another amine producing a new α -aminoalkyl radical⁵ (Figure II.8).

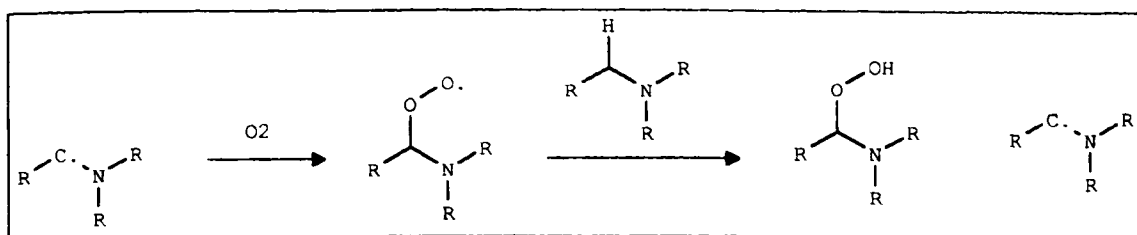


Figure II.8 Reaction of amines with oxygen.

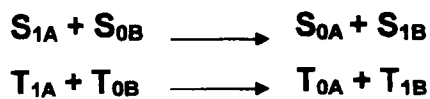
Atmospheric oxygen is known to be a very efficient quencher of triplet states⁶. Molecular oxygen has a triplet ground state and this diradical can also react with propagating radicals during polymerisation decreasing the efficiency of initiation as well as the polymerisation rate and product molecular weight distribution and average molecular weight.

This process makes amines effective additives to counteract oxygen inhibition in radical photopolymerisation. This process can explain the role of amine on the

polymerisation of acylphosphine oxides PIs where the reduction of oxygen inhibition is also appreciable⁷.

II.3.3 Energy transfer

Energy transfer may occur when a molecule in its lowest vibrational state S_1 or T_1 transfer its energy to another molecule in its ground state, consequently this molecule is excited to its S_1 or T_1 state whilst the original one reverts to its ground state.



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III. CHAPTER III PHOTOINITIATION OF POLYMERISATION

III.1 Introduction

There are two basic categories of free radical photoinitiators. The first group involves Type I photoinitiators, which undergo a direct photofragmentation process (α or less commonly β cleavage) upon absorption of light and formation of initiating radicals capable of inducing polymerisation. The second group, known as Type II photoinitiators undergo a primary process of hydrogen atom abstraction from the environment, which may be the resin itself or a solvent, but usually a tertiary amine co-synergist is used for enhanced efficiency. The reaction usually occurs from the lowest excited 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 α -methylene-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 in order to overcome oxygen inhibition. 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.

III.2 Type I Photoinitiators

III.2.1 α -Cleavage photoinitiators

Alkylarylketones are the most important type of PIs due to their high reactivity and thermal stability. Some of the applications in which α cleavage PIs are used are clear coatings, printing inks, printing plates, white lacquers. The most important families are:

III.2.1.1 Benzoin ethers

Benzoin ether derivatives are efficient photoinitiators for the radical polymerisation of vinyl systems. They undergo homolytic fission (Norrish Type I) of the C-C bond which is adjacent to the carbonyl group¹ (Figure III.1). In comparison to other α -cleavage PIs they lead to a shorter pot life of the formulations containing them.

Benzoin itself is not a very effective PI. Additionally, it can provoke gelation on storage in the presence of some pigments.

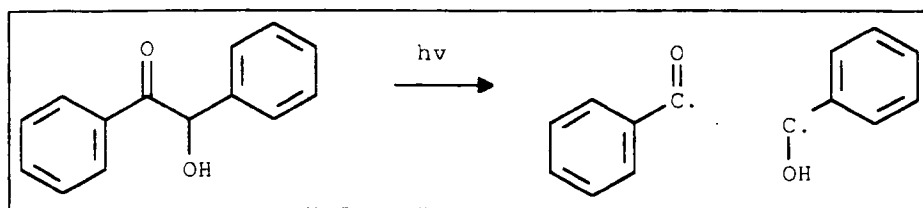


Figure III.1 Fragmentation of Benzoin upon absorption of light.

Benzoin ethers turn out to be more reactive and stable. Different products can be produced upon irradiation such as benzil through hydrogen atom abstraction, dimerisation of the benzoyl radical and pinacol derivative formation from the dimerisation of benzyl radicals² (Figure III.2).

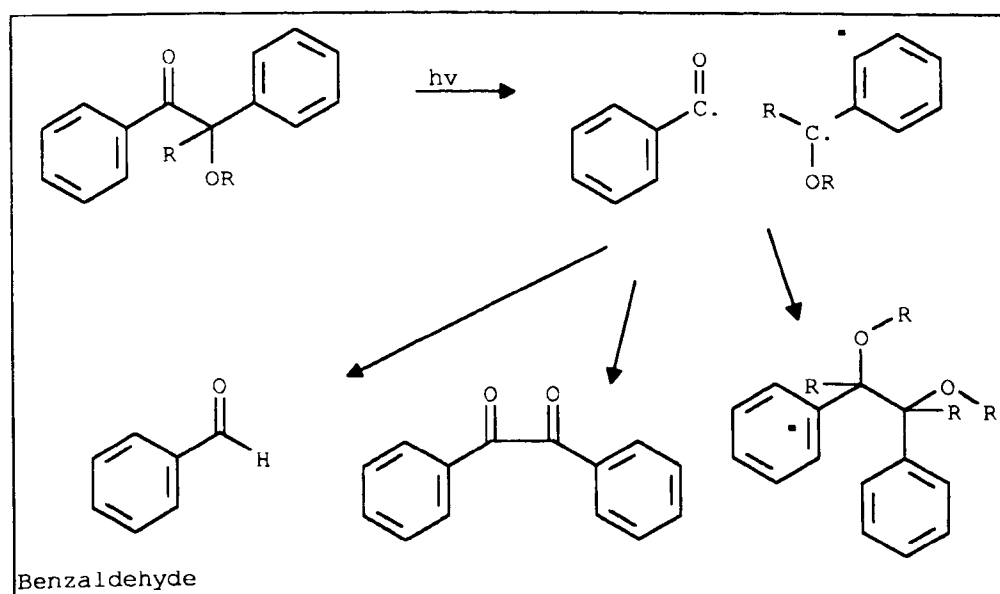


Figure III.2 Reactions of benzoin ethers upon absorption of light.

III.2.1.2 Benzil ketals

Benzil ketals represent a versatile family of photoinitiators. 2,2-dimethoxy-2-phenylacetophenone (DMPA or BDK) is one of the most important commercial photoinitiators of the α -cleavage family. It possesses the following properties:

- high reactivity and initiating efficiency
- high thermal stability
- easy synthetic route with an outstanding price/performance ratio.

The major drawback of this compound is its considerable yellowing. BDK found its first commercial application in unsaturated polyester resins for wood coatings.

Acrylate based inks and coatings for metal, paper, plastic and wood commonly make use of this photoinitiator.

Methyl benzoate was found to be the main product besides benzaldehyde and benzil. The primary benzoyl radical can dimerise to give benzil, which can also react with a methyl radical to form acetophenone or benzaldehyde³ via hydrogen atom abstraction from a molecule in the near environment. In the presence of molecular oxygen it can form benzoic acid and methyl benzoate (Figure III.3).

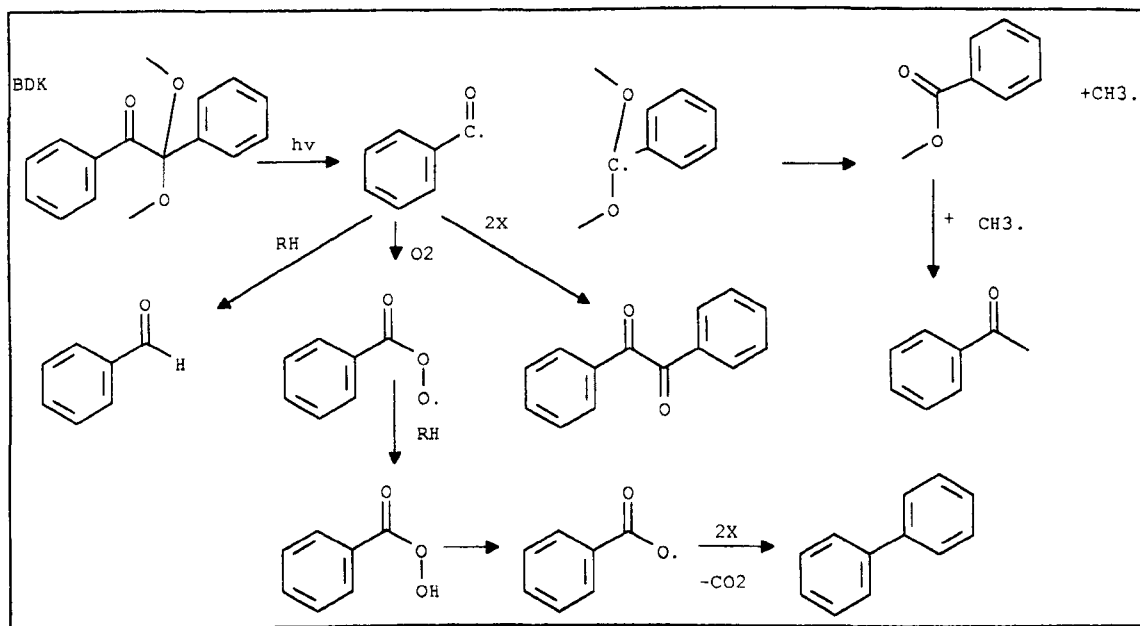


Figure III.3 Reactions of BDK upon absorption of light.

BDK is difficult to deactivate by quenchers due to its very short lifetime, precluding bimolecular reactions and making it suitable for curing styrene systems.

III.2.1.3 α - α -Dialkoxyacetophenones

α - α -Dialkoxyacetophenones are structurally similar to benzil ketal. α - α -Diethoxyacetophenone (DEAP) is the most frequently used PI of its class. The excited state undergoes two competitive reactions⁴ as shown in Figure III.4.

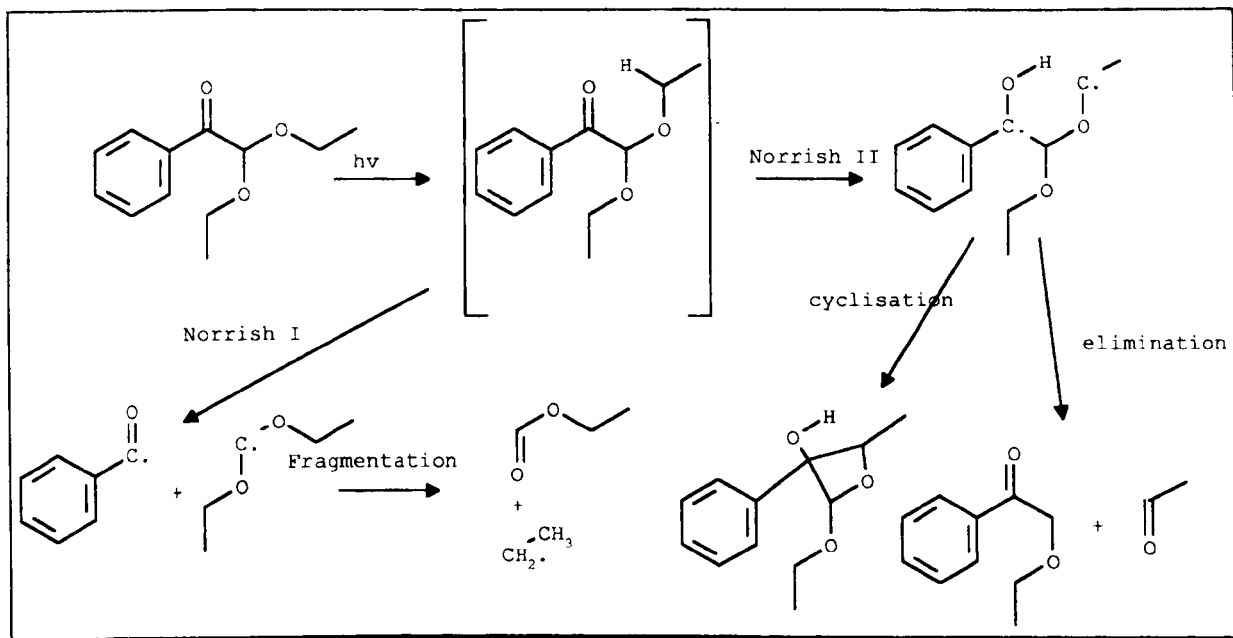


Figure III.4 α - α -Diethoxyacetophenone reactions upon absorption of light.

Norrish I cleavage gives a benzoyl radical and a ketyl radical. The latter fragments to give an alkyl ester of formic acid and an initiating alkyl radical. Both the benzoyl and the alkyl radicals initiate the polymerisation process.

Norrish Type II intramolecular abstraction gives a 1,4 radical intermediate, which decomposes to an oxetane by cyclisation, an acetophenone derivative and an aldehyde via elimination. The Norrish Type II reactions do not initiate the polymerisation reactions.

III.2.1.4 α -Hydroxy alkylphenones

α -Hydroxy alkylphenones are highly reactive, at the same time they possess high thermal stability as benzil ketals. Additionally, they exhibit better colour characteristics imparting very low yellowing in comparison to other commercial PIs. This low yellowing makes its use a necessity when clear coatings are designed.

1-Hydroxy-cyclohexylphenylketone (HCPK or Irgacure 184) is the most common representative PI of this family. Its aliphatic cyclic group at the α position has better properties⁵ than its acyclic counterparts.

Triplet lifetimes for α -hydroxy alkylphenones⁶ are considerably longer than benzoin ethers, DEAP, acylphosphine oxides, due to this fact it can be easily quenched and a subsequent decrease of reactivity can be observed in styrene formulations.

Upon irradiation benzoyl radicals are formed (Figure III.5). As with other PIs, the benzoyl radical is mainly responsible for the initiation of the polymerisation. The α -hydroxyalkyl radical can also participate in the initiation process.

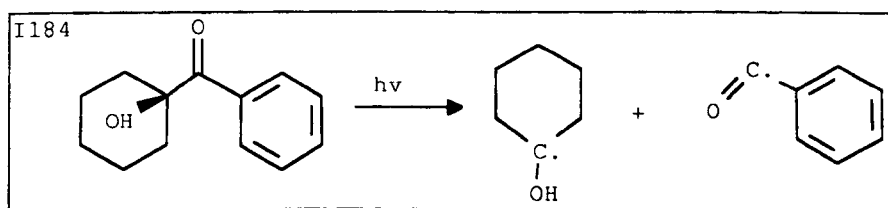


Figure III.5 Unimolecular reaction of Irgacure 184.

In Figure III.6 are shown the different pathways by which α -hydroxyalkylphenones can react. Recombination reactions yield benzil, benzoin and pinacol, whilst disproportionation gives benzaldehyde and acetone⁷.

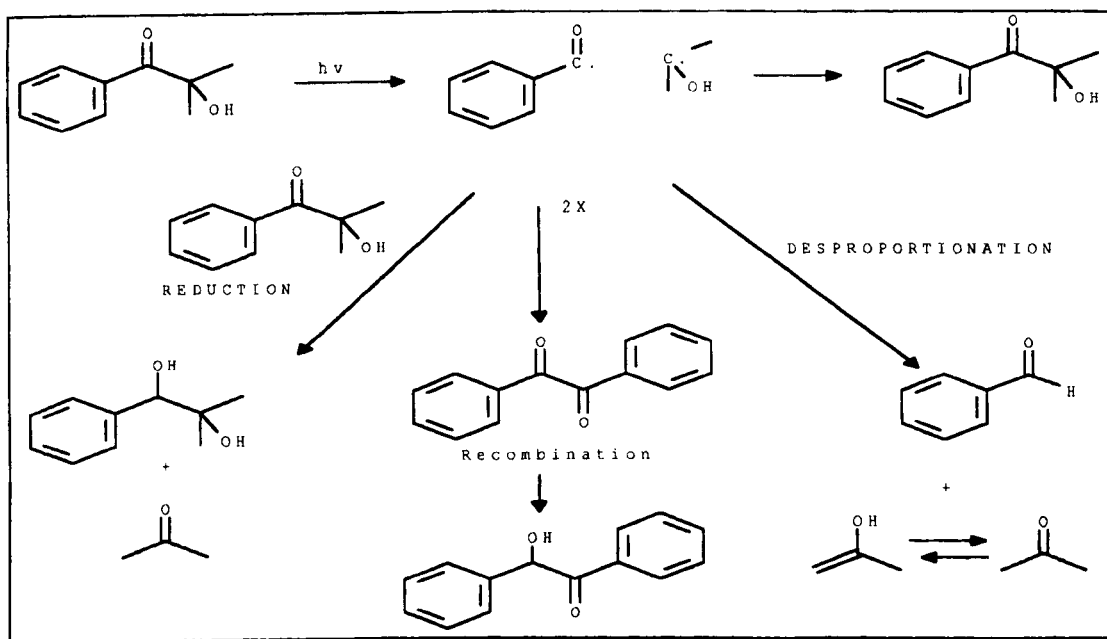


Figure III.6 Reactions of α -hydroxy alkylphenones in solution.

III.2.1.5 α -Aminoalkylphenones

α -Aminoalkylphenones are a relatively new class of Type I photoinitiators. The most important types are substituted at the para position of the aromatic ring by highly electron donating groups such as alkylthio or dialkylamino. The resulting effect is a red shift of the photoinitiator absorption above 300 nm.

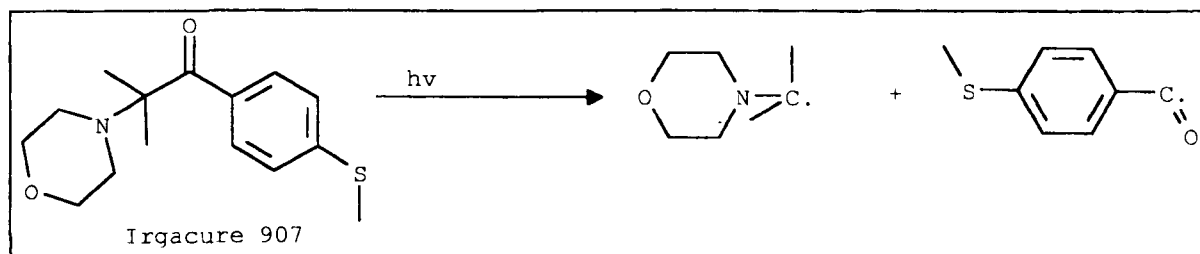


Figure III.7 Unimolecular reaction of Irgacure 907 upon absorption of light.

Two types of α -aminoacetophenone PIs are currently available: 2-methyl-1-4-(methylthio)phenyl)-2-morpholino-propan-2-one (MMMP or Irgacure 907, Figure III.7) and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (BDMB or Irgacure 369).

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 behaviour in pigmented systems⁸. Their curing performance depends on the type of pigment and its absorption spectrum between 250–400 nm.

α -Aminoacetophenone PIs can be sensitised by thioxanthenes⁹ (Figure III.8) or other sensitisers, allowing an extension of reactivity into the visible. Depending on the formulation a several fold increase in reactivity is observed. The reactivity enhancement is due to the fact that thioxanthenes have longer wavelength absorption in the near UV/Visible than most of the common photoinitiators. Thioxanthenes sensitise selectively α -aminoalkylphenones. However it is not possible to sensitise benzoin ethers, benzil ketals or α -hydroxyketones.

Sensitisation occurs via energy transfer and electron transfer. Triplet states of α -aminoalkyl phenones are around 61–63 kcal/mol. Thioxanthenes have triplet energies in the range 59–63 kcal/mol, consequently, energy transfer is possible because the triplet energy of the sensitiser is higher than that of the α -aminoalkylphenone¹⁰. Other PIs present higher triplet state energy than thioxanthenes, subsequently no sensitisation can occur due to the endergonic character of the transition.

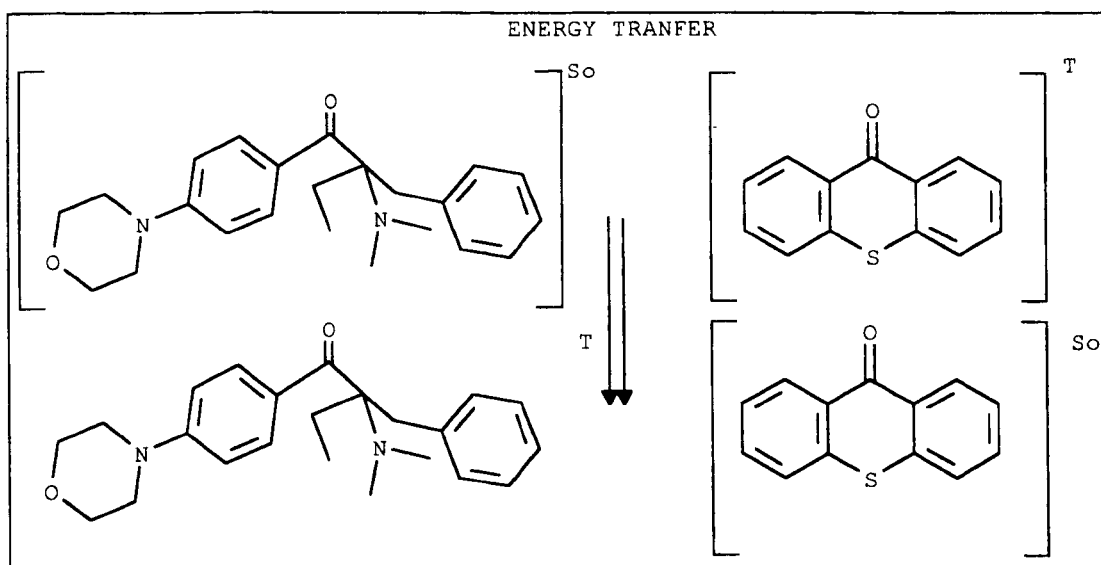


Figure III.8 Sensitisation of Irgacure 369 by a thioxanthone.

Electron transfer can also occur between the excited thioxanthone and the amino group of the α -aminoalkylphenone molecule. MMMP can transfer an electron from the non bonding orbital to the thioxanthone, followed by a fast back electron transfer and proton transfer to give a ketyl radical in the thioxanthone and an α -aminoalkyl radical. No evidence has been found of the involvement of this α -aminoalkyl radical in the initiation process. α -Aminoalkylphenones present a high initiating efficiency and long term stability in the presence of pigments. This factor as well as their insolubility in water complies with the performance requirements of offset lithographic inks.

BDMB is more extensively used due to its lower odour characteristics in comparison to MMMP. MMMP has been replaced in some applications such as printing inks due to its odour. It has been shown by chemically induced dynamic nuclear polarisation $^1\text{H-NMR-CIDNP}^{11}$ experiments that BDMB in solution undergoes predominantly α -cleavage from its triplet state and a minor β -cleavage¹² (See Figure III.9).

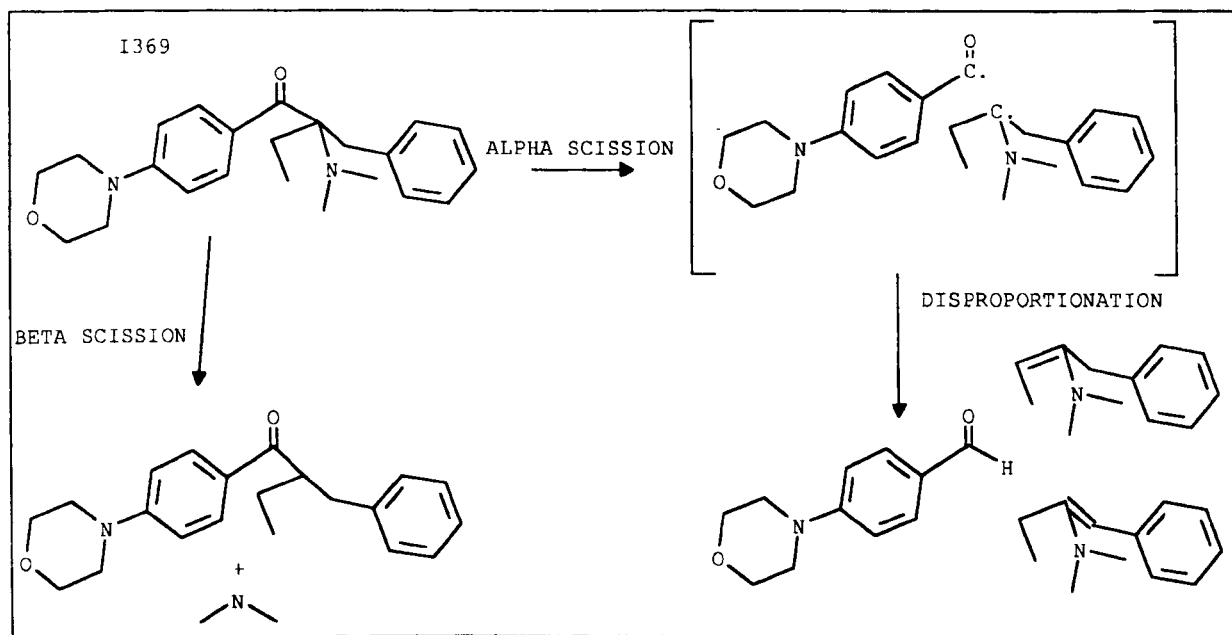


Figure III.9 α -cleavage and β -cleavage reactions of Irgacure 369 upon absorption of light.

III.2.1.6 Acylphosphine Oxides

Acylphosphine oxides were introduced some years ago as a new class of α -cleavage PIs, derived from DEAP by replacing C-H by P=O and alkoxy by aryl groups (see Figure III.10). A relatively high oxygen inhibition may decrease their reactivity in the curing of thin films¹³.

Acylphosphine oxides have absorption bands in the near UV/visible region, which bleach upon irradiation, hence there is a decrease of absorbance in the near UV-Visible range and radiation can penetrate into deeper layers.

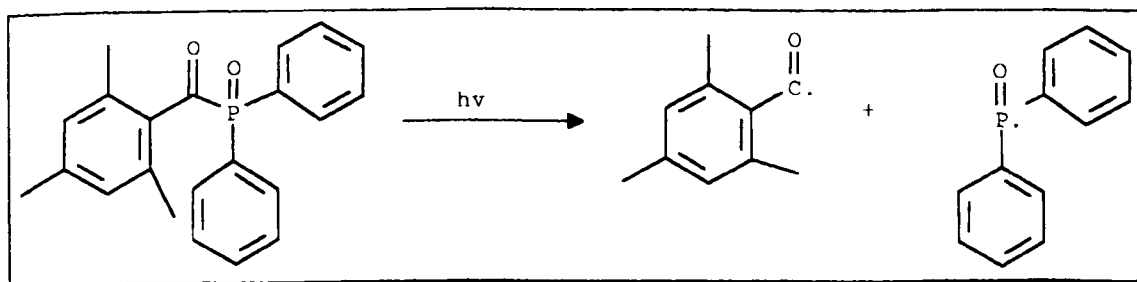


Figure III.10 Unimolecular reaction of TPO upon absorption of light.

Acylphosphine oxides and bisacylphosphine oxides produce very little yellowing immediately after curing and upon long term exposure, therefore they have been

used in applications where low yellowing requirements are demanded such as white and pale inks.

Acylphosphine oxides possess short-lived excited states and present low quenching characteristics being suitable in styrene based formulations for the furniture manufacturing industry.

III.3 Type II photoinitiators

A variety of bimolecular photoinitiators have been used in the curing of pigmented and clear systems. Tertiary amines are mostly used as coinitiators, since they react as oxygen scavengers and thereby help to overcome oxygen inhibition.

III.3.1 Benzophenones

Benzophenone (BP) and its derivatives are the most industrially used bimolecular photoinitiators due to their low cost despite their relatively low reactivity and hardness of cured films. Benzophenone combined with tertiary amines is commonly used in blends combined with other photoinitiators.

A eutectic liquid 1:1 blend of benzophenone and 1-hydroxycyclohexyl-phenyl ketone (Irgacure 500) has high reactivity which is only slightly inferior to 1-hydroxycyclohexyl-phenyl ketone¹⁴.

4,4'-bis-(dimethylamino)-benzophenone, known as Michler's ketone, is an aromatic ketone, which has amino substituents, hence it is reactive by its own even without the presence of additional amine. The combination of Michler's ketone and benzophenone gives a synergistic effect, which far exceeds the reactivity efficiency of the two compounds by their own even in the presence of amine¹⁵ (Figure III.11).

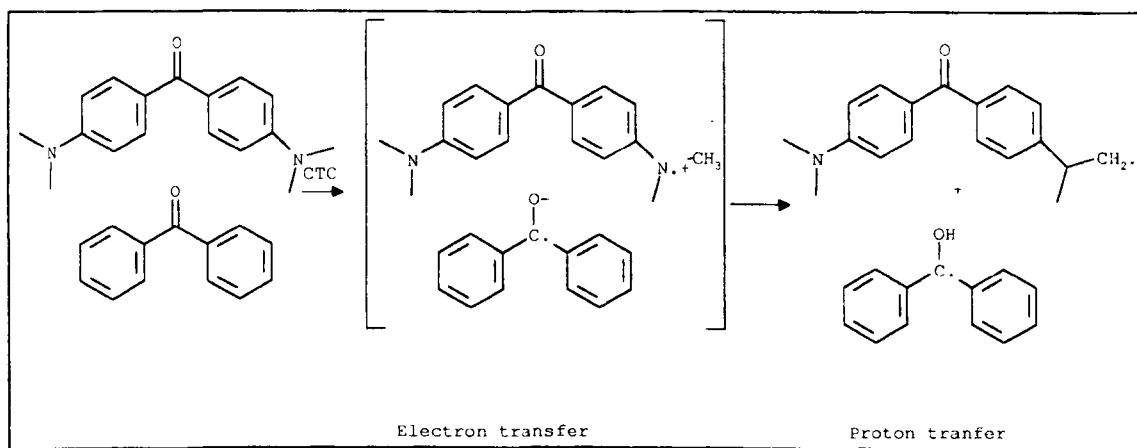


Figure III.11 Charge transfer complex between Michler's ketone and benzophenone.

Michler's ketone is suspected of being a carcinogen¹⁶, consequently its usage has been abandoned in most applications.

III.3.2 Thioxanthenes

Thioxanthone derivative photoinitiators have been widely used for the UV and in particular visible crosslinking of acrylic coatings and inks. Their particular value in these areas is associated with the ability of this chromophore to absorb radiation in the near UV region of the spectrum, thus avoiding much of the absorption/screening by the presence of coloured pigments. For most applications the thioxanthone chromophore relies on the presence of a tertiary amine co-synergist in order to form an excited triplet-exciplex through which electron or hydrogen atom abstraction may take place. Hence, thioxanthenes react similarly to that of benzophenone in the presence of tertiary amines¹⁷. The main difference is their absorption characteristics exhibiting absorption in the near ultraviolet range. Therefore, these photoinitiators are mainly used in pigmented systems such as printing inks.

The photochemical and photophysical properties of a range of thioxanthone^{18, 19} photoinitiators have been extensively studied and reviewed²⁰ 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. As a consequence of this, several

thioxanthone derivatives are currently used in the UV curing industry in various applications.

As for benzophenone derivatives, the ketyl radicals formed are not efficient initiating species. Flash photolysis¹⁸ studies of different thioxanthone derivatives revealed that the α -amino radical acts as the initiating species for these systems.

Isopropyl thioxanthone (ITX) is the most widely used thioxanthone in the market for pigmented systems in combination with tertiary amines (Figure III.12).

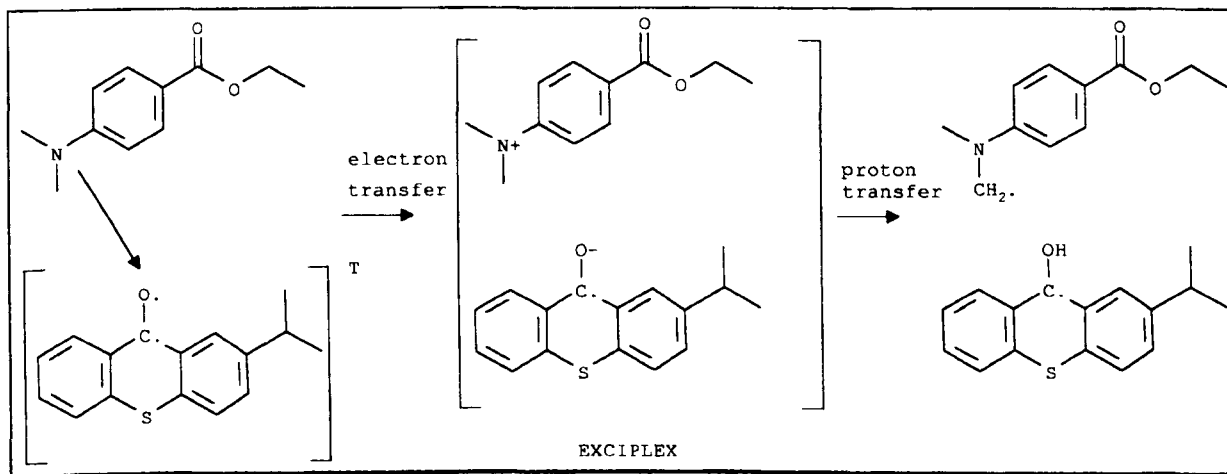


Figure III.12 Reaction mechanism of ITX and a commercial aromatic tertiary amine (Quantacure EPD).

1-Chloro-4-propoxythioxanthone (CPTX) has been introduced in the market and has been claimed to be twice as reactive as ITX in the presence of methyl diethanolamine in a blue printing ink¹⁹. A methyl group in the 1-position probably deactivates the molecule via hydrogen atom abstraction, whilst a chlorine group leads to an enhancement of reactivity. The ether group in the 4-position results in an increase in reactivity in comparison to alkyl substitution at 4-position.

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IV. CHAPTER IV EXPERIMENTAL DESIGN

IV.1 *Introduction to Experimental Design*

Experimental design provides a systematic approach to obtain knowledge of system behaviour based on statistically analysed experimental results. Response surface methodology^{1,2} consists of a group of techniques used in the empirical study of relationships between one or more responses (such as number of passes to get through cure or film hardness measurements), and on the other hand, a number of variables such as photoinitiator type and concentration.

Response surface designs are used to quantify the relationships between one or more measured responses and any number number of input factors. The design factors may be either quantitative continuous variables or they can also be qualitative or discrete variables. The objective is to find a desirable location in the design space. This could be a maximum, a minimum or an area where the response is stable over a range of the factors. Goals might include meeting a set of specifications for several responses simultaneously.

The classical one variable at a time strategy presents certain weakness because it assumes that the optimum value of one variable is independent of the level of the other. Response surface techniques have been used since about 1950 on a wide variety of systems³. Factorial^{4,5} and Mixture⁶ designs are statistically based techniques, which permit an investigation of linear, non linear and interactive effects of independent variables on a response.

IV.2 *Mixture design*

A **Mixture design** is used when the response is a function of the proportions of the ingredients in a composition, which normally corresponds to a total of 100%. There are several mixture design choices, the simplex design can be used whenever there are no upper limit constraints in the concentration of components presenting symmetry.

IV.3 *Design types*

A **simplex** is the simplest figure having $n+1$ boundary points in an n dimensional space. In a zero dimension it is a point, in one dimension, a line, in two dimensions a triangle and in three dimensions a tetrahedron.

A **simplex lattice** design of degree m consists of $m+1$ points of equally spaced values between 0 and 1 for each component. If $m=2$ then possible fractions are 0, $\frac{1}{2}$, 1. For $m=3$ the possible fractions are 0, $\frac{1}{3}$, $\frac{2}{3}$, 1. The points include the pure components and enough points between them to estimate an equation of degree m . This design differs from a simplex-centroid design by having enough points to estimate a pure cubic model. The simplex design will also be available when the range of each component is the same.

A **simplex-centroid** design consists of all points that are equally weighted mixtures of 1 to q components. Included are permutations of the pure blends (1, 0, ..., 0), permutations of binary blends ($\frac{1}{2}$, $\frac{1}{2}$, 0, ..., 0), permutations of tertiary blends ($\frac{1}{3}$, $\frac{1}{3}$, $\frac{1}{3}$, 0, ..., 0) and so on to the overall centroid ($\frac{1}{q}$, $\frac{1}{q}$, ..., $\frac{1}{q}$). The design cannot be used to estimate the full cubic model. It is also possible to choose the type of points, which will be included in the design by choosing a simplex-screening design. Adding axial check blends and constraint plane centroids will provide for lack of fit measurements in the model. Centroid points are added for pure error determination. Finally, this design does not allow space constraints. In the case of a constrained design space, many vertices are possible. The design uses the D-optimal algorithm to ensure that the vertices selected are as far as possible from each another.

D-optimal selection maximises the determinant of the Fisher information matrix, the optimisation is performed to minimise the general variance of the coefficients in the polynomial model. D-optimal selection chooses points from the candidate point set, which are spread throughout the design region. The candidate point set generation includes:

- **Linear model** based on a Scheffe mixture polynomial model⁷ contains only linear or main effect terms (A, B, C, ... linear coefficients), vertices of feasible regions, axial check points (50-50 combinations) of the overall centre at each vertex for extra design points inside the design space, and the overall centroid.
- **Quadratic model** based on a Scheffe mixture polynomial model contains linear and two factor terms (Linear model + AB, AC, BC, ... two factor coefficients), midpoints of the edges.
- **Special cubic model** based on a Scheffe mixture polynomial contains quadratic and three factor terms (quadratic model + ABC, ... three factor coefficients), triple blends, the centre of the plane where two edges meet.

- **Full cubic model** based on a Scheffe mixture polynomial contains special cubic terms + AB (A-B), AC (A-C), coefficients at a third of the edges.

Mixture polynomials account for the fact that for mixtures the terms in the ordinary polynomials are not independent. The sum of the mixture components must equal 100%. In D-optimal point selection, the points are selected in order to test a specified model. For an adequate design several points should be replicated to provide an estimation of pure error. If the correct independent variables have been selected the model should, adequately predict the response within the design space.

When pure error SS is subtracted from the model residual SS the resulting SS is that associated with lack of fit. The degrees of freedom of pure error equal n_e , which is the number of repeated points. n_r equals the degrees of residuals SS and n_{lof} "lack of fit" is obtained by subtraction $n_r - n_e$.

A comparison of $S^2_{lof} / S^2_{\text{pure error}}$ provides a test of model adequacy. If this F test is significant the model is said to suffer from lack of fit. This, in turn suggests that there are factors, other than those considered by the model, that are affecting the response.

F distribution is a probability distribution used to compare variances by examining their ratio. If they were equal then the **F value** would equal 1 and have a high p value ($p > 0.1$). The F value in **Analysis of Variance or ANOVA** is the ratio of the term mean square **MS** to the appropriate error mean square. The larger their ratio, the greater the F values and the more likely that the variance contributed by the term is significantly greater than random error. The F distribution is dependent on the degrees of freedom DF for the variance in the numerator and the DF of the variance in the denominator of the F ratio. The number of DF can be defined as the number of independent measurements available to estimate a parameter. Usually, it is calculated by the number of model parameters minus one, analogous to the denominator in the definition of sample variance.

ANOVA

ANOVA is a statistical technique, which subdivides the total variation of a set of data into component parts associated with specific sources of variation for the purpose of testing a hypothesis on the parameters of a model. Suppose a set of experiments is conducted and replicated and a response is measured, such as

the number of passes under a lamp necessary to obtain through-cure of a coating. In an ideal world the replicates would give identical results, but in the real world experimental error is present. In one-way ANOVA the total variation is split in two parts: variation related to the model and variation related to experimental error (residual error). ANOVA shows whether the variation from the model is significant when compared to the variation due to residual error. ANOVA takes into consideration the following:

- Source of variation or **residual error**. Difference between the observed response and the value predicted by the model.
- The sum of squares for the model is calculated by summing over all the experiments the squared difference between the averages of the replications and the grand average. The average of the replicates is the average of the results obtained for each experiment. The grand average is the average over all of the experiments.
- The sum of squares for the residual error is calculated by summing over all of the experiments and all of the replications the squared difference between replication and its average. It is a measure of the variation of the experimental error. If there were no experimental error the difference between each replication and its average would be zero.
- Degrees of freedom **DF**
- The number of degrees of freedom for the total sum of squares is equal to the number of experiments minus one.
- The number of degrees of freedom for the sum of squares due to the residual error equals the total number of experiments minus the number of terms in the model.
- Mean square **MS** or variance corresponds to the sum of squares divided by the number of degrees of freedom.
- **F ratio**

The variation due to the model can be compared with the variation due to residual error by means of the F ratio. The F ratio is calculated by dividing the mean squares of the model by the mean squares of the residual error. This test can indicate whether the variance due to the model is significantly different from the variance due to the random error. The significance of the ratio is evaluated using the **F distribution**.

IV.4 *Significance of the model*

Assuming the null hypothesis that all variation in the response is due to random error alone, the F ratio is expected to be near one. If the null hypothesis is rejected and the model is introducing variation into the results, the F ratio is expected to be much greater than could be expected by random error. Hence, above a certain critical value the null hypothesis can be rejected. In a suitable statistical Table at an appropriate significance level ($\alpha < 0.05$) can be found a critical value X. If the calculated F value is greater than the critical value X, the model is significant at 95% significance.

Design Ease software (Stat-Ease Inc.) computes the F statistic for each term. This calculation is expressed by $\text{prob} > F$ that represents the probability that all the variation in the results are due to random error. Consequently, a low $\text{prob} > F$ indicates that the results are not random.

An **aliased** model implies the existence of parameters that cannot be estimated independently, due to the fact that there are fewer points in the design than there are terms in the model.

There are a number of test statistics available, such as:

A **lack of fit test** can be done when there are replicates to provide an estimate of pure error. Lack of fit is not desirable, however, the nature of the design (choice of variables, number of variable levels, etc) may make lack of fit unavoidable. When lack of fit occurs, it is a warning to the researcher that more work must be done before a final predictive model can be built.

The **model summary statistics** of models fit shows the following terms:

Root MSE - or square root of the residual mean square error- provides an estimation of the experimental error.

R-SQR - R squared or the multiple correlation coefficient. A number between 0 and +1 that indicates the amount of variation observed in the data that is explained by the model.

ADJ R-SQR or adjusted R-squared is an estimate of the fraction of the overall variation in the data accounted for by the model, but modified to take into account the number of terms in the model relative to the number of points in the design

PRE R-SQR -or Predicted R-squared- measures the amount of variation in new data explained by the model.

$$\text{PRE R-SQR} = 1 - \frac{\text{SS}_{\text{PRESS}}}{(\text{SS}_{\text{TOTAL}} - \text{SS}_{\text{BLOCK}})}$$

PRESS (PRESS statistic or predicted residual sum of squares) is a measure of the fitness of the model to the points in the design. The model is used to estimate each point using all the design points except that one. The difference between the predicted value and actual value at each point is squared and summed over all the points. The smaller the PRESS statistic the better the model fits to the data points.

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V. CHAPTER V INSTRUMENTATION

V.1 *Colour measurements*

The difference in colour between two samples, can be represented by a three-dimensional geometric representation or colour space. Munsell introduced the concept of colour space as a three dimensional system in which all colours can be defined. An international committee, the Commission Internationale de l'Eclairage (CIE) introduced illumination standards in order to create a standard colour measurement system in 1931. The Colour Measurement Committee of the society of dyers and colourists created another system termed CMC. In the CMC system the ellipsoid semi-axes are calculated from the CIELab, Luminosity L is the value of the colour, the apparent lightness or brightness of the colour, Chroma C, and Hue H which is governed by the dominant wavelength of a colour, hence Hue distinguishes one colour from another. The latest CIELab equation was introduced in 1976. The total colour difference is commonly represented by ΔE . Mathematically ΔE has been expressed by different equation systems. In the CMC system ΔE is expressed by:

$$\Delta E = (\Delta C^2 + \Delta H^2 + \Delta L^2)^{0.5}$$

ΔE is normally calculated for illuminant D65. ΔC represents the Chroma or colour difference. The Chroma can be expressed by $C = (a^2 + b^2)^{0.5}$ where a and b represent colour axes. The Hue difference ΔH and the lightness difference ΔL are introduced into the CIELab equation to calculate the ΔE^1 .

V.2 *Ultraviolet absorption measurements*

Most organic molecules are transparent in the UV/Visible region, that is, the region whose wavelengths range from 190 nm to 800 nm. When radiation passes through a transparent material, a portion of the radiation may be absorbed. If this occurs, the residual radiation, when it is passed through a prism, will yield a spectrum with windows. This is called an absorption spectrum. As a result of energy absorption, atoms and molecules pass from a state of low energy to a state of higher energy. In the case of UV/Visible spectroscopy, the transitions, which result in the absorption of electromagnetic radiation in the UV/Visible region, are transitions between electronic energy levels.

The extent of light absorption is dependent on the number of molecules capable of absorbing light of a given wavelength. Furthermore, the more effective a molecule is in absorbing light of a given wavelength, the greater will the extent of light absorption. The Beer-Lambert's Law² is an empirical formula, which may be expressed by:

$$A = \log (I_0/I) = \epsilon C L \text{ for a given wavelength}$$

A = Absorbance

I₀ = Intensity of the incident light upon the sample cell

I = Intensity of the light leaving the sample cell

C = molar concentration of solute (M)

L = length of sample cell (cm)

ε = Molar extinction coefficient

The molar extinction coefficient ϵ is a property of the molecule undergoing an electronic transition and is not a function of the variable parameters involved in preparing a solution.

V.3 Luminescence measurements

The determination of phosphorescence quantum yields using optically dilute solutions is the most common method currently employed³. The optically dilute measurements rely on Beer-Lambert's Law, which can also be expressed by:

$$I_0B = I_0(1 - 10^{-AL})$$

where **B** is the fraction of light absorbed by the sample, **I₀** is the intensity of the incident light, **A** is the absorbance and **L** is the path length. The exponential equation can be expanded in a power series of **AL**, consequently the expression of the fraction of light absorbed by the sample **B** becomes

$$B = 1 - (1 - 2.303AL + (2.303AL)^2/2 + \dots)$$

which can be simplified to **B = 2.303AL** at low **AL** values.

Phosphorescence quantum yields ($\phi_{\text{phosphorescence } X}$) can be calculated by the relative method with the following expression^{4, 5}:

$$\phi_{\text{phosphorescence } X} = \phi_{\text{phosphorescence } R} (B_R/B_X) (I_R/I_X) (\eta_X^2/\eta_R^2) (Area_X/Area_R)$$

$$\phi_{\text{phosphorescence } X} = \phi_{\text{phosphorescence } R} (A_R/A_X) (\eta_X^2/\eta_R^2) (Area_X/Area_R)$$

where $\phi_{\text{phosphorescence } R}$ is the known quantum yield of the reference, B is the fraction of incident light absorbed, A_R and A_X are the absorbance at the excitation wavelength of the reference and sample solution respectively, I_R and I_X are the intensities of the light at the excitation wavelength λ for reference and sample respectively, η_R and η_X are the refractive indexes of the solvents used in the reference and sample respectively, $Area_R$ and $Area_X$ are the integrated areas under the corrected emission spectra.

For sample and reference it is assumed that the integrated luminescence intensity ($Area_R$ and $Area_X$) measured at 77 K is proportional to the fraction of light absorbed (A_R and A_X) as measured at room temperature, all geometrical factors are identical (cells of constant path length L , reproducible positioning of cell in the instrument), the excitation beams are monochromatic, reflection losses are the same (same cell thickness), internal reflection effects are equal (more feasible in high diluted solutions), reabsorption and reemission are negligible and isotropic light is emitted.

Triplet lifetimes can be calculated from a first order rate equation from the following equation:

$$dI_t/dt = -kI_t \quad \int dI/I = \int -k dt \Rightarrow \ln I_t = \ln I_0 - k t$$

where I_t is the phosphorescence intensity at time t , I_0 is the phosphorescence intensity at time zero and k is kinetic constant.

The triplet lifetime τ can be defined as the time required for the intensity to decrease to a value $I_t = 1/e I_0$. Substitution of $I_t = 1/e I_0$ in the equation shows that the triplet lifetime is obtained from the inverse of the kinetic constant k .

$$\ln I_t = \ln I_0 - k t \Rightarrow I_t = I_0 e^{-kt} \quad \text{and at } t = \tau \quad I_t = 1/e I_0 = I_0 e^{-k\tau} \Rightarrow \tau = k^{-1}$$

V.4 Microsecond flash photolysis measurements

The use of a flash of light to induce photochemical reaction forms the basis of flash photolysis. The method was developed by Norrish and Porter in an attempt to identify the reactive intermediates in a photochemical system.

Light absorption occurs very rapidly (10^{-4} s) but the decay processes cover a wider range of times from picoseconds for vibrational relaxation, to nanoseconds for radiative processes (from lower singlet states) and from microseconds to seconds for triplet decay processes, radicals and long-lived species.

The concentration of transients (triplets, singlets or radicals) is normally too low to be detected by their absorption spectra. The use of a high intensity flash source can populate sufficiently the excited states to produce a high enough transient concentration to be measured by absorption spectroscopy. The changes with respect to time of the intermediate concentration can be monitored from absorption measurements. The decay time of phosphorescence and fluorescence can be measured by this method^{6, 7}.

The monitoring source is switched on and a wavelength is selected at which the species of interest absorbs radiation. The photolysis lamp is then fired and the absorbance at this wavelength is observed on an oscilloscope. The wavelength can be changed as required to measure the absorbance of the intermediates at different wavelengths of interest.

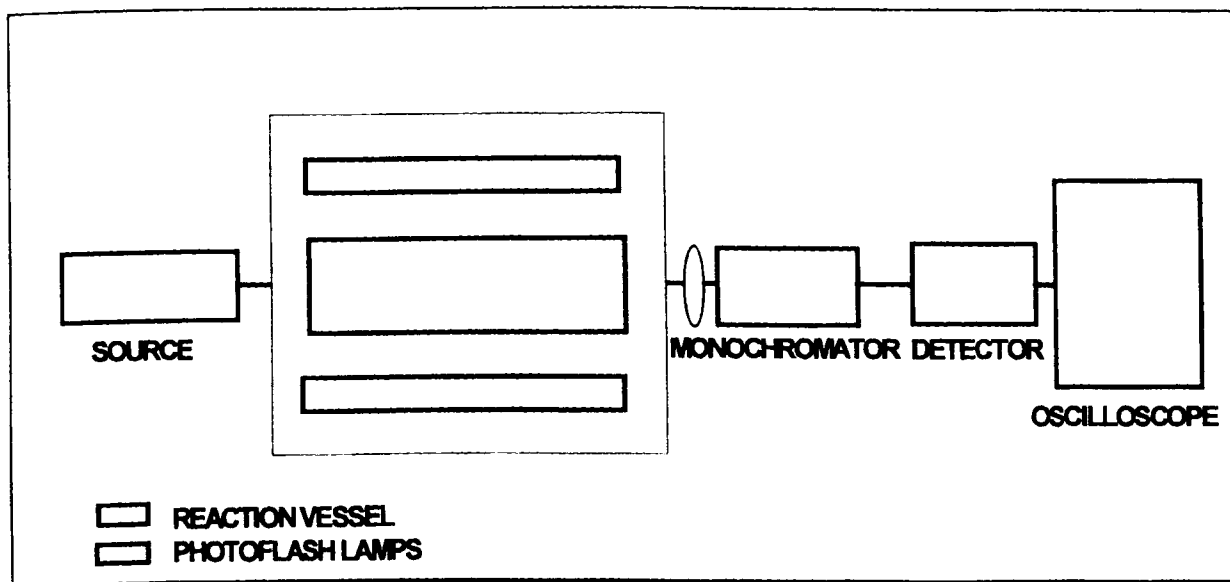


Figure V.1 Flash photolysis apparatus set up.

The absorption spectra of new species of the transients formed during flash photolysis are calculated from oscilloscope deflection values χ . It is assumed that the photomultiplier response is linear with respect to the light intensity. Oscilloscope deflection χ is then proportional to the light intensity I .

$$I_0 = k \chi_0 \text{ and } I = k \chi$$

where k is a constant which depends on the sensitivity of the detector. It is necessary to assume the validity of the Beer-Lambert's law over the concentration region studied to calculate kinetic constants. Beer-Lambert's law can also be expressed as:

$$A_\lambda = -\log T = \log(I_0/I) = \log(\chi_0/\chi) = \epsilon_\lambda c L \text{ where } T = I/I_0$$

where A_λ is the absorbance of the solution at wavelength λ , ϵ is the molar extinction coefficient at wavelength λ and L is optical pathlength.

This equation provides the possibility of measuring the transient absorption spectra, the transient lifetimes and the kinetic constants. Transient (triplets or radicals) decay can follow unimolecular or bimolecular processes depending on the type of initiating system. The order rate constants can be calculated by considering a first or a second order reaction mechanism.

A first order rate constant assumes that the rate of disappearance of a chemical species is proportional to its concentration (unimolecular process). Since the absorbance is proportional to the species concentration a first order reaction equation can be expressed by:

$$dA_t/dt = -k A_t \text{ and } \int dA_t/A_t = \int -k dt \Rightarrow \ln A_t = \ln A_0 - kt$$

where A_t is the absorbance at time t and A_0 is the absorbance before the flash.

Plots of $\ln A_t$ versus time can be analysed and the first order rate constant can be calculated from the slope.

A second order rate constant assumes that the rate of disappearance of a chemical species (intermediate) is proportional to the square of its concentration (bimolecular process). A second order reaction can be expressed by;

$$dA_t/dt = k A_t^2 \text{ and } \int dA_t/A_t^2 = \int k dt \Rightarrow 1/A_t = 1/A_0 + kt$$

Plots of $1/A_t$ versus t can be analysed and the second order rate constant can be calculated from the slope.

The model, which provides the best correlation when measuring the slope of the line, is considered to be the predominant decay mechanism. For first and second order models the same time range around 0.1 ms was measured after the flash to calculate the rate constants by regression analysis.

The transient decay lifetime can be measured for both models by measuring the time required to the transient concentration fall a $1/e$ the initial concentration.

V.5 Photopolymerisation measurements

Different techniques for measuring the reactivity and curing of UV systems have been developed to date, which can be divided into two types:

- Direct methods, based on the measurement of parameters which change with time during the polymerisation process, such as the heat of reaction which can be monitored with differential photocalorimetry and the decrease of the carbon-carbon double bond absorbance, which can be monitored with real time infrared spectroscopy RTIR^{4, 5}.

- Indirect methods, based on the measurement and evaluation of properties of the system after the system is polymerised, such as the hardness of coatings and inks measured with the pendulum hardness method, the pencil hardness test and the thumb-twist resistance.

One of the advantages of direct methods of analysis for measuring the reactivity of UV curing systems is to allow the evaluation of kinetic aspects such as polymerisation rate, induction time and residual unsaturation content.

Real time infrared spectroscopy

Real time infrared spectroscopy^{8,9} (RTIR) is based on the decrease in absorbance at 812 cm^{-1} , which corresponds to the twisting of the carbon-carbon double bond, during the polymerisation reaction. The sample is polymerised with UV radiation whilst the infrared beam measures the decrease of absorbance at 812 cm^{-1} . A reference 100% conversion was given to the

baseline, which it was calculated by drawing a line from the shoulders of the peak at 812 cm^{-1} .

Hardness measurements

Pendulum Hardness

Pendulum hardness measures the damping by the coating of the oscillations of a pendulum. The harder the film (the higher the degree of cure) the longer the number of oscillations. The pendulum suspension points rock on a small area, hence is possible to measure the hardness on several points to avoid surface imperfections which could affect the measurements. Replication of at least five measurements is desirable to prevent experimental error due to imperfections on the film surface.

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VI. CHAPTER VI EXPERIMENTAL

VI.1 *Materials*

The chemical structures, chemical names and suppliers of the photoinitiators, resins and reactive diluents studied are shown in Appendix I. The solvents methylcyclohexane, acetonitrile and isopropanol used in this work to obtain the UV spectra were of HPLC grade quality.

VI.2 *Colour measurements*

The yellowing of commercial photoinitiators has been measured with a Datacolour colorimeter following the CMC system. The measurement of colour has been carried out on coatings of a commercial alkoxylated tetrafunctional acrylate Actilane 440 PPTTA (Akcros Ltd., Manchester) at 2% photoinitiator level. All the coatings have been applied at 75 microns with a Brown K wired bar (number 7) over transparent glass and have been cured with a tunnel conveyor with a medium pressure mercury lamp of 80 W/cm during one pass at 50 ft/min. The total colour difference (ΔE), hue difference (ΔH), lightness difference (ΔL), and Chroma (ΔC) have been measured with D65 day light at 2 degree angle. The values have been taken by difference between films of PPTTA with photoinitiators and films of PPTTA without photoinitiators. The colour measurements were carried out after 24 hours. Replicated samples were measured in order to have an estimation of the accuracy. The results have been expressed as mean values, the relative error was estimated to be inferior to 5% for all the samples.

VI.3 *Ultraviolet absorption measurements*

Absorption spectra were obtained using a Perkin-Elmer Lambda 7 absorption spectrometer on solutions of photoinitiators in three solvents of different polarity in order to study the effect of solvent polarity on the absorption properties of photoinitiators such as hyperchromic and hypochromic effects and hypsochromic and bathochromic shifts. Methylcyclohexane, acetonitrile and isopropanol were the chosen solvents. The solutions were analysed by UV spectroscopy at different concentrations in order to obtain the best correlation by regression analysis. From the slope of the linear regression lines the photoinitiators 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 and 500 nm and the extinction coefficients were calculated using the Beer-Lambert's Law.

UV spectra of pigments have been run in suspensions due to the insoluble nature of pigments. The solvent used with each pigment has been selected via solubility tests and 1 L volume suspensions were used in order to minimise errors when weighing pigments in the 10 mg range. The pigment extinction coefficients have not been measured due to the low accuracy of the measurements carried out in suspensions.

Interpretation of the recorded spectra of photoinitiators and pigments showed the maximum absorption range of the photoinitiators hence allowing the pigment absorption windows to be deduced.

VI.4 Luminescence measurements

Benzophenone has been used as the reference assuming a phosphorescence quantum yield of 0.74 in absolute ethanol at 77 K¹. Phosphorescence quantum yields and triplet lifetimes were measured in methyl cyclohexane with a Perkin-Elmer LS-5 luminescence spectrometer. All the spectra were corrected using a Perkin-Elmer IBM-compatible GEM package with an appropriate file for this purpose.

The integrated luminescence intensity is normally proportional to the fraction of light absorbed at the excitation wavelength over a relative large range, but for high optical densities the luminescence may be confined to the front surface on the cell (filter effect) thereby destroying this proportionality².

Linear proportionality between the phosphorescence emission intensities (area measurements) and the absorbance at the excitation wavelength $\lambda=290$ nm has been measured over a range of optical densities. Similar low absorbance values around 0.05 at the excitation wavelength $\lambda=290$ nm in methyl cyclohexane have been used in both reference and sample in order to avoid the need of any correction factor due to the systematic error created by the power series approximation (5% systematic error for $AL=0.043$)³.

Absorbance values were obtained from more concentrated solutions of known absorbance (absorbance around 1) by diluting the sample by a certain factor. This method presented a higher accuracy than the direct measurement due to the error

obtained when measuring low absorbance values (20% relative error is obtained when measuring the absorbance of a solution around 0.05 considering the detector sensitivity around 0.01)⁴.

The solvent selection is an important aspect, which should be considered when measuring phosphorescence quantum yields at 77 K since solvents of high purity are required for the formation of a transparent glass⁵. Traces of water should be avoided since water traces form non-transparent glasses. Isopropanol does not form a transparent glass and presents reproducibility problems due to variability on the transparency and quality (cracking) of the glass. Absolute ethanol and methylcyclohexane form transparent glasses and provide reproducible results.

VI.5 Microsecond flash photolysis measurements

End of pulse transient absorption spectra of different photoinitiators in isopropanol ($C=1 \times 10^{-5}$ M) on the microsecond time scale were obtained using a kinetic flash photolysis apparatus utilising two 16 k xenon filled flash lamps with 300 J energy output (operated at 10 kV) and a 150 W tungsten/halogen monitoring source. Transient decay profiles were stored using a Gould model 1425 storage oscilloscope and solutions were degassed using white spot nitrogen gas.

VI.6 Real time infrared spectroscopy RTIR

The irradiation source used was a Xenon lamp ILC 302UV (Laser Lines Ltd) connected to a infrared spectrophotometer. A sample of a solution of a photoinitiator in a resin or reactive diluent was positioned between two sodium chloride salt plates covered with two pieces of low density polyethylene film using a Teflon separator to give a film thickness of 50 microns. Two polyethylene films were placed in the reference beam in order to subtract the polyethylene absorption from the sample. Different samples of photoinitiators were dissolved in a resin or low viscosity acrylate and cured following the method described.

Another method has been set up in order to evaluate the effect of oxygen inhibition on the curing efficiency of a range of photoinitiators. The liquid samples were applied with calibrated wire bars⁶ on sodium chloride plates to give specific film thickness and it was positioned uncovered in the sample holder as before. Consequently, the reactivity of photoinitiators, resins and reactive diluents was assessed in the presence of atmospheric oxygen as is common practice in industrial applications.

Plots of conversion percentage and polymerisation rate versus irradiation time were obtained. The derivative of conversion versus irradiation time plots were calculated and the maximum polymerisation rates (R_p maximum) were obtained from the maximum of the derivative curves (Figure VI.1).

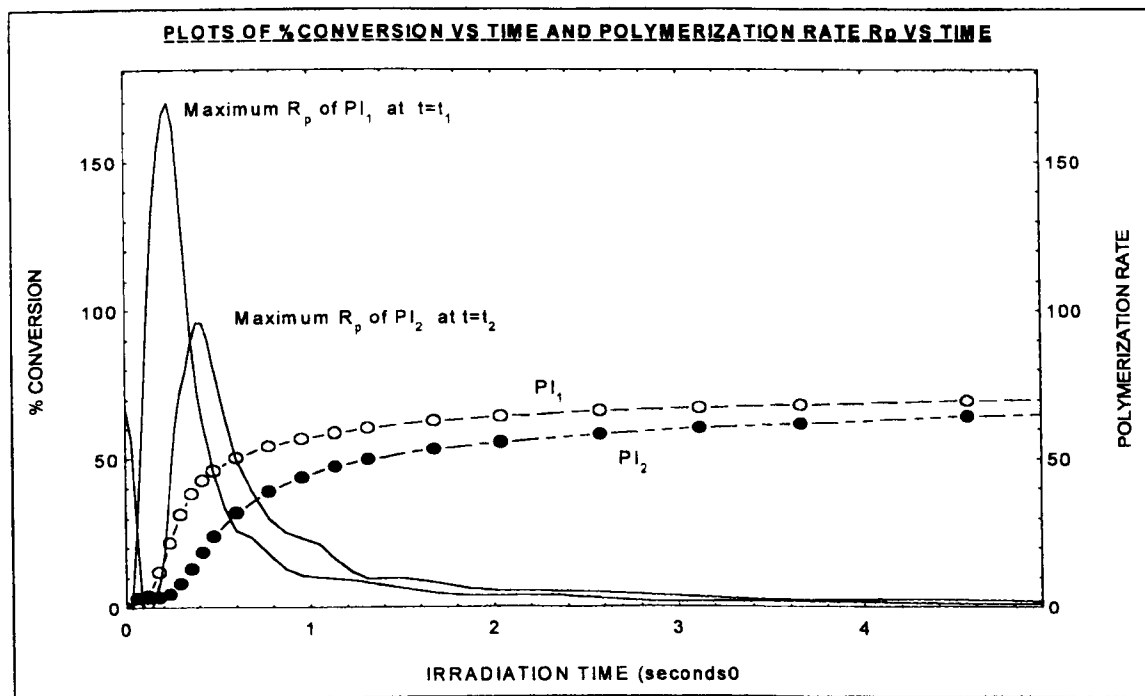


Figure VI.1 Plots of conversion and polymerisation rate ($R_p = -d\text{conversion}/dt$) versus irradiation time.

For those photoinitiators exhibiting slow cure rates, the polymerisation rates were calculated by regression analysis from the slope of conversion versus time plots at short irradiation times. For each sample replication has been done in order 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.

VI.7 Hardness measurements

VI.7.1 Pendulum Hardness

Hardness measurements have been done with a pendulum hardness instrument supplied by Sheen Instruments. The measurements were run with films on glass at different film thickness. Calibrated K wired bars were used to apply the wet

films. The films were cured with a medium pressure mercury lamp of around 80 W/cm (Primarc) at one pass at certain speed (ft/min) using a tunnel conveyor. The average number of oscillations was obtained from at least five replicate measurements.

VI.7.2 Thumb twist resistance

Hardness measurements have also been done by measuring the number of passes required to obtain through cure of coatings cured at certain speed using the same tunnel conveyor mentioned before. The higher number of passes required to cure the coating, the lower the reactivity of the system.

VI.8 *Rheological measurements*

Rheology measurements have been done with different viscometers, and a comparative study of resins and acrylates has been performed using the following techniques: ICI cone and plate viscometer at 35°C, Laray falling rod viscometer for calculating viscosity and yield values of high viscosity resins and a controlled stress viscometer: Rheometer Haake Rheostress RS75 for the analysis of thixotropy, zero shear stress viscosity, shear stress gradient flow curves, shear rate gradient flow curves and creep.

Tack of resins (0.5 ml) have been measured on a tackmeter at 25°C using a metal and a rubber roller at 300 rpm and the tack value was measured after 90 seconds.

VI.9 *Misting measurements*

Misting of inks samples (0.5 g) has been measured at 35°C over the course of 30 minutes at 1000 rpm on a tackmeter. The effect of low viscosity acrylates (reactive diluents) on the misting properties of inks has been evaluated. The basic formulations consisted of resin, talc, pigment and different low molecular weight acrylates.

The experimental series was performed maintaining constant the tack of the final formulation. Different proportions of low viscosity acrylates were added to obtain a constant tack value.

Another series of experiments was performed maintaining the constant proportion of acrylate (26.9% acrylate added to the basic formulation).

The basic formulations were composed of Ebecryl 657 (80.46%), pigment blue 15:3 (17.24%) and IT Extra talc (2.30%). It was necessary to add different

percentage of acrylates to the basic formulation in order to get a tack value between 11 and 13.

During the experiment a piece of white paper was situated on the surface of the tackmeter in a fixed position. Measurement of misting was achieved by weight and colour density using a colour densitometer. Weight measurements did not show reliable results due to the small quantities of material weighed. Consequently colour density measurements were used to evaluate the misting of inks.

VI.10 Volatility measurements

The volatility of photoinitiators has been compared by thermogravimetric analysis with a Netzsch TG 209 instrument. Volatility measurements were carried out at a heating rate of 20°C/min. Plots of mass loss versus temperature were represented.

VI.11 References

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VII. CHAPTER VII Photoyellowing and discoloration of UV cured clear coatings systems: influence of photoinitiator type.

VII.1 Introduction

The discoloration or yellowing of coatings and inks is an important matter to take into account since the final product quality depends on the colour stability. Different components of coatings and inks can contribute to their discoloration. The vehicle system can cause yellowing especially if it is composed of aromatic or chromophoric functional groups since they may absorb light in the visible region. Photoinitiators also cause discoloration of the system. Pale pigmented inks and clear coatings are more prone to suffer discoloration by the photoinitiators since it is common practice to use around a 7-10% photoinitiator level to attain the fast curing systems demanded by the printing ink industry. The objective of this investigation is to study the yellowing properties of the most important commercially available photoinitiators and to relate their yellowing properties to their chemical composition.

The discoloration and yellowing of acrylated coating films after photocuring with a broad range of photoinitiators have been measured by colorimetry with the CMC (CIELab) system. The yellowing of the photoinitiators was evaluated and related to the chemical structure of the photoinitiator fragments and to the unreacted photoinitiator itself. The total colour difference was related to the type of chromophoric substituent in the basic structure of the photoinitiator. The implications of these results are discussed in relation to clear coats.

VII.2 Results and discussion

Benzophenone derivatives substituted in the para position by alkyl/aryl thio groups are characterised by exhibiting a bathochromic shift permitting their use in pigmented systems. The yellowing properties of a range of commercial benzophenone derivatives are compared in Figure VII.1.

The para-methylphenylthio derivative of benzophenone, Quantacure BMS, caused higher yellowing than the benzophenones substituted with methyl groups, Esacure TZT and Speedcure BEM. The presence of the paramethylphenylthio chromophoric group induces a red shift of the maximum absorption band (π, π^* transition) of the photoinitiator, which causes discoloration by absorption of near UV/Visible light. The paramethylphenylthio moiety may also suffer C-S bond cleavage into radicals, fission can occur either side of the

sulphur atom to produce two aryl and two thioaryl radicals¹. The methylthio radicals can then react with different species to form coatings with pronounced odour.

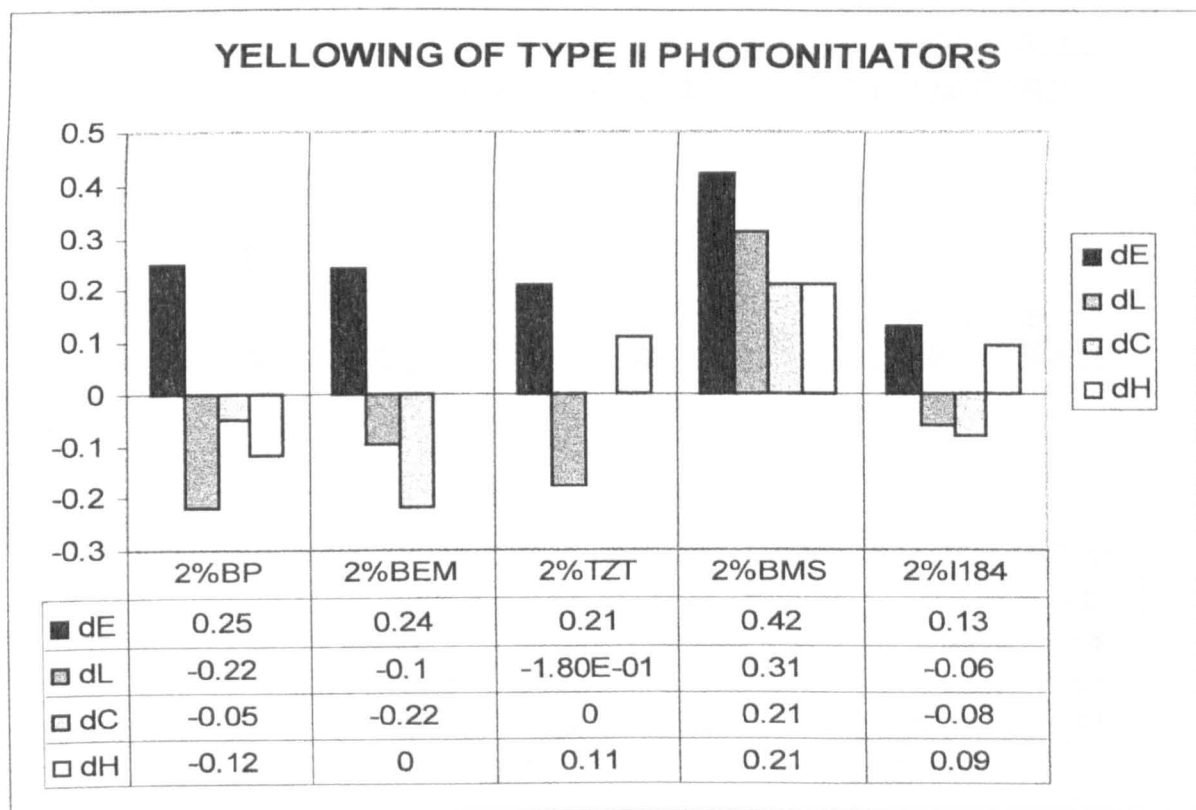


Figure VII.1 Yellowing of benzophenone derivatives.

The benzophenone derivatives have been compared with 1-hydroxycyclohexylphenyl ketone (Irgacure 184) which is claimed to be the most important commercial non-yellowing photoinitiator. Irgacure 184 caused lower yellowing than the benzophenone derivatives due to the absence of any aromatic substituents in the hydroxycyclohexyl moiety which prevents the formation of chromophoric compounds.

The yellowing properties of some photoinitiators of the α -hydroxyalkylphenone and the α - α -dialkoxyacetophenone families are compared in Figure VII.2.

The aromatic substituted α - α -dialkoxyacetophenone, 2,2-dimethoxy-2-phenyl acetophenone DMPA (also known as benzyl dimethyl ketal BDK) caused a higher degree of yellowing than its counterparts due to the formation of coloured compounds with a semiquinoid structure² in the cage, and by reactions of the dimethoxybenzyl radical with other species. H-NMR-CIDNP experiments³ demonstrated the formation of semi-benzenes produced in a cage by

recombination of the primary benzoyl and ω - ω -dimethoxybenzyl radicals to give benzoyl substituted methylbenzoates.

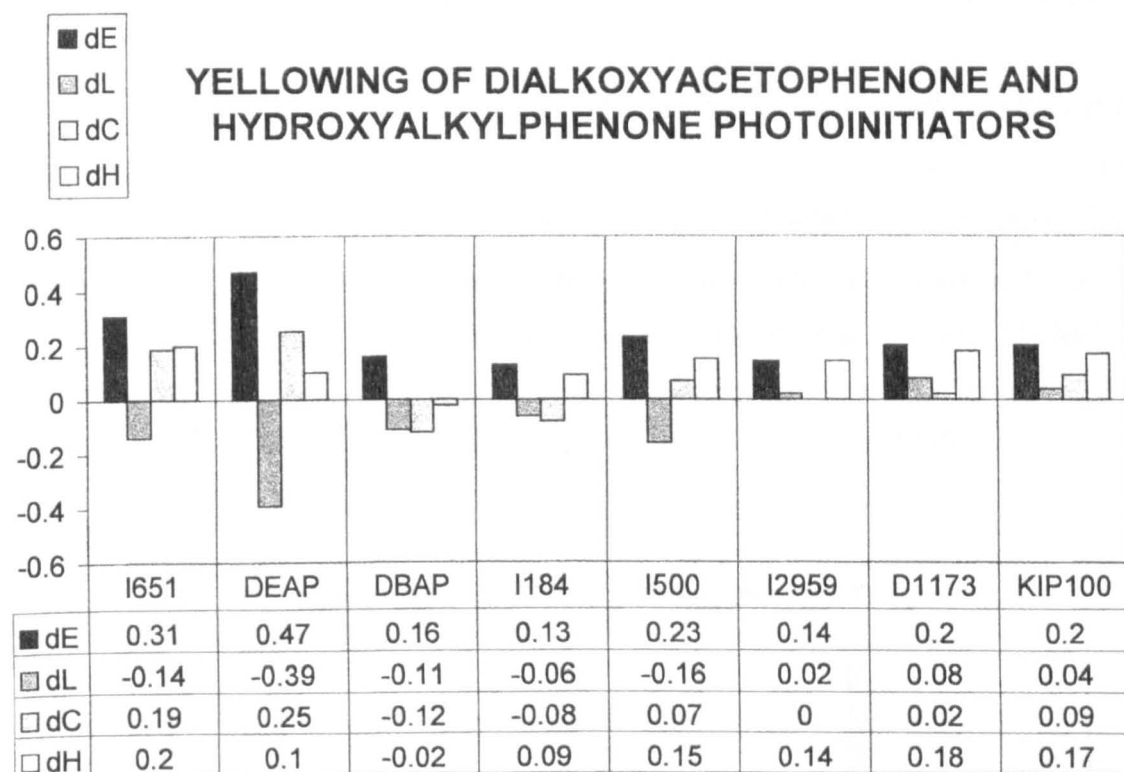


Figure VII.2 Yellowing of the α - α -dialkoxyacetophenone and α -hydroxyalkylphenone type photoinitiators.

These results were confirmed by isolating these products in film curing experiments⁴. The yellowing of films cured with BDK increase upon exposure to daylight. Photoinitiator molecules, which are not consumed during the curing process may undergo slow cleavage reactions in the solid matrix to render in cage recombination products such as semi-benzene⁵ and contribute to the increased yellowing observed at long exposure times to daylight.

1-Hydroxycyclohexylphenyl ketone (Irgacure 184) gave the most transparent film of all the photoinitiators studied. 2-Hydroxy-2-methyl-1-phenyl-propan-1-one (HMMP or Darocur 1173) and its oligomeric counterpart Esacure KIP150 had similar yellowing properties. They exhibited higher yellowing than their para 2-hydroxy ethoxy derivative (Irgacure 2959) and than 2,2-di-sec-butoxyacetophenone DBAP.

The low yellowing properties of photoinitiators of the α -hydroxyalkylphenone and α - α -dialkoxyacetophenone families can be attributed to the absence of the benzil radical as with benzil ketals, consequently, yellowing is not caused by formation of recombination products with a semi-benzene structure.

The yellowing of some near UV photoinitiators commonly used in pigmented systems have also been compared (Figure VII.3). 2-Benzil-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone (DBMP or Irgacure 369) exhibited significant yellowing due to its absorption extending well beyond 400 nm. 2-Methyl-1-(4-(methylthio)phenyl)-2-morpholino propan-1-one (MMMP or Irgacure 907) also imparts a high degree of yellowing in comparison to 2,4,6-trimethyl benzoyl diphenyl phosphine oxide (MAPO or Lucirin TPO).

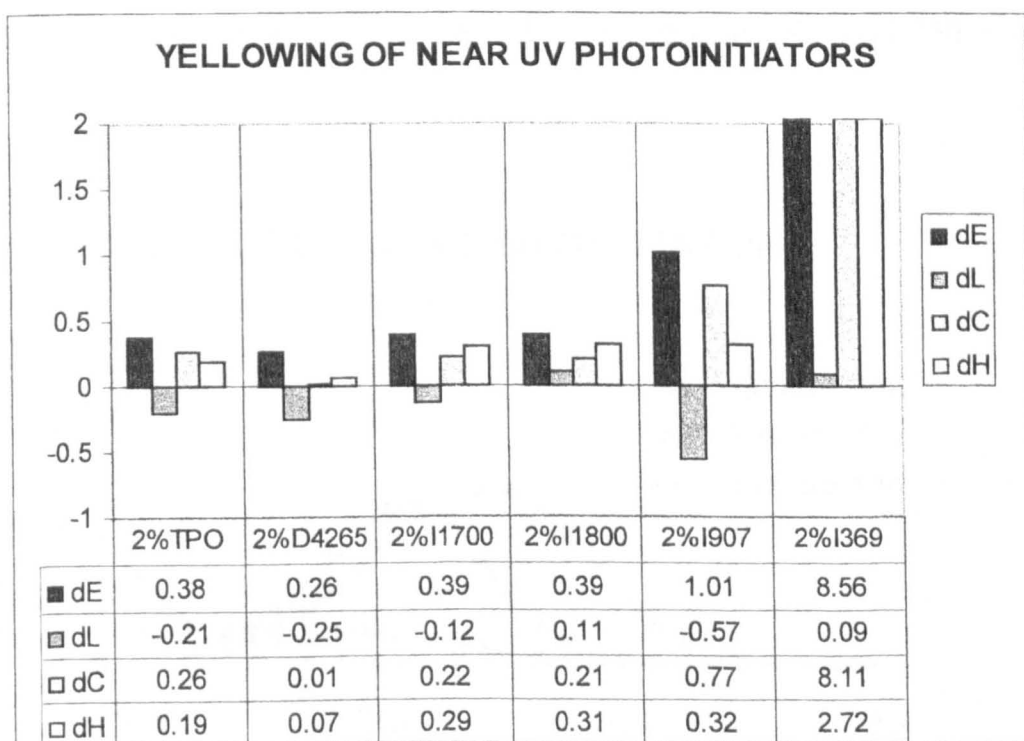


Figure VII.3 Yellowing of Near UV photoinitiators.

The two α -amino-acetophenone derivatives Irgacure 369 and 907 are strongly red shifted due to their morpholino and methylthio substitution in the para positions of the benzoyl chromophore. The para-substituents can engender an absorption, which tails into the visible⁶ region. Irgacure 369 has been investigated by ¹H NMR CIDNP⁷, confirming that the α -cleavage from the triplet

is the principal reaction. 4-Morpholino benzaldehyde results from α -cleavage to engender a benzoyl and α -aminoalkyl radical pair. The α -aminoalkyl radical can also initiate polymerisation⁸. The fragmented products were isolated by means of trapping experiments. A minor β -cleavage route could be responsible for the formation of alkyl aminated products.

The photochemistry of Irgacure 907 has also been investigated by ^1H NMR CIDNP⁹ and trapping experiments. Para-methylthiobenzaldehyde was identified as the predominant α -cleavage photoproduct. Disproportionation and hydrogen atom abstraction reactions with the α -aminoalkyl radical in the cage give rise to para-methylthio-benzaldehyde and 4-isopropylmorpholine.

A colour difference chart has been set-up comparing all the photoinitiators studied in this work where it is evident that the Irgacure 907 and 369 give the most prominent discoloration.

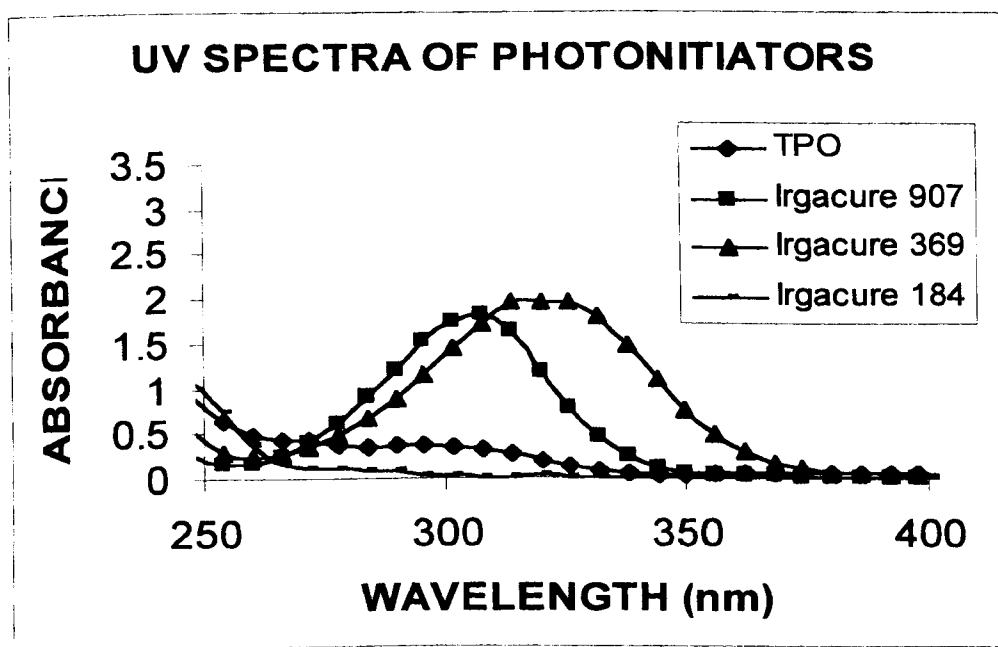


Figure VII.5 UV spectra of near UV photoinitiators in isopropanol ($C=1.0 \times 10^{-4}\text{M}$).

In Figure VII.5 the absorption spectra of these two commercial α -amino-acetophenones derivatives in comparison with those of TPO and Irgacure 184 are shown. The non-substituted benzoyl chromophore has its main absorption

around 250 nm (π, π^* transition) and exhibits a low transition band around 320 nm. As was expected, the introduction of electron donating functional groups such as methylthio or amino groups in the para position shifts the main absorption band towards longer wavelengths causing yellowing of the unreacted photoinitiator and its by-products. Consequently, Irgacure 369 is not used in white lacquers, except in thin layers at short irradiation time and low photoinitiator percentage. Irgacure 907 gives films exhibiting less yellowness than Irgacure 369. Irgacure 369 can still be used in thin white films at short exposure time. Unfortunately, in thick films significant yellowing can be expected. In contrast to TPO which bleaches¹⁰ upon radiation, Irgacure 369 and 907 increase their yellowing upon prolonged daylight exposure.

Acylphosphine oxides and bis-acylphosphine oxides produce little yellowing which may decrease under prolonged exposure to daylight¹¹. 2,4,6-methylbenzoyl and phosphinoyl radicals were found to be the main products under different curing conditions, besides other non-reactive products from different radical recombination and disproportionation processes. The bleaching of this photoinitiator occurs because of the carbonyl and phosphonyl interaction disappearance upon absorption of light, consequently absorption of this photoinitiator decreases due to the disappearance of the near UV/Visible absorbing chromophore.

Absorption spectra for the three main benzophenones are shown in Figure VII.6 where it can be seen that the BMS (methylthio) derivative exhibits the long wavelength tail into the near UV region and as seen from the colour difference chart gives the greatest yellowing of these derivatives.

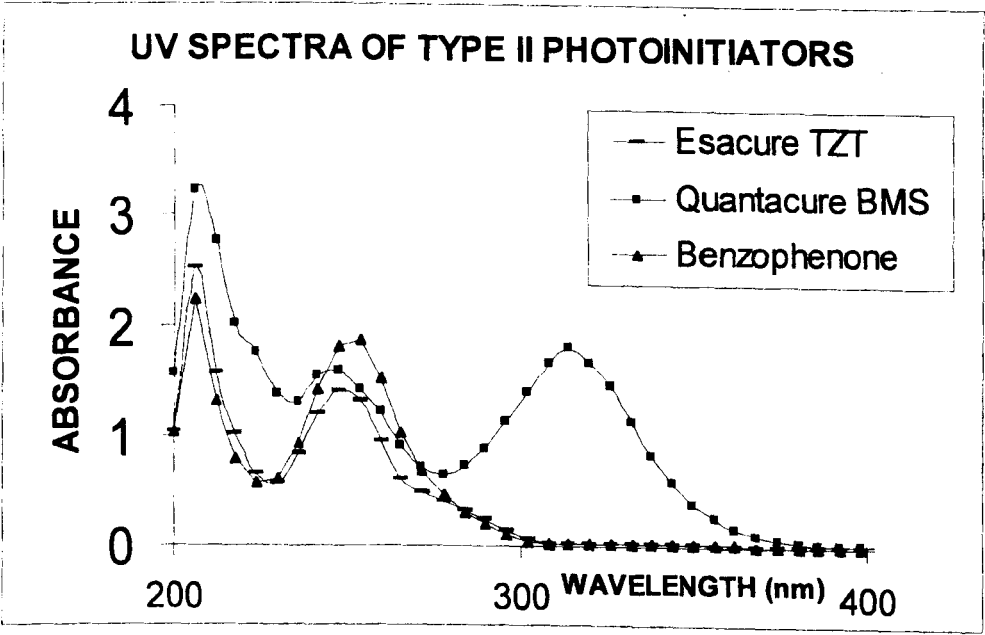


Figure VII.6 UV spectra of benzophenone derivative photoinitiators in isopropanol ($C=1.0 \cdot 10^{-4}M$).

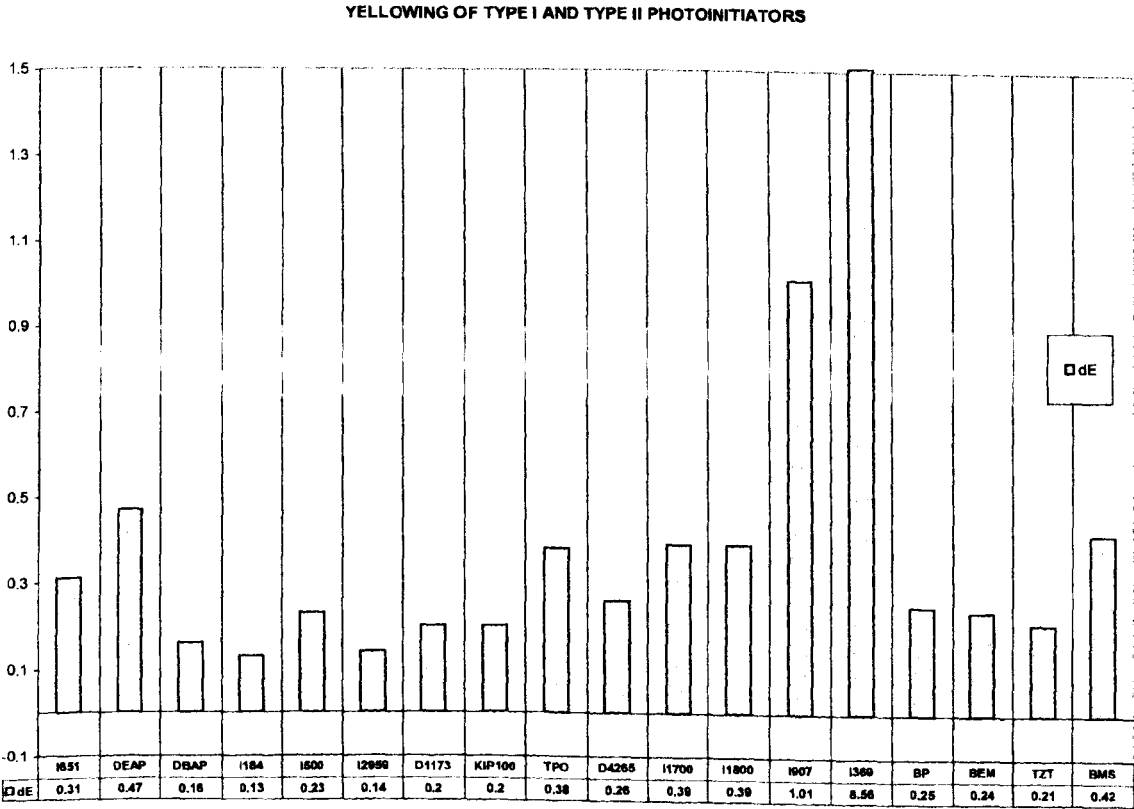


Figure VII.7: Total colour difference ΔE of the most important photoinitiators of the market.

VII.3 Conclusions

The yellowing properties of the most important commercial free radical photoinitiators have been analysed (Figure VII.7). 1-Hydroxycyclohexylphenyl ketone (Irgacure 184) exhibited very little discoloration and gave the best results of all the photoinitiators studied. The para-methylphenylthio derivative of benzophenone Quantacure BMS caused higher yellowing than benzophenone and its methylated derivatives Esacure TZT and Speedcure BEM.

1-Hydroxycyclohexylphenyl ketone (Irgacure 184) gave the most transparent films of all the photoinitiators compared. 2-Hydroxy-2-methyl-1-phenyl-propan-1-one (HMMP or Darocur 1173) and its oligomeric counterpart Esacure KIP150 had similar yellowing properties. They exhibited higher yellowing than their para 2-hydroxy ethoxy derivative (Irgacure 2959). On the other hand, 2,2-diethoxyacetophenone DEAP exhibited higher yellowing than its counterpart 2,2-di-sec-butoxyacetophenone DBAP.

The yellowing of some near UV photoinitiators such as Irgacure 369, Irgacure 907 and Lucirin TPO exhibited higher yellowing than most of the far UV photoinitiators due to their extended absorption extending into the visible. TPO caused lower yellowing than α -aminoalkylketone photoinitiators due to photobleaching of the photoinitiator after the absorption of light.

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VIII. CHAPTER VIII A comparative kinetic study of UV curable resins: structural and rheological inter-relationships

VIII.1 Introduction

The curing performance and kinetics of several UV resins commonly used in UV offset lithographic and UV flexographic printing inks have been investigated by Real Time Infrared Spectroscopy RTIR. The maximum polymerisation rates and final conversion were measured for the different resins and their reactivity was related to their mechanical properties by pendulum hardness at different thickness. The rheological properties of the resins were also measured and related to their polymerisation kinetics. The structure and functionality of the resin play an important role in controlling its tack and rheological properties and these, in turn, have an important influence on their rate of photocuring. Radical migration rates exhibit an inverse relationship with increasing resin functionality and viscosity due to increasing cage effects.

VIII.2 Results and Discussion

Reactivity of resins by RTIR and Pendulum Hardness

The reactivity of a broad range of resins is compared in Figure VIII.1 and Table VIII.2. From the reaction rate curves the reactivity of resins of different chemical family, functionality, viscosity and molecular weight were compared.

The maximum polymerisation rate (R_p max), conversion and final unsaturation content of resins have been measured. Some resins have higher initial polymerisation rate but lower conversion, probably due to the gel effect of high functional resins at high conversions.

Pendulum hardness measurements have been carried out for the same number of resins (Figure VIII.2, Table VIII.2).

REACTIVITY OF UV RESINS CURED WITH UV LIGHT IN THE PRESENCE OF AIR

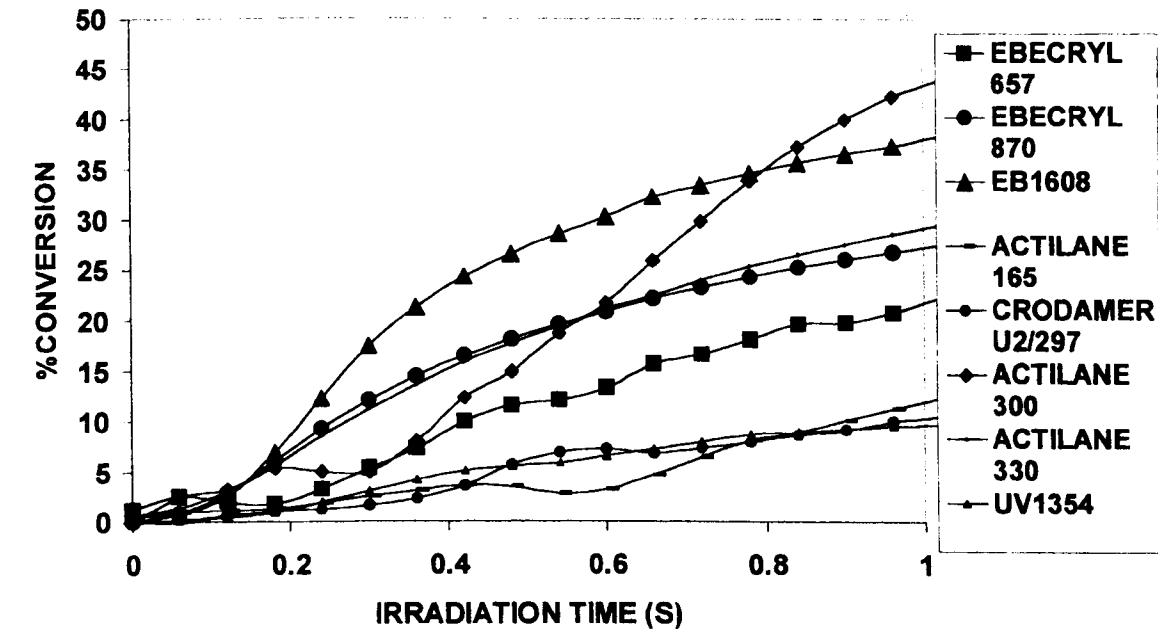


Figure VIII.1 Reactivity of resins by RTIR at 8% Irgacure 500 at 4 microns.

RESIN	Rp maximum (mol L ⁻¹ s ⁻¹)	%Conversion at 25s ± SD	N ^o of runs
Eb 657	0.448 ± 0.054	64.2 ± 1.7	3
Eb 870	0.539 ± 0.018	61.3 ± 4.0	3
Eb 1608	0.870 ± 0.257	69.6 ± 4.6	3
Actilane 165	0.277 ± 0.041	50.1 ± 1.8	4
Crodamer U2/297	0.085 ± 0.0002	60.7 ± 0.2	2
Actilane 300	1.043 ± 0.291	88.4 ± 1.7	3
Actilane 330	0.434 ± 0.054	59.5 ± 0.6	3
Uvecryl 1354	0.036 ± 0.002	39.1 ± 0.8	4

Table VIII.1 Reactivity of different acrylated resins at 8%Irgacure 500 by RTIR in the presence of air.

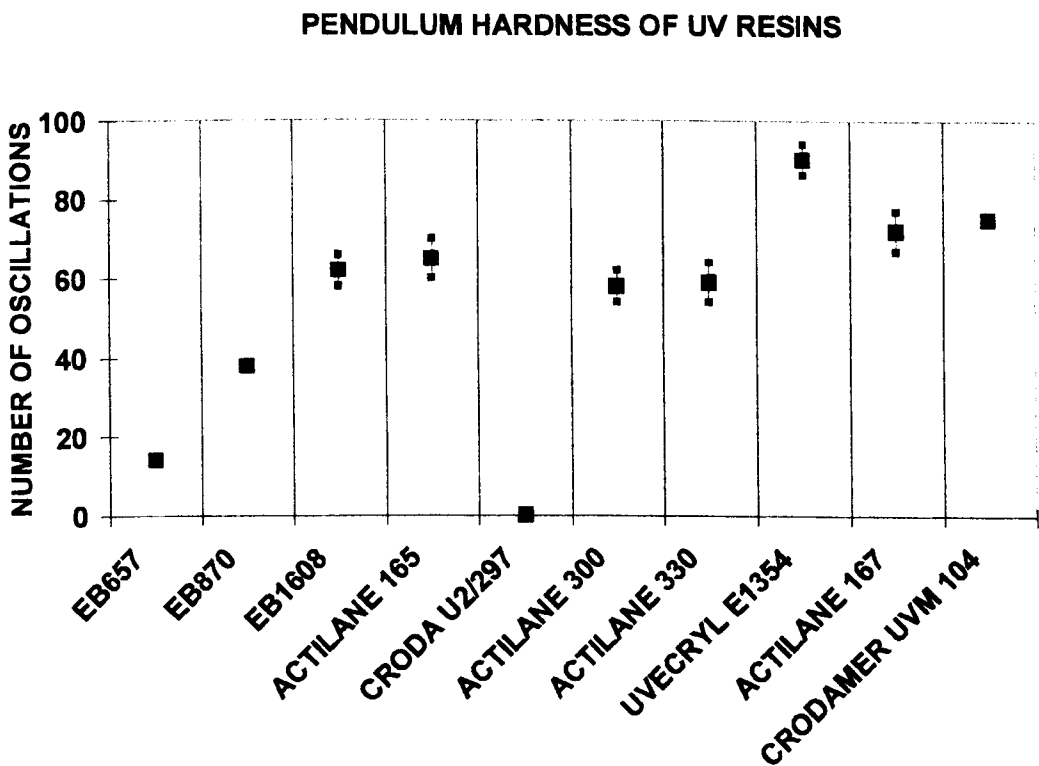


Figure VIII.2 Hardness of resins at 8% Irgacure 500 at 75 microns.

%RESIN	Number of oscillations ± SD
92%EB657	14 ± 1
92%EB870	38 ± 1
92%EB1608	62 ± 4
92%ACTILANE 165	65 ± 5
92%CRODA U2/297	No cured
92%ACTILANE 300	58 ± 4
92% ACTILANE 330	59 ± 5
UVECRYL E1354	90 ± 4
ACTILANE 167	72 ± 5

Table VIII.2 Pendulum hardness of acrylated resins at 8%Irgacure 500 measured immediately after curing (75 microns).

The curing performance of resins has been compared with two different photoinitiating systems consisting of 8% Irgacure 500 and 10% PI blend B. The coatings were printed at film thickness of 75 microns with K bars and cured under a conveyor during one pass at 100 feet per minute. The hardness was measured immediately after curing.

Functionality is an important factor to consider, an increase of functionality imparts a higher concentration of growing radicals and hence a higher polymerisation rate, it also gives a higher degree of crosslinking density and as a consequence the hardness, scratch resistance and tensile properties are enhanced. Oxygen inhibition is also reduced in systems containing the high concentration of growing radicals found in high functionality systems.

Uvecryl E1354 is an aromatic urethane hexafunctional resin based on pentaerythritol, which exhibits a low polymerisation rate and conversion due perhaps to steric hindrance of the reactive sites typical of high functionality systems. Its aromatic backbone may also contribute to its low reactivity due to the low mobility and the rigidity of the propagating radical. It gives very hard films due to its high functionality and low backbone flexibility, despite its low reactivity.

Actilane 165 is a tetrafunctional aromatic urethane acrylate based on an aliphatic polyester backbone which gives softer film properties, although it possesses a higher polymerisation rate (and conversion) than Uvecryl E1354. Its relatively high reactivity in comparison to Uvecryl E1354 can be explained by a higher backbone mobility, which can influence the reactivity of the reactive macro-radical.

Actilane 300 (acrylated epoxidised oil) exhibits a high polymerisation rate and conversion percentage due to its high flexibility and mobility of the propagating radical. Actilane 300 is a fast curing acrylated epoxidised oil which exhibits excellent pigment wetting, however it has a low surface cure and a low hardness which is comparable to Ebecryl 657 and Ebecryl 870.

Actilane 330 is a trifunctional acrylated aliphatic epoxy resin of similar hardness and lower reactivity than Actilane 300.

Croda U2/297 is a difunctional acrylated urethane alkyd resin in 20% GPTA of very low reactivity and low curing properties mainly due to its low functionality and soft chemical backbone.

Ebecryl 870 exhibits a higher reactivity than Ebecryl 657 due to its higher functionality and perhaps lower viscosity, on the other hand, it exhibits a lower

conversion percentage due to its higher functionality and steric hindrance. Ebecryl 657 and Ebecryl 870 present good lithographic performance¹, since they impart short water release times and low tack increase. They are used as the main resin systems in UV offset lithographic inks, however they are softer than other resins such as Ebecryl 1608, Actilane 165, Uvecryl E1354, Actilane 167 and Crodamer UVE 104. These low hardness properties can be due to their chemical composition, which are based on polyester oligomers of high flexibility. Ebecryl 870 is a slightly harder due to its higher functionality (6 acrylates per molecule) in comparison to Ebecryl 657 (4 acrylates per molecule), which provides a higher crosslinking density.

Ebecryl 1608 is based on a diacrylate ester of Bisphenol A diglycidyl ether with a molecular weight around 500 g/mol (Ebecryl 1600) of high viscosity, and is commercialised at 20% in OTA 480 to reduce its viscosity and improve its handling properties. It exhibits, at the same time, a high polymerisation rate and high hardness properties. On the other hand, its lithographic performance is not as good as its polyesters counterparts² since it requires more time for water release and presents higher tack increase. It also has worse pigment wetting than its polyester counterparts.

Actilane 167 is an aromatic urethane acrylate of low functionality, its low functionality is balanced with a rigid aromatic backbone, consequently, it forms hard films.

The reactivity and hardness properties of the resins studied showed the following order:

- **Rp maximum:** Actilane 300>Ebecryl 1608>Ebecryl 870>Ebecryl 657>Actilane 330>Actilane 165>Crodamer U2/297>Uvecryl E1354.
- **Conversion_{25s} :** Actilane 300>Ebecryl 1608>Ebecryl 657>Ebecryl 870=Crodamer U2/297=Actilane 330>Actilane 165>Uvecryl E1354
- **Hardness of the pure resins:** Uvecryl E1354>Actilane 167>Actilane 165>Ebecryl 1608>Actilane 330=Actilane 300>Ebecryl 870>Ebecryl 657>Croda U2/297
- **Hardness of resins at 30% PPTTA:** Uvecryl E1354>Actilane 165>Ebecryl 1608>Actilane 167>Ebecryl 870>Ebecryl 657=Actilane 300=Actilane 330

The reactivity of a resin is not a direct measurement of the mechanical properties of a resin. As explained before, the crosslinking density and the chemical and

physical characteristics of a resin such as the rigidity and flexibility of the chain backbone, physical-chemical interactions between chains, molecular weight, molecular weight distribution and branching can influence either on the glass transition temperature of a resin or in mechanical properties such as elasticity, elongation and tensile strength. Actilane 300 exhibits a very high polymerisation rate but it is very soft showing low hardness properties and a low rub and scratch resistance.

It can be postulated that high functional resins possess better mechanical properties with respect to tensile strength. Generally a high crosslinking density imparts rigidity if it is not balanced with a relatively flexible backbone. Ebecryl 870 is a hexafunctional polyester acrylate but it is very soft mainly due to the flexibility of its backbone.

Hardness measurements of resins diluted with GPTA and PPTTA

Reactive diluents are commonly used to reduce the viscosity of resins. Ebecryl 657 and Ebecryl 870 are commonly used in offset lithographic printing inks combined with reactive diluents in order to adjust viscosity. GPTA and PPTTA are commonly used in these systems due to their high reactivity, good viscosity cutting properties and reasonable cost. The hardness of these low viscosity reactive diluents is higher than formulations containing 60% Ebecryl 657 and 60% Ebecryl 870 at 10% photoinitiator blend B (Figure VIII.3, Table VIII.3) due to the poor mechanical properties of these polyester acrylates. PPTTA is harder than GPTA due to its higher functionality, which imparts a higher crosslinking density. Formulations of Ebecryl 657 containing PPTTA are also harder than those containing GPTA for the same reason. The results obtained confirm that a better surface cure can be obtained in combined systems resin/acrylate when PPTTA is used rather than GPTA.

PENDULUM HARDNESS OF UV ACRYLATES

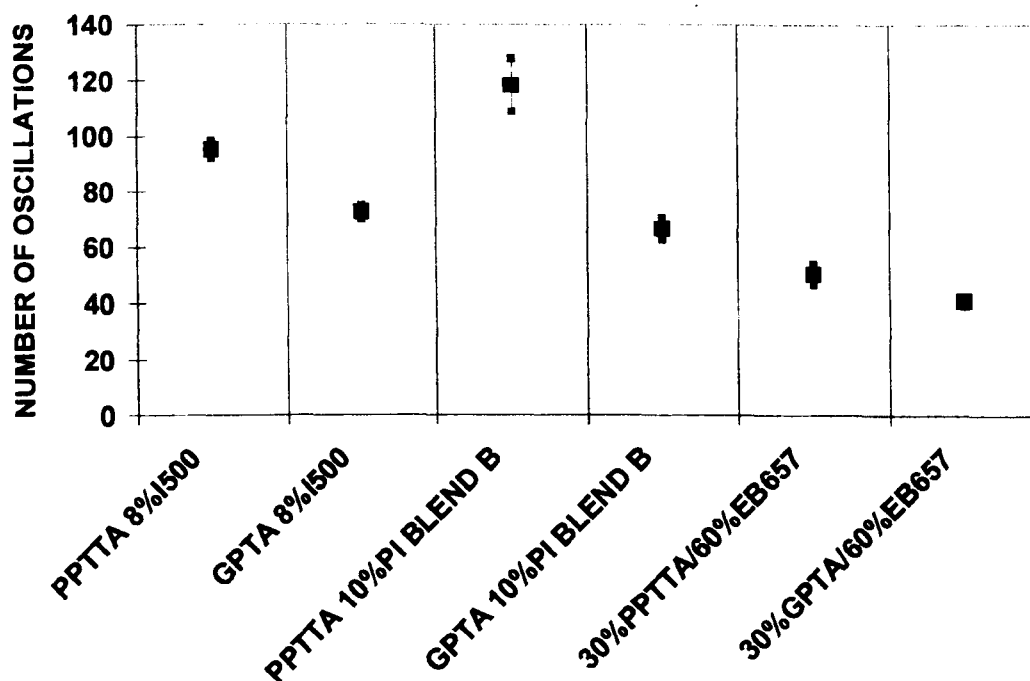


Figure VIII.3 Hardness of GPTA and PPTTA with and without Ebecryl 657.

%Acrylate	%Resin	N° of oscillations $\pm$ SD	N. of runs
30%PPTTA	60%EB 657	50 ± 4	5
30%GPTA	60%EB 657	41 ± 2	5
90%PPTTA	0%	118 ± 9	5
90%GPTA	0%	67 ± 4	5

Table VIII.3 Pendulum hardness of GPTA and PPTTA at 10% photoinitiator blend B by themselves and combined with Ebecryl 657 measured immediately after curing (75 microns).

Hardness of resins formulated with PPTTA and GPTA

The hardness properties of some resins at 60% have been studied in formulations containing 30%PPTTA, 30%GPTA and a 10%PI blend B (Figure VIII.4, Tables VIII.4 and VIII.5). The formulations based on PPTTA gave harder films than those based on GPTA in the systems studied.

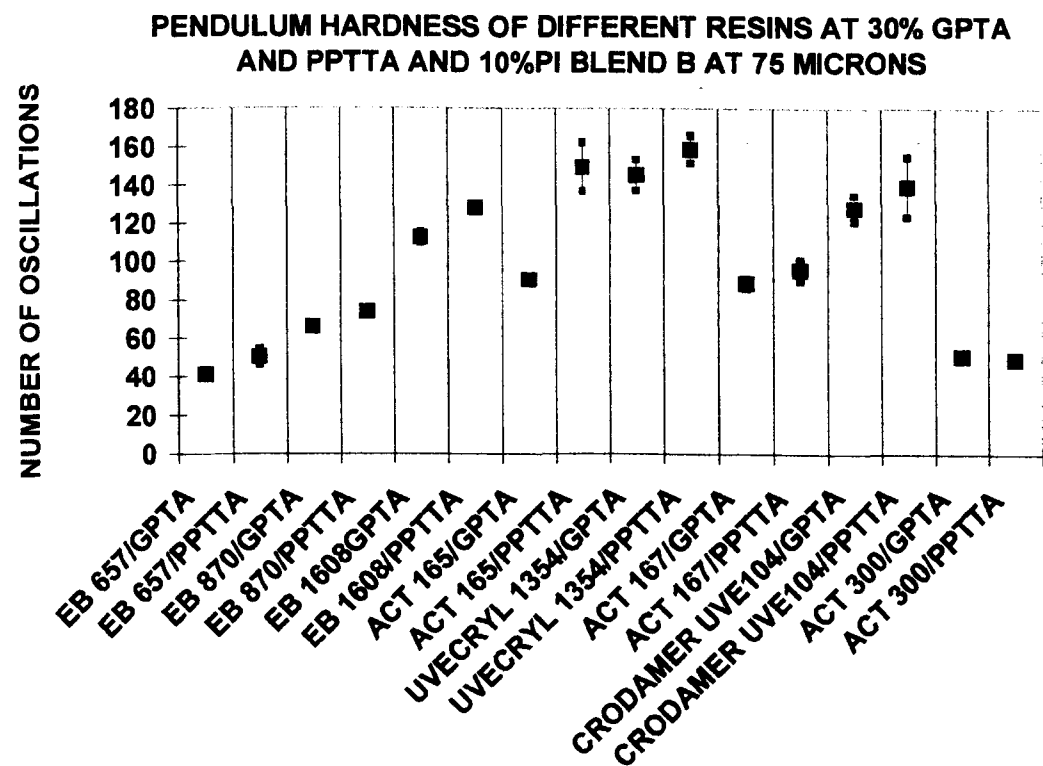


Figure VIII.4 Hardness of GPTA and PPTTA (reactive diluents) with some UV resins.

%PPTTA	%Resin	Number of oscillations ± SD
30%	60%EB 657	50 ± 4
30%	60%EB 870	74 ± 2
30%	60%EB1608	128 ± 2
30%	60%ACT 165	149 ±13
30%	60%CRODA U2/297	Soft
30%	60%ACT 300	49 ±1
30%	60%UVECRYL 1354	158 ±7
30%	60%ACT 167	95 ± 5
30%	60%CRODA UVE 104	139 ±16

Table VIII.4 Pendulum hardness of acrylated resins at 30%PPTTA and 10%photoinitiator blend B measured immediately after curing (75 microns).

%GPTA	%Resin	N. of oscillations
30%	60%EB 657	41 ± 2
30%	60%EB 870	66 ± 2
30%	60%EB1608	112 ± 3
30%	60%ACT 165	90 ± 2
30%	60%CRODA U2/297	Soft
30%	60%ACT 300	51 ± 7
30%	60%UVECRYL 1354	145 ± 8
30%	60%ACT 167	88 ± 2
30%	60%CRODA UVE 104	128 ±7

Table VIII.5 Pendulum hardness of acrylated resins at 30%GPTA and 10%photoinitiator blend B measured immediately after curing (75 microns).

Effect of film thickness on the hardness of resins

The same type of experiments has been carried out under the same conditions in order to evaluate the effect of thickness (Figure VIII.5, Tables VIII.4, VIII.6 and VIII.7). K wire bars have been used to apply wet films of approximately 12, 24 and 75 microns. The films were cured under a conveyor at one pass at 100 feet per minute. The hardness was measured immediately after curing.

The samples have higher number of oscillations at 12 microns than at 24 and 75 microns due to the effect of the glass on the hardness. The hardness of the glass substrate has been measured and has an average hardness of 446 ± 10 oscillations, consequently the hardness of the substrate affects the results obtained for a specific film thickness. The effect of the substrate on the hardness can be easily appreciated at low film thickness because of the significant pendulum head indentation into the film, consequently the hardness can be affected noticeably by the substrate.

The relative hardness of the resins shows the same tendency at the different thickness, hence it is possible to extrapolate these results to real lithographic and flexographic inks, which are normally printed at very thin film thickness around 1-2 microns.

PENDULUM HARDNESS OF UV RESINS

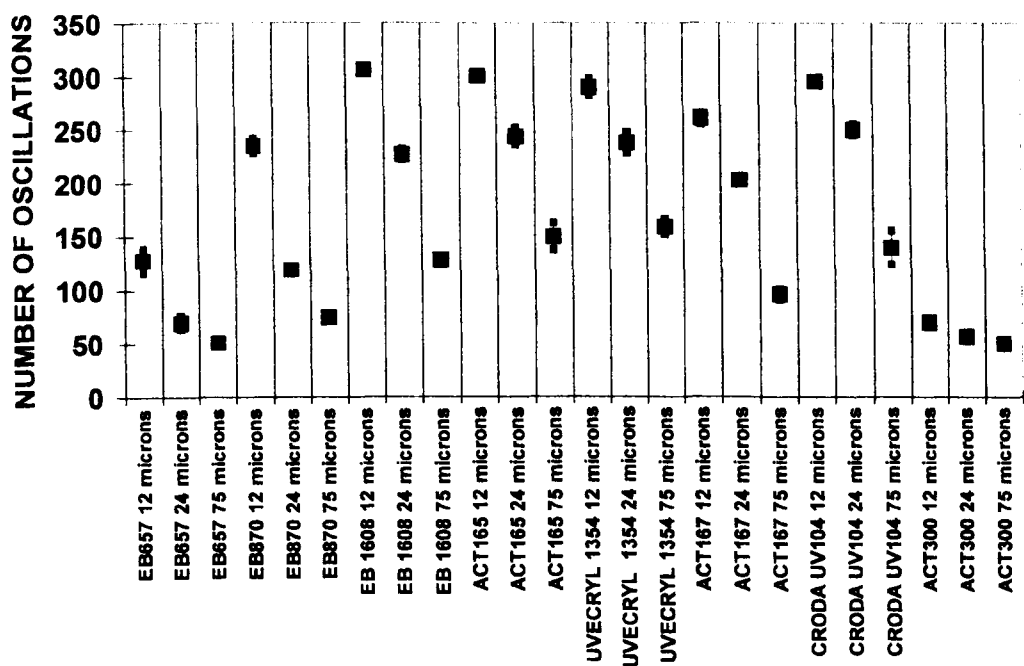


Figure VIII.5 Hardness of UV resins at different film thickness (12, 24 and 75 microns).

12microns 30%PPTTA	EB 657	EB 870	EB 1608	ACT 165	Croda U2/297	ACT 300	Uvecryl 1354	ACT 167	Croda UV104
Average	127	234	306	300	Soft	69	289	260	295
Std deviation	11	7	3	2		3	8	5	3

Table VIII.6 Pendulum hardness of acrylated resins at 30%PPTTA and 10%photoinitiator blend B measured immediately after curing (12 microns).

24microns 30%PPTTA	EB 657	EB 870	EB 1608	ACT 165	Croda U2/297	ACT 300	Uvecryl I1354	ACT 167	Croda UV104
Average	69	118	226	243	Soft	56	237	202	250
Std deviation	6	3	5	8		1	10	3	5

Table VIII.7 Pendulum hardness of acrylated resins at 30%PPTTA and 10%photoinitiator blend B measured immediately after curing (24 microns).

Rheological properties of resins

The rheological properties of resins are shown in Table VIII.8. Figure VIII.6 shows the viscosity of resins at 100 s⁻¹ and 500 s⁻¹ shear rate.

Commercial name	Viscosity at 100s ⁻¹ (Pas)	Viscosity at 500 s ⁻¹ (Pa s)	Thixotropy (10 ⁵ Pa/s)	Viscosity at 10 Pa (Pa s)
EB 657	88	76	11	92.3
EB 870	39	37	2.9	40.2
EB 1608	62	56	3.0	62.7
ACTILANE 165	32	29	2.6	27.7
CRODAU2/297	12	10.7	0.9	12.6
ACTILANE 300	7.9	7.3	0.3	7.8
ACTILANE 330	36	34	1.9	33.9
UVECRYL E1354	18.8	18	0.8	17.9
ACTILANE 167	38	36	1.4	40.1
ACTILANE 515	31	24	1.7	30.4

Table VIII.8 Rheological properties of acrylated resins.

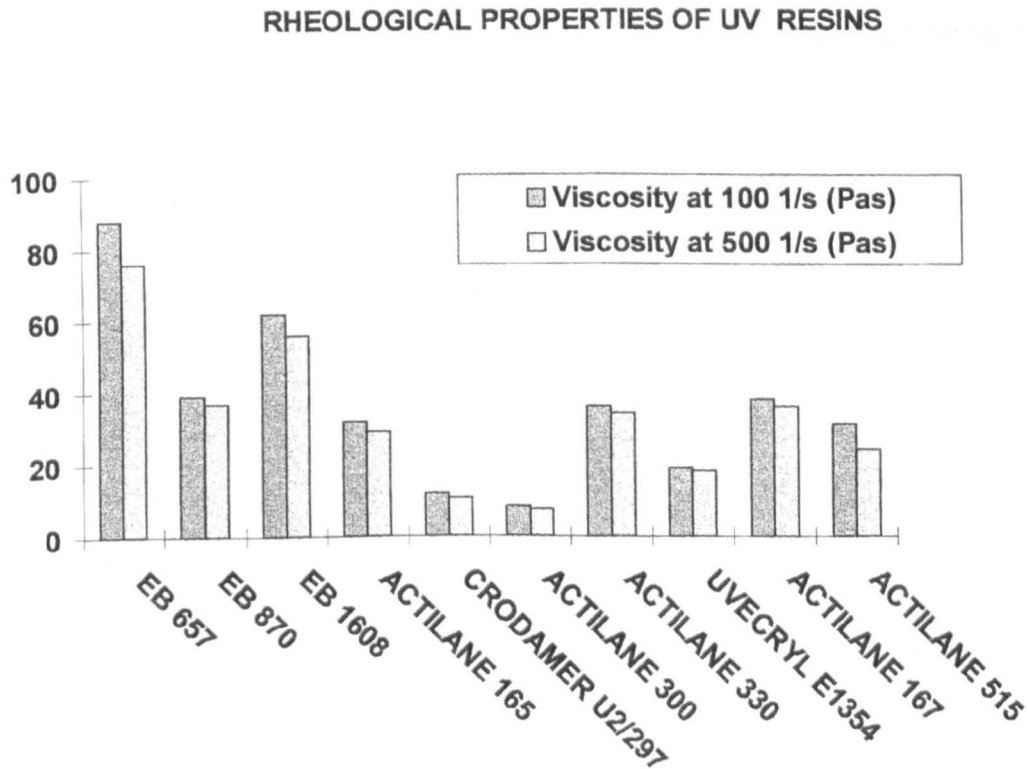


Figure VIII.6 Viscosity of resins at 100 and 500 s⁻¹.

The results show that the viscosity decreases when the shear rate increases, giving rise to what is called "shear thinning" behaviour or pseudoplasticity. Ebecryl 657 has the highest viscosity of all the resins studied; its polymerisation rate should be controlled by the diffusion rate of the propagating radical in the matrix. This diffusion-controlled rate (steric hindrance) may justify the higher polymerisation rates exhibited by resins of lower viscosity such as Actilane 300 and 330.

Thixotropy is generally confused with pseudoplasticity. Thixotropy is the gradual decrease of the viscosity under a constant shear. The viscosity decreases with shear time for thixotropic resins. A highly thixotropic resin is in principle not desired due to its unstable performance in the press. By performing loop tests it is possible to measure the thixotropy of a system by increasing the shear rate steadily and linearly in time from zero to 500 s^{-1} and then decreasing to zero in the same way. The area measured between the two curves is an indication of the thixotropy of the material. The thixotropic properties of resins can influence the final ink thixotropy. The thixotropy of different resins is shown in Figures VIII.7 and VIII.8. In some cases, the thixotropic properties of resins may disappear once the resins have been milled with pigments. Ebecryl 657 has the highest thixotropy compared to the other resins but it shows little thixotropy after being dispersed with pigments.

RHEOLOGICAL PROPERTIES OF UV RESINS

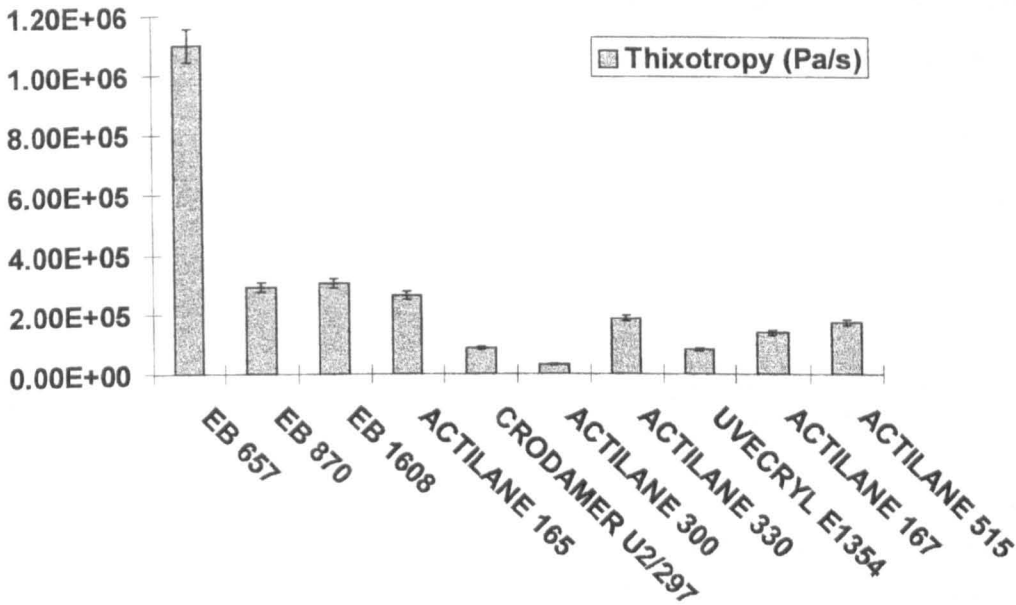


Figure VIII.7 Thixotropy of resins.

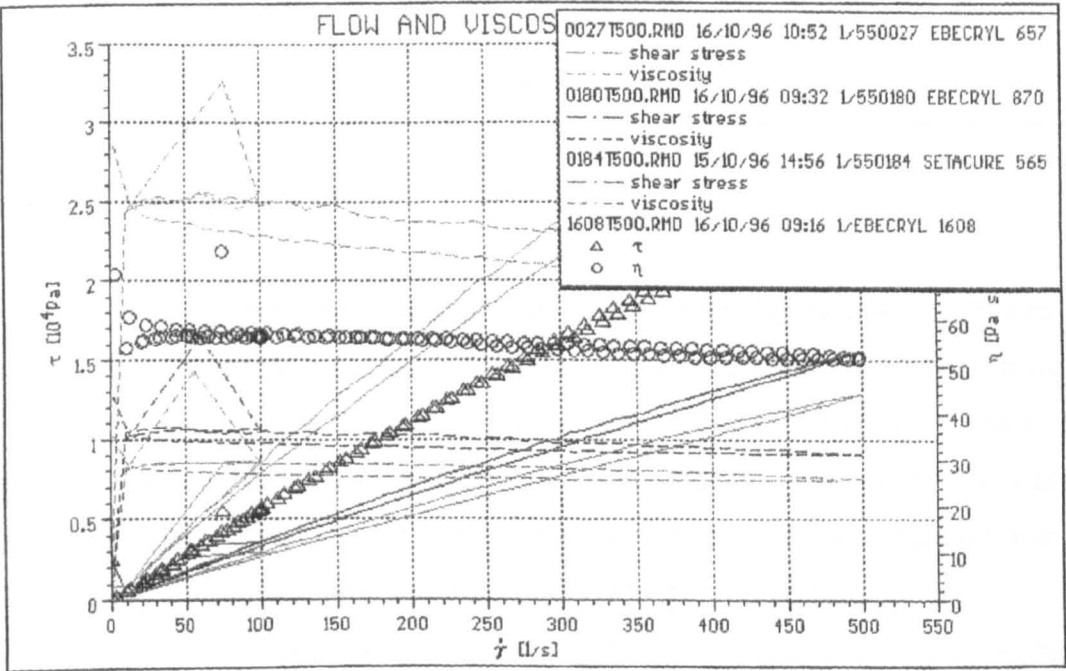


Figure VIII.8 Thixotropy of resins.

Viscoelasticity is the simultaneous existence of viscous and elastic properties. The elastic nature of a resin is a desired property due to the tendency of the resin to recover its original shape. This property could give improved printing performance and a better dot sharpness with lower dot gain. Creep tests at constant shear stress have been performed on a broad range of commercial resins (Figure VIII.9).

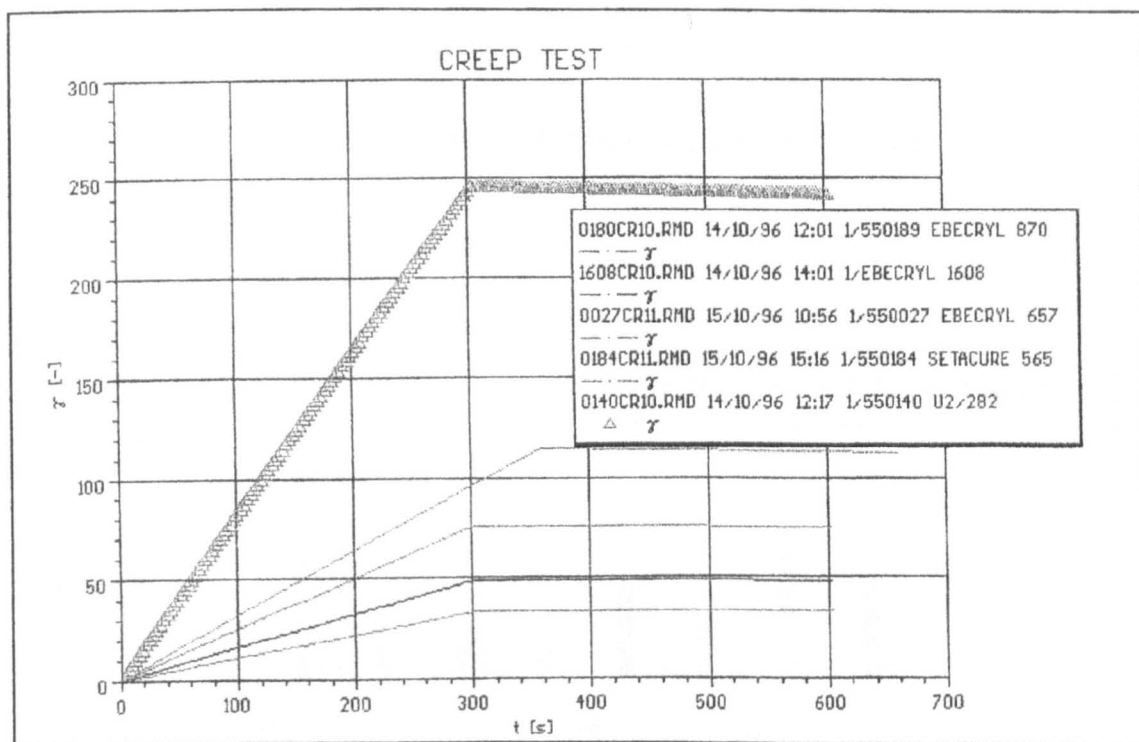


Figure VIII.9 Creep test of several resins.

A constant shear stress was applied for 25 seconds. Suddenly, the stress was removed and the recovery measured. Pure viscous materials do not show any recovery of position. On the other hand, pure elastic materials recover their original position. A viscoelastic material possesses both components and partially recovers its original position. The resins studied have a pure viscous behaviour at 10 Pa. None of them possess an appreciable elastic component.

An increase of viscoelasticity can be obtained by using resins of higher molecular weights than Ebecryl 657 or Ebecryl 870 ($M_w=1500$ g/mol) and/or chemical gel resins. Chemical gel resins are formed by creating chemical bonds, of covalent or associative nature, between the resin molecules by using a gel catalyst. The chemical gel or the higher molecular weight resin can then provide the required

elastic component necessary to obtain a low dot gain. At the same time, chemical gel resins would resist breakdown under heat at high shear conditions. Misting could be reduced due to the resistance of the ink to become more fluid.

The yield value is the force needed to cause a fluid to flow. Obviously, at lower stresses values than the yield value the material behaves as a pure elastic material. In Figure VIII.10 the yield value, viscosity and tack of different resins are given. Actilane 300 and Croda U2/297 have high yield values with relatively low viscosity.

RHEOLOGICAL PROPERTIES OF UV RESINS

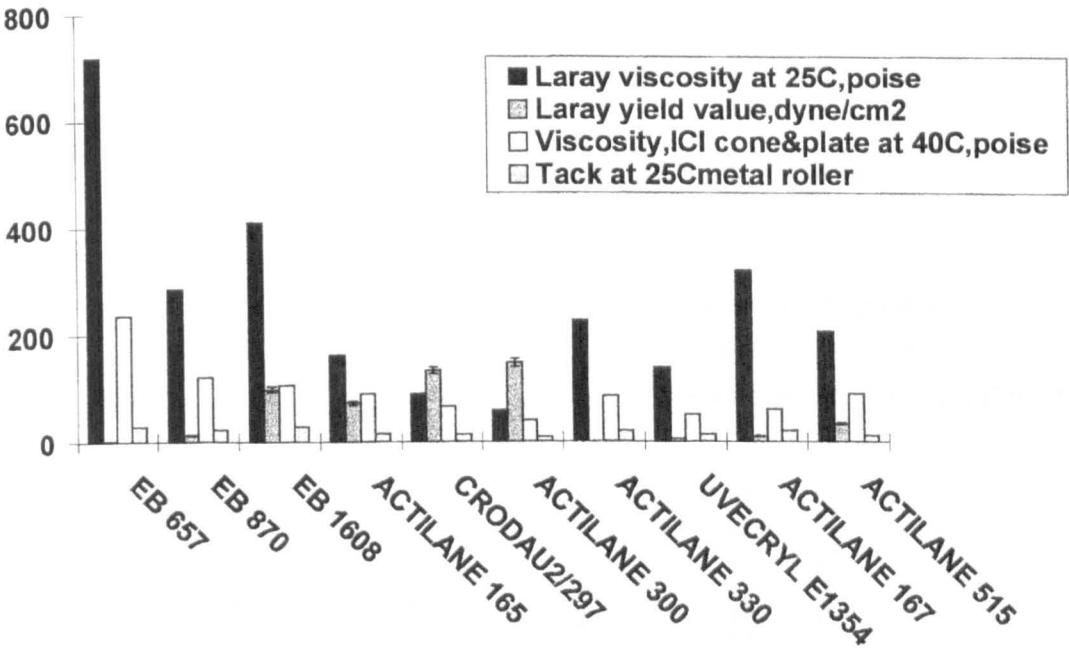


Figure VIII.10 Laray yield value, Laray viscosity, ICI cone and plate viscosity and tack of resins.

The yield value of an ink can help to prevent an enlargement of the dot size after the ink has been printed. An excessive yield value can make the feeding of the ink difficult in the printing duct. Additives can also affect the yield value; fumed silica can increase the yield value of inks having little influence on tack, but may affect adversely on gloss. Hydrophobic and hydrophilic silica are commonly used to improve the lipophilic-hydrophilic balance HLB in offset lithographic inks.

Tack is relevant since the ink transfer properties are dependent on its value. Too high a tack value can cause some type of rupture in the substrate and the paper

may be pulled onto the surface of the offset blanket. Where the tack is only marginally too high for the strength of the substrate, a small degree of coating pick up (picking) may occur. Low tack values can have insufficient cohesion to transmit the frictional forces across the nips in the press resulting in roller slippage and inadequate ink feed and distribution. It can also cause back trapping from subsequently printed, higher tack inks³. Excessive low tack inks may also provoke high dot gain due to low dot cohesion, which may provide dot squashing. The tack of a resin affects the final ink tack. Formulators commonly use talc to decrease ink misting and ink tack since talc increases slightly the ink rheology and consequently it is required to add reactive diluents in order to adjust the ink viscosity. The overall effect results in a decrease of the original ink tack. The use of certain resins of different tack and viscosity ratio may facilitate the formulation task (Figure VIII.11).

RHEOLOGICAL PROPERTIES OF UV RESINS

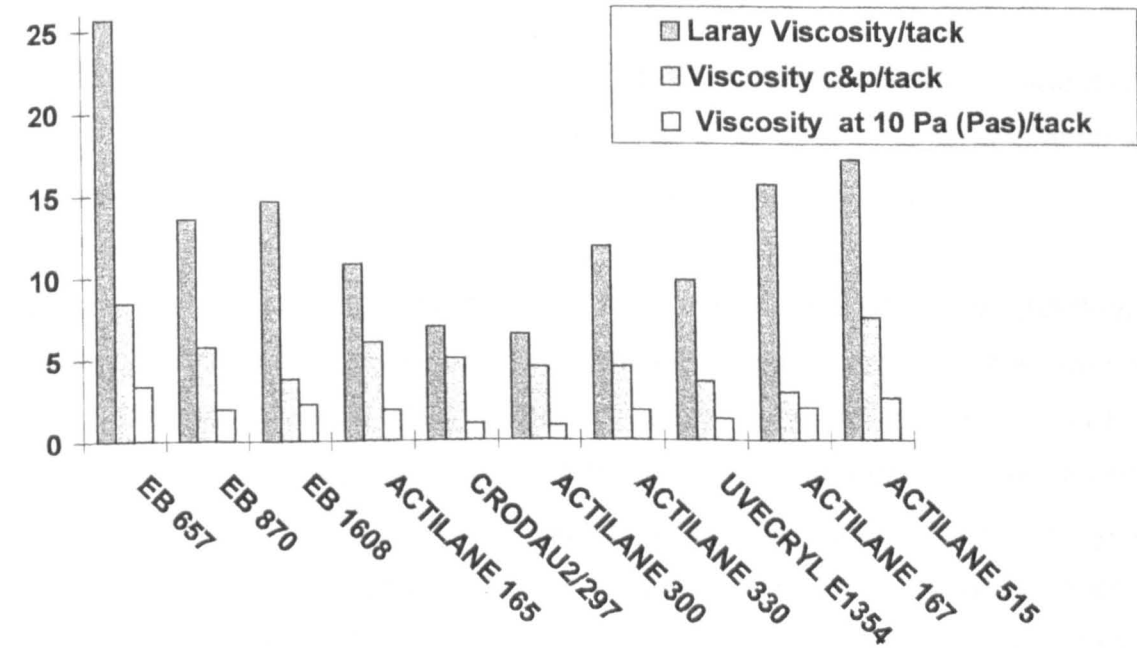


Figure VIII.11 Ratio of viscosity and tack of resins.

Ebecryl 657 has a much higher viscosity/tack ratio than the other resins studied. On the other hand, Actilane 300 and Croda U2/297 have a very low viscosity/tack ratio. They can be used to decrease the viscosity without significantly decreasing the tack values.

VIII.3 Conclusions

From this investigation the following conclusions can be highlighted:

- PPTTA imparts harder film properties than GPTA due to its higher functionality.
- Ebecryl 870 is harder than Ebecryl 657 mainly due to its higher functionality.
- Ebecryl 870 and Ebecryl 657 (polyester acrylates) are resins of high reactivity and low hardness, which have good pigment wetting and good lithographic performance. Gel effect (by steric hindrance) can limit the final conversion and the final unsaturation content of these resins.
- PPTTA and GPTA are harder than formulations of Ebecryl 657 and 870 with PPTTA and GPTA.
- Epoxy acrylates and urethane acrylates give hard films with good rub and scratch resistance properties. Crodamer UVE 104 and Ebecryl 1608 (epoxy acrylates) and Uvecryl E1354, Actilane 167 and Actilane 165 (urethane acrylates) are twice as hard as Ebecryl 657 and 870 (polyester acrylates).
- Actilane 300 (acrylated epoxidised oil) is a resin of high reactivity and low hardness which can be used in low percentage (5-10%) to improve the pigment wetting of inks.
- Resin functionality influences the cure rate and extent of conversion and this, in turn, influences the final film properties. Steric effects on radical migration and propagation are important in resins of high functionality.

A compromise should be considered between mechanical properties (hardness), reactivity, wetting and lithographic performance. Combinations of cost effective resins possessing good mechanical properties such as epoxy acrylates (of medium lithographic performance and medium pigment wetting characteristics) combined with resins of good lithographic performance such as some polyester acrylates (Ebecryl 657 and Ebecryl 870) and good pigment wetters, such as acrylated soya bean oils, can provide cost effective formulations with excellent lithographic performance and good mechanical properties for the cured inks. PPTTA is a cost-effective reactive diluent, which gives hard films and high surface cure due to its high crosslinking density, which is reflected in a good rub and scratch resistance.

VIII.4 References

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IX. CHAPTER IX A comparative kinetic study of UV curable reactive diluent monomers: structural and rheological inter-relationships

IX.1 Introduction

The reactivity and mechanical properties of several low viscosity acrylates (reactive diluents) were analysed and correlated with their chemical composition such as chemical backbone and functionality. The rheological properties of several acrylates such as viscosity and thixotropy were also measured as well as their misting characteristics in a reference offset lithographic ink. The acrylate functionality appears to play a crucial role in controlling the cure rate and final film properties associated with the crosslink density.

IX.2 Results and Discussion

Reactivity and hardness of different reactive diluents

Functionality and reactivity are important parameters to consider when choosing reactive diluents. For example, hardness, scratch and thumb twist resistance increase with functionality. Flexibility can be obtained with low functional reactive diluents due to their slow cure rate, low shrinkage and low crosslink density. The results obtained are shown in Figure IX.1 and Table IX.1. The reactivity of a range of low viscosity acrylates is compared by RTIR at 8% Irgacure 500 at 4 microns. Laromer 8889 (amine modified ether acrylate) has the highest polymerisation rate and final conversion among all the acrylates investigated, possibly due to its co-synergistic amine function which can act as an electron/proton donor with benzophenone. On the other hand, it exhibits low hardness due to its low functionality and crosslinking.

DITMPTA and PPTTA exhibit at the same time high reactivity and hardness due to their high functionality and high concentration of growing radicals capable of overcoming oxygen inhibition. GPTA and OTA 480 present lower reactivity and hardness due to their lower functionality, which results in a higher oxygen inhibition affecting the overall polymerisation rate and in a lower crosslink density.

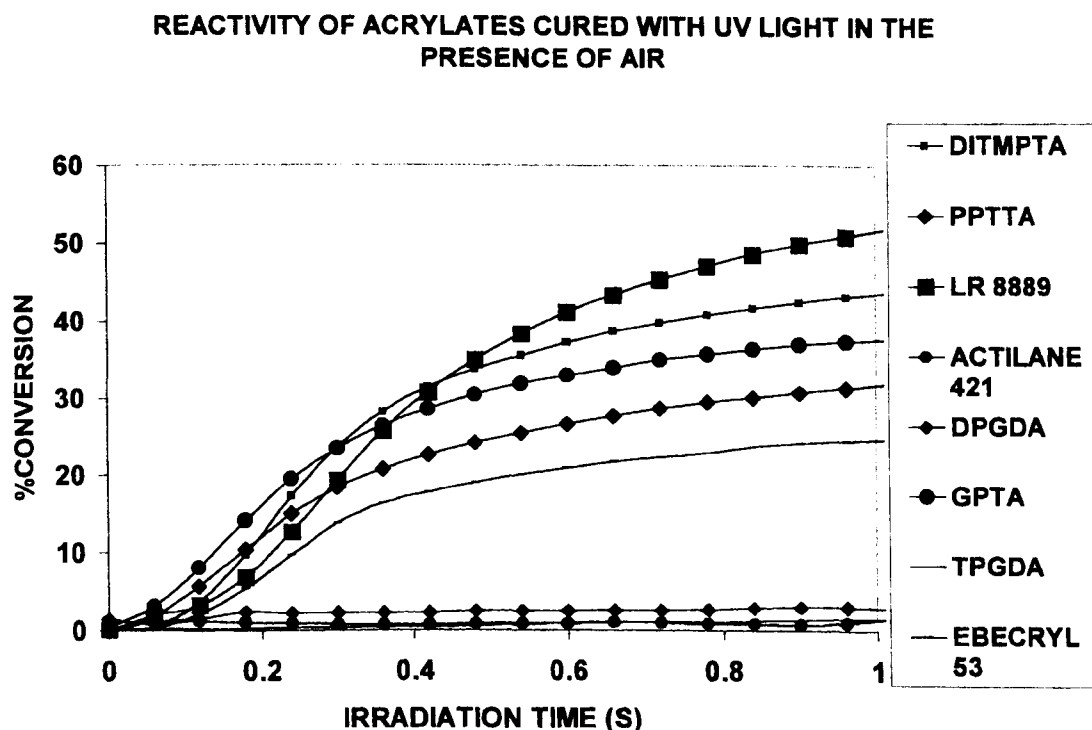


Figure IX.1 Reactivity of different reactive diluents with 8% Irgacure 500 by RTIR with UV light (Xenon lamp with a cut off at 390 nm) at 4 microns in the presence of air.

Acrylate	Rp maximum (mol L ⁻¹ s ⁻¹) ± SD	Conversion at 25 s ± SD	N ^o runs	Number of oscillations ± SD
DITMPTA	1.165 ± 0.068	70.7 ± 3.1	2	104 ± 3
PPTTA	0.980 ± 0.226	71.5 ± 6.6	2	94 ± 2
LR 8889	1.152 ± 0.244	82.9 ± 2.6	3	55 ± 2
ACT 421	0.158 ± 0.021	28.7 ± 2.3	3	<30
DPGDA	0.015 ± 0.005	15.6 ± 3.1	2	No cured
GPTA	0.914 ± 0.101	63.4 ± 3.5	2	66 ± 3
TPGDA	0.024 ± 0.003	29.3 ± 6.9	2	No cured
OTA480	0.711 ± 0.049	57.5 ± 0.8	2	74 ± 5

Table IX.1 Reactivity of different reactive diluents with 8%Irgacure 500 by RTIR in the presence of air. Pendulum Hardness of films (75 microns) cured under a conveyor at 80 W/cm and 100 ft/min, measured immediately after curing.

Difunctional reactive diluents such as DPGDA, TPGDA and Actilane 421 present even lower reactivity due to low crosslink density and low surface cure due to the high inhibition effect of oxygen acting as a terminating agent of the polymerisation process.

Viscosity of the system is also an important factor to take into account since the oxygen diffusion rate constant depends on the viscosity of the system, hence since high functionality acrylates exhibit higher viscosity than low functionality acrylates they have lower oxygen inhibition and consequently enhanced reactivity. On the other hand, systems of very high viscosity can exhibit low reactivity due to reduced mobility of the propagating macro-radical (diffusion rate controlled reaction).

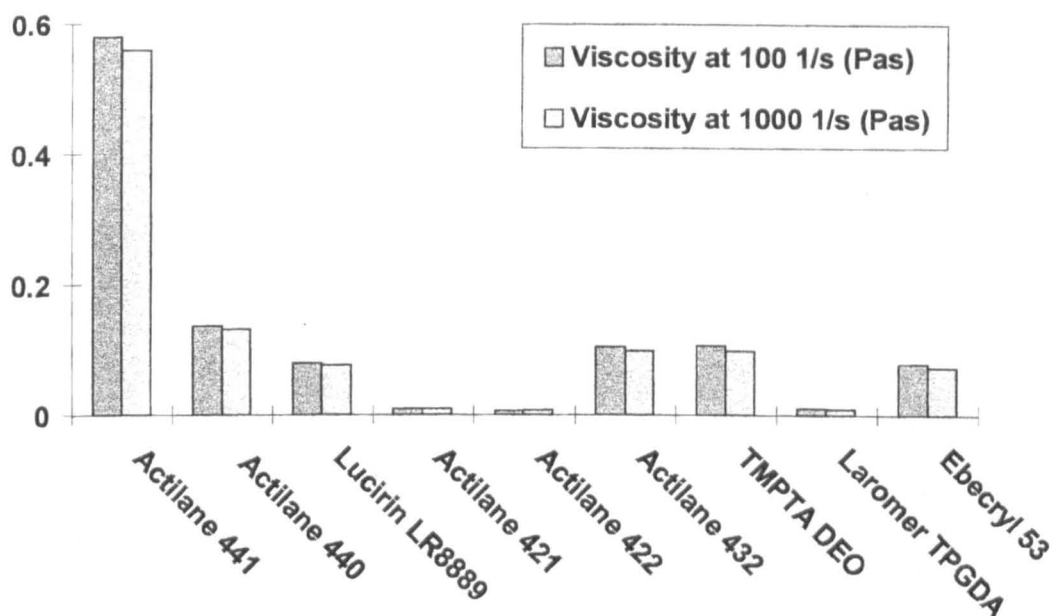
Actilane 440 (PPTTA) is a form of ATTA (alkoxylated tetra-acrylate) that possesses very low odour and gives hard films with good toughness and abrasion resistance. The Draize rating is very low at 0.1(non-toxic), therefore it is ideally suited for food contact inks. GPTA has a similar viscosity and a slightly lower reactivity and hardness than PPTTA. GPTA has a good hydrophilic-lipophilic balance (HLB) making it particularly important for lithographic inks. GPTA has good wet offset lithographic performance and a good balance of tensile strength and elongation. The Draize value of GPTA is lower than 0,1.

Rheological properties of acrylates

The viscosity of different UV reactive diluents (Table IX.2) at 100 and 1000 s⁻¹ is shown in Figure IX.2.

Actilane 421, DPGDA and TPGDA (difunctional acrylates) have the lowest viscosity of the low viscosity acrylates studied, due to their lower molecular weight and low functionality. GPTA and OTA 480 (trifunctional acrylates) exhibit higher viscosity than their difunctional counterparts. High functionality acrylates such as DITMPTA and PPTTA exhibit higher viscosity due to their higher molecular weight and branched structure.

RHEOLOGICAL PROPERTIES OF UV ACRYLATES

Figure IX.2 Viscosity of low reactive diluents at 100 and 1000s⁻¹.

Commercial name	Viscosity at 100 1/s (Pas)	Viscosity at 1000 1/s (Pas)	Thixotropy (Pa/s)	Zero shear stress viscosity
Actilane 441	0.58	0.56	133.3	1.36
Actilane 440	0.137	0.132	84.91	0.68
Lucirin LR8889	0.08	0.076	686.5	0.53
Actilane 421	0.0085	0.0085	786	0.44
Actilane 422	0.006	0.0072	825	0.58
Actilane 432	0.106	0.1	453.1	0.365
TMPTA DEO	0.108	0.1	474.4	0.33
Laromer TPGDA	0.0105	0.01	843	0.41
Ebecryl 53	0.08	0.074	565.9	0.7

Table IX.2 Rheological properties of acrylates.

The viscosity, at zero shear stress³, of acrylates has been measured and it can be compared in Figure IX.3.

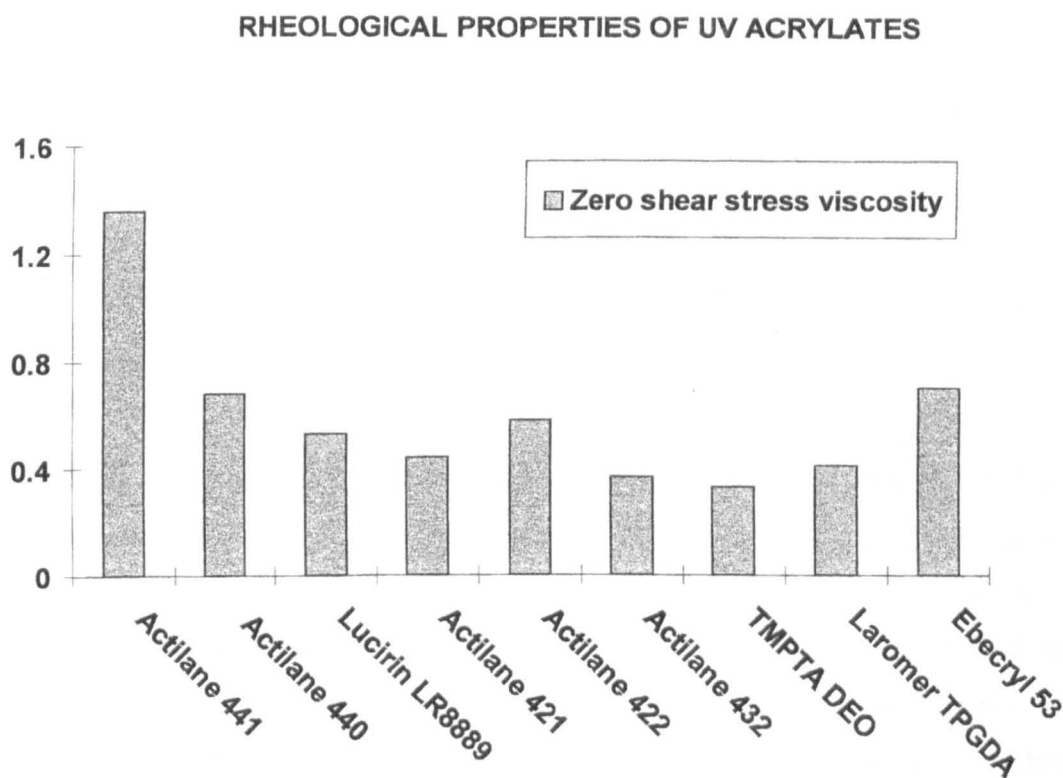


Figure IX.3 Zero shear viscosity of reactive diluents.

In Figure IX.4 is shown the zero shear viscosity plot of GPTA where its higher initial viscosity is observed at zero shear stress. Actilane 441 (DITMPTA) has a higher zero shear stress viscosity than the other reactive diluents studied. Actilane 440 (PPTTA) and OTA 480 present a slightly higher zero shear stress viscosity than the rest of the acrylates.

These results show a clear correspondence with the rheological measurements, obtained at shear rate gradient flow curves, for the different acrylates. The viscosity at zero shear stress is higher than the viscosity measured at 100 or 1000 s^{-1} due to the higher energy required to break the original static intermolecular interaction.

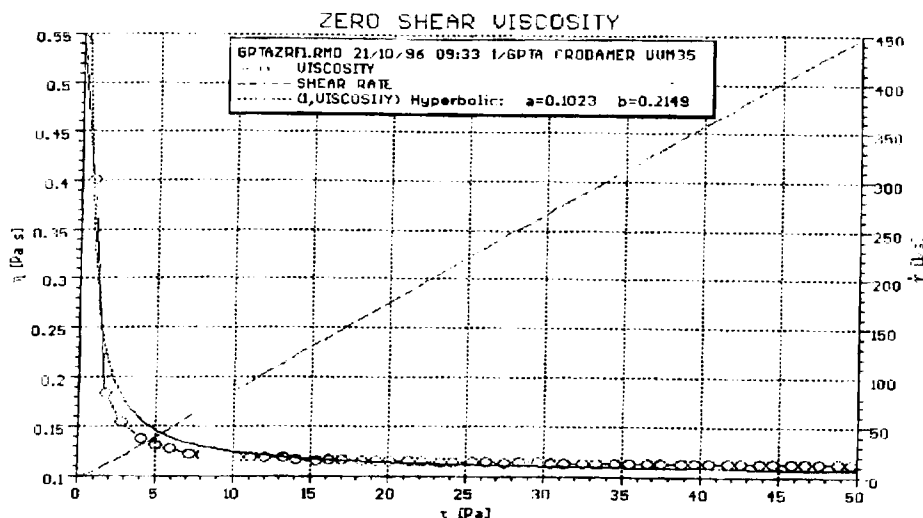


Figure IX.4 Zero shear stress viscosity of GPTA

Thixotropy is generally confused with pseudoplasticity. Thixotropy is the gradual decrease of the viscosity under shear stress or shear rate followed by a gradual recovery of structure when the stress is removed¹. The process is time dependent², therefore, the viscosity decreases with time of shearing for thixotropic resins. A high thixotropic reactive diluent is in principle not desired due to its unstable performance in the press. By performing loop tests, it is possible to measure the thixotropy of a system by increasing the shear rate steadily and linearly in time from zero to 1000 s^{-1} and then decreasing to zero in the same way. The area measured between the two curves is an indication of the thixotropy of the material (Figures IX.5 and IX.6).

The thixotropic properties of reactive diluents can influence the final ink thixotropy. Thixotropic measurements have also been analysed and show that DITMPTA and PPTTA show much lower thixotropy than the other acrylates analysed. On the other hand, low functionality acrylates such as DPGDA, TPGDA and Actilane 421 show higher thixotropy than higher functional acrylates such as GPTA, OTA 480. These results indicate that there is a direct relationship between thixotropy and molecular weight, functionality and branching of the molecules. It can be postulated that highly branched molecules may interact physically by intermolecular interpenetration and may maintain an interpenetrating structure even at high shear conditions. The difunctional acrylates exhibit higher thixotropy due to their lower intermolecular interaction resulting from their linear structure.

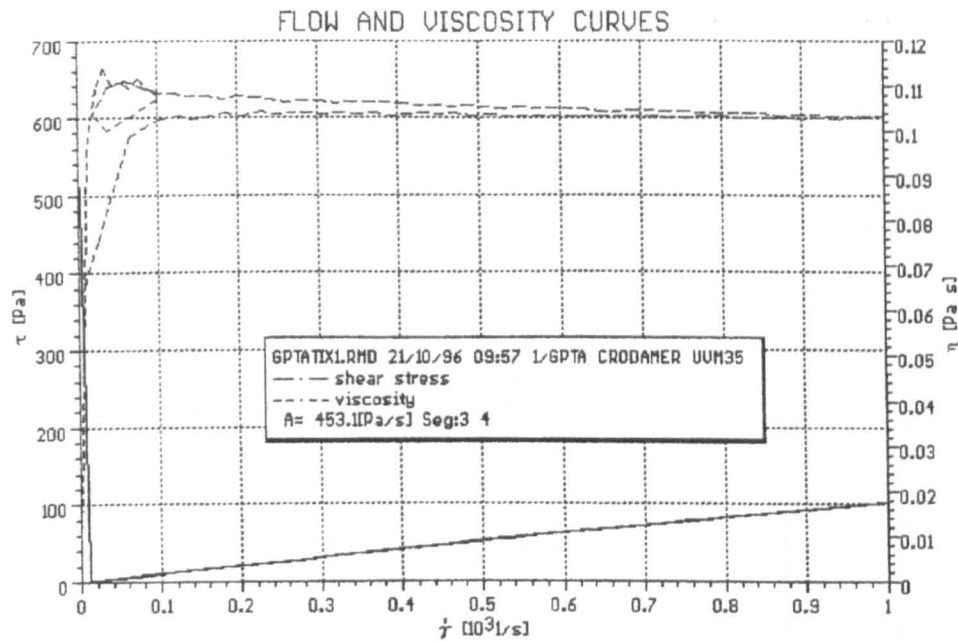


Figure IX.5 Thixotropy plot of GPTA.

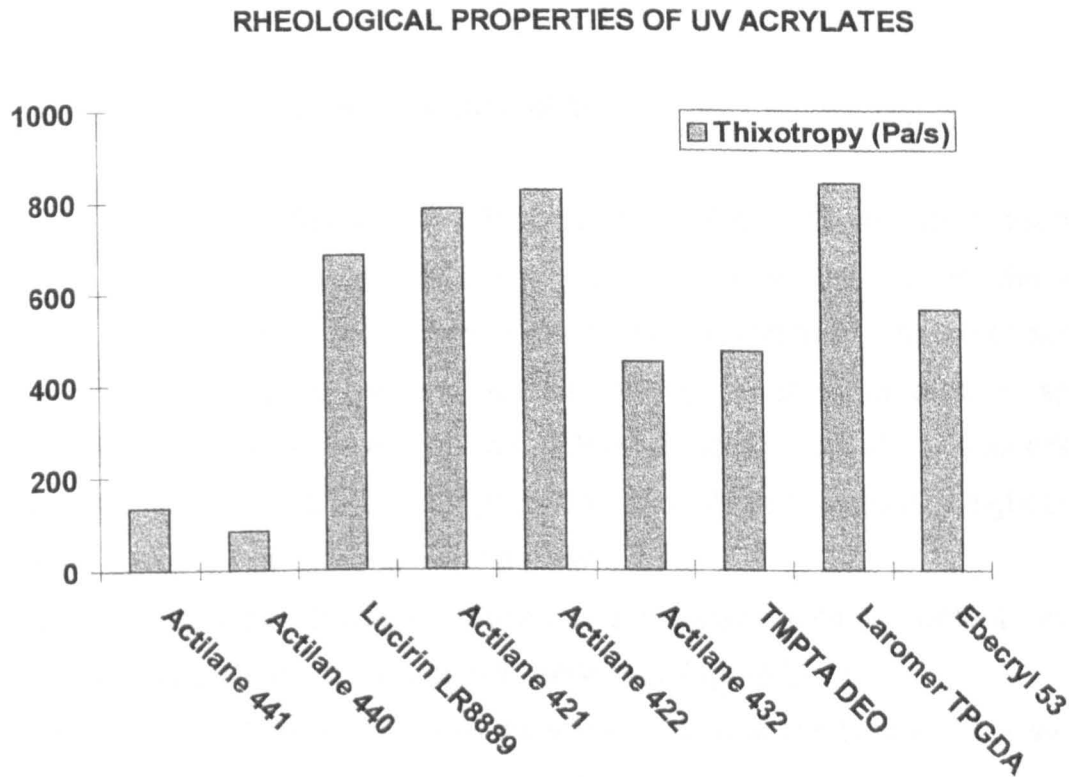


Figure IX.6 Thixotropy of reactive diluents.

Misting properties of acrylates

The misting properties of inks at constant tack are displayed in Figure IX.7.

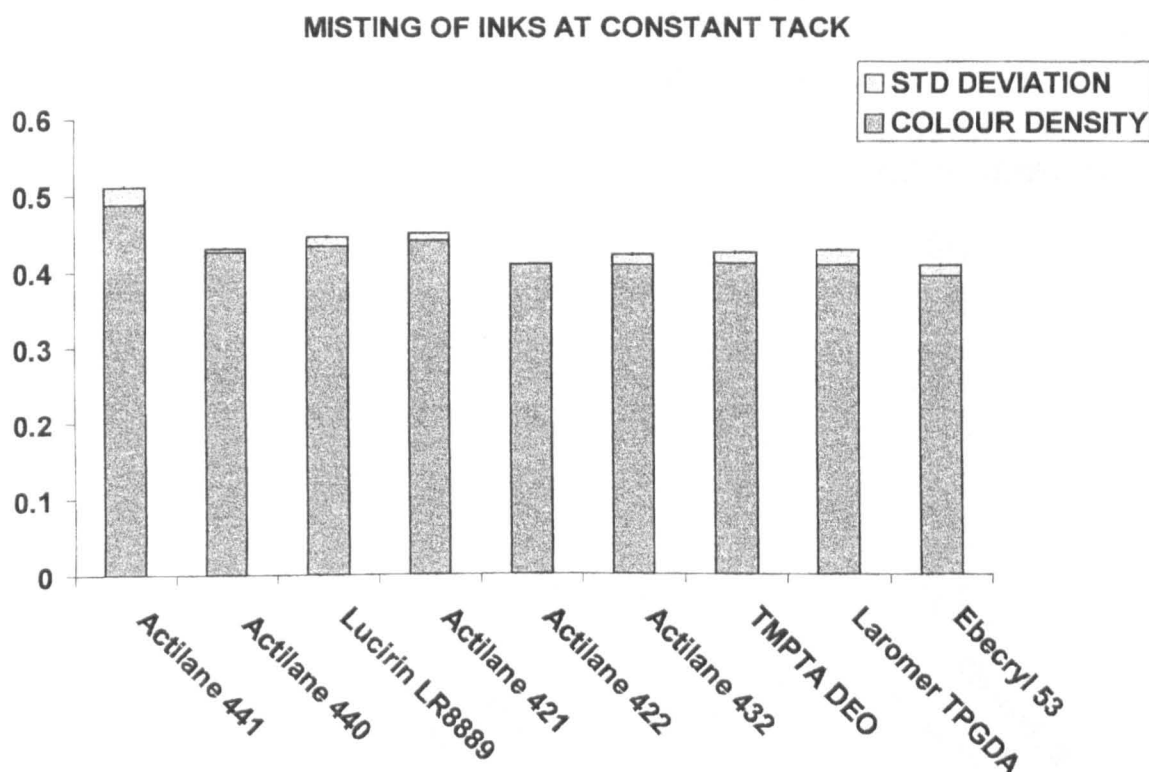


Figure IX.7 Misting of inks at constant tack.

The inks diluted with Actilane 441 (high viscosity diluent) show higher misting than the other counterparts at the same tack. This may be due to the higher percentage of Actilane 441 added to obtain the desired tack. The other acrylates compared in the study present similar misting at constant tack. It appears reasonable that once a level of low molecular weight acrylate is exceeded the misting is increased due to the high percentage of low molecular weight acrylate forming strings as the ink splits in the rollers.

Measurement of the degree of misting at a constant acrylate content has been performed for a series of low viscosity acrylates (Figure IX.8).

Actilane 422 and Laromer TPGDA gave low misting at low tack and low viscosity. In principle, it is not possible to understand this phenomenon; possibly, colour density measurements are not always representative results of the real process. Indeed, it is thought, that low viscosity and low tack inks form smaller particle size

droplets, which spread in the atmosphere giving very fine misting. On the other hand, relatively high viscosity and tack inks do not spread to such an extent in the atmosphere, since higher particle size misting with lower volatility is formed. It is expected that colour density measurements are affected by this fact, consequently, this can lead to misinterpretation of the results.

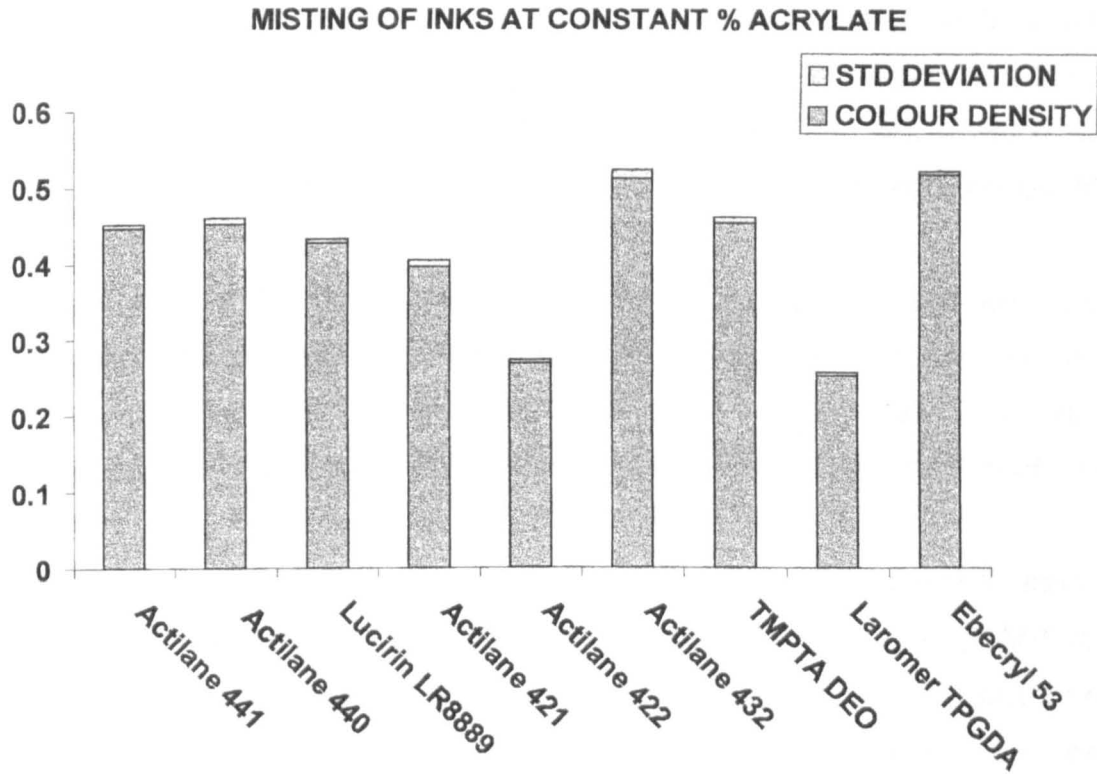


Figure IX.8 Misting of inks at constant acrylate content.

IX.3 Conclusions

The selection of high performance reactive diluents affects the final properties of the cured coatings and inks. Highly functionality acrylates such as PPTTA and DITMPTA are indispensable for getting high tack-free crosslinked systems with good hardness characteristics especially in the printing ink industry, due to the high oxygen inhibition effect found in thin films. Low functionality acrylates present low crosslinking density and deficient surface cure, due to oxygen inhibition. This deficient cure and low crosslinking density has a plasticizer effect which can be used to enhance the flexibility of the cured film and improve adhesion on difficult substrates.

Actilane 421, DPGDA and TPGDA (difunctional acrylates) have lower viscosity than higher functionality acrylates due to their lower molecular weight and low functionality. They suffer oxygen inhibition in a more extent than higher viscosity acrylates due to their high oxygen diffusion rate and low concentration of growing radicals.

GPTA and OTA 480 (trifunctional acrylates) exhibit higher viscosity than their difunctional counterparts. High functionality acrylates such as DITMPTA and PPTTA exhibit even higher viscosity due to their higher molecular weight branch structure, which may increase their intermolecular interaction by forming interpenetrating structures.

Thixotropic measurements indicated that the tetrafunctional acrylates DITMPTA and PPTTA had lower thixotropy than the other acrylates analysed. On the other hand, low functionality acrylates such as DPGDA, TPGDA and Actilane 421 showed higher thixotropy than higher functionality acrylates such as GPTA, OTA 480. These results indicate that there is a direct relationship between thixotropy and molecular weight, functionality and branching of the molecules. Highly branched molecules may interact physically by intermolecular interpenetration. These interpenetrating structures may maintain their interaction even at high shear conditions. The difunctional acrylates exhibit higher thixotropy due to their lower intermolecular interaction resulting from their linear structure.

IX.4 References

1. Barnes, H. A., Hutton, J. F., and Walters, K., *"An introduction to Rheology"*, Elsevier, 3 (1989).
2. Mewis, J., Thixotropy, "A general review", *J. non-Newtonian Fluid Mech*, 6 (1979)1-20.
3. Ferry, J. D., *"Viscoelastic Properties of Polymers"*, 3rd edition, John Wiley & Sons.

X. CHAPTER X Photochemistry and photopolymerisation activity of several Type II commercial photoinitiators

X.1 Introduction

Some of the most important commercial benzophenone and thioxanthone photoinitiators have been analysed by various spectroscopic techniques to evaluate the relationship between their photophysical properties and photoinitiation activity for photocuring of commercial acrylated monomers. The types of electronic transitions occurring upon absorption of light are established via UV spectroscopy. Phosphorescence spectroscopy has been used to study their triplet energies and lifetimes and phosphorescence quantum yields. Microsecond flash photolysis has also been undertaken to determine the nature of the free radical semiquinone (ketyl) intermediates. The free radical intermediate decay kinetics of the different photoinitiators have also been determined, as well as the first and second order rate constants, the transient radical absorption and radical lifetimes. Photopolymerisation studies have been undertaken by Real Time Infrared Spectroscopy RTIR at different photoinitiator concentrations in the presence and absence of oxygen using a low viscosity reactive diluent and a commercial resin of higher viscosity. Pendulum hardness measurements were also carried out to correlate the film hardness properties with the kinetic results obtained with RTIR. Analysis of the data shows that whilst Type II initiator photoactivity is predominantly dependent upon the absorption maxima of the chromophore structural influences play a major role in controlling the nature of the lowest excited triplet state and the formation of radical intermediates.

The photochemical and photophysical properties of a wide range of benzophenone¹⁻⁴ and thioxanthone⁵ photoinitiators (Type II photoinitiators) have been extensively studied and reviewed⁶ in the literature. Benzophenone represents the most important bimolecular photoinitiator since the use of benzophenone combined with amines makes possible the formulation of cost effective UV inks and coatings. Benzophenone is frequently used in combination with unimolecular photoinitiators (Type I) as well as with tertiary amines for enhanced reactivity. Thioxanthenes are used in printing inks due to the longer wavelength absorption characteristics in the near UV range of the spectrum. They

react similarly to that of benzophenone, but here tertiary amines must also be used. The thioxanthenes are also often used in conjunction with Type I photoinitiators to design cost effective synergistic photoinitiator blends.

Modification of the structure of conventional photoinitiator chromophores for improved property requirements is a subject of much interest and activity¹⁻⁵. In this context, structures based on the thioxanthone and benzophenone chromophore have attracted intensive academic and industrial interest. As a consequence of this, several benzophenone and thioxanthone derivatives are currently used in the UV curing industry in several applications.

In this study the photocuring kinetic characteristics of the most important benzophenone and thioxanthone derivatives on the market have been compared and related to their photophysical and photochemical characteristics. This was undertaken firstly, to compare the photoactivities of the latest range of initiators and to ascertain the most important photophysical requirements in relation to their chemical structure. Whilst such studies have been undertaken on ranges of novel esoteric non-commercial initiators no such comparative study has been undertaken on the latest commercial systems.

X.2 Results and Discussion

UV spectroscopic results

The most important UV transitions of the photoinitiators studied in isopropanol, acetonitrile and methylcyclohexane are shown in Figures X.1, X.2 and in Tables X1, X2. Benzophenone derivatives exhibit a main $\pi \rightarrow \pi^*$ transition around 250 nm and a weak forbidden $n \rightarrow \pi^*$ transition around 340 nm.

The benzophenone derivative substituted in the para position by an methylphenylthio group, Quantacure BMS, is characterised by showing a strong red shifted absorption around 315 nm, since the thioether group introduces a charge transfer character into the lowest lying $\pi \rightarrow \pi^*$ transition. This increased absorption in the spectral window leads to higher photoactivity and permits its use in pigmented systems. Adversely, its strong absorption around 310-320 nm, which tails off up to 380 nm imparts a small degree of inherent yellowness to this compound and limits its application in clear coatings. Additionally, Quantacure BMS presents C-S bond cleavage reactions producing alkyl and alkylthio radicals¹⁶. Triganol 12 also exhibits a red shifted absorption due to extension of π

conjugation, because of para substitution by a phenyl group. This bathochromic effect on its $\pi \rightarrow \pi^*$ transition is accompanied by an increase in the absorption intensity (hyperchromic effect). The lowest lying triplet state of Triganol 12 is $\pi\pi^*$ whilst that of benzophenone is $n\pi^*$.

The thioxanthone derivatives 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 strongly mixed $n\pi^*/\pi\pi^*$ states. CPTX shows a more pronounced red shifted maximum than ITX, which may be due to the inductive effect by the chlorine atom substituted, in the 1-position and by resonance by the propoxy substituent in the 4-position.

UV SPECTRA OF TYPE II PHOTOINITIATORS

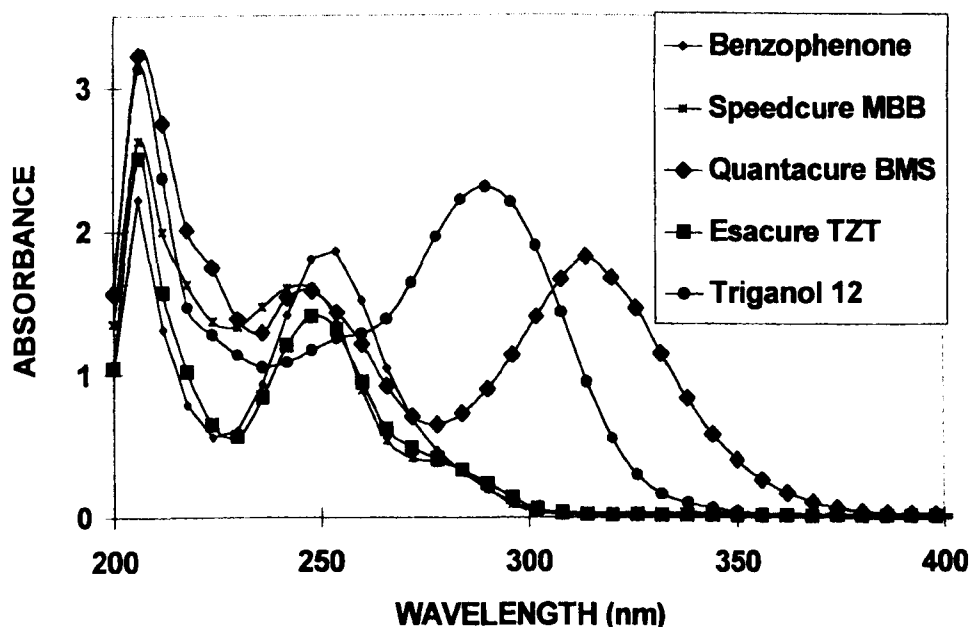


Figure X.1 UV absorption spectra of photoinitiators in isopropanol ($C=1.0 \times 10^{-4}$ M).

UV SPECTRA OF NEAR UV TYPE II PHOTOINITIATORS

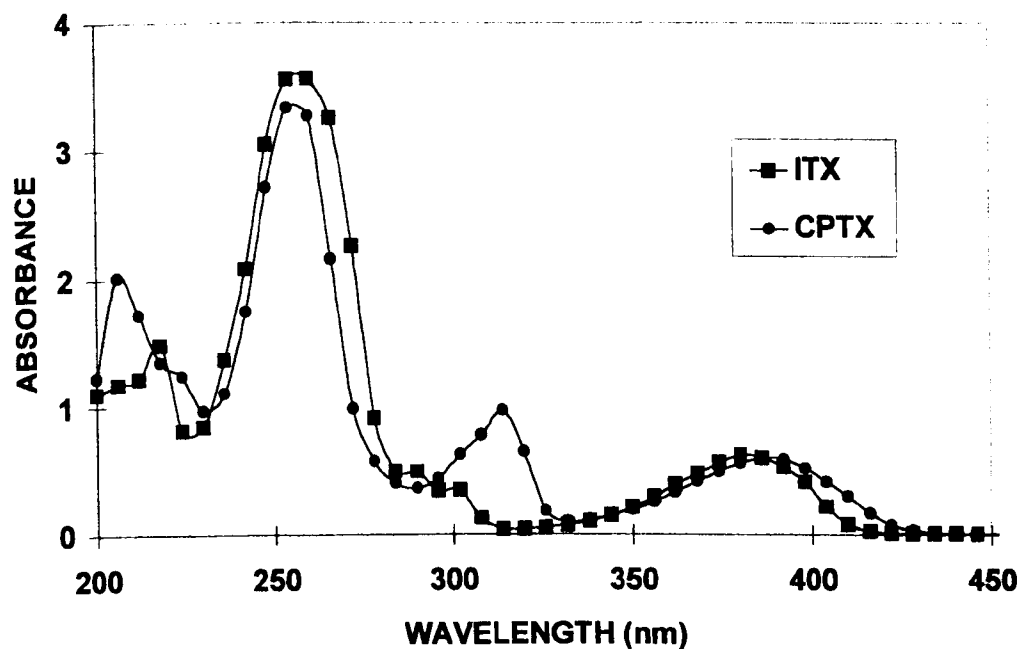


Figure X.2 UV absorption spectra of photoinitiators in isopropanol (C=1.0x10⁻⁴ M).

	Methylcyclohexane		Acetonitrile		Isopropanol	
	λ max	log ϵ	λ max	log ϵ	λ max	log ϵ
Benzophenone	248.2	4.30	250.3	4.19	251.5	4.27
Speedcure MBB	239.5	4.18	243.9	4.19	245.2	4.21
Genocure MBF	252.8	4.00	254.3	4.05	253.6	4.10
Quantacure BMS	311.9	4.30	311.8	4.25	315.6	4.26
Esacure Tzt	244.3	4.16	247.6	4.15	249.6	4.15
Triganol 12	283.4	4.40	288.5	4.35	289.7	4.36
Quantacure ITX	255.4	4.58	257.3	4.56	257.0	4.55
Quantacure CPTX	255.4	4.58	257.3	4.51	256.8	4.59

Table X.1 $\pi \rightarrow \pi^*$ transition of several photoinitiators in different solvent systems.

	Methylcyclohexane		Acetonitrile		Isopropanol	
	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$
Benzophenone	345.4	2.05	341.5	2.16	331.3	2.18
Speedcure MBB	335.2	1.98	332.9	2.00	326.8	2.08
Quantacure BMS	*		*		*	
Esacure TZT	349.3	1.91	340.0	2.04	333.3	2.07
Triganol 12	*		*		*	
Quantacure ITX	380.7	3.85	381.8	3.84	382.3	3.79
Quantacure CPTX	385.0	3.81	385.0	3.75	388.0	3.78

The $n \rightarrow \pi^$ transitions were buried under the more intense $\pi \rightarrow \pi^*$ transitions

Table X.2 $n \rightarrow \pi^*$ transition of several photoinitiators in different solvent systems.

Phosphorescence results

Phosphorescence quantum yields in methylcyclohexane of the Type II photoinitiators are compared in Table X.3.

	Phosphorescence quantum yields	Lifetime (ms)
Benzophenone	0.74	5.5 (444 nm)
Triganol 12	0.68	39.8 (472 nm)
Quantacure BMS	0.75	24.5 (481 nm)
Speedcure MBB	0.61	4.2 (445 nm)
Esacure TZT	0.12	4.6 (449 nm)
Quantacure ITX	0.76	47.2 (450 nm)
Quantacure CPTX	0.43	53.6 (484 nm)

Table X.3 Phosphorescence quantum yields and lifetimes of several benzophenone derivatives in methylcyclohexane.

All the photoinitiators present a high degree of intersystem crossing ISC as reflected by their high phosphorescence quantum yields. Quantacure BMS exhibits the highest phosphorescence quantum yields among all the benzophenone derivatives studied ($\phi_p \text{ BMS} = 0.75$). Quantacure BMS has a longer triplet lifetime and lower triplet energy than benzophenone in agreement with the higher polymerisation rate observed in the polymerisation kinetic experiments to be discussed below. On the other hand, Esacure TZT has a low phosphorescence quantum yield ($\phi_p \text{ TZT} = 0.12$) and a short triplet lifetime ($\tau = 4.6 \text{ ms}$ $\lambda = 449 \text{ nm}$) as well as a low polymerisation rate in comparison to the other photoinitiators. There

is a correspondence between phosphorescence quantum yields and triplet lifetimes since Type II photoinitiators follow a bimolecular reaction mechanism via hydrogen atom abstraction¹ with hydrogen atom donors such as tertiary amines. Since Type II photoinitiators react from their lowest lying excited triplet states it should be expected that long-lived triplets would have a higher probability to form an exciplex with a molecule of the environment. On the other hand, photoinitiators prone to quenching by molecules in the environment possessing relative long-lived triplet states, can be more easily quenched than those showing shorter triplet lifetimes. This could be the case of Triganol 12, which exhibits a relatively high quantum yield of phosphorescence and a long triplet lifetime. Its long triplet lifetime is accompanied with by a low triplet energy ($\tau=39.8$ ms $\lambda=472$ nm) which diminishes its hydrogen atom abstraction capability. Triplet states with lifetimes in the range 10-100 ms tend to be primarily of a mixed $n\pi^*/\pi\pi^*$ character.

CPTX displays a lower phosphorescence quantum yield and a longer lived red shifted triplet state ($\phi_p=0.43$ $\tau=53.6$ ms $\lambda=484$ nm) than ITX ($\phi_p=0.76$ $\tau=47.2$ ms $\lambda=450$ nm) in methylcyclohexane.

Flash photolysis results

End of pulse transient absorption spectra of the photoinitiators in isopropanol are compared in Table X.4 and in Figures X.3 and X.4 where absorption maxima and the first and second order rate constants K_1 and K_2 are compared and recorded. Benzophenone exhibits a higher maximum transient absorption spectrum than its derivatives, resulting from the formation of a high concentration of transient intermediates.

	Maximum Absorbance	K_1 s ⁻¹	τ_1 s	R_1	K_2 s ⁻¹	τ_2 s	R_2
Benzophenone	0.546 (320 nm)	18.68	0.054	0.967	110.30	0.009	0.994
Triganol 12	0.230 (340 nm)	29.37	0.034	0.966	662.68	0.001	0.985
Quantacure BMS	0.143 (360 nm)	41.03	0.024	0.988	635.99	0.001	0.977
Speedcure MBB	0.470 (340 nm)	19.18	0.052	0.986	115.25	0.009	0.985
Esacure TZT	0.265 (320 nm)	15.19	0.066	0.981	141.49	0.007	0.990
Quantacure ITX	0.019 (380 nm)	15.23	0.066	0.980	1485.80	0.0007	0.956
Quantacure CPTX	0.0136 (370 nm)	8.82	0.113	0.962	1065.9	0.0009	0.933

Table X.4 First and second order kinetic results by microsecond flash photolysis in isopropanol ($C=1 \times 10^{-5}$ M).

The spectrum of benzophenone is normally assigned to that of the ketyl radical formed by abstraction of a hydrogen atom by the excited triplet state from isopropanol.

Quantacure BMS ((4-(4-methylphenylthio)phenyl) phenylmethanone) and Triganol 12 (p-phenyl benzophenone) exhibit red shifted absorption spectra and lower maxima absorptivity. Speedcure MBB (methyl o- benzoylbenzoate) also exhibits a red shifted absorption maximum with a slightly lower maximum absorptivity than benzophenone. The methylated benzophenone Esacure T2T does not exhibit an absorption shift, but exhibits a two fold lower absorbance than benzophenone and hence a lower radical transient formation mainly due to intramolecular hydrogen atom abstraction from the ortho methyl substituent. This effect will also rapidly deactivate the excited triplet state of the benzophenone chromophore and reduce the triplet quantum yield, as is the case in Table X.4. The intensity of transient formation follows this sequential order:

BP>MBB>T2T>T12>BMS>ITX>CPTX

The majority of the photoinitiators studied follow a second order kinetic decay mechanism evidenced by regression analysis (R_1 and R_2). Some photoinitiators such as Quantacure BMS and Speedcure MBB also give transients that follow a first order kinetic decay since, by instance, C-S¹⁶ and C-O³ bond cleavage occur upon absorption of light. CPTX also follows a unimolecular deactivation mechanism since dehalogenation (C-Cl bond cleavage) occurs as indicated by earlier solution photolysis studies¹⁶.

Benzophenone, Triganol 12 and Esacure T2T exhibit a bimolecular deactivation mechanism for the transient radical. The second order lifetimes τ_2 of the radical intermediates were calculated and followed the order:

BP>MBB>T2T>BMS $\approx$ T12>CPTX>ITX

Consequently, benzophenone derivatives present a longer radical intermediate lifetimes than the thioxanthenes studied supposing a bimolecular deactivation mechanism. Additionally, benzophenone exhibits a longer-lived ketyl radical than its derivatives, presenting a certain correlation with the kinetic measurements

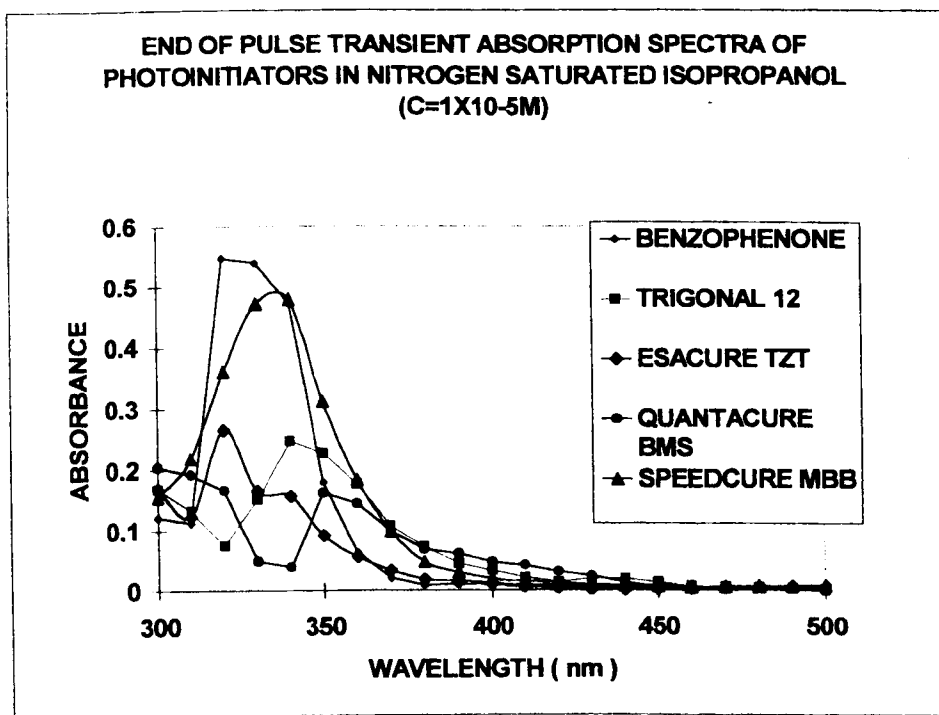


Figure X.3 End of pulse transient absorption spectra of type II photoinitiators in nitrogen saturated isopropanol ($C=1 \times 10^{-5}M$) produced on microsecond flash photolysis.

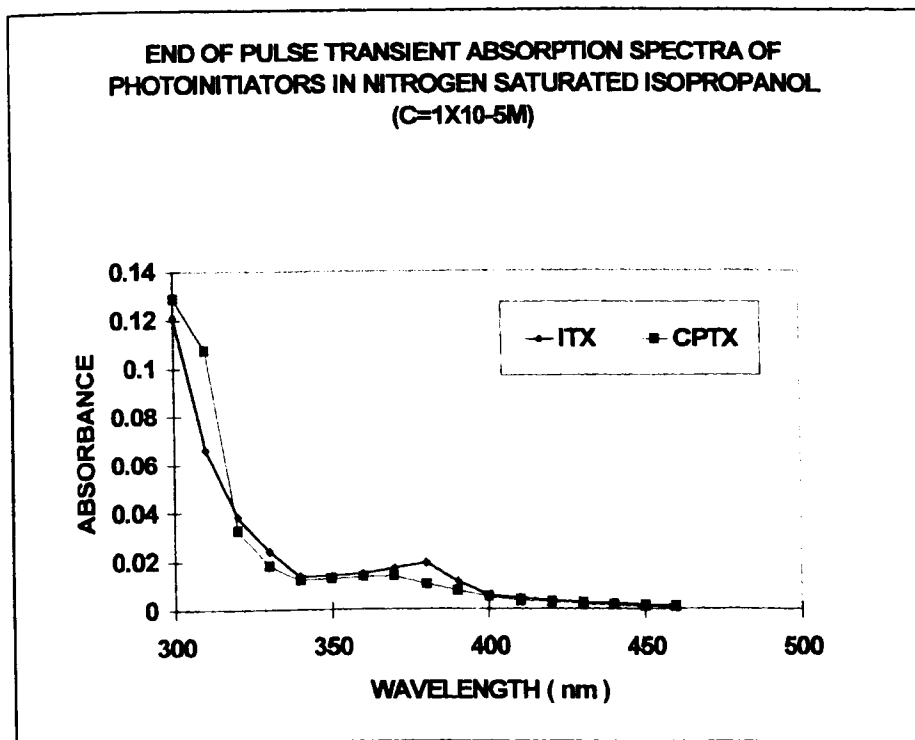


Figure X.4 End of pulse transient absorption spectra of ITX and CPTX in nitrogen saturated isopropanol ($C=1 \times 10^{-5}M$) produced on microsecond flash photolysis.

carried out by RTIR where benzophenone gave higher polymerisation rates than Esacure TZT, Triganol 12 and Speedcure MBB.

On the other hand, supposing the transient decay follows a first order kinetic decay mechanism the lifetimes of the radical intermediates would have an opposite tendency than in a second order mechanism. The radical intermediate lifetimes follow this order:



The higher radical lifetime of CPTX in comparison to ITX can be responsible for the higher polymerisation rate of CPTX observed in photopolymerisation experiments⁴. The narrow absorption bands with maxima at 370 and 380 nm for CPTX and ITX respectively reflect a higher ketyl radical formation for ITX than for CPTX, formed by abstraction of a hydrogen atom from the solvent by the excited triplet state of the thioxanthone chromophore^{19, 20}.

Photopolymerisation results

The photoreactivity of some Type II photoinitiators is compared in Tables X.5, X.6 and in Figures X.5, X.6.

Photoinitiators at 8% in Crodamer U2/297	Rp maximum (mol L ⁻¹ s ⁻¹) ± SD	% Conversion at 25s ± SD	No. of runs
Benzophenone	0.0103 ± 0.0002	19.6 ± 0.6	3
Speedcure MBB	0.0061 ± 0.0009	11.3 ± 0.6	3
Quantacure BMS	0.0114 ± 0.0001	23.9 ± 0.8	3
Esacure TZT	0.0057 ± 0.0003	11.7 ± 2.2	4
Triganol 12	0.0050 ± 0.0001	9.1 ± 0.4	3
Speedcure BEM	0.0099 ± 0.0003	20.8 ± 1.1	3

Table X.5 Reactivity of photoinitiators at 8 % w/w in Crodamer U2/297 by RTIR in the presence of air (uncovered method).

Photoinitiators at 2% in PPTTA	R _p maximum (mol L ⁻¹ s ⁻¹) ± SD	%conversion at 15 s ± SD	No of oscillations ± SD (5 runs)	No. of runs
Benzophenone	0.133 ± 0.041	62.0 ± 5.7	49 ± 14	2
Speedcure MBB	0.111 ± 0.052	56.0 ± 7.3	25 ± 7	2
Quantacure BMS	0.146 ± 0.053	64.9 ± 8.5	75 ± 5	3
Esacure TZT	0.121 ± 0.044	52.8 ± 9.4	26 ± 3	2
Triganol 12	0.053 ± 0.021	57.1 ± 5.8	No cured	2
Speedcure BEM	0.132 ± 0.042	61.8 ± 4.81	47 ± 12	2

Table X.6 Reactivity of photoinitiators at 2%w/w in PPTTA by RTIR at 50 microns (covered method) in the absence of air and pendulum hardness measurements of coatings cured at 50ft/min with a film thickness of 75 microns (measured after 24 hours).

Quantacure BMS displayed the highest photoinitiation activity (polymerisation rate) both in the presence and in the absence of air. These kinetics results were in agreement with the pendulum hardness measurements.

Benzophenone and Speedcure BEM (eutectic mixture of benzophenone and methylated benzophenones) had similar polymerisation rates and final percentage conversion. Esacure TZT gave lower reactivity than benzophenone and Esacure BEM in the absence of a tertiary amine despite having a similar composition. Norrish Type II intramolecular hydrogen atom abstraction may occur from the methyl group in the ortho position. On the other hand, Esacure TZT showed enhanced reactivity in the presence of a tertiary amine showing similar hardness properties than benzophenone (Figure X.6).

Genocure MBB (Methyl o-benzoylbenzoate) gave similar results to that of Esacure TZT. Substitution of benzophenone by an ester group in the ortho position decreased its reactivity, by a factor of two, in the absence of an amine co-synergist. Triganol 12 (paraphenylbenzophenone) gave the poorest results in the absence of an amine exhibiting very low polymerisation rates and poorly cured films. Its low reactivity results from lower hydrogen atom abstraction ability resulting from the lower energy of its triplet state due to a charge transfer by the phenyl group in the para position. Its photoreactivity is increased dramatically in

the presence of an efficient electron proton donor such as a tertiary amine giving harder films than films cured with benzophenone (Figure X.6).

CPTX exhibited a higher reactivity and hardness than ITX in the presence of an amine. CPTX and ITX exhibited a higher kinetic reactivity and gave harder films than benzophenone (Figure 9). On the other hand, other experiments evidenced that ITX has a higher reactivity than CPTX in the absence of an amine, due to the lowest triplet state of CPTX resulting in a lower energy $n-\pi^*$ transition by charge transfer and a consequent lower hydrogen atom abstraction ability.

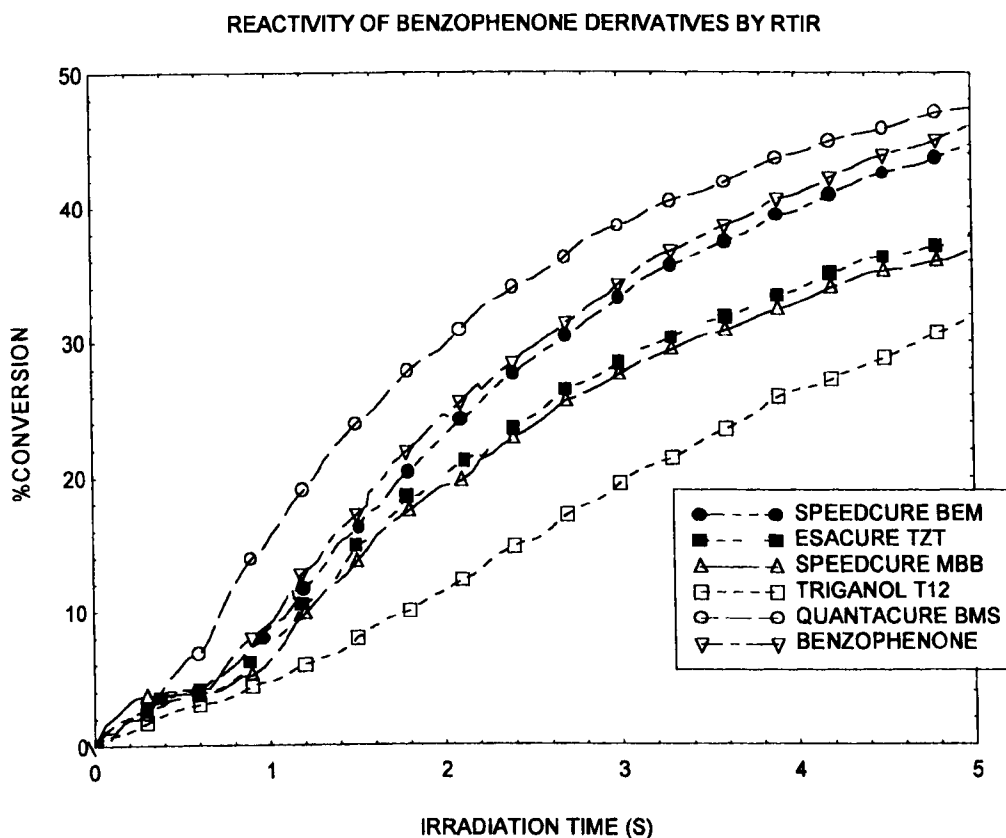


Figure X.5 Reactivity of several benzophenone derivatives at 2% w/w in PPTTA at 50 microns in the absence of air.

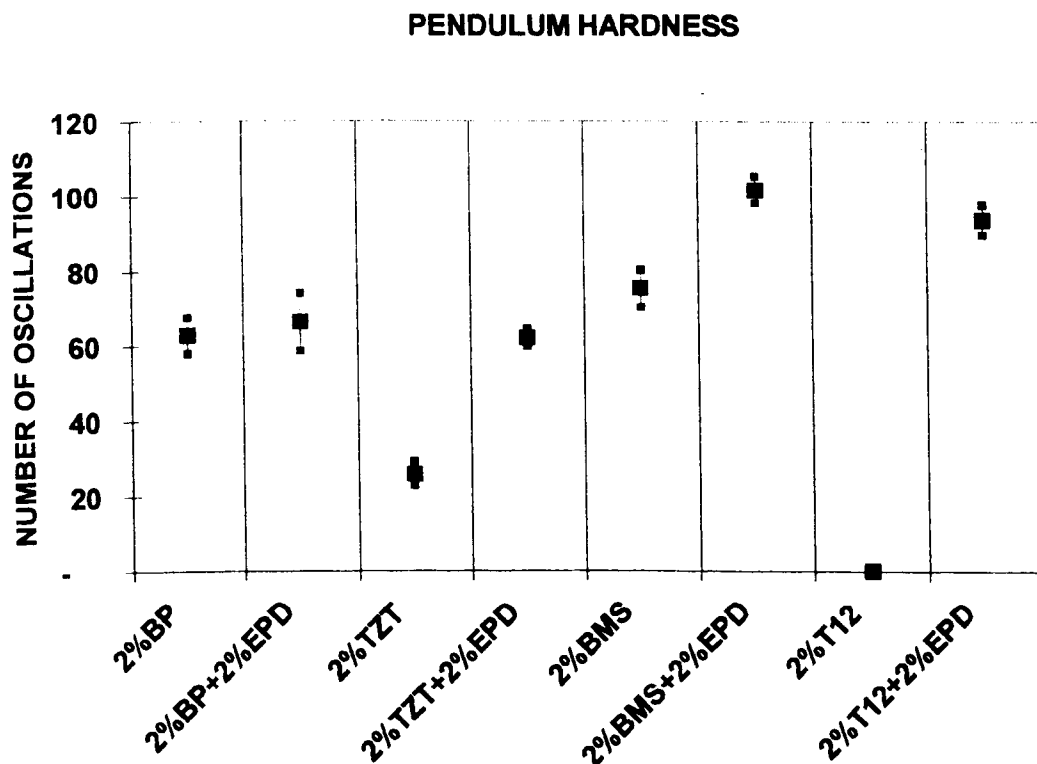


Figure X.6 Pendulum hardness of several benzophenone derivatives with and without tertiary amine EPD.

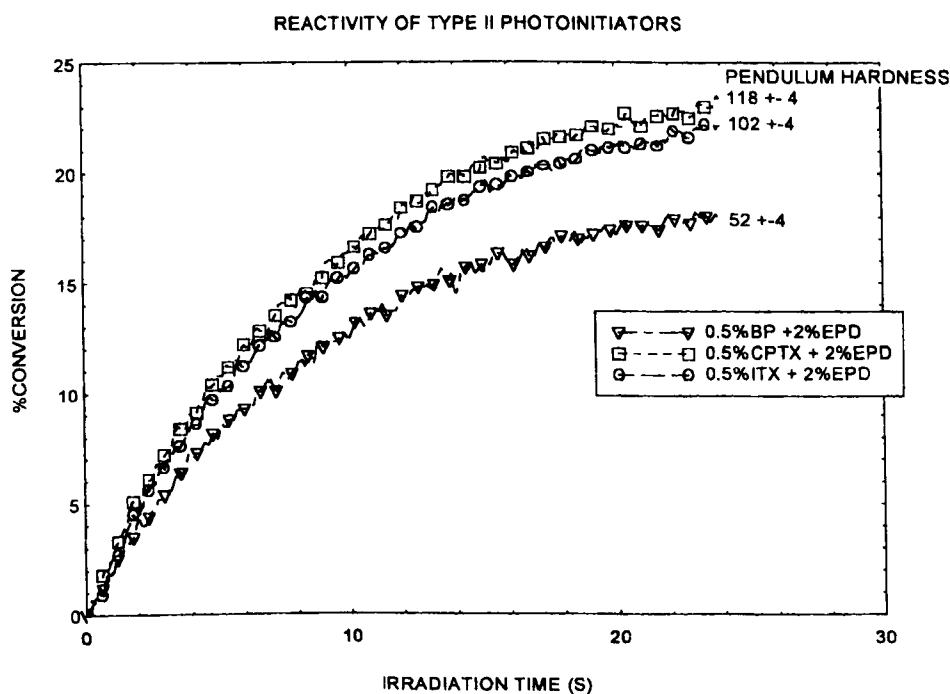


Figure X.7 Reactivity of benzophenone, ITX and CPTX at 2%EPD at 50 microns in the absence of air.

Volatility

The volatility of photoinitiators has been studied in order to ensure that the photoinitiators exhibit acceptable organoleptic properties and to assess the potential contamination of foodstuff.

Benzophenone shows the highest volatility among all the photoinitiators studied. On the other hand, the para phenyl derivative of benzophenone Triganol 12 shows the lowest volatility. The photoinitiators had the following volatility order (Figure X.8):

BP>Quantacure BMS>Esacure TZT>CPTX>Ebecryl P36> Speedcure
MBB>ITX>Speedcure BEM>T12

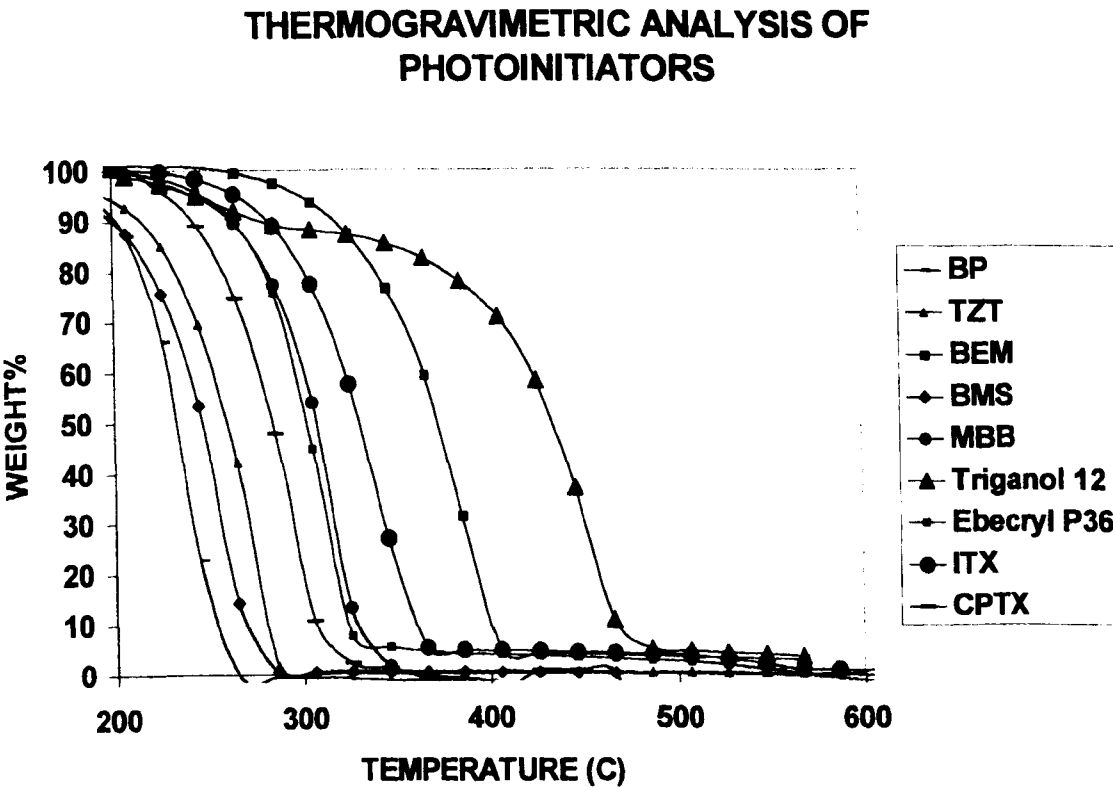


Figure X.8 Thermogravimetric analysis of several Type II photoinitiators.

X.3 Conclusions

The photopolymerisation activities of benzophenone and thioxanthone derivatives are highly dependent upon the degree of substitution of the chromophore, which controls the degree of charge transfer content and the energy of the lowest lying triplet state. Reaction of the photoinitiators occurs by ketyl radical formation due to either electron or proton abstractions in the presence of an efficient donor such as a tertiary amine or by direct hydrogen atom abstraction from the photoexcited triplet state of the chromophore.

Quantacure BMS exhibits a higher polymerisation rate than the other benzophenone derivatives studied due to the charge transfer character of the methylphenylthio substituent and its extended absorption in the near ultraviolet range. The unsubstituted benzophenone shows higher reactivity than its methyl ester derivative Speedcure MBB, and than its phenyl derivative Triganol 12 in the absence of an amine. Speedcure BEM shows a similar reactivity to that of benzophenone and a higher reactivity than its similar counterpart Esacure TZT. Since Esacure TZT is substituted in the ortho position by a methyl group it may exhibit a Norrish Type II intramolecular hydrogen atom abstraction process which will reduce the photoactivity of the lowest excited triplet state of the chromophore toward intermolecular hydrogen atom abstraction.

CPTX showed higher photoreactivity than ITX as reflected by its higher polymerisation rate and hardness. Dehalogenation on photolysis can be responsible for the observed enhanced reactivity of CPTX since the chlorine atom can either form a chloride anion and a thioxanthonyl radical or form an intramolecular hydrogen bond and produce amine hydrochloride and a thioxanthonyl radical for further reaction⁴.

X.4 References

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XI. CHAPTER XI Photochemistry and photopolymerisation activity of several Type I commercial photoinitiators

XI.1 Introduction

Some of the most important commercial Type I far UV photoinitiators have been analysed by various spectroscopic techniques to evaluate the relationship between their photophysical properties and photoinitiation activity for photocuring of commercial acrylated monomers. The type of electronic transitions occurring upon absorption of light are established via UV spectroscopy. Phosphorescence spectroscopy has also been used to study their triplet energies and lifetimes and phosphorescence quantum yields. Microsecond flash photolysis has been undertaken to determine the nature of the free radical (benzoyl radical) intermediates. The free radical intermediate decay kinetics of the different photoinitiators have also been determined, as well as the first and second order rate constants, the transient radical absorption and radical lifetime. Photopolymerisation studies have been undertaken by Real Time Infrared Spectroscopy RTIR at different photoinitiator concentrations in the presence and absence of oxygen using a reactive diluent monomer. Pendulum hardness measurements were also carried out to correlate the film hardness properties with the kinetic results obtained with RTIR. Analysis of the data shows that whilst Type I initiator photoactivity is predominantly dependent upon the absorption maxima of the chromophore, structural influences play an important role in controlling the formation of benzoyl radical intermediates. Triplet lifetimes are very short-lived (<10 ms) indicative of a predominantly $n-\pi^*$ low lying triplet state. Photocuring rates by RTIR appear to be closely linked to benzoyl radical formation while in the presence of oxygen variable quenching effects are observed on the curing reactivity.

XI.2 Results and Discussion

UV spectroscopic results

The π - π^* and n - π^* absorption bands in the UV spectra of the Type I photoinitiators are shown in Tables XI.1 and XI.2 respectively.

Photoinitiator	Methylcyclohexane		Acetonitrile		Isopropanol	
	λ max	log ϵ	λ max	log ϵ	λ max	log ϵ
Irgacure 184	243.5	4.05	243.8	4.00	244.0	4.05
Irgacure 651	248.3	4.13	251.2	4.11	251.8	4.12
Darocur 1173	242.7	4.05	243.0	4.04	244.2	4.00
Irgacure 2959	no soluble		272.4	4.21	275.3	4.21
Genocure MBF	252.8	4.00	254.3	4.05	253.6	4.10
Genocure DEAP	245.5	4.10	246.7	4.11	246.5	4.33

Table XI.1 $\pi \rightarrow \pi^*$ transition of several photoinitiators in different solvent systems.

Photoinitiator	Methylcyclohexane		Acetonitrile		Isopropanol	
	λ max	log ϵ	λ max	log ϵ	λ max	log ϵ
Irgacure 184	*		325.0	1.98	328.3	2.00
Irgacure 651	344.1	2.38	342.1	2.39	337.4	2.42
Darocur 1173	*		*		*	
Irgacure 2959	*		*		*	
Genocure MBF	338.6	1.54	341.0	1.60	336.1	1.64
Genocure DEAP	349.4	1.56	330.1	1.94	327.8	2.19

* the values were too low to be measured accurately.

Table XI.2 $n \rightarrow \pi^*$ transition of several photoinitiators in different solvent systems.

The extinction coefficients of the most important UV transitions of the photoinitiators studied are shown in Table XI.3 corresponding to the main emission lines from the UV irradiation source.

Photoinitiator	253 nm	303 nm	313 nm
Irgacure 184	3.92	1.97	1.91
Irgacure 651	4.11	2.54	2.24
Darocur 1173	3.85	2.26	1.99
Irgacure 2959	3.81	3.46	2.69
Genocure MBF	4.10	2.81	2.21
Genocure DEAP	4.25	2.54	2.23

Table XI.3 Extinction coefficients ϵ (L / mol.cm) of different photoinitiators in isopropanol at the most important emission wavelengths of the medium pressure mercury lamp.

Solvents have the ability to shift the wavelength of ultraviolet light, which can be absorbed. 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 excited states. Polar solvents may not form hydrogen bonds as readily with excited states as with ground states of polar molecules, and 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 will have 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 stabilised more strongly with the excited state than with the ground state. As a result, the transition is shifted to longer wavelengths (bathochromic shift).

UV curing is associated with the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions (or combination of these) that occur between 250 to 400 nm. $\pi \rightarrow \pi^*$ Transitions are shifted to longer wavelengths by an increase of the extension of the conjugation and by an increase in solvent polarity. $\pi \rightarrow \pi^*$ Transitions are also more intense than $n \rightarrow \pi^*$ transitions which are shifted to shorter wavelengths by an increase in solvent polarity.

All the photoinitiators studied exhibit $\pi \rightarrow \pi^*$ transitions below 300 nm with maximum absorption between 240 and 250 nm. The non-substituted benzoyl chromophore has its main absorption ($\pi \rightarrow \pi^*$ transition) around 250 nm and exhibits a low intensity $n \rightarrow \pi^*$ transition band around 340 nm. This is the case of the acetophenone type photoinitiators Irgacure 651 and Genocure DEAP, which absorb at around 250 nm and 245 nm respectively. The α -

hydroxyalkylphenone type photoinitiators Darocur 1173 and Irgacure 184 (non-substituted in the phenyl ring) also involve a $\pi \rightarrow \pi^*$ transition between 242 nm and 244 nm and probably an $n \rightarrow \pi^*$ transition centred at 325 nm. The latter is often extremely weak and difficult to measure accurately.

The α -hydroxyalkylphenone derivative photoinitiator Irgacure 2959 exhibits a transition having a charge transfer character (bathochromic effect) showing an absorption maximum ($\pi \rightarrow \pi^*$ transition) at 275 nm. This is mainly due to substitution by a 2-hydroxyethoxy substituent group (electron donating group) at the para position within the aromatic ring of the benzoyl group.

Phosphorescence results

Phosphorescence quantum yields and triplet lifetimes in methylcyclohexane of the photoinitiators are compared in Table XI.4.

	Wavelength (nm)	$\phi_{\text{phosp.}}$	$\tau_{1/2}$ (ms)
Irgacure 184	435	0.25	2.10
Irgacure 651	444	0.62	2.59
Darocur 1173	431	0.62	3.22
Irgacure 2959*	-	-	-
Genocure MBF	468	0.49	2.99
Genocure DEAP	427	0.61	2.62

*Irgacure 2959 was insoluble in methylcyclohexane

Table XI.4 Phosphorescence quantum yields and triplet lifetimes of type I photoinitiators in methylcyclohexane at 77 K.

Irgacure 651, Darocur 1173 and Genocure DEAP exhibit similar phosphorescence quantum yields ($\phi=0.62$, $\phi=0.62$, $\phi=0.61$ respectively). Darocur 1173 exhibits a slightly longer triplet lifetime ($\tau=3.22$) than the other photoinitiators covered in this study ($\tau<3\text{ms}$). They exhibit higher phosphorescence quantum yields than Genocure MBF ($\phi=0.49$) and Irgacure 184 ($\phi=0.25$, $\tau=2.10\text{ms}$) which exhibits the lowest phosphorescence quantum yields and shortest triplet lifetime among all the other photoinitiators studied. The short phosphorescence lifetimes in all cases is indicative of a predominantly $n-\pi^*$ triplet state with strong oxygen sensitivity.

Flash photolysis results

End of pulse microsecond transient absorption spectra of the photoinitiators in isopropanol are compared in Figures XI.1-3. Absorption maxima and the first and second order rate constants are compared and recorded in Table XI.5. The transient of all the Type I far UV photoinitiators studied follow a first order kinetic decay mechanism evidenced by regression analysis. Type I photoinitiators exhibit transient absorption maxima between 320 and 360 nm, which are all very similar and may be assigned to the benzoyl radical formed by a Norrish Type I α -cleavage reaction¹.

The α -hydroxy-alkyl phenones Darocur 1173, Irgacure 184, Irgacure 2959 and the α - α -dialkoxyacetophenone Genocure DEAP exhibit a weaker end of pulse absorption than Irgacure 651 and Genocure MBF. These lower absorptions indicate a lower radical formation from the former photoinitiators. This particular result is interesting and may possibly be associated in some way with the presence of the α -hydroxy substituent to the carbonyl group forming an intramolecular hydrogen bond. This would have a deactivating influence on the excited state of the chromophore and is evident in all three cases.

The dialkoxyacetophenone Irgacure 651 shows higher radical formation than Genocure DEAP. Irgacure 651 and Genocure DEAP undergo Norrish Type I α -cleavage to give a benzoyl radical and an alkyl radical^{1,2}. Both the benzoyl and the alkyl radicals are considered to initiate the polymerisation process. In the case of Genocure DEAP, the latter fragments to give an alkyl ester of formic acid and an initiating alkyl radical². Norrish Type II intramolecular hydrogen atom abstraction gives a 1,4 radical intermediate, which decomposes to an oxetane by cyclisation, an acetophenone derivative and an aldehyde via elimination. The Norrish Type II reactions do not initiate polymerisation reactions.

Irgacure 651 undergoes a secondary cleavage to give a methyl radical. This radical may also initiate the polymerisation.

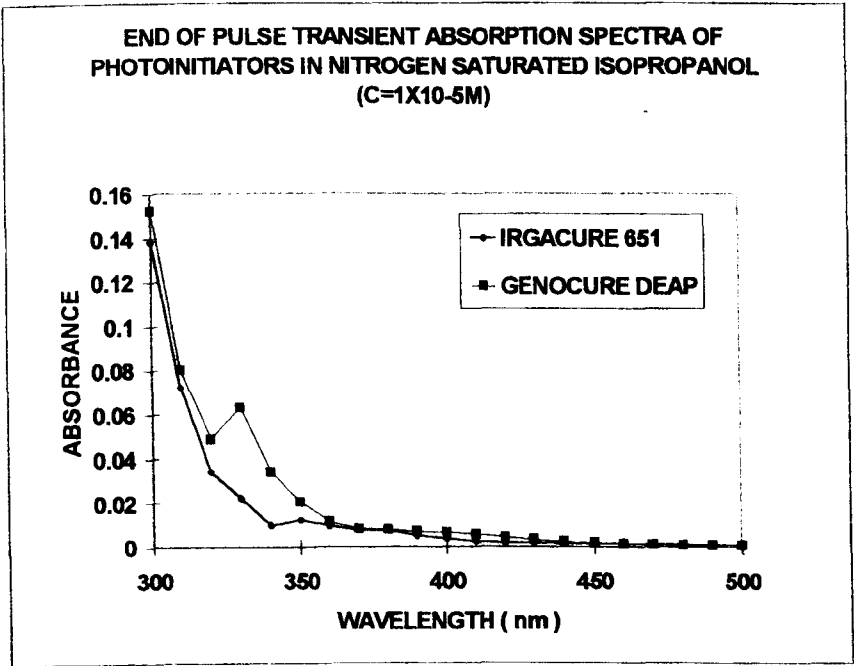


Figure XI.1 End of pulse microsecond transient absorption spectra of photoinitiators in nitrogen saturated isopropanol (C=1x10⁻⁵ M).

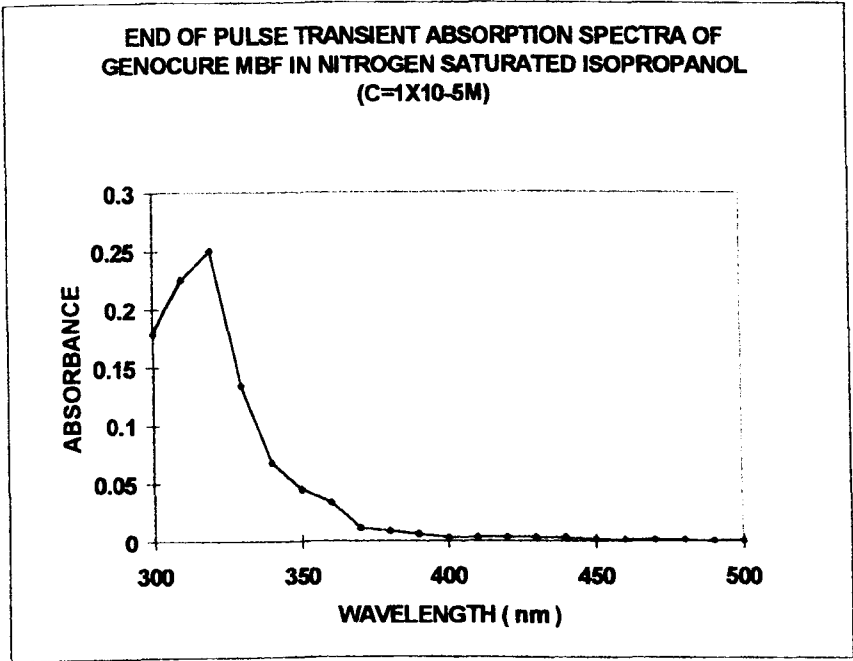


Figure XI.2 End of pulse microsecond transient absorption spectra of photoinitiators in nitrogen saturated isopropanol (C=1x10⁻⁵ M).

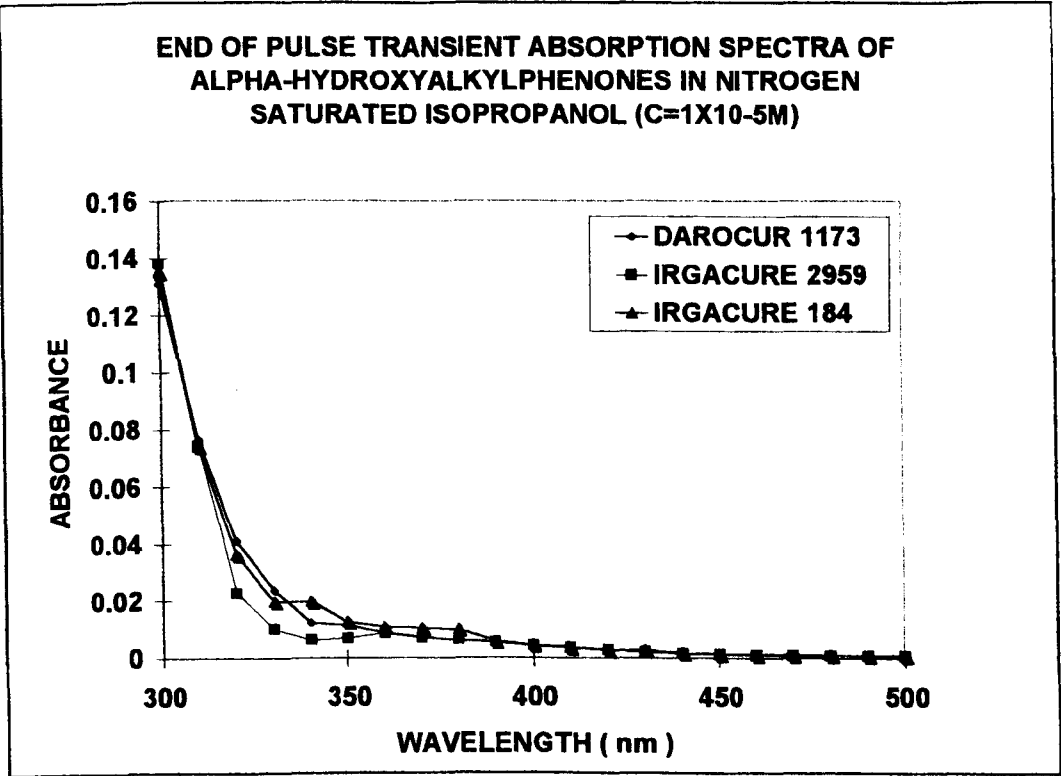


Figure XI.3 End of pulse microsecond transient absorption spectra of photoinitiators in nitrogen saturated isopropanol (C=1x10⁻⁵ M).

	λ (nm)	Abs.	K_1 (s ⁻¹)	τ (s)	R_1	K_2 (s ⁻¹)	τ (s)	R_2
Irgacure 184	340	0.019	11.9	0.08	0.968	977.3	0.0010	0.920
Irgacure 651	330	0.060	9.3	0.10	0.992	228.9	0.0043	0.987
Darocur 1173	340	0.012	9.9	0.10	0.928	1364.1	0.0007	0.884
Irgacure 2959	360	0.008	9.8	0.10	0.948	407.8	0.0024	0.935
Genocure MBF	320	0.250	11.3	0.09	0.991	912.4	0.0010	0.987
Genocure DEAP	350	0.012	11.0	0.09	0.974	1527.6	0.0006	0.945

Table XI.5 End of pulse transient absorption properties by microsecond flash photolysis of Type I photoinitiators in nitrogen saturated isopropanol (C=1*10⁻⁵ M).

Photopolymerisation results

▪ Reactivity of photoinitiators cured with UV light in the absence of air

The photoreactivity of the photoinitiators at 2% w/w in PPTTA cured with UV light in the absence of air are compared in Figure XI.4 and in TableXI.6.

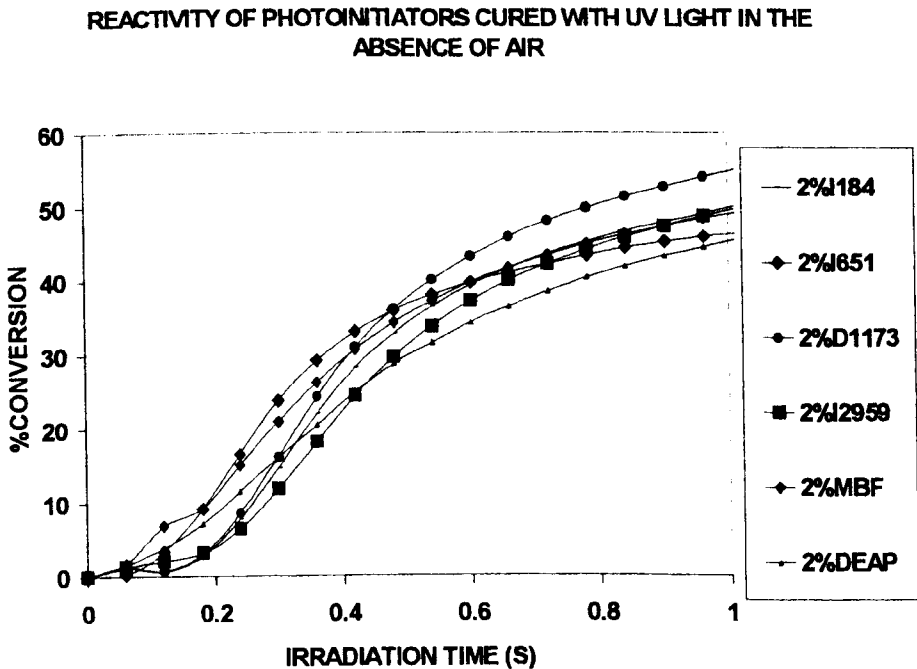


Figure XI.4 Reactivity of photoinitiators by RTIR at 2% w/w photonitiator level in PPTTA cured with UV light (Xenon lamp with a cut off at 390 nm) at 50 microns (covered method) in the absence of air.

	Rp maximum (mol L ⁻¹ s ⁻¹) ± SD	%Conversion (15 s) ± SD	No. of runs	No. of oscillations ± SD
Irgacure 184	1.240 ± 0.028	77.6 ± 0.2	2	126 ± 8
Irgacure 651	1.365 ± 0.180	78.8 ± 3.6	2	145 ± 9
Darocur 1173	1.335 ± 0.160	74.0 ± 2.6	2	145 ± 5
Irgacure 2959	1.147 ± 0.262	78.0 ± 4.2	2	112 ± 9
Genocure MBF	0.965 ± 0.007	70.1 ± 3.5	2	119 ± 7
Genocure DEAP	0.875 ± 0.147	75.0 ± 3.1	4	152 ± 6

TableXI.6 Reactivity of photoinitiators by RTIR at 2% w/w/ photonitiator level in PPTTA cured with UV light (Xenon lamp with a cut off at 390 nm) at 50 microns (covered method) in the absence of air. Pendulum hardness measurements of coatings cured at 50 ft/min with a film thickness of 75 microns (measured after 24 hours).

Irgacure 651 and Darocur 1173 displayed slightly higher polymerisation rate than the other photoinitiators in the absence of air. All the photoinitiators exhibited high acrylate double bond conversion (over 70 % conversion) at long irradiation times (15 s). Pendulum hardness results also indicate that Genocure DEAP, Darocur 1173 and Irgacure 651 gave harder films than Irgacure 184, Genocure MBF and Irgacure 2959 (Table XI.6). Generally, the far UV spectra below 300 nm for all these initiators are similar (Table XI.1). Some exhibit near UV absorptions as shown in Table XI.3 with the Irgacure 651 having the highest extinction coefficients.

▪ **Reactivity of photoinitiators cured with UV light in the presence of air**

The photoreactivity of the photoinitiators at 5% w/w in PPTTA cured with UV light in the absence of air are compared in Figure XI.5 and in Table XI.7. In the presence of air, Irgacure 651 showed the highest polymerisation rate among all photoinitiators studied followed by Genocure MBF, which exhibited the highest conversion at long irradiation time (15 s). In comparison with the above data at 2% w/w in the absence of air (oxygen) the conversions are significantly less even at 5% w/w concentration of initiator. From the phosphorescence analysis the triplet lifetimes are very short-lived indicative of an $n-\pi^*$ triplet state which has strong oxygen sensitivity. In commercial reality however, the removal of oxygen is an expensive process resulting in photocuring processes operating in air.

These results agree with the flash photolysis data, which indicates that a higher radical concentration was formed for Irgacure 651 and Genocure MBF in comparison to the other photoinitiators. Irgacure 184 has a slightly higher reactivity than Darocur 1173 in conformity with a slightly higher radical formation resulting from flash photolysis. Genocure DEAP shows the lowest reactivity reflected by a low polymerisation rate and conversion.

**REACTIVITY OF PHOTOINITIATORS CURED WITH UV LIGHT IN THE
PRESENCE OF AIR**

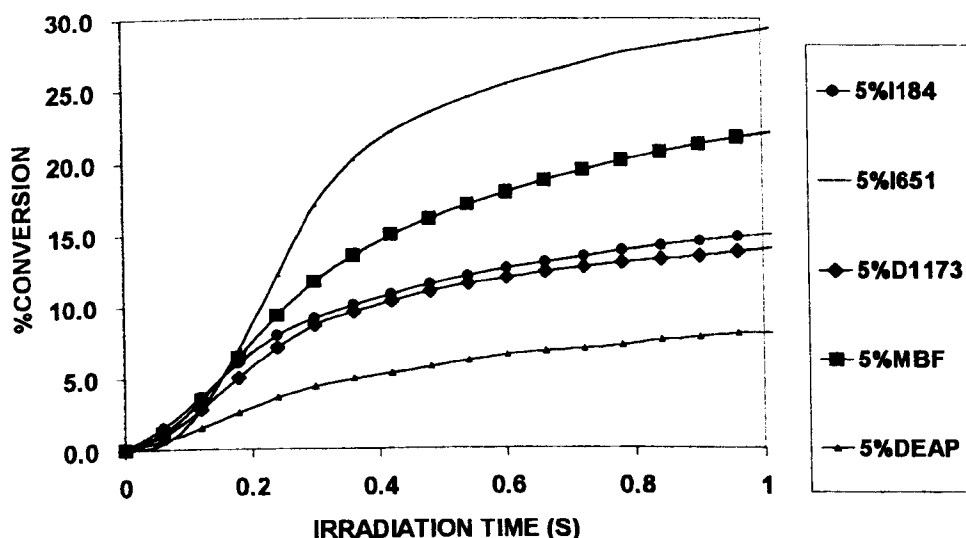


Figure XI.5 Reactivity of photoinitiators by RTIR at 5% w/w photoinitiator level in PPTA cured with UV light (Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

	Rp maximum (mol L ⁻¹ s ⁻¹) ± SD	%Conversion (15 s) ± SD	No. of runs
Irgacure 184	0.412 ± 0.011	37.8 ± 4.0	2
Irgacure 651	0.865 ± 0.008	45.7 ± 1.9	2
Darocur 1173	0.370 ± 0.005	37.2 ± 2.1	2
Irgacure 2959	-	-	-
Genocure MBF	0.511 ± 0.003	52.3 ± 2.2	2
Genocure DEAP	0.181 ± 0.004	20.9 ± 2.6	2

Table XI.7 Reactivity of photoinitiators by RTIR at 5% w/w photoinitiator level in PPTA cured with UV light (Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

XI.3 Conclusions

The majority of the photoinitiators studied exhibit $\pi \rightarrow \pi^*$ transitions with maximum absorptions between 240 and 250 nm. Irgacure 651 exhibits strong far and near UV absorptions associated with both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and is the most effective initiator. The α -hydroxyalkylphenone derivative Irgacure 2959 exhibits a transition having a charge transfer character (bathochromic effect) showing an absorption maximum ($\pi \rightarrow \pi^*$ transition) at 275 nm. This is mainly due to substitution by a 2-hydroxyethoxy substituent at the para position within the aromatic ring of the benzoyl group.

Irgacure 651 and Genocure MBF exhibit stronger end of pulse absorptions than Darocur 1173, Irgacure 184, Irgacure 2959 and Genocure DEAP. Irgacure 651 and Darocur 1173 displayed a higher polymerisation rate than the other photoinitiators in the absence of air. All the photoinitiators showed high acrylate double bond conversion (over 70 %conversion) at long irradiation times (15 s). Pendulum hardness results indicate that Genocure DEAP, Darocur 1173 and Irgacure 651 gave harder films than Irgacure 184, Genocure MBF and Irgacure 2959.

In the presence of air, Irgacure 651 showed the highest polymerisation rate of all the photoinitiators studied followed by Genocure MBF, which exhibited the highest conversion at long irradiation time. These results agree with the flash photolysis results, which indicated that a higher benzoyl radical concentration was formed for Irgacure 651 and Genocure MBF in comparison to the other photoinitiators. Irgacure 184 exhibits a higher reactivity than Darocur 1173 in conformity with a slightly higher radical formation resulting from flash photolysis. Genocure DEAP shows the lowest reactivity reflected by a low polymerisation rate and conversion.

Phosphorescence analysis and oxygen quenching effects on curing rates suggest the presence of some triplet quenching behaviour suppressing the polymerisation rate. For the α -hydroxyalkylphenone initiators low concentrations of benzoyl radicals are formed which may be associated with an intramolecular hydrogen atom transfer process. This may also suppress initiator photoactivity.

XI.4 References

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XII. CHAPTER XII Photochemistry and photopolymerisation activity of several commercial near UV photoinitiators

XII.1 Introduction

Some of the most important commercial near UV photoinitiators in the market were analysed by UV spectroscopy to evaluate the type of electronic transitions occurring upon absorption of light. Phosphorescence spectroscopy was used to study the triplets energy, the phosphorescence lifetimes and the phosphorescence quantum yields of different photoinitiator chromophores. Microsecond flash photolysis has also been undertaken to determine the nature of the free radical intermediates. The free radical intermediate decay kinetics of the different photoinitiators has been studied, as well as the first and second order rate constants, the transient radical absorption intensities and radical lifetimes.

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 thioxanthenes, 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 emission lines from the excitation source.

The volatility of the photoinitiators has also been measured by thermogravimetric analysis.

XII.2 Results and Discussion

UV spectroscopic results

The most important UV transitions of the photoinitiators studied in isopropanol, acetonitrile and methylcyclohexane are shown in Tables XII.1 and XII.2 for the short and long wavelength bands respectively.

PHOTOINITIATOR	Methylcyclohexane		Acetonitrile		Isopropanol	
	λ max	log ϵ	λ max	log ϵ	λ max	log ϵ
Irgacure 369	311.7	4.36	315.0	4.23	317.5	4.31
Irgacure 907	300.4	4.31	302.8	4.27	307.1	4.25
Lucirin TPO	282.0	3.75	288.2	3.62	294.7	3.57
Irgacure 819	291.0	3.96	291.0	3.90	292.7	3.91
Quantacure ITX	255.4	4.58	257.3	4.56	257.0	4.55
Quantacure CPTX	255.4	4.58	257.3	4.51	256.8	4.59

Table XII.1 $\pi \rightarrow \pi^*$ Transitions of photoinitiators in different solvents.

PHOTOINITIATOR	Methylcyclohexane		Acetonitrile		Isopropanol	
	λ max	log ϵ	λ max	log ϵ	λ max	log ϵ
Irgacure 369	*		*		*	
Irgacure 907	*		*		*	
Lucirin TPO	381.8	2.61	380.4	2.72	379.9	2.76
Irgacure 819	371.4	2.93	368.7	2.97	367.9	2.98
Quantacure ITX	380.7	3.85	381.8	3.84	382.3	3.79
Quantacure CPTX	385.0	3.81	385.0	3.75	388.0	3.78

***The $n \rightarrow \pi^*$ transitions were buried under the more intense $\pi\text{-}\pi^*$ transitions**

Table XII.2 $n \rightarrow \pi^*$ Transitions of photoinitiators in different solvents.

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 XII.1 and XII.2. The extinction coefficients of the respective photoinitiators corresponding to the emission output lines of the spectral emission source are also shown in Table XII.3 for activation comparisons.

PHOTOINITIATOR	253 nm	303 nm	313 nm	365 nm	404 nm
Irgacure 369	3.53	4.16	4.29	3.34	1.90
Irgacure 907	3.09	4.24	4.22	2.06	
Lucirin TPO	3.80	3.52	3.39	2.70	2.33
Irgacure 819	3.97	3.89	3.81	2.97	2.71
Quantacure ITX	4.60	3.51	2.57	3.63	3.32
Quantacure CPTX	4.55	3.82	3.99	3.57	3.62

Table XII.3 Extinction coefficients ϵ (l/mol.cm) of different photoinitiators in isopropanol at the most important emission wavelengths of the medium pressure mercury lamp.

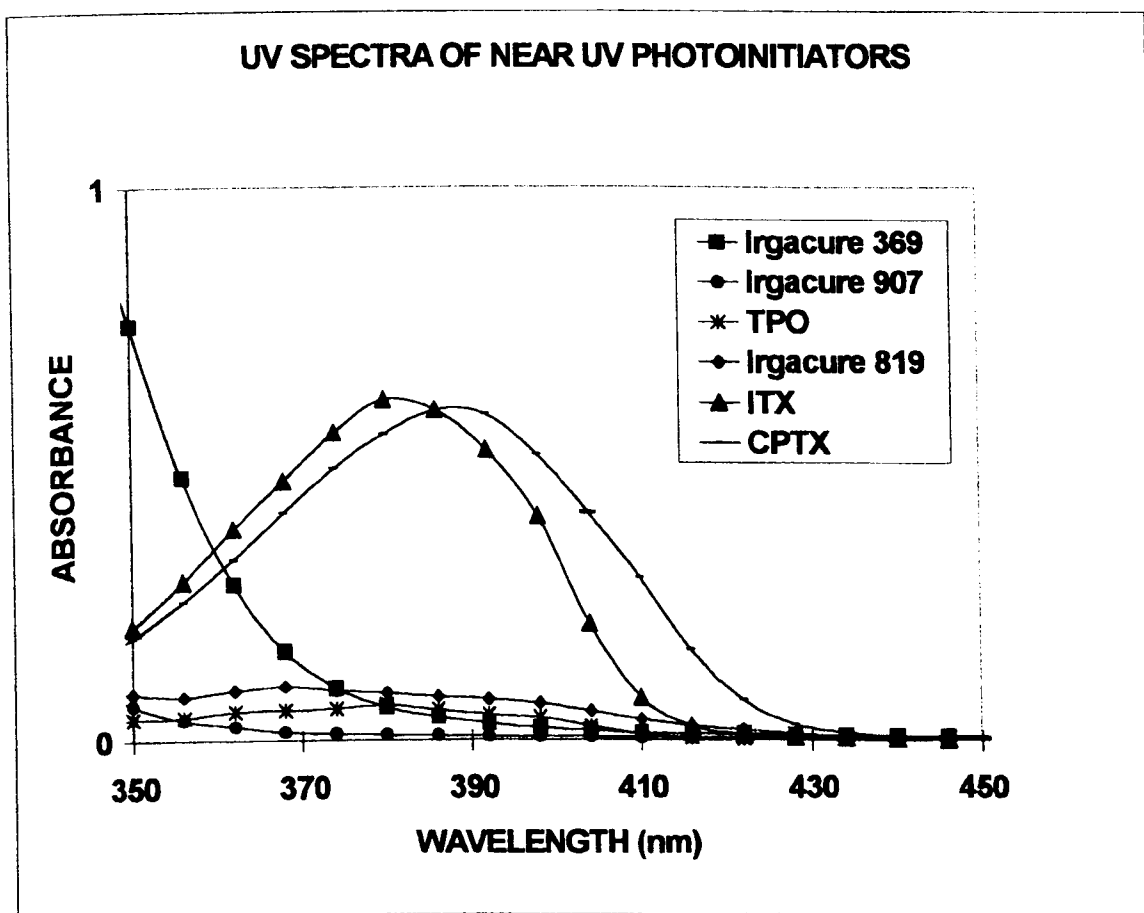


Figure XII.1 UV absorption spectra of photoinitiators in isopropanol ($C=1.0 \times 10^{-4}$ M).

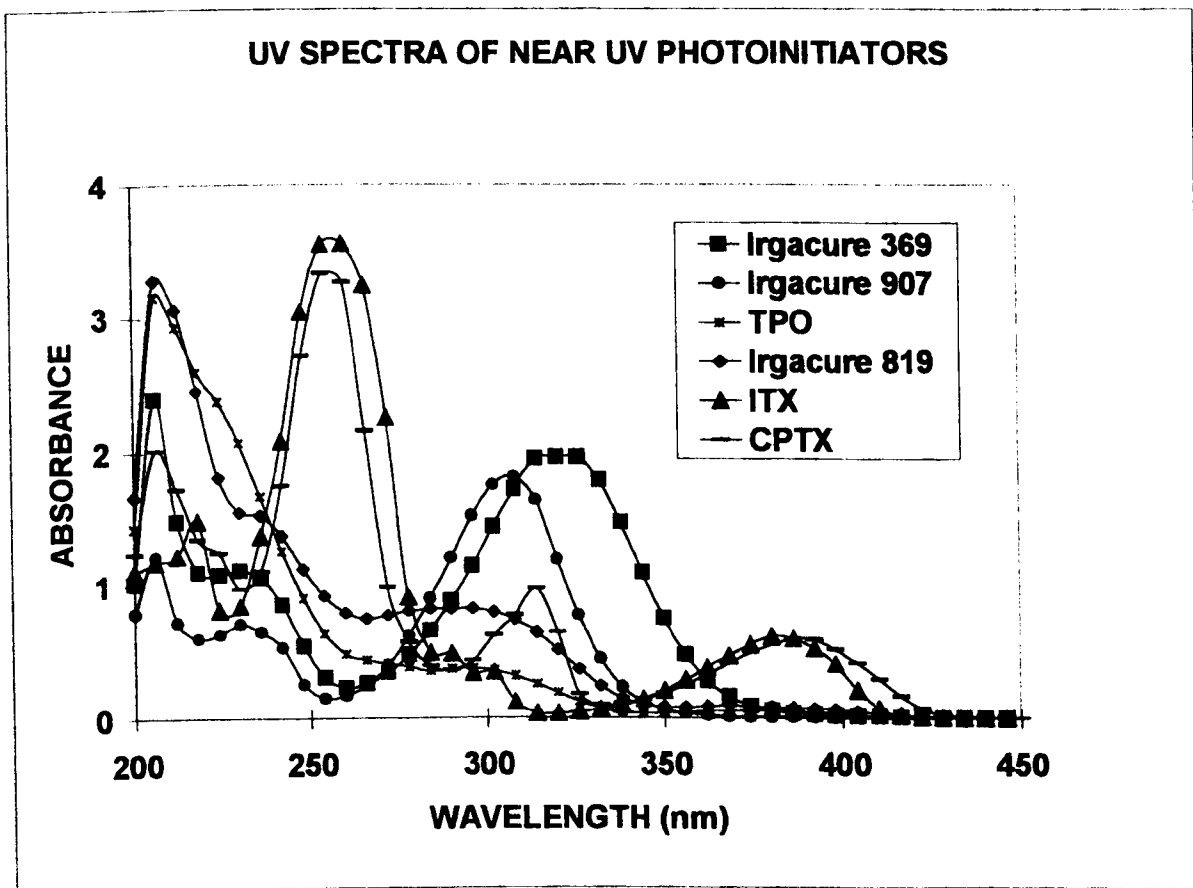


Figure XII.2 UV absorption spectra of photoinitiators in isopropanol ($C=1.0 \times 10^{-4}$ M).

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. The α -aminoalkylphenone derivative type photoinitiators Irgacure 369 and Irgacure 907 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.

Acylphosphine oxides (Lucirin TPO and Irgacure 819) 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 thioxanthenes, there is a variable red/blue shift in the absorption maxima with increasing solvent polarity, indicative of strongly mixed $n\pi^*/\pi\pi^*$ states. CPTX shows a more pronounced red shifted maximum than ITX may be due to inductive effect by the chlorine atom substituted in the 1-position and by resonance by the propoxy substituent in the para position.

Phosphorescence results

Phosphorescence quantum yields in methylcyclohexane of several near UV photoinitiators are compared in Table XII.4.

PHOTOINITIATOR	Wavelength (nm)	$\phi_{\text{phosp.}}$	$\tau_{1/2}$ (ms)
Irgacure 369	466	0.27	11.2
Irgacure 907	438	0.69	55
Lucirin TPO	453	0.20	11.3
Irgacure 819	516	0.13	5.9
Quantacure ITX	450	0.76	47.1
Quantacure CPTX	484	0.43	53.6

Table XII.4 Phosphorescence quantum yields and triplet lifetimes of photoinitiators in methylcyclohexane at 77 K.

Irgacure 907 exhibits higher phosphorescence quantum yields and longer triplet lifetime than the other Type I near UV photoinitiators studied. Irgacure 819 exhibits lower phosphorescence quantum yields and shorter triplet lifetime than TPO and Irgacure 369.

CPTX displays a lower phosphorescence quantum yield and a longer lived red shifted triplet state ($\phi_p=0.43$ $\tau=53.6$ ms $\lambda=484$ nm) than ITX ($\phi_p=0.76$ $\tau=47.2$ ms $\lambda=450$ nm) in methylcyclohexane.

Flash photolysis results

End of pulse transient absorption spectra of the photoinitiators in isopropanol are compared in Figures XII.3-5. Absorption maxima and the first and second order rate constants are compared and recorded in Table XII.5.

Irgacure 369 and Irgacure 907 exhibit higher maximum absorptivity spectra than TPO and Irgacure 819, resulting from the formation of a high concentration of transient radical intermediates.

TPO and Irgacure 819 exhibit red shifted absorption spectra in comparison to Irgacure 369 and Irgacure 907. Irgacure 819 exhibits a higher maximum absorptivity and consequently a higher radical formation than TPO. All the Type I near UV photoinitiators follow a first order kinetic decay mechanism evidenced by regression analysis. CPTX also follow a unimolecular deactivation mechanism since dehalogenation (C-Cl bond cleavage) occurs as indicated by solution photolysis studies¹.

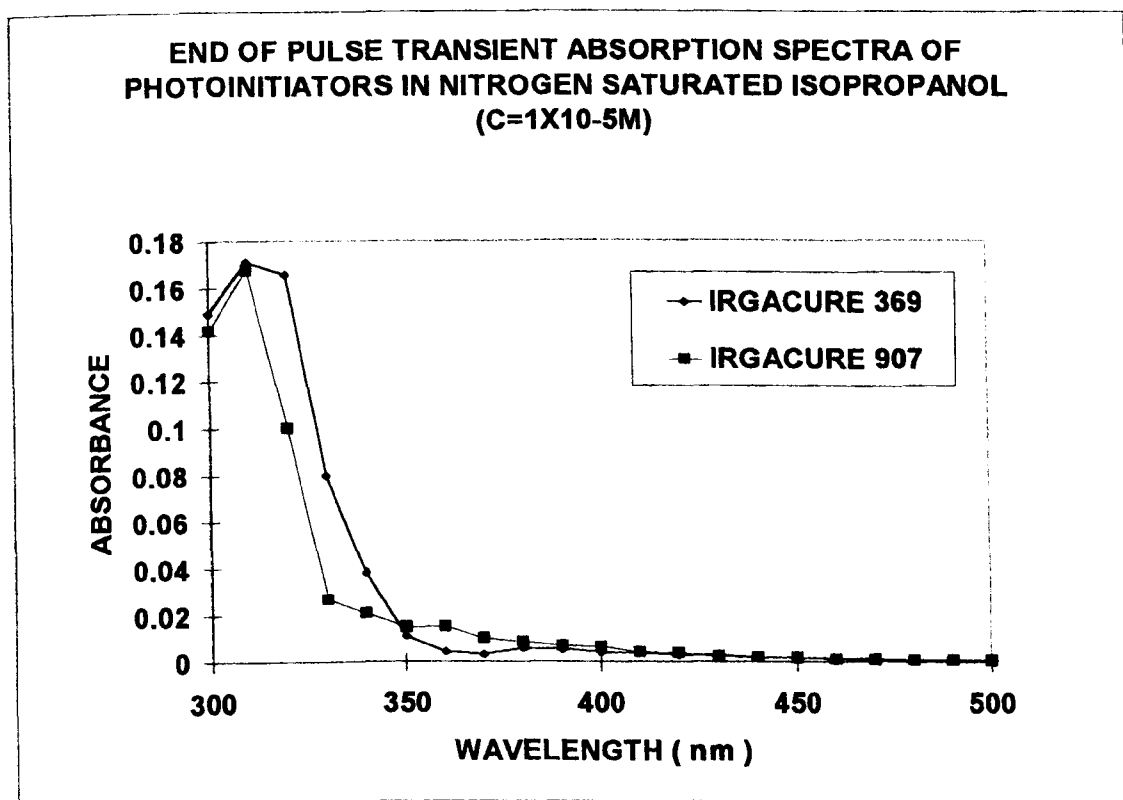


Figure XII.3 End of pulse transient absorption spectra of photoinitiators in nitrogen saturated isopropanol (C=1x10⁻⁵ M).

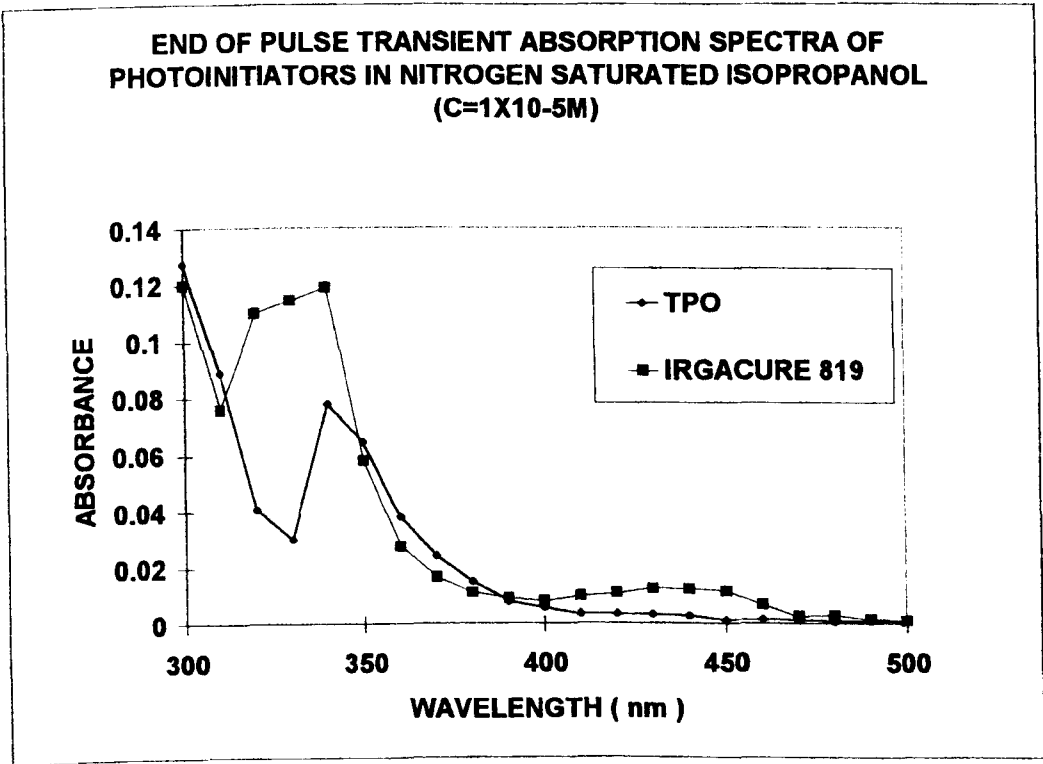


Figure XII.4 End of pulse transient absorption spectra of photoinitiators in nitrogen saturated isopropanol (C=1x10⁻⁵ M).

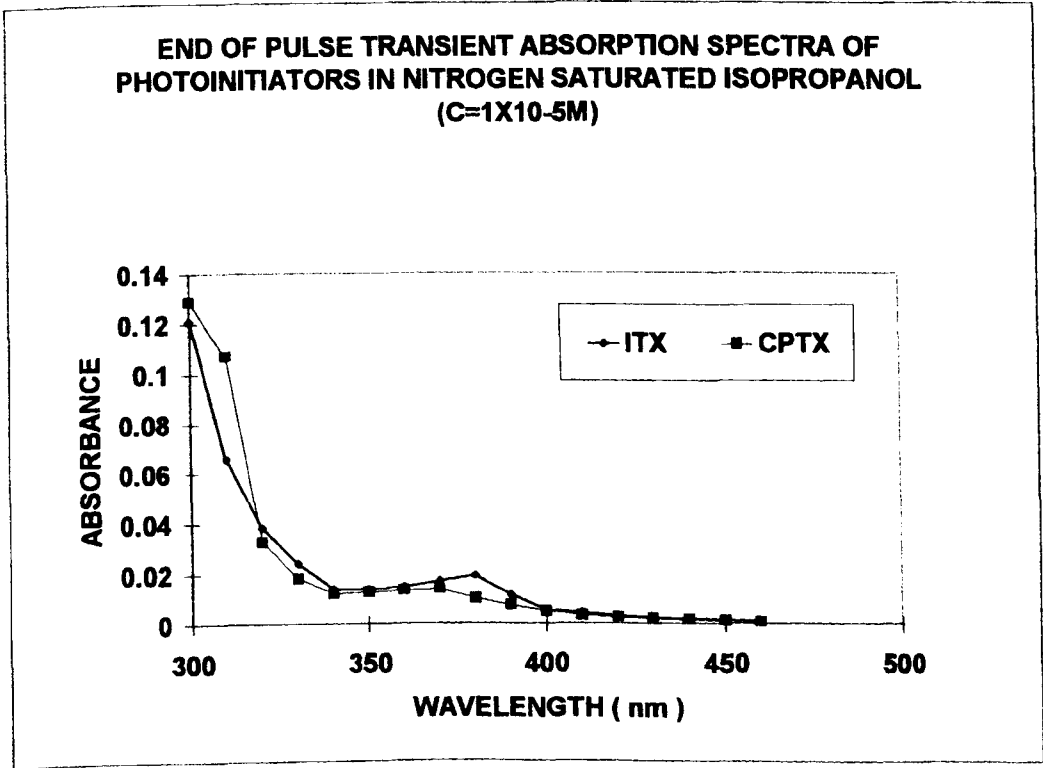


Figure XII.5 End of pulse transient absorption spectra of photoinitiators in nitrogen saturated isopropanol (C=1x10⁻⁵ M).

	λ (nm)	Abs.	K_1 (s^{-1})	$\tau_{1/2}$ (s)	R_1	K_2 (s^{-1})	$\tau_{1/2}$ (s)	R_2
Irgacure 369	310	0.172	10.2	0.10	0.983	116.8	0.0085	0.969
Irgacure 907	310	0.168	10.0	0.10	0.985	77.1	0.0130	0.967
Lucirin TPO	240	0.126	12.5	0.08	0.982	327.5	0.0030	0.979
Irgacure 819	340	0.125	15.8	0.06	0.997	238.0	0.0042	0.987
Quantacure ITX	380	0.019	15.2	0.06	0.979	1485.8	0.0006	0.986
Quantacure CPTX	370	0.013	8.8	0.11	0.961	1065.9	0.0009	0.933

Table XII.5 End of pulse transient absorption by flash photolysis of photoinitiators in nitrogen saturated isopropanol ($C=1 \times 10^{-5}$ M).

The slightly higher absorption band at 370 and 380 nm of ITX in comparison to CPTX reflect a higher ketyl radical formation for ITX than for CPTX formed by direct abstraction of a hydrogen atom from the solvent by the excited state of the thioxanthone chromophore^{2, 3}. The higher radical lifetime of CPTX in comparison to ITX can be responsible for the higher polymerisation rate of CPTX observed in photopolymerisation experiments⁴ in the presence of an electron/proton donor such as tertiary amines.

Photopolymerisation 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 XII.6 and XII.7 showing Rp and conversion values at 0.5 and 2.5% w/w of the initiators.

	0.5%PHOTOINITIATOR UV LIGHT			0.5%PHOTOINITIATOR VISIBLE LIGHT		
	Rp maximum (mol L s ⁻¹) ± SD	%Conversion (15s) ± SD	No of runs	Rp maximum (mol L s ⁻¹) ± SD	%Conversion (15 s) ± SD	No of runs
I369	1.224 ± 0.020	41.9 ± 0.7	2	0.002 ± 0.001	1.6 ± 0.2	2
I907	1.064 ± 0.007	47.6 ± 2.1	3	0.000 ± 0.000	1.3 ± 0.2	2
TPO	0.641 ± 0.085	31.6 ± 0.9	2	0.193 ± 0.023	14.3 ± 0.2	2
I819	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 XII.6 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.

	2.5%PHOTOINITIATOR UV LIGHT			2.5%PHOTOINITIATOR VISIBLE LIGHT		
	Rp maximum (mol L s ⁻¹) ± SD	%Conversion (15s) ± SD	No of runs	Rp maximum (mol L s ⁻¹) ± SD	%Conversion (15 s) ± SD	No of runs
I369	2.164 ± 0.182	71.1 ± 0.6	2	0.473 ± 0.030	39.2 ± 0.7	2
I907	1.508 ± 0.148	71.2 ± 1.7	3	0.002 ± 0.001	3.1 ± 0.9	3
TPO	1.374 ± 0.117	60.6 ± 1.0	3	0.958 ± 0.046	42.6 ± 2.2	3
I819	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

Table XII.7 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.

Figures XII.6 and XII.7 show the corresponding rate curves from the actual RTIR experiments. Irgacure 369 displayed the highest photoinitiation activity (polymerisation rate and conversion) in the presence of air at two different photoinitiator concentrations. Irgacure 907 showed higher reactivity than TPO and Irgacure 819 possibly due to the higher degree of oxygen inhibition typically found in phosphine oxide radicals at low film thickness in the presence of air. Irgacure 819 exhibited a similar polymerisation rate and conversion to TPO.

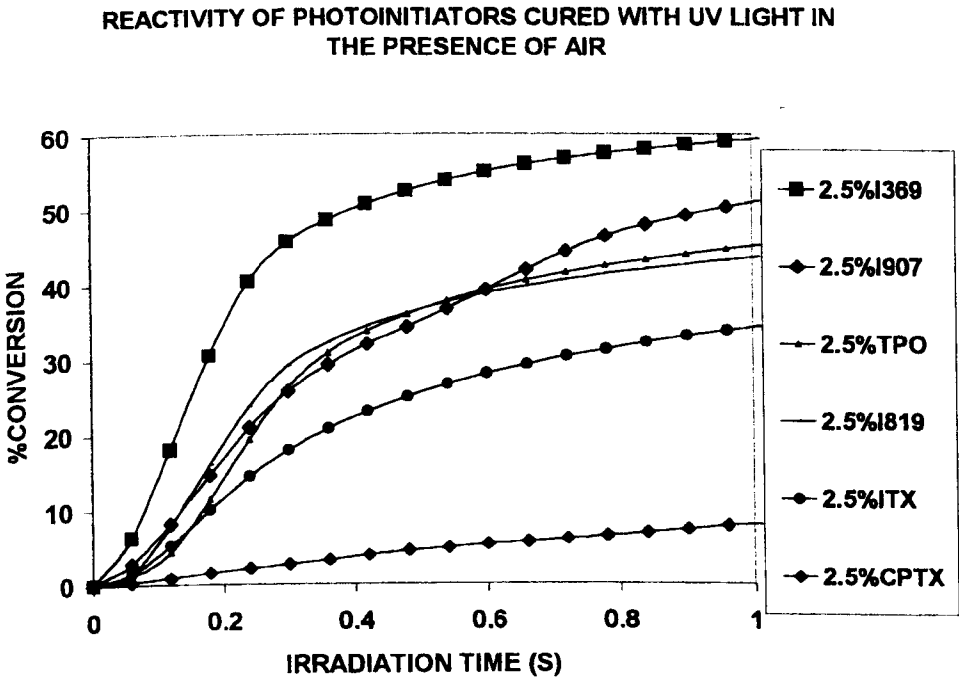


Figure XII.6 Reactivity of photoinitiators by RTIR at 0.5 % w/w photoinitiator level in 50/50 Ebecryl 870/GPTA cured with UV light (Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

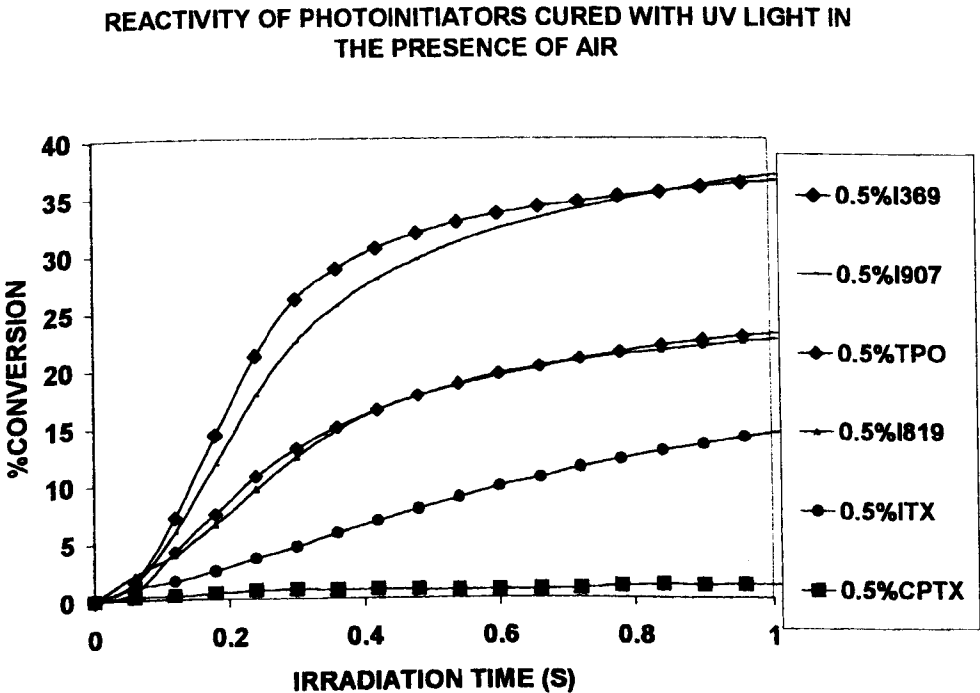


Figure XII.7 Reactivity of photoinitiators by RTIR at 2.5% w/w photoinitiator level in 50/50 Ebecryl 870/GPTA cured with UV light (Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

Irgacure 369 exhibits a very strong near UV transition with a broad weak tail extending beyond 400 nm. As it can be seen from the extinction coefficients in Table XII.3 for the source emission lines, the Irgacure 369 exhibits the highest values followed by the Irgacure 907. The TPO and Irgacure 819 exhibit lower extinction coefficients and comparable activities in the near UV.

The thioxanthone photoinitiators showed much less activity in this system with ITX exhibiting higher reactivity than CPTX in the absence of a tertiary amine. Although the thioxanthenes 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 XII.6 and XII.7 showing the R_p and % conversion values. Figures XII.8 and XII.9 show the corresponding rate curves from the RTIR plots. Generally, the conversions were all very low under visible light irradiation.

However, Irgacure 819 displayed the highest photoinitiation activity (polymerisation rate and conversion) in the presence of air at two different photoinitiator concentrations. Above 400 nm the Irgacure 819 exhibits the strongest extinction coefficients of the photofragmenting initiators as seen by the data in Table XII.3. TPO showed a higher polymerisation rate than ITX. On the other hand, at long irradiation times ITX gave higher conversion than TPO and Irgacure 819 at low photoinitiator concentration (0.5%). ITX exhibited a higher polymerisation rate than both Irgacure 369 and Irgacure 907 due to the low absorptivity of these photoinitiators in the visible region. Obviously, both the thioxanthenes exhibit some degree of hydrogen atom abstraction ability under visible light irradiation.

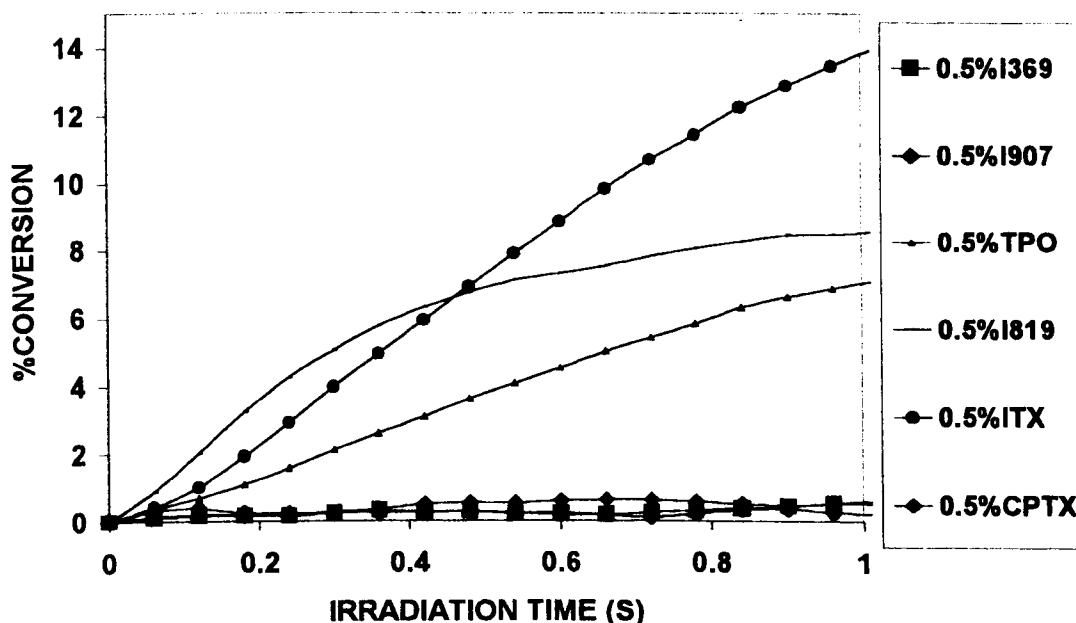
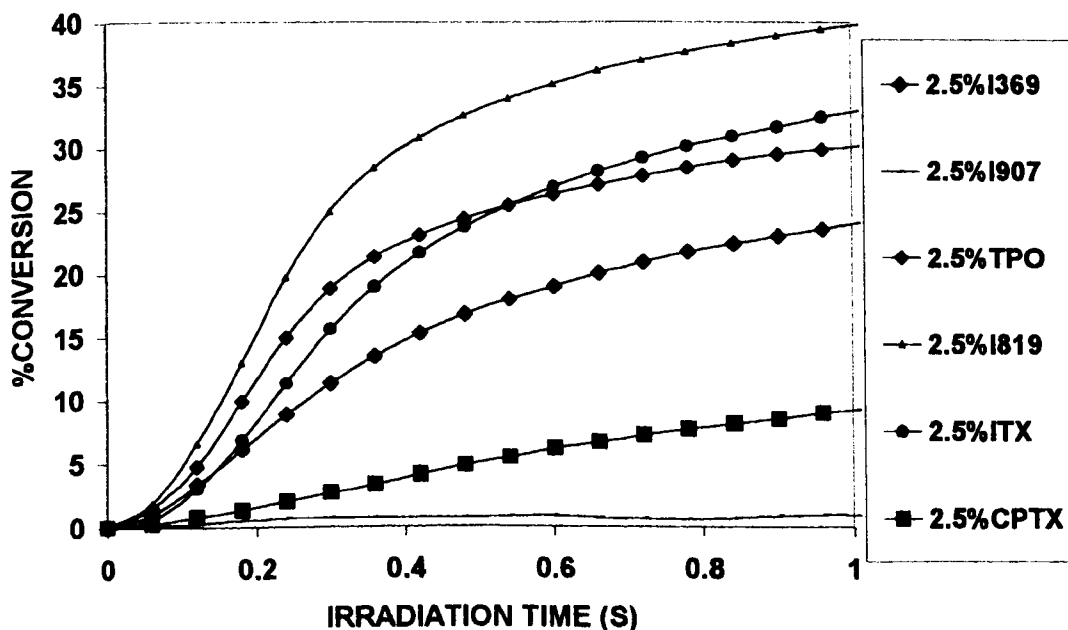


Figure XII.8 Reactivity of photoinitiators by RTIR at 0.5% w/w photoinitiator level in 50/50 Ebecryl 870/GPTA cured with Visible light

REACTIVITY OF PHOTOINITIATORS CURED WITH VISIBLE LIGHT
 IN THE PRESENCE OF AIR



(Xenon lamp with a cut off at 390 nm) at 6 microns in the presence of air.

Figure XII.9 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.

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 XII.8-11 for black, cyan, magenta and yellow pigmented inks. These tables show both R_p and % conversion values. Figures XII.10 to XII.13 show the corresponding rate curves from the RTIR plots. There was no observable cure under visible light exposure.

4.5%PHOTOINITIATOR IN A BLACK INK			
	R_p maximum (mol L s^{-1}) $\pm$ SD	%Conversion (15 s) $\pm$ SD	No of runs
I369	1.978 ± 0.077	70.2 ± 0.03	2
I907	0.580 ± 0.003	54.3 ± 0.7	2
TPO	0.381 ± 0.002	20.8 ± 0.6	2
I819	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 XII.8 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 CYAN INK			
	R_p maximum (mol L s^{-1}) $\pm$ SD	%Conversion (15 s) $\pm$ SD	No of runs
I369	2.129 ± 0.375	75.6 ± 2.1	2
I907	1.163 ± 0.064	66.5 ± 1.8	2
TPO	0.993 ± 0.015	38.2 ± 0.8	2
I819	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

Table XII.9 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 MAGENTA INK			
	R_p maximum (mol L s^{-1}) $\pm$ SD	%Conversion (15 s) $\pm$ SD	No of runs
I369	1.837 ± 0.104	80.9 ± 0.5	2
I907	1.455 ± 0.001	72.2 ± 0.7	2
TPO	1.296 ± 0.169	49.5 ± 0.7	2
I819	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 XII.10 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 YELLOW INK			
	Rp maximum (mol L s ⁻¹) ± SD	%Conversion (15 s) ± SD	No of runs
Irgacure 369	2.53 ± 0.009	76.9 ± 0.1	2
I907	1.328 ± 0.241	70.4 ± 1.6	2
TPO	1.334 ± 0.100	51.7 ± 2.4	2
I819	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

Table XII.11 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.

Irgacure 369 displayed the highest photoinitiation activity (polymerisation rate and conversion) in the presence of air in the four colour process inks studied. Irgacure 907 showed higher conversion at long irradiation times than TPO and Irgacure 819 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, Irgacure 819 exhibited higher maximum polymerisation rate than both Irgacure 907 and TPO. 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 thioxanthenes 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 reflected by its low conversion below 10% after 15 seconds of irradiation time.

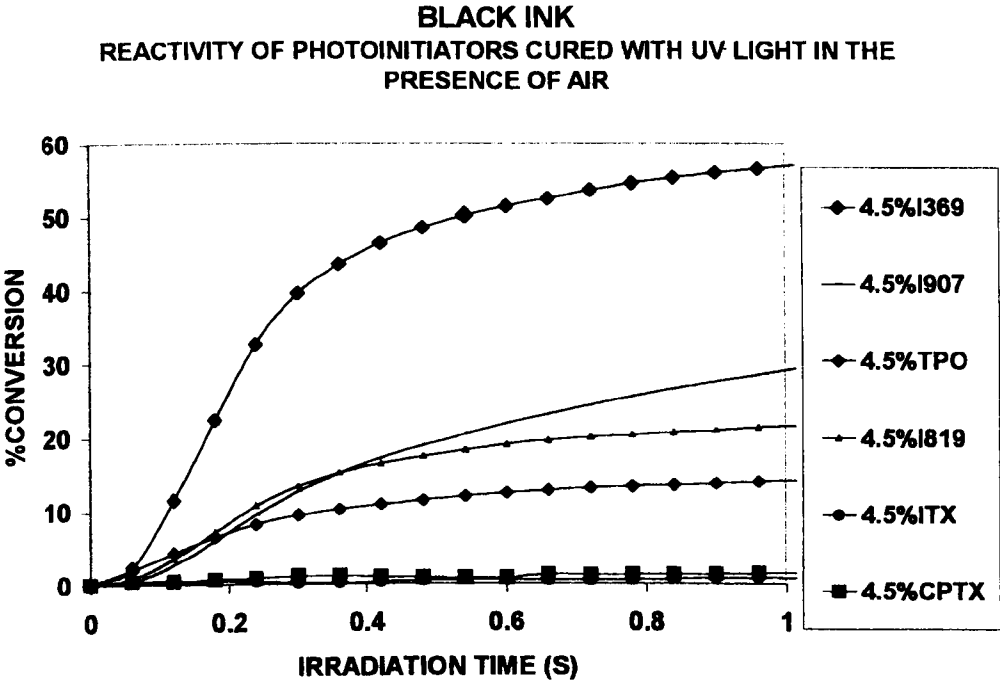


Figure XII.10 Reactivity of photoinitiators in a black ink (2%w/w pigment black 7) cured with UV light at 6 microns in the presence of air.

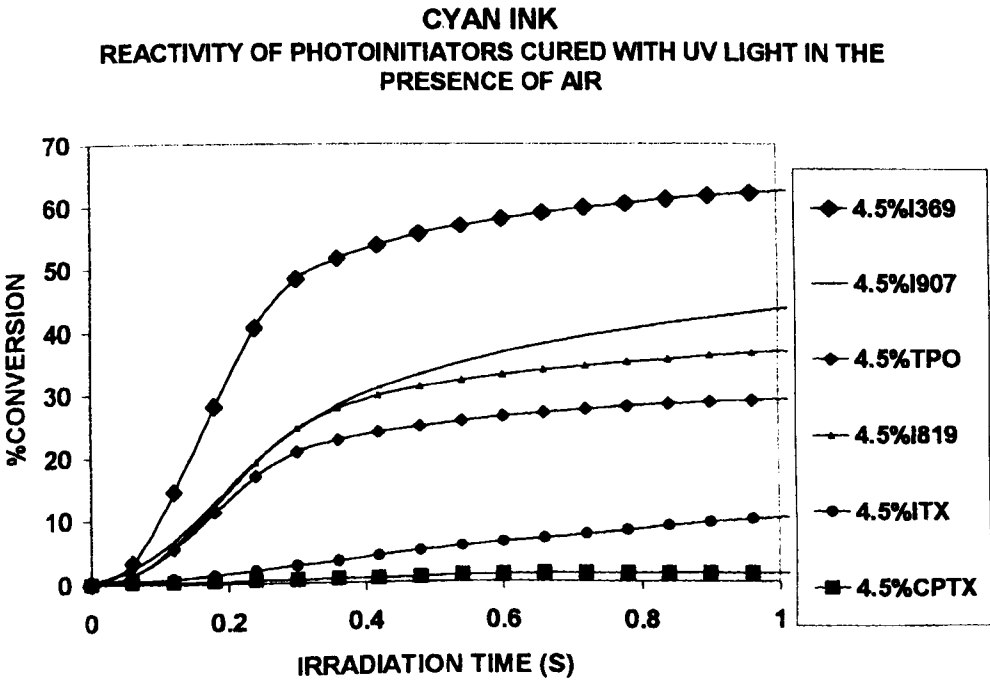


Figure XII.11 Reactivity of photoinitiators in a cyan ink (2%w/w pigment blue 15:3) cured with UV light at 6 microns in the presence of air.

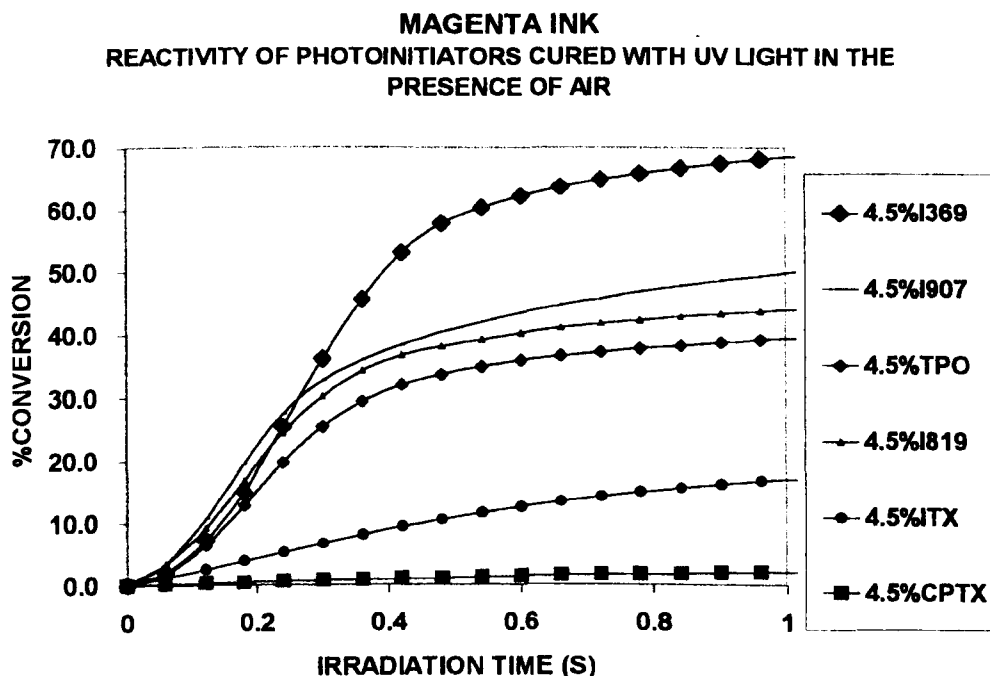


Figure XII.12 Reactivity of photoinitiators in a magenta ink (2%w/w pigment red 57:1) cured with UV light at 6 microns in the presence of air.

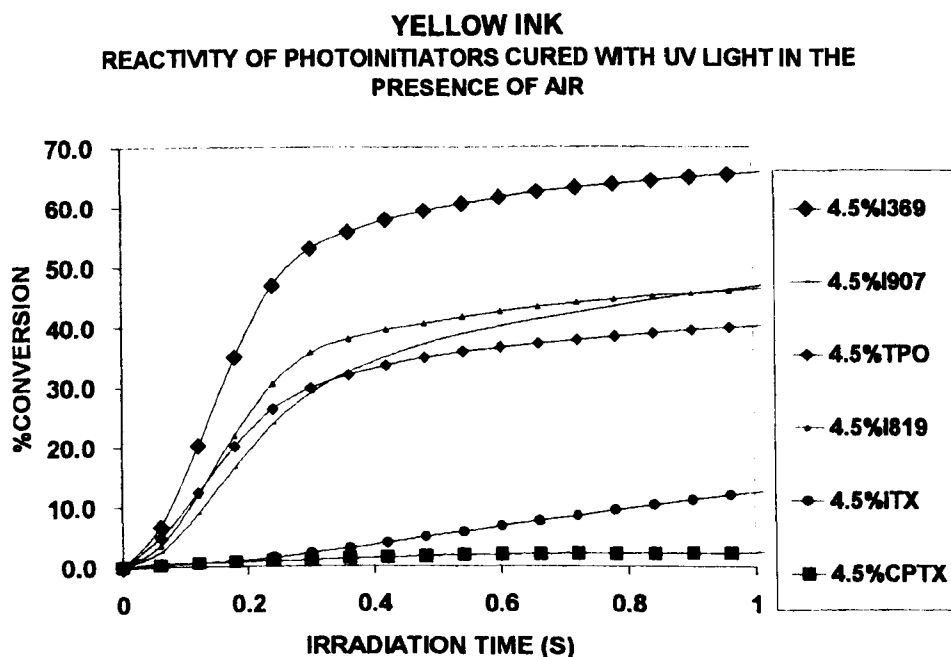


Figure XII.13 Reactivity of photoinitiators in a yellow ink (2% w/w pigment yellow 13) cured with UV light at 6 microns in the presence of air.

Volatility

All the photoinitiators studied showed very low volatility until 200°C. TPO showed slightly higher volatility than the other photoinitiators studied. The photoinitiators had the following volatility order (Figure XII.14):

TPO > CPTX $\cong$ Irgacure 369 $\cong$ Irgacure 819 > Irgacure 907 $\cong$ ITX

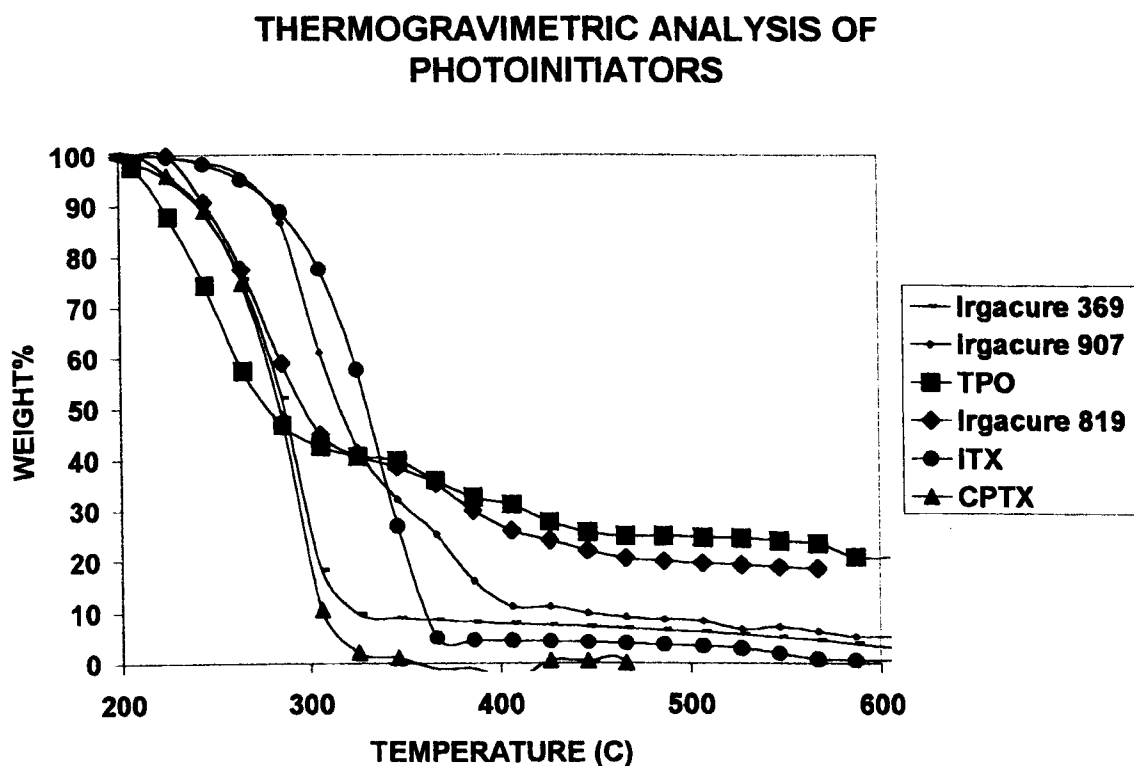


Figure XII.14 Volatility of near UV photoinitiators measured by thermogravimetric analysis.

XII.3 Conclusions

The photopolymerisation activities of the most important commercial near UV photoinitiators are highly dependent upon 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 Irgacure 369 and Irgacure 907 exhibit higher initiation efficiency than acylphosphine oxide type photoinitiators such as Irgacure 819 and TPO 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, Irgacure 819 displayed the highest initiation efficiency in films cured with visible light. Irgacure 819 showed higher polymerisation rate than TPO and ITX. Even in the absence of amine, ITX exhibited a similar (slightly lower) reactivity than TPO, which makes possible the design of cost effective photoinitiation systems. Irgacure 369 and Irgacure 907 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 Irgacure 369 exhibited the highest reactivity among all the photoinitiators studied. Irgacure 819 showed slightly higher polymerisation rate than Irgacure 907 whilst it gave lower conversion at long irradiation times. Irgacure 819 is also more reactive than TPO 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 higher photoreactivity (polymerisation 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 state energy. Consequently, the direct hydrogen atom abstraction ability might decrease and justify its lower reactivity in the absence of an efficient electron/proton donor.

XII.4 References

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2. Allen, N. S., Catalina, F., Green, P. N. and Green, W. A., *Eur. Polym. J.*, **21** (1985) 841.
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XIII. CHAPTER XIII Design of synergistic near eutectic photoinitiator blends by Mixture Design

XIII.1 Introduction

The optimisation of photoinitiator systems used in UV printing inks and coatings has been carried out by means of Design of Experiments DOE (Mixture Designs). Mixture Designs have been used to improve the reactivity of photoinitiator blends in order to design cost effective, synergistic, near eutectic photoinitiator blends for curing UV printing inks. Both the reactivity and bulk stability of photoinitiator blends have been studied. The photoinitiator blends consisted of three commercial photoinitiators benzophenone (BP), isopropyl thioxanthone (ITX), which are Type II photoinitiators and benzil dimethyl ketal (BDK), a Type I photoinitiator. Ethyldimethylamino benzoate (EPD), a commercial aromatic tertiary amine, which is an efficient electron/proton donor was used to enhance the reactivity of the Type II photoinitiators.

The results highlighted that the EPD content plays a crucial role in the final reactivity of the photoinitiator blends. Relatively high proportions of EPD with respect to the overall centroid (25% each component) were required to design photoinitiator blends of enhanced reactivity. These results agreed with mechanistic studies published in the literature where it was observed that with Type II photoinitiators, such as BP and ITX, the tertiary amine synergist acted as the main initiating radicals of the polymerisation process.

On the other hand, from the stability point of view, high proportions of EPD decreased the stability (eutectic properties) of the photoinitiator blends. Benzophenone BP showed good solvating properties in the photoinitiator blends and had the highest influence on the stability of the photoinitiators studied. Relatively high proportions of BP enhanced the stability of photoinitiator blends. Multiple response optimisation for stability and reactivity resulted in photoinitiator blends that exhibited both enhanced reactivity and stability.

The selection of a photoinitiator blend is of prime importance in the design of UV curing systems, since the polymerisation 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.

Reactivity and bulk stability of the photoinitiator blends are the most important factors to bear in mind. One of the most important advantages of using near eutectic photoinitiator blends is speeding up the manufacturing process. The ink manufacturing process of a printing ink company consisted of dissolving the single solid photoinitiators in the vehicle system (resins and acrylates) before milling the pigments. This was a time consuming process, which limited the increase of the production output. Photoinitiator blends should be carefully designed because of the natural tendency of the photoinitiators to crystallise from the photoinitiator blend. By carefully designing near eutectic photoinitiator blends is possible to reach a compromise between reactivity and bulk stability.

Two important aspects are especially important to design cost effective formulations:

- The selection of cost effective photoinitiators
- The determination of the "ideal" photoinitiator content in the photoinitiator blend to obtain reactive stable photoinitiator eutectic blends.

XIII.2 Experimental

XIII.2.1 Materials

Speedcure BP (Benzophenone) was supplied by Lambson, Quantacure ITX (mixture of 2- and 4-isopropyl-thioxanthone isomers) and Quantacure EPD (Ethylidimethylamino benzoate) were supplied by Great Lakes. Irgacure 651 (BDK benzyl dimethyl ketal) was supplied by Ciba. The reactive diluent used Actilane 440 (PPTTA alkoxyated tetrafunctional acrylate monomer) was supplied by Akcros Ltd, Manchester.

XIII.2.2 Preparation of photoinitiator blends

The solid photoinitiators BDK, BP, ITX, and EPD at specific ratios (see mixture design procedure) were heated until dissolution in a recipient whilst stirring. The liquid photoinitiator blends (100 g) were left at 8 °C. Stability of the samples was evaluated by measuring photoinitiator crystallisation after certain time. Those samples, which apparently showed stability, were seeded (nuclei formation) by rubbing the metallic wall of the recipient with a spatula in order to test their stability. The samples were left at 8 °C for another week. Scale up was done at 2 Kg batches to evaluate the stability of the eutectic photoinitiator blends. A response value of 0 was assigned to those photoinitiator blends which were

unstable, whilst a value of 1 was assigned to those samples exhibiting near eutectic properties.

XIII.2.3 Reactivity of photoinitiator blends: Measure of cure

The reactivity of the photoinitiator blends has been evaluated at a constant photoinitiator content (8%w/w) in PPTTA. The measurements were run with films of 6 microns thickness on board. A K wired bar (No 1) was used to apply the wet films. The films were cured with a medium pressure mercury lamp of around 80 W/cm (Primarc) using a tunnel conveyor. The reactivity of the photoinitiator blends was assessed as the number of passes at 230 ft/min necessary to get through cure. The fewer number of passes required to cure the coating the higher the reactivity of the photoinitiator blend.

XIII.2.4Design of photoinitiator blends

In a mixture, the proportions of each component must satisfy the summation constraint, that implies that the component proportions must add up to 100%. If the proportion of a component is changed, the proportion of at least another component must also change. Simplex designs can be used when the design points include pure components or there are no limit constraints on the components. If one or more components are constrained by a maximum level the design space is no longer a simplex, so simplex lattice designs cannot be used.

Our design had multicomponent constraints on the components level (see Table XIII.1 and Table XIII.2 for experimental data).

Components	Minimum constraint	Maximum constraint
%BP	0.00	50.00
%BDK	15.00	40.00
%EPD	15.00	40.00
%ITX	10.00	40.00

Table XIII.1 Component constraints.

Distance based point selection chooses points from the candidate point set which are spread throughout the design region. There is a risk that the number of points might not be sufficient to estimate the model coefficients or to provide an estimate of pure error or to judge lack of fit.

D-optimal point selection minimises the determinant of the Fisher information matrix. The optimisation is performed to minimise the general variance of the coefficients in the model. The points selected are model dependent and are selected with only these criteria in mind. A D-optimal design was generated to permit the investigation of all the terms in a full cubic model. A 2D contour plot of the standard errors can be used to assess the ability of the chosen design to permit the investigation of the region of interest (Figure XIII.1).

RUN	%BP	%BDK	%EPD	%ITX	STABILITY	N. OF PASSES
1	50.00	15.00	25.00	10.00	0	4
2	17.50	15.00	27.50	40.00	0	6
3	26.25	20.83	20.83	32.08	1	6
4	11.25	23.33	33.33	32.08	0	5
5	50.00	25.00	15.00	10.00	0	5
6	50.00	15.00	15.00	20.00	0	6
7	35.00	40.00	15.00	10.00	0	5
8	0.00	40.00	20.00	40.00	0	7
9	17.50	27.50	15.00	40.00	0	8
10	22.50	40.00	27.50	10.00	0	5
11	15.00	40.00	15.00	30.00	0	8
12	20.00	15.00	40.00	25.00	0	4
13	35.00	15.00	40.00	10.00	0	4
14	16.67	40.00	23.33	20.00	0	5
15	30.00	15.00	35.00	20.00	0	4
16	0.00	20.00	40.00	40.00	0	4
17	0.00	40.00	40.00	20.00	0	4
18	35.00	40.00	15.00	10.00	0	5
19	30.00	35.00	15.00	20.00	0	7
20	31.67	23.33	35.00	10.00	0	4
21	0.00	20.00	40.00	40.00	0	4
22	30.00	15.00	15.00	40.00	0	8
23	50.00	15.00	25.00	10.00	0	4
24	10.00	40.00	40.00	10.00	0	5
25	0.00	33.33	33.33	33.33	0	5
26	15.00	31.67	40.00	13.33	0	4
27	36.25	20.83	20.83	22.08	1	5
28	35.00	15.00	40.00	10.00	0	4
29	0.00	40.00	20.00	40.00	0	7
30	39.00	23.00	23.00	15.00	1	4
31	25.00	25.00	25.00	25.00	1	5
32	43.00	18.00	24.00	15.00	1	4

Table XIII.2 Experimental data.

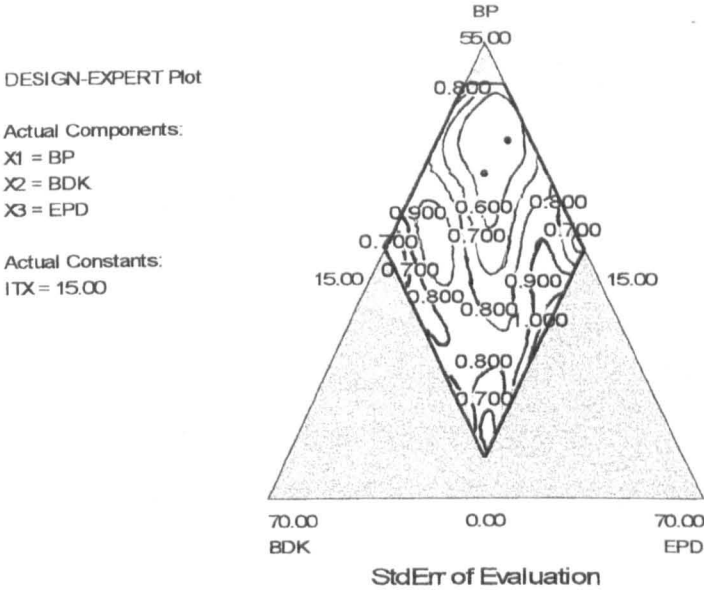


Figure XIII.1 2D contour plot of standard errors of evaluation.

Once the polynomial model has been selected for investigation and the experiments have been done, regression methods are used to determine which, if any, independent variables are significant.

There are several types of regression:

- In the **full model regression** all blocks and candidate terms are fitted to the data regardless of their contribution to the model.
- **Stepwise regressions** can be categorised in 3 basic types:
 - Forward selection with replacement. A factor is added, eliminated or exchanged at each step.
 - Backward elimination. A factor is eliminated at each step.
 - Forward selection. A factor is added at each step.

For data from designed experiments, all three stepwise methods should yield the same reduced model if all the experiments gave a measurable response. However, if some design points did not provide data, then different methods may give different models.

XIII.2.5 Stability

From the **ANOVA** Table it is possible to **evaluate the model coefficients** predicted values, statistics and residuals or difference between the observed stability and the value predicted by the model (Table XIII.3).

T for H_0 parameter=0

For a Null Hypothesis H_0 , the coefficient is considered equal zero. By using the t distribution where t is defined as the number of standard deviations that the parameter estimate is away from zero ($t = \text{parameter estimate} / \text{parameter standard error}$) it is possible to test the significance of the distance of the parameter value from zero. $\text{Prob} > t$ is defined as the probability of a larger t value if the Null hypothesis is true. Small values of this probability indicate significance and rejection of the Null hypothesis.

Component	Coefficient estimate	DF	Std error	T for H ₀ Coeff=0	Prob > t
A-BP	-1.35	1	0.30	Not applicable	
B-BDK	10.79	1	10.84	Not applicable	
C-EPD	40.77	1	9.04	Not applicable	
D-ITX	-9.88	1	4.78	Not applicable	
AC	-75.66	1	17.02	-4.45	0.0008
AD	22.41	1	9.84	2.28	0.0418
BC	-96.14	1	23.12	-4.16	0.0013
CD	-59.61	1	17.69	-3.37	0.0056
ABC	111.59	1	26.17	4.26	0.0011
ACD	71.09	1	21.49	3.31	0.0062
BCD	96.34	1	37.34	2.58	0.0241
AB(A-B)	20.30	1	10.49	1.94	0.0768
AC(A-C)	53.08	1	9.61	5.53	0.0001
BC(B-C)	25.35	1	17.82	1.42	0.1803
BD(B-D)	-29.89	1	10.94	-2.73	0.0182
CD(C-D)	-59.41	1	12.38	-4.80	0.0004

Table XIII.3 ANOVA for mixture cubic model. Stability analysis.

The fit of the mathematical model to the real response values can be assessed by residual analysis (Table XIII.4). Design expert® facilitates assessment of the model by providing plots of residuals, student residuals, Cook's distances and outliers.

Std order	Actual Value	Predicted value	Residual	Leverage	Student residual	Cook's distance	Outlier t	Run order
1	0.000	-0.037	0.037	0.483	0.355	0.006	0.341	13
2	1.00	0.85	0.15	0.236	1.178	0.021	1.199	31
3	1.00	0.75	0.25	0.263	2.055	0.075	2.444	32
4	1.00	0.91	0.094	0.300	0.776	0.013	0.763	30
5	0.000	-0.037	0.037	0.483	0.355	0.006	0.341	28
6	0.000	-0.0002	0.0002	0.491	0.002	0.000	0.002	16
7	0.000	-0.0002	0.0002	0.491	0.002	0.000	0.002	21
8	0.000	-0.002	0.002	0.892	0.038	0.001	0.037	6
9	0.000	-0.039	0.039	0.914	0.913	0.441	0.906	5
10	0.000	-0.004	0.004	0.491	0.040	0.000	0.039	18
11	0.000	-0.004	0.004	0.491	0.040	0.000	0.039	7
12	0.000	-0.024	0.024	0.784	0.357	0.023	0.344	24
13	0.000	0.045	-0.045	0.854	-0.808	0.190	-0.796	17
14	0.000	0.078	-0.078	0.467	-0.739	0.024	-0.724	1
15	0.000	0.078	-0.078	0.467	-0.739	0.024	-0.724	23
16	0.000	-0.012	0.012	0.881	0.244	0.022	0.234	22
17	0.000	0.041	-0.041	0.483	-0.393	0.007	-0.378	29
18	0.000	0.041	-0.041	0.483	-0.393	0.007	-0.378	8
19	0.000	0.017	-0.017	0.831	-0.283	0.020	-0.272	12
20	0.000	-0.036	0.036	0.730	0.486	0.032	0.470	10
21	0.000	-0.031	0.031	0.891	0.655	0.174	0.638	2
22	0.000	-0.016	0.016	0.926	0.407	0.103	0.392	9
23	0.000	-0.16	0.16	0.837	2.680	1.841	4.049*	11
24	0.000	-0.019	0.019	0.883	0.390	0.058	0.376	26
25	0.000	0.14	-0.14	0.659	-1.689	0.276	-1.852	20
26	0.000	0.013	-0.013	0.611	-0.141	0.002	-0.135	15
27	0.000	-0.11	0.11	0.811	1.745	0.654	1.934	25
28	0.000	0.16	-0.16	0.695	-2.024	0.467	-2.389	19
29	0.000	0.071	-0.071	0.750	-0.981	0.145	-0.980	14
30	0.000	0.091	-0.091	0.572	-0.967	0.063	-0.964	4
31	1.00	1.15	-0.15	0.315	-1.294	0.039	-1.336	27
32	1.00	1.09	-0.093	0.535	-0.942	0.051	-0.937	3

Table XIII.4 Diagnostics case statistics for stability.

Figure XIII.2 is a normal probability plot of residuals. Normal probability plots indicate whether the residuals follow a normal distribution. On normal probability plots the points should be close to a straight line. The assumption is that the errors are normally distributed. If there is a definite pattern, such as an "S-shaped" curve, then a transformation of the response might be indicated to make the data more normal. Possible outliers can also be identified on this plot.

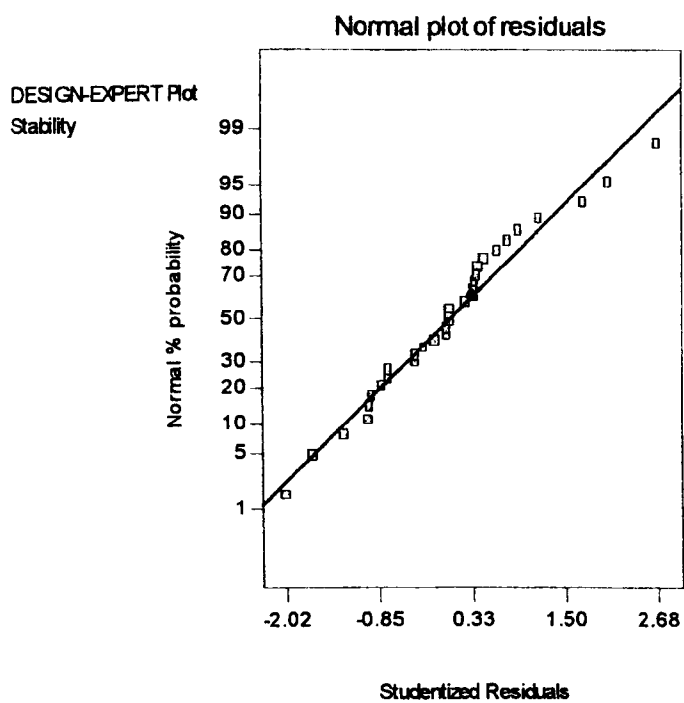


Figure XIII.2 Normal plot of residuals for stability.

The plot of residuals versus the predicted values (Figure XIII.3) tests the assumption of constant variance regardless of the size of the response. If the variance expands with larger predicted values ("megaphone" shape) then a transformation of the response may be necessary. The plot should be random scatter about the zero axes with no discernible pattern. The plot of absolute value of residuals versus the predicted values may indicate more clearly if a pattern exists (Figure XIII.4). The results do not show appreciable change in variation as the level increases.

Residuals versus run order plots provide a test for time dependency. Values above 3.5 should be investigated (Figure XIII.5). All the values are less than 3.

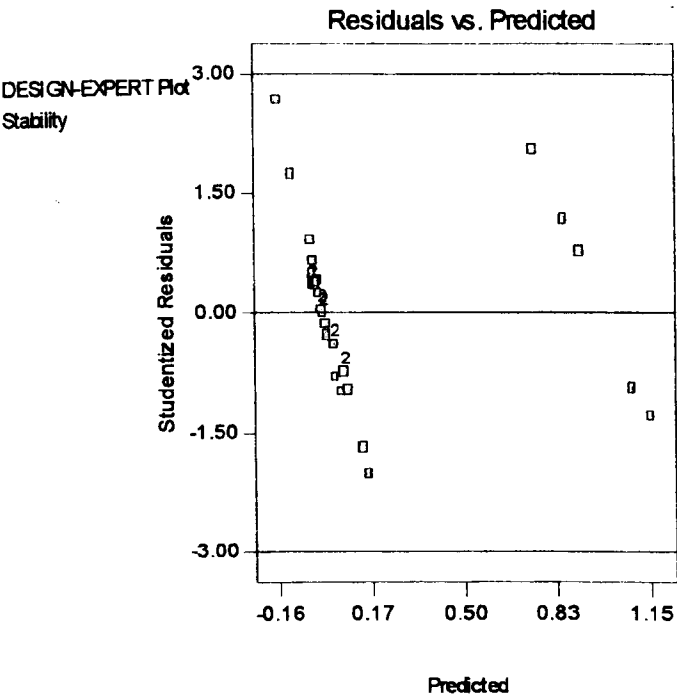


Figure XIII.3 Residuals versus predicted plot for stability.

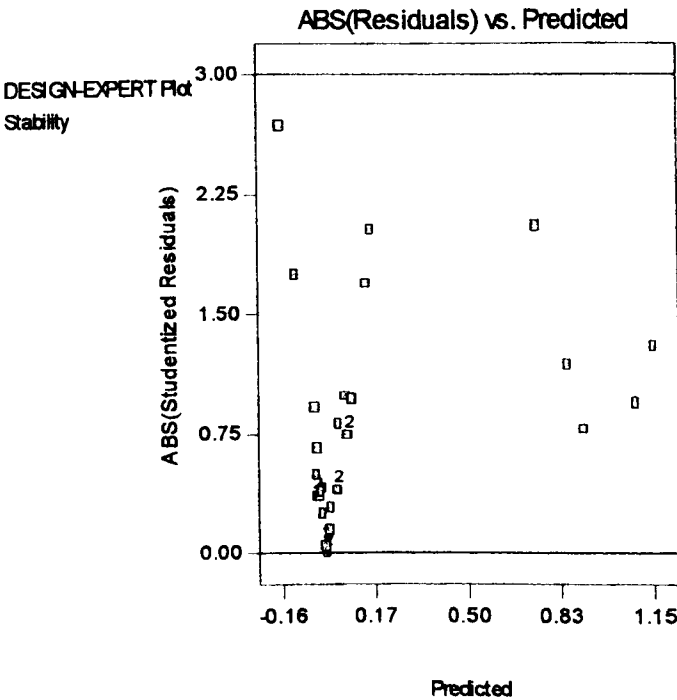


Figure XIII.4 Absolute residuals versus predicted plot for stability.

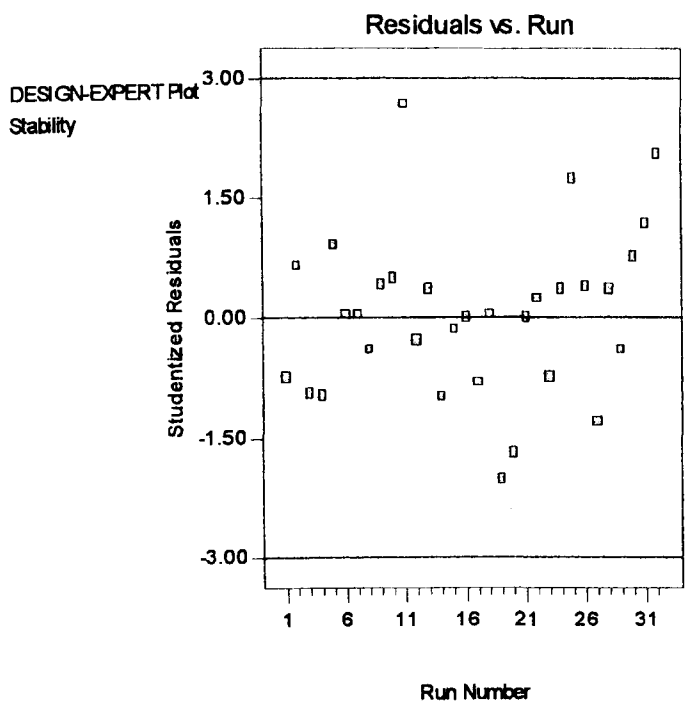


Figure XIII.5 Residuals versus run number plot for stability.

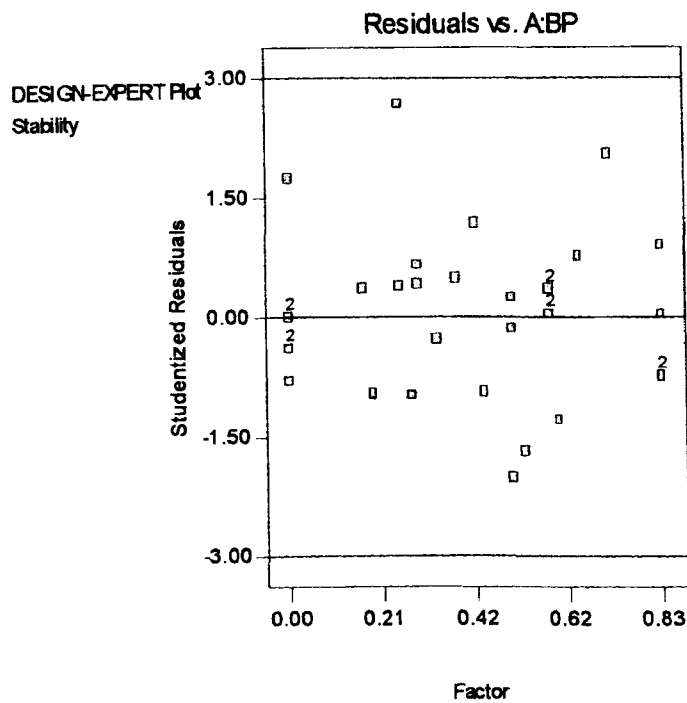


Figure XIII.6 Residuals versus factor (BP) plot for stability.

The plot of residuals versus component checks whether the variance not accounted for by the model is different for different levels of a variable. The plot should be a random scatter. Pronounced curvature may indicate a systematic contribution of the independent variable that is not accounted for by the model (Figure XIII.6). The plots for the four components are randomly scattered.

As well as residuals versus run order plots, plots of outliers t versus run order plots show whether a run is significantly different from the other cases. Values above 3.5 should also be investigated (Figure XIII.7). An outlier with a value of 4 (run order 11) has been identified.

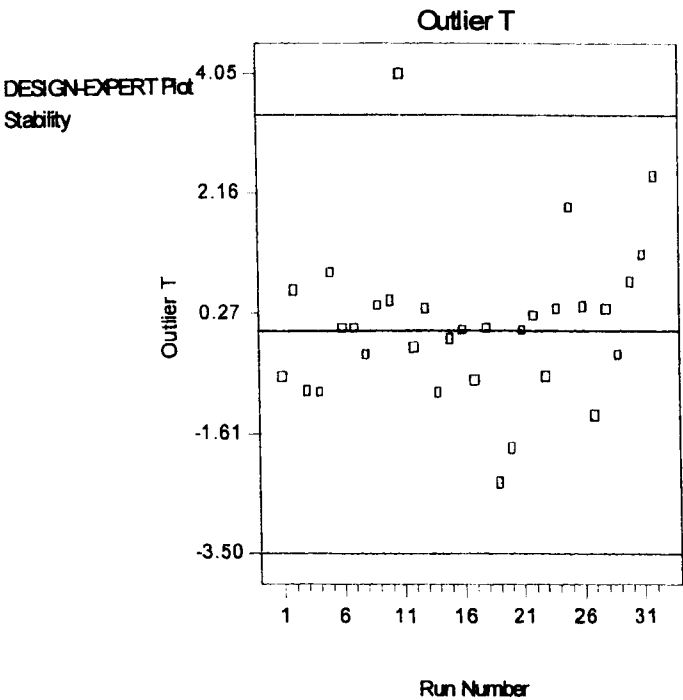


Figure XIII.7 Outliers T versus run number plot for stability.

Cook's distance plots may also be useful to notice whether a run is significantly different from the other cases. Cook's distance analysis measures how much the estimated coefficients would change if that particular run was omitted from the analysis. The values are relative. Large values, relative to the rest of the data points, are important because may indicate an outlier. Figure XIII.8 also indicates the presence of the same outlier identified before.

Similarly, leverage versus run plots may give a better perspective on whether a run is an influential data point. Leverages near one indicate an inordinate

influence for a design point. Figure XIII.9 shows the existence of several runs with values around 0.9.

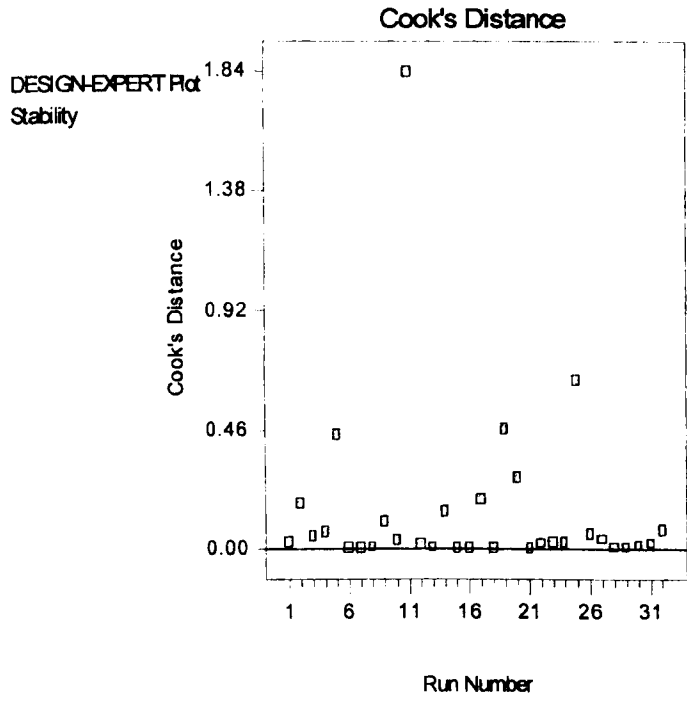


Figure XIII.8 Cook's distance versus run number plot for stability.

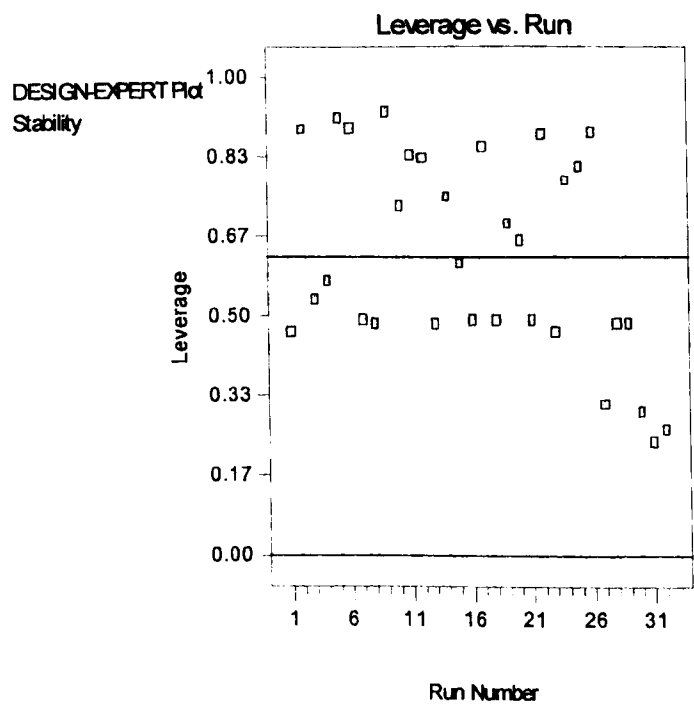


Figure XIII.9 Leverage versus run number plot for stability.

XIII.2.6Reactivity of photoinitiator blends

Table XIII.5 is a summary of the model coefficient predicted values, statistics and residuals or difference between the observed response and the value predicted by the model. Figure XIII.10 is a normal probability plot of residuals. The residuals follow a normal distribution as indicated by their straight line plot. There are no outliers.

Figure XIII.11 is a plot of residuals versus the predicted values. The plot does not show appreciable variance expansion with large predicted values. As mentioned before, plots of absolute value of residuals versus the predicted values may indicate more clearly if a pattern exists (Figure XIII.12). The data points are spread randomly in the plot area indicating that there is not any appreciable pattern.

Component	Coefficient estimate	DF	Std error	T for H ₀ Coeff=0	Prob > t
A-BP	5.14	1	0.28	Not applicable	
B-BDK	-20.69	1	9.98	Not applicable	
C-EPD	-31.26	1	8.37	Not applicable	
D-ITX	-12.86	1	4.51	Not applicable	
AB	48.36	1	18.88	2.56	0.0306
AC	64.93	1	15.75	4.12	0.0026
AD	47.33	1	9.24	5.12	0.0006
BC	120.44	1	21.34	5.64	0.0003
BD	99.17	1	24.29	4.08	0.0027
CD	103.15	1	16.58	6.22	0.0002
ABC	-144.26	1	24.29	-5.94	0.0002
ABD	-112.56	1	29.56	-3.81	0.0042
ACD	-158.01	1	20.29	-7.79	< 0.0001
BCD	-254.59	1	34.81	-7.31	< 0.0001
AB(A-B)	-27.39	1	9.72	-2.82	0.0201
AC(A-C)	-44.25	1	9.00	-4.92	0.0008
AD(A-D)	-29.15	1	5.44	-5.36	0.0005

Table XIII.5 ANOVA for mixture cubic model. Reactivity (number of passes) analysis.

Residuals versus run order plots did not identify any outliers (Figure XIII.13). All the values were less than 3.

The plot of residuals versus component, shown in Figure XIII.14 diagnoses whether the variance not accounted for by the model is different for different levels of a variable. All four component plots were randomly scattered and did not indicate any systematic contribution of the independent variable that is not

accounted for by the model. The plot of outliers t versus run order (Figure XIII.15) shows an outlier with a value of 3.7 (run order 4). The Cook's distance plot (Figure XIII.16) shows two large values suggesting the possible of other outliers (run order 14 and 25).

Leverage versus run plots usually give a better perspective on whether a particular value is an outlier. Figure XIII.17 shows the existence of several runs (run order 5, 6, 9, and 26) with values around 0.9 indicating the possible existence of outliers.

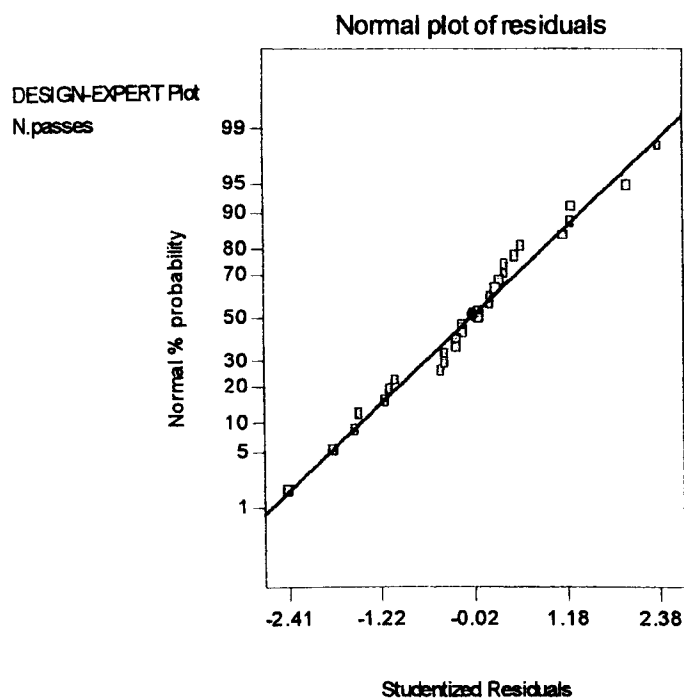


Figure XIII.10 Normal plot of residuals for the number of passes.

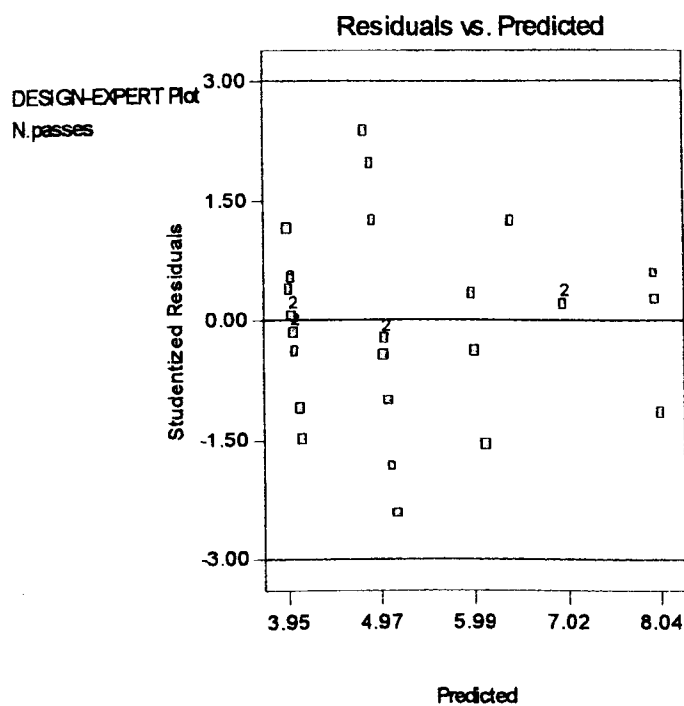


Figure XIII.11 Residuals versus predicted for reactivity (number of passes).

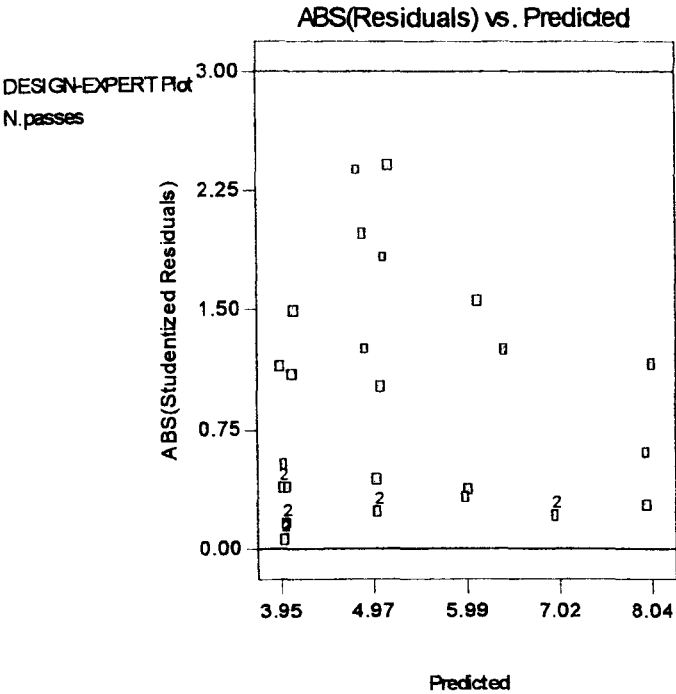


Figure XIII.12 Absolute residuals versus predicted plot for reactivity (number of passes).

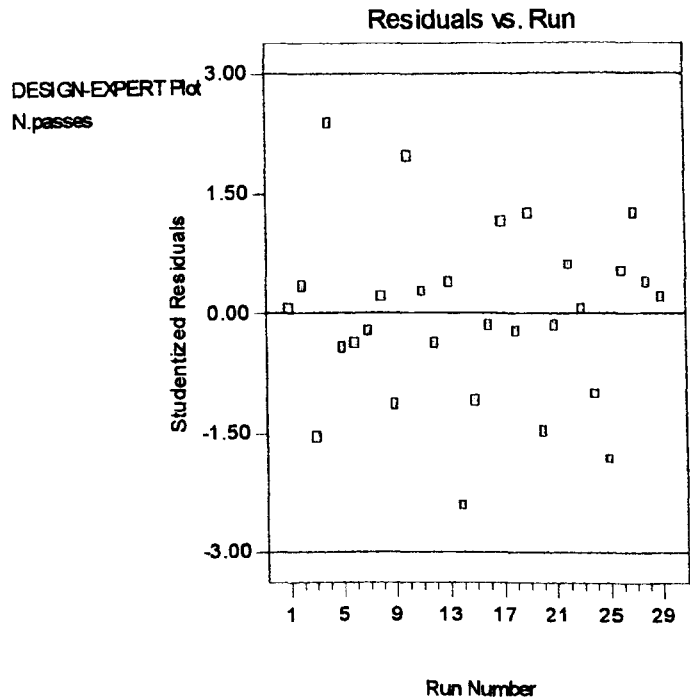


Figure XIII.13 Residuals versus run number plot for reactivity (number of passes).

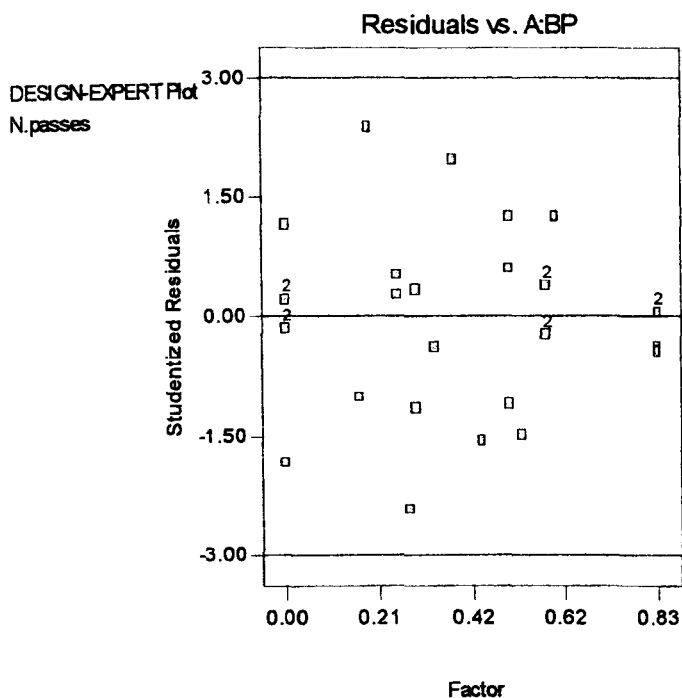


Figure XIII.14 Residual versus factor (BP) plot for reactivity (number of passes).

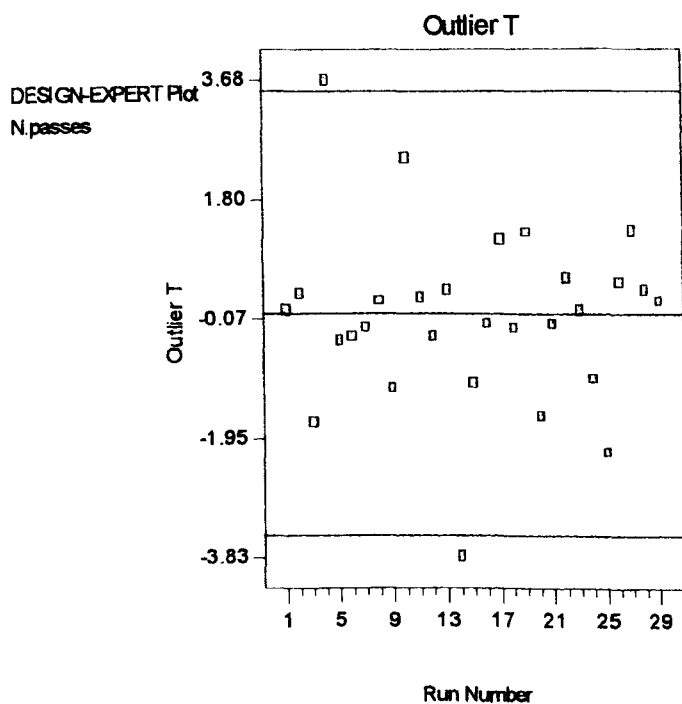


Figure XIII.15 Outlier T versus run number plot for reactivity (number of passes).

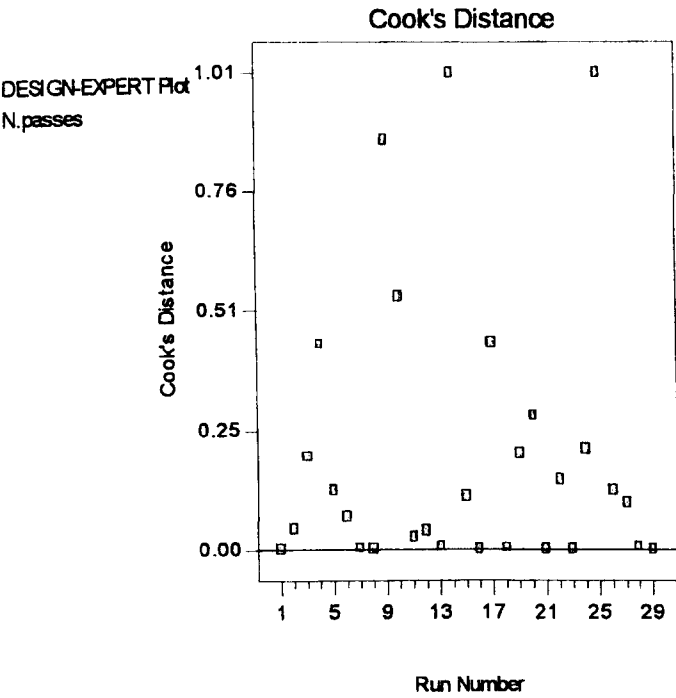


Figure XIII.16 Cook’s distance versus run number plot for reactivity (number of passes).

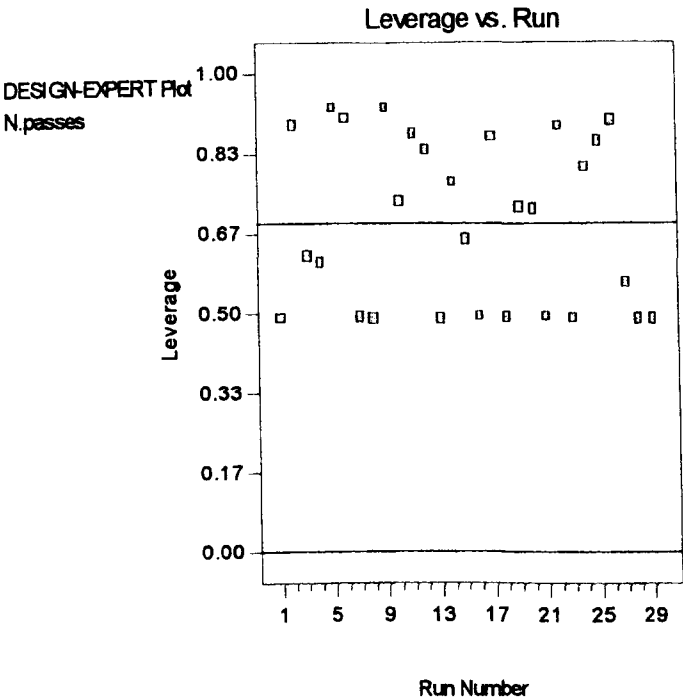


Figure XIII.17 Leverage versus run number plot for reactivity (number of passes).

XIII.3 Results and discussion

XIII.3.1 Stability

In order to gain insights about the mixture system, it is useful to look at response graphs. Trace plots are very helpful in multicomponents systems. These plots reveal how the response changes when changing the proportion of each component while keeping all the others constant. The overall centroid has been used as a starting point (25% BP, 25% BDK, 25% EPD, 25% ITX).

The trace plot for stability of a photoinitiator blend based on 25% of each component is shown in Figure XIII.18. It indicates that an increase in the proportion of BP, and to a minor extent of ITX, improves the stability until certain level when it starts to decrease. On the other hand, a decrease of the proportion of EPD, and to a minor extent of BDK, improves the stability of the photoinitiator blends.

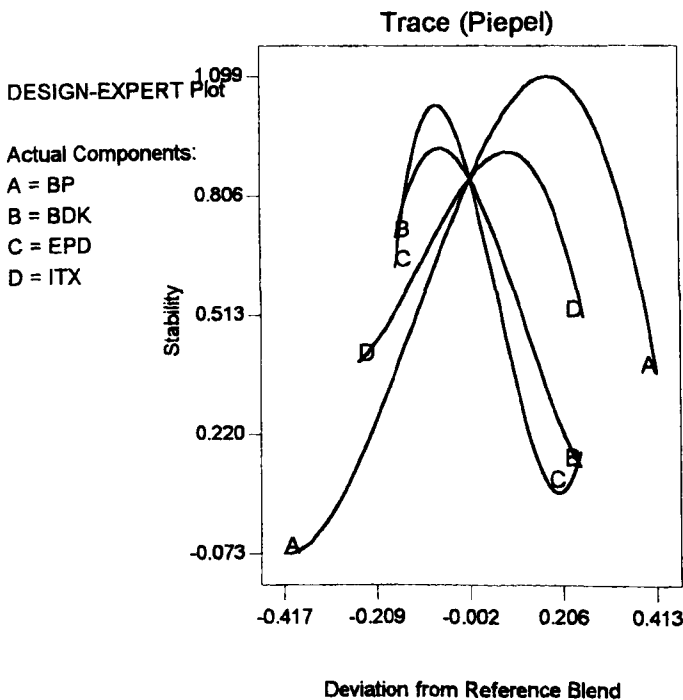


Figure XIII.18 Trace plot for stability considering as starting a photoinitiator blend based on 25% of each component.

Two-dimensional contour plots provide numerical predictions of stability as a function of the component proportions. Only three components can be displayed at once. Figure XIII.19 illustrates the 2D contour plot for stability at a constant ITX concentration of 15%. Three-dimensional plots provide 3D perspectives of the shape of the surfaces. Figure 20 illustrates a 3D plot for showing a region of maximum stability. Similarly, plots of standard errors can be represented graphically. Figure XIII.21 illustrates a 2D contour plot for standard errors of stability at a constant ITX concentration of 15% where it can be observed that the standard errors associated with the model are around 0.1.

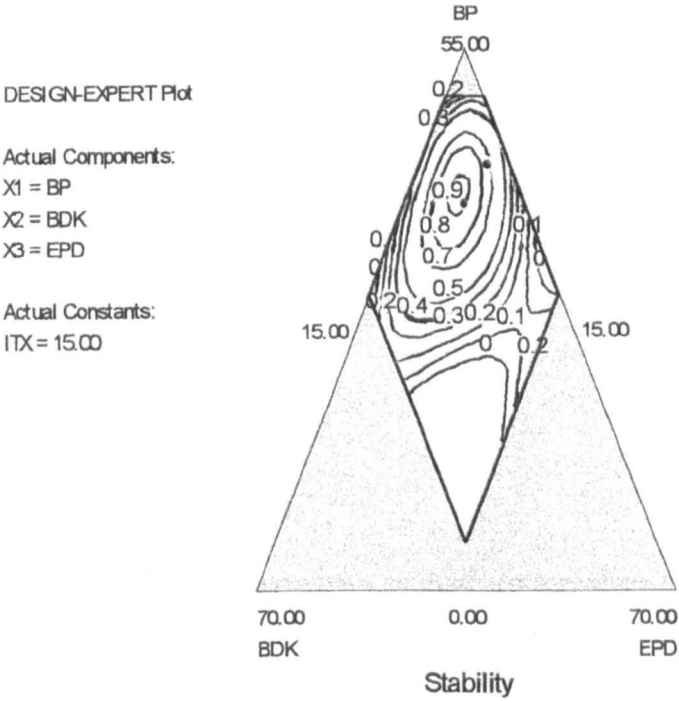


Figure XIII.19 2D contour plot for stability at 15%ITX.

Positive high values of the terms indicate the term contribution to the stability function and negative values indicate a negative contribution to the stability of the system.

DESIGN-EXPERT Plot

Actual Components:

X1 = BP

$$X_2 = BDK$$

X3 = EPD

Actual Constants:

ITX = 15.00

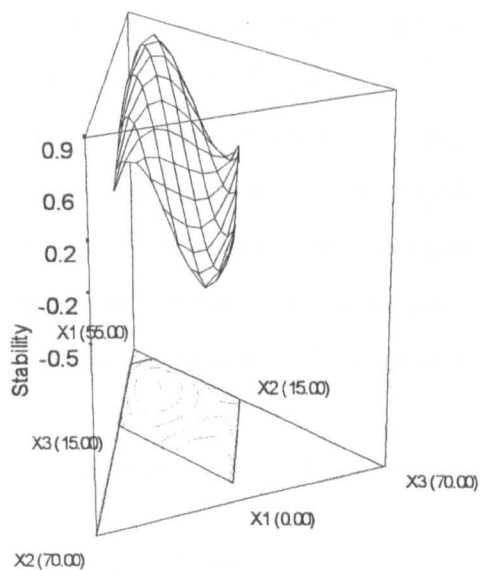


Figure XIII.20 3D contour plot for stability at 15%ITX.

DESIGN-EXPERT Plot

Actual Components:

X1 = BP

$$X_2 = BDK$$

X3 = EPD

Actual Constants:

ITX = 15.00

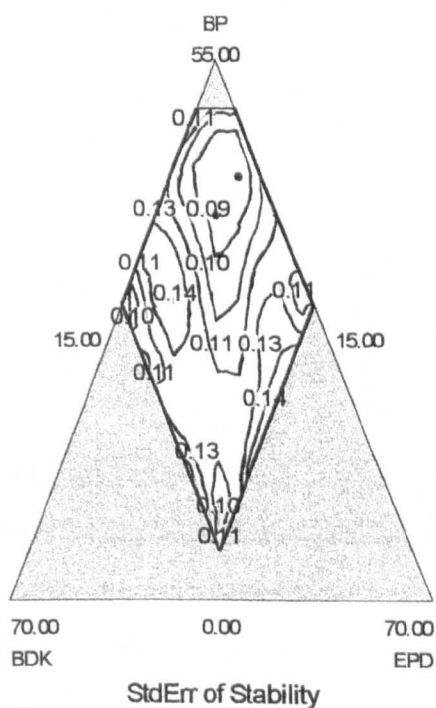


Figure XIII.21 2D contour plot of standard error of stability.

XIII.3.2Reactivity of photoinitiator blends

The overall centroid has been used as a starting point (25% BP, 25% BDK, 25% EPD, 25% ITX). This blend has been optimised from this starting point by trace plot analysis. Figure XIII.22 shows the trace plot for reactivity (number of passes). It indicates that an increase of the EPD proportion decreases dramatically the number of passes required to achieve through cure, so the reactivity of the formulations can be improved significantly by increasing the proportion of EPD. Similarly, to a lesser extent an increase of BP also improves the reactivity of the photoinitiator blends. On the other hand, a decrease of ITX level increases the reactivity of the system, whilst an increase of the proportion of ITX decreases the reactivity of the formulations.

From the reactivity point of view, the proportion of BDK is nearly optimal.

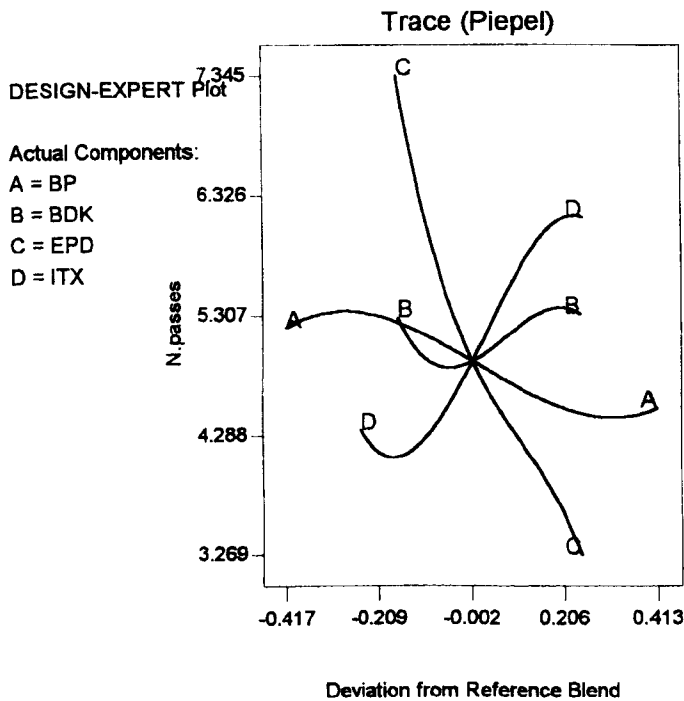


Figure XIII.22 Trace plot for reactivity (number of passes) considering as a starting point a photoinitiator blend based on 25% of each component.

Figures XIII.23 and XIII.24 illustrate 2D and 3D contour plots for number of passes at a constant ITX concentration of 15%. It is clear that the surface exhibits a maximum gradient in the EPD axis indicating that the reactivity of the formulations increases dramatically when increasing the proportion of EPD.

DESIGN-EXPERT Plot

Actual Components:

X1 = BP

X2 = BDK

X3 = EPD

Actual Constants:

ITX = 15.00

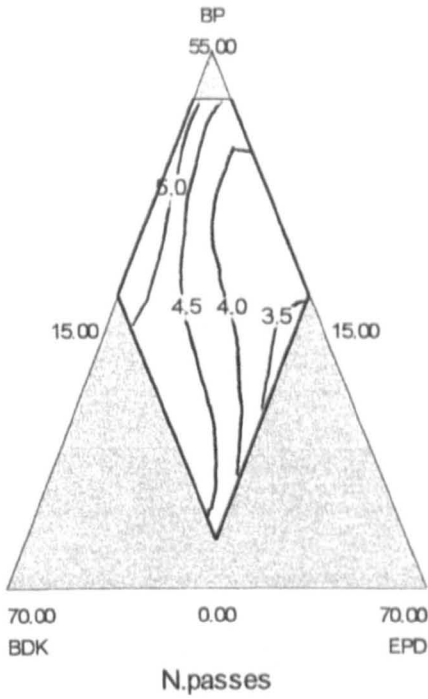


Figure XIII.23 2D contour plot for reactivity (number of passes) at 15%ITX.

DESIGN-EXPERT Plot

Actual Components:

X1 = BP

X2 = BDK

X3 = EPD

Actual Constants:

ITX = 15.00

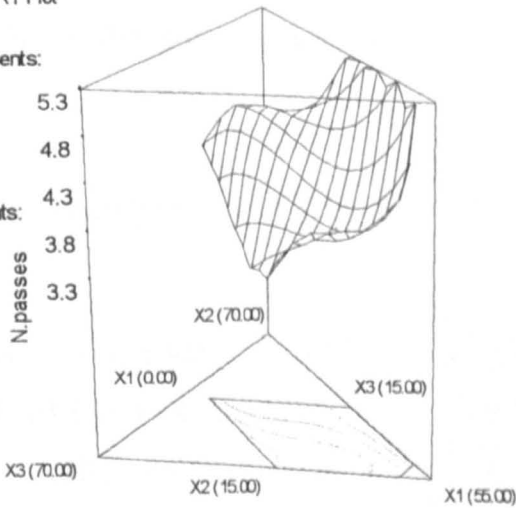


Figure XIII.24 3D contour plot for reactivity (number of passes) at 15%ITX.

Similarly, plots of standard errors can be represented graphically. Figure XIII.25 illustrates a 2D contour plot for standard errors of the number of passes at a constant ITX concentration of 15%, where it can be observed that the standard errors associated with the model are around 0.1.

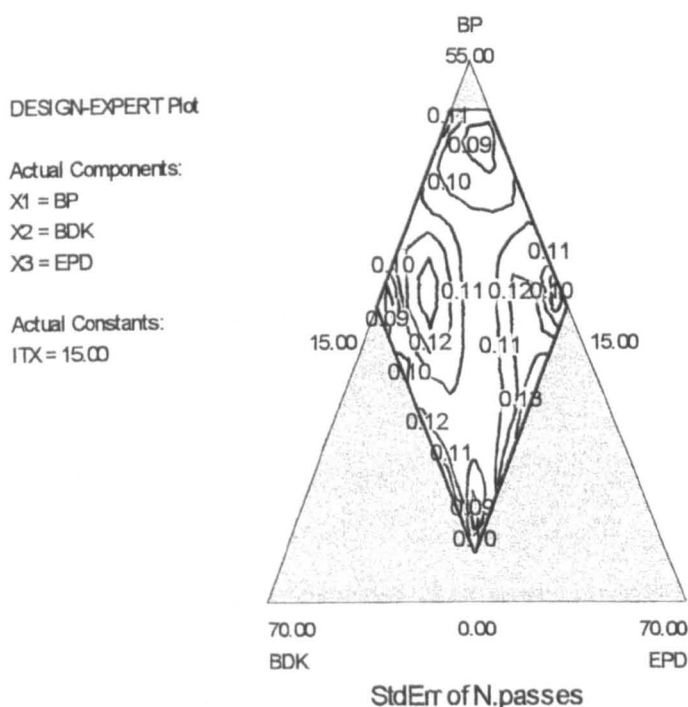


Figure XIII.25 2D contour plot of standard error of reactivity (number of passes).

The final polynomial equation in terms of actual components for reactivity is shown below

$$\begin{aligned} \text{N.passes} = & + 0.20\text{BP} - 1.02\text{BDK} - 1.13\text{EPD} - 0.93\text{ITX} + 0.019(\text{BP}-\text{BDK}) + \\ & + 0.023(\text{BP}-\text{EPD}) + 0.022(\text{BP}-\text{ITX}) + 0.046(\text{BDK}-\text{EPD}) + 0.045(\text{BDK}-\text{ITX}) + \\ & + 0.045(\text{EPD}-\text{ITX}) - 6.679\text{E-}04(\text{BP}-\text{BDK}-\text{EPD}) - 5.211\text{E-}04(\text{BP}-\text{BDK}-\text{ITX}) - 7.315\text{E-} \\ & - 04(\text{BP}-\text{EPD}-\text{ITX}) - 1.179\text{E-}03(\text{BDK}-\text{EPD}-\text{ITX}) - 1.268\text{E-}04(\text{BP}^2-\text{BDK}) + 1.268\text{E-} \\ & - 04(\text{BP}-\text{BDK}^2) - 2.049\text{E-}04(\text{BP}^2-\text{EPD}) + 2.049\text{E-}04(\text{BP}-\text{EPD}^2) - 1.349\text{E-}04(\text{BP}^2- \\ & - \text{ITX}) + 1.349\text{E-}04(\text{BP}-\text{ITX}^2) \end{aligned}$$

From which the contribution of the term coefficients to the model can be evaluated:

- Linear terms which represent pure blends of each component
- Quadratic terms, which represent 50%: 50% binary blends and give an idea of the degree of synergism/antagonism in the blend.
- Special Cubic terms which represent 33.3%: 33.3%: 33.3% ternary blends
- Cubic terms which represent third of the edges; 66.6%: 33.3% binary blends

XIII.3.3 Multiple response optimisation

The objective for optimisation is to design cost effective synergistic photoinitiator blends of optimum reactivity and bulk stability. An algorithm is applied to find the optimum. A hill-climbing approach method is used. Numerical optimisation for the stability and reactivity of the photoinitiator blends have been carried out separately.

Stability has been optimised without bearing in mind the reactivity of the system (goal: maximum stability). The numerical optimisation results (Table XIII.6) gave nine photoinitiator blends of high stability (maximum desirability). Several photoinitiator blends give stability values above one. The approximate optimal stability coordinates for the different blends are in a relatively narrow range around; 29-40%BP, 18-26%BDK, 18-25%EPD and 21-31%ITX.

	%BP	%BDK	%EPD	%ITX	Stability	Desirability
1	28.27	18.36	21.91	31.45	1.1	1.000
2	39.69	21.14	17.93	21.24	1.0	1.000
3	32.37	21.72	22.06	23.85	1.2	1.000
4	29.13	21.18	20.69	29.01	1.2	1.000
5	36.27	18.83	18.83	26.07	1.2	1.000
6	37.10	17.94	22.44	22.52	1.1	1.000
7	30.61	26.03	20.05	23.31	1.0	1.000
8	31.46	17.63	20.25	30.66	1.1	1.000
9	29.72	20.22	25.06	25.00	1.0	1.000

Table XIII.6 Optimisation of stability. Predicted photoinitiator blends of maximum stability.

The reactivity of photoinitiator blends has also been optimised having only this criteria in mind (goal: minimum number of passes). Seven photoinitiator blends were obtained by numerical optimisation (Table XIII.7). The approximate optimal

reactivity coordinates for the different blends are in a relatively wide range around; 2-45%BP, 17-36%BDK, 23-40%EPD and 10-24%ITX.

In multiple response optimisation a desirability function is commonly used in which the several responses contribute to the final desirability function. In our case, equal weightings were given to stability and reactivity. Numerical optimisation gave an optimal predicted photoinitiator blend having, at the same time, high reactivity and stability (Table XIII.8).

Run	%BP	%BDK	%EPD	%ITX	N.passes	%Desirability
1	1.90	35.81	39.07	23.22	4	1.000
2	17.98	18.63	39.58	23.81	4	1.000
3	40.12	17.34	26.44	16.11	4	1.000
4	42.94	20.82	23.49	12.74	4	1.000
5	17.65	27.47	37.92	16.95	4	1.000
6	45.30	19.98	24.53	10.19	4	1.000
7	36.85	18.67	30.13	14.35	4	1.000

Table XIII.7 Optimisation of reactivity. Predicted photoinitiator blends of minimum number of passes required to obtain through cure.

%BP	%BDK	%EPD	%ITX	Stability	N.passes	Desirability
38.08	21.05	23.00	17.88	1.0	4	0.979

Table XIII.8 Multiple response optimisation of reactivity and stability.

Benzophenone (BP) due to its high volatility and high migration rate can potentially contaminate foodstuffs in direct food contact inks. One of the goals is to reduce the level of BP in UV inks and coatings. Table XIII.9 shows the optimal photoinitiator blends exhibiting the highest reactivity (minimum number of passes) at the minimum BP level. Unfortunately, at these low BP levels the photoinitiator blends are unstable (low stability values).

	%BP	%BDK	%EPD	%ITX	N.passes	Desirability
1	0.00	25.88	38.84	35.28	4	1.000
2	0.00	36.41	39.71	23.88	4	1.000
3	0.00	21.17	39.76	39.07	4	1.000
4	0.00	39.95	39.83	20.22	4	1.000
5	1.19	40.00	40.00	18.81	4	0.991
6	6.88	20.19	40.00	32.92	4	0.946

Table XIII.9 Optimal photoinitiator blends exhibiting the highest reactivity (minimum number of passes) at the minimum level of BP.

On the other hand, for most applications maximisation of the level of BP is desired in UV formulations due to its low cost, good pigment wetting, good solubility in photoinitiators and resins, and stabilising function in photoinitiator blends. Having these criteria in mind, numerical optimisation has been carried out with a maximum BP level (Table XIII.10). Two cost-effective photoinitiator blends of high reactivity were obtained at 50% BP. The predicted stability of the samples are low (0.2 and 0.4 respectively).

	%BP	%BDK	%EPD	%ITX	N.passes	Desirability
1	50.00	15.22	23.11	11.66	4	1.000
2	50.00	18.37	20.97	10.67	4	1.000

Table XIII.10 Optimal photoinitiator blends exhibiting the highest reactivity (minimum number of passes) at the maximum level of BP.

Multiple response optimisation has been carried out for reactivity and stability at the same contribution level to desirability function. The goal is to maximise the proportion of BP in order to design cost effective formulations whilst maintaining stability. Numerical optimisation gave an optimal predicted photoinitiator blend having, at the same time, high reactivity and stability (Table XIII.11).

%BP	%BDK	%EPD	%ITX	Stability	N.passes	Desirability
42.83	20.24	22.10	14.83	0.86	4	0.911

Table XIII.11 Multiple response optimisation of reactivity and stability at the maximum level of BP.

XIII.4 Conclusions

The reactivity and stability of photoinitiator blends are dependent on the level of each single photoinitiator in the final formulation. Design of Experiments DOE-Mixture Design has provided profound insights about the formulation of eutectic photoinitiator blends by predicting the optimum percentage of each single photoinitiator in the photoinitiator blends.

A computer aided statistical approach to mixture experimentation provided profound insights about synergistic photoinitiator combinations within a relatively short time. Mixture experiments provided a clear advantage in comparison to the limited one factor at a time approach. In this study, synergistic eutectic photoinitiator blends have been designed to comply with several industrial demands.

3-D stability plots identified regions of maximum stability at certain photoinitiator proportions. Evaluation of the component coefficients gave information about photoinitiator interactions such as synergism and antagonism. Trace plot analysis indicated that for the overall centroid, an increase of the proportion of BP (and to a minor extent ITX) improved the stability whilst, on the other hand, an increase of the proportion of EPD (and to a minor extent BDK) has a negative effect on the photoinitiator blend stability.

3-D reactivity plots demonstrated the positive influence of the tertiary aromatic amine cosynergist, EPD, on the overall reactivity of photoinitiator systems. Analysis of reactivity plots indicated that, for the overall centroid, an increase of the proportion of EPD dramatically decreased the number of passes required to obtain through cure, so the reactivity of the formulations can be improved significantly by increasing the proportion of EPD. Similarly, to a lesser extent an increase of the concentration of BP also improves the reactivity of the photoinitiator blends, whilst a decrease of the ITX level increased the reactivity of the system.

Both the reactivity and stability of photoinitiator blends were optimised simultaneously. Several aspects were taken into account. Firstly, since BP is the least expensive photoinitiator on the market, cost effective photoinitiator blends of enhanced reactivity and stability were designed at high BP content.

Secondly, the use of BP should be avoided to prevent foodstuff contamination in direct food contact inks due to its volatile nature. For such applications highly reactive photoinitiator blends were designed at minimum BP content.

XIV. CHAPTER XIV Optimisation of the photopolymerisation performance of commercial offset lithographic inks

XIV.1 Introduction

Two synergistic near eutectic photoinitiator blends designed by Mixture design have been used to improve the curing properties of UV offset lithographic inks.

Spectroscopic properties of pigments

The absorption properties of pigments and photoinitiators, combined with reactivity studies of photoinitiators have served to design and improve the curing of different UV inks. The knowledge of the pigment absorption window facilitated the design of cost-effective photoinitiator blends. By knowing the UV spectra of pigments and photoinitiators, photoinitiator systems were designed, which exhibited absorption in the pigment spectral windows, hence the pigment filter effect can be partially overcome.

The UV spectra of pigments have been measured in different solvents. The relative absorptivities of the pigments are represented in bar graphs at the most important emission lines of the mercury lamp at 253, 302, 313, 365 and 404 nm (Figure XIV.1).

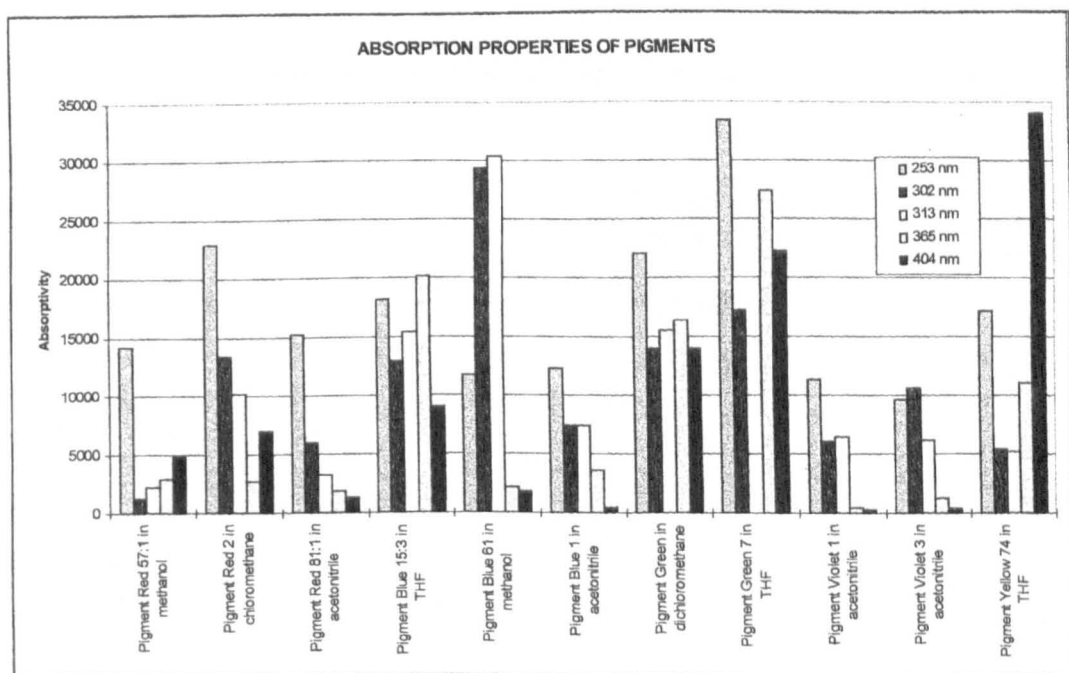


Figure XIV.1 Approximate extinction coefficients ($\text{Lmol}^{-1} \text{cm}^{-1}$) of pigments in suspensions at the most important emission lines of a mercury lamp.

It is important to confirm if the pigment ultraviolet absorption spectra measured in

pigment suspensions in solvents present the same ultraviolet absorption spectrum as the final formulations where the pigment is wetted by wetting agents and resins. The UV spectra have been measured on the inks without any photoinitiator and the spectra have been analysed by transmittance. The inks were applied on polypropylene transparent film at thin films to let the UV beam cross the film. Both spectra were found to coincide exactly, confirming the validity of the results.

Photoinitiator blends

Instead of using different photoinitiator systems for each specific pigment, it has been designed photoinitiator eutectic blends, which exhibit a widened absorption in the UV/visible range.

Two photoinitiator near eutectic liquid blends have been formulated by design of experiments DOE-Mixture Design for curing both dark and light colour inks. These two blends possess high stability and high absorbance in the short UV balanced with a relatively lower absorbance in the near UV/visible range. Consequently, it is possible to cure a broad range of pigmented inks owing to the broad absorption range of the two photoinitiator blends, this fact makes possible to maximise the light absorbed at the different emissions lines of the Hg lamp.

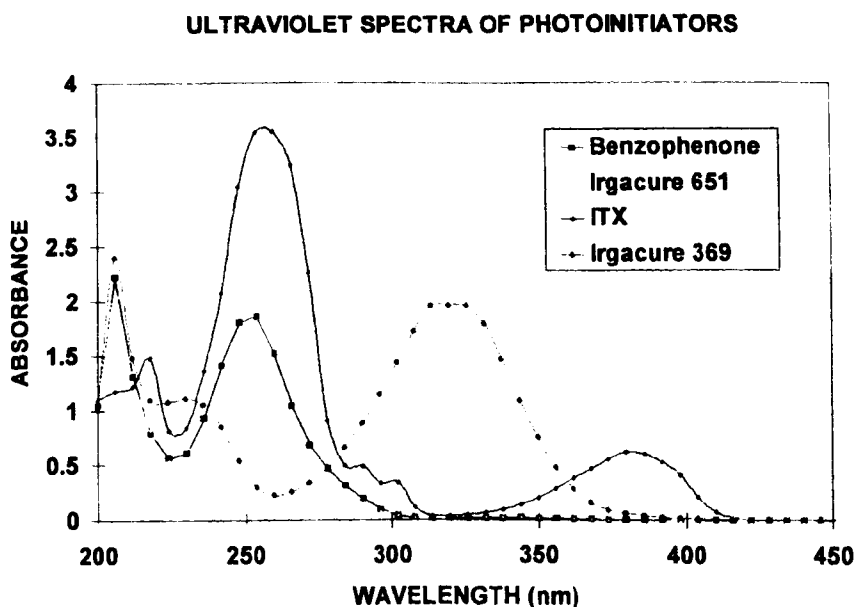


Figure XIV.2 UV absorption spectra of BP, BDK, ITX and Irgacure 369 in isopropanol ($C=1.0 \times 10^{-4}$ M).

The two eutectic blends were the following:

- Photoinitiator eutectic liquid blend A is based on BP, BDK, EPD and ITX as a Type II near UV/visible photoinitiator for absorbing the mercury lamp emission lines in the near UV/visible range (366 and 404 nm), Figure XIV.2.
- Photoinitiator eutectic blend B is based on BP, BDK, EPD and Irgacure 369 as a Type I near UV photoinitiator for absorbing the mercury lamp emission lines in the near UV range (313 and 365 nm), Figure XIV.2.

Both samples exhibit near eutectic properties and have the same proportion of BP, BDK, and EPD. The only difference between the two photoinitiator blends consists on the type of near UV/visible PI used.

In order to get cost effective formulations, it is suggested that photoinitiator blend A should be used with photoinitiator blend B at different ratios for different pigments in order to maximise the absorption of light. Combinations of PI blend A and PI blend B present synergism by energy transfer from ITX to Irgacure 369 being highly efficient for most of the pigments.

REFERENCE	%BP	%BDK	%EPD	%ITX	%I369	%TOTAL
BLEND A	A	B	C	15	0	100
A75%/B25%	A	B	C	11.25	3.75	100
A50%/B50%	A	B	C	7.5	7.5	100
A25%/B75%	A	B	C	3.75	11.25	100
BLEND B	A	B	C	0	15	100

Table XIV.1 Compositions of blends of photoinitiators eutectic blends A and B at different ratios. A, B, and C indicate constant proportions of BP, BDK and EPD.

XIV.1.1 Curing performance of black inks

A standard black base has been formulated with the new universal PI blends. The different ink formulations (0.4 ml of ink) have been printed on a reference polymeric film at the same colour density and film thickness and they have been cured with a tunnel conveyor with a normal pressure mercury lamp of 80 W/cm at different speeds.

The curing evaluation has been performed by using the thumb twist resistance method after passing the print several times under the curing unit. The number of passes necessary to obtain surface and through cure were recorded at different conveyor speeds.

Black base	100 ft/min	150 ft/min
Commercial ink	3-4	5
A100 12%	3-4	6
A25/B75 12%	3-4	4
A10/B90 12%	3-4	4
B100 12%	3	4

Table XIV.2 Curing performance of a black ink base cured with combinations of the photoinitiators blends A and B at different ratios with one lamp in a tunnel conveyor at different speeds.

The results shown in Table XIV.2 indicate that the photoinitiator blend B at 12% has similar curing performance than the commercial blend. These results show that the curing performance of photoinitiator blend B is better than photoinitiator blend A at the same photoinitiator level, consequently Irgacure 369 presents better curing performance than ITX in black inks. Combinations of the photoinitiator blends A and B give cost effective formulations.

A standard commercial black base ink has also been reformulated by using the universal blends A and B.

The results shown in Table XIV.3 indicate that combinations of photoinitiator blends A and B exhibit better curing performance than several commercial photoinitiator blends.

Black Base		100 ft/min	230 ft/min
Commercial ink 1 12%		6-7	>14
Commercial ink 2 12%		5-6	14
Commercial ink 3 12%		6-7	11-12
A25/B75	12%	5-6	13
A10/B90	12%	5-6	11

Table 3 Curing performance of a black ink base cured with combinations of the photoinitiators blends A and B at different ratios with two lamps in tunnel conveyor at different speeds.

XIV.1.2 Curing performance of cyan inks

A standard cyan base has been formulated with the new universal PI blends. The different ink formulations have been printed and cured at the same conditions as explained previously.

Cyan base	100 ft/min	150 ft/min	200 ft/min	230 ft/min
Commercial ink	3-4	4	5	7
A100 12%	4	5	5	5-6
A75/B25 12%	4	5-6	6	7
A50/B50 12%	3-4	4	5	5
A25/B75 10%	3	5	5-6	6-7
A25/B75 12%	3	5	5	6
B100 12%	3-4	4	5	7

Table XIV.4 Curing performance, measured as the number of passes required to obtain total cure (thumb twist resistance), of a cyan ink base cured with combinations of the photoinitiators blends A and B at different ratios with one lamp in a tunnel conveyor at different speeds.

The results shown in Table XIV.4 indicate the existence of very little differences between the different formulations studied. These results reflect that the curing performance of photoinitiator blend B is slightly better than photoinitiator blend A at the same photoinitiator level, consequently Irgacure 369 has slightly better curing performance than ITX in cyan inks. This little difference of reactivity may be due to the extended absorption of ITX into the visible range and the existence of a pigment absorption window in the near UV/visible range.

XIV.1.3 Curing performance of magenta inks

A standard magenta base ink and magenta process ink have been formulated with the new universal photoinitiator blends. The different ink formulations have been printed and cured at the same conditions as explained previously.

Magenta Base Ink	100 ft/mn	230 ft/min
Commercial ink 8%	1-2	2
A100 7%	1-2	2
A100 8%	1-2	2
A25/B75 8%	1	2
A25/B75 9%	1	1-2
B100 8%	1	1

Table XIV.5 Curing performance of a magenta ink base cured with combinations of the photoinitiators blends A and B at different ratios with a tunnel conveyor at different speeds.

Magenta Process Ink	100 ft/min	150 ft/min	200 ft/min	230 ft/min
Commercial ink 10%	1	1-2	2	2-3
A100 10%	1-2	2	2-3	3
A25/B75 9%	1-2	2	2-3	3
A25/B75 10%	1	1-2	2	2-3
B100 10%	1	1	2	2.3

Table XIV.6 Curing performance of a magenta process ink cured with combinations of the photoinitiators blends A and B at different ratios with a tunnel conveyor at different speeds.

The relative curing performance is compared below in a decreasing order:

- **B100 10% > Commercial ink $\approx$ A25/B75 10% > A25/B75 9% $\approx$ A100 10%**

These results, shown in Tables XIV.5 and XIV.6, indicate that the curing performance of photoinitiator blend B is better than photoinitiator blend A at the same photoinitiator level. Consequently Irgacure 369 exhibits higher reactivity than ITX in magenta inks.

XIV.1.4 Curing performance of yellow inks

A standard yellow base has been formulated with the new universal PI blends. The different ink formulations have been printed and cured at the same conditions as explained previously.

Yellow Process Ink	100 ft/mn	230 ft/min
A100 7%	1-2	2
A100 8%	1	1-2
A75/B25 7%	1	1-2
A75/B25 8%	1	1-2
A25/B75 7%	1	1
A25/B75 8%	1	1
B100 7%	1	1
B100 8%	1	1

Table XIV.7 Curing performance of a yellow process ink cured with combinations of the photoinitiators blends A and B at different ratios with a tunnel conveyor at different speeds.

These results shown in Table XIV.7 indicate that the curing performance of photoinitiator blend B is better than photoinitiator blend A at the same photoinitiator level. These results confirm that Irgacure 369 exhibits better curing performance than ITX in yellow inks.

XIV.2 Conclusions

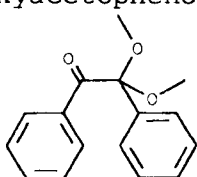
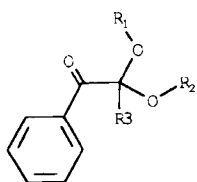
The manufacturing process of a printing ink manufacturing company was based on a “dry process” characterised by the dispersion of solid photoinitiators in resins during the first step of the production process. This photoinitiator dispersion process often lasted around one and a half hour and it was one of the most important limiting factors affecting the production output. The objective of this project was to design eutectic liquid photoinitiators blends of outstanding reactivity and stability in bulk. Kinetic and stability studies have been carried out in order to determine which photoinitiator combinations presented the best balance of reactivity and stability for the most number of pigments. Two near eutectic liquid photoinitiator blends have been designed for curing both dark and light colour inks. These two blends possess high absorbance in the short UV balanced with a relatively lower absorbance in the near UV. The two near eutectic liquid photoinitiator blends A and B resulted in a high curing performance exhibiting higher reactivity than most commercial ink formulations. Blends A and B are being used in the manufacture of all the range of UV offset lithographic and flexographic inks of a printing ink manufacturing company.

APPENDIX

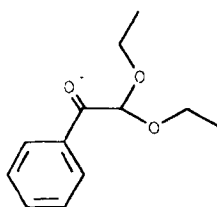
Commercial name	Chemical name	Supplier
IRGACURE 184	HCPK 1-Hydroxycyclohexyl phenylketone	CIBA
IRGACURE 369	DBMP2-Benzyl-2-N,N-dimethylamino-1-(4morpholinophenyl)-1-butanone	CIBA
IRGACURE 500	HCPK/Benzophenone (BP)1:1	CIBA
IRGACURE 651	BDK Benzyl Dimethyl Ketal or 2,2-dimethoxy-2-phenyl acetophenone	CIBA
IRGACURE 907	MMMP 2-Methyl-1-(4-(methylthio)phenyl)-2-morpholino propan-1-one	CIBA
DAROCUR 1173	HMPP 2-Hydroxy-2-methyl-1-phenyl-propan-1-one	CIBA
IRGACURE 2959	4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-methyl propyl) ketone	CIBA
IRGACURE 819	Bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide	CIBA
SPEEDCURE BP	Benzophenone	Lambson
SPEEDCURE BEM	BP/methyl- BP mixture	Lambson
SPEEDCURE MBB	Methyl o- benzoylbenzoate	Lambson
GENOCURE MBF	Methylbenzoylformate	RAHN
GENOCURE DEAP	2,2-Diethoxyacetophenone	RAHN
DBAP	2,2-Di-sec-butoxyacetophenone	First Chemicals
QUANTACURE BMS	(4-(4-methylphenylthio) phenyl)phenylmethanone. 4-benzoyl-4'-methyldiphenyl sulphide	G. Lakes
ESACURE TZT	Eutectic mixture of 2,4,6-trimethylbenzophenone and 4-methylbenzophenone	Lamberti
TRIGANOL 12	p-phenyl benzophenone	AKZO
LUCIRIN TPO	2,4,6-trimethyl benzoyldiphenyl phosphine oxide	BASF
QUANTACURE ITX	Isopropylthioxanthone (mixture of 2- and 4-isomers)	G. Lakes
QUANTACURE CPTX	1-Chloro-4-propoxythioxanthone	G. Lakes

Table A.1 List of commercial photoinitiators

I Alpha-alpha-dialcoxyacetophenones

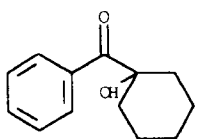
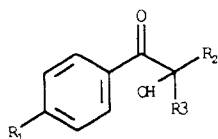


DMPA (BDK)

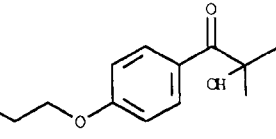


DEAP

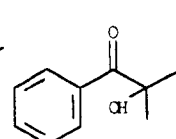
II Alpha-hydroxy alkyl phenones



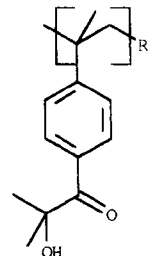
Irgacure 184



Irgacure 2959

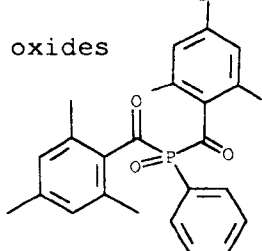
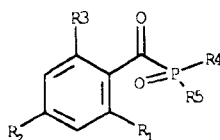


Darocur 1173

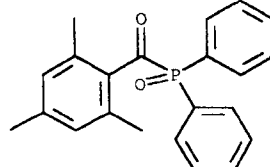


Esacure KIP150

III Benzoyl phosphine oxides

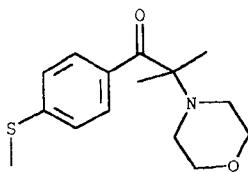
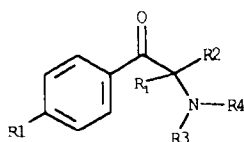


Irgacure 819

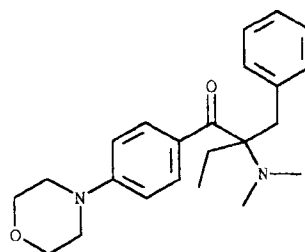


Lucirin TPO

IV Alpha-amino ketones



Irgacure 907



Irgacure 369

Figure A.1 Type I photoinitiators

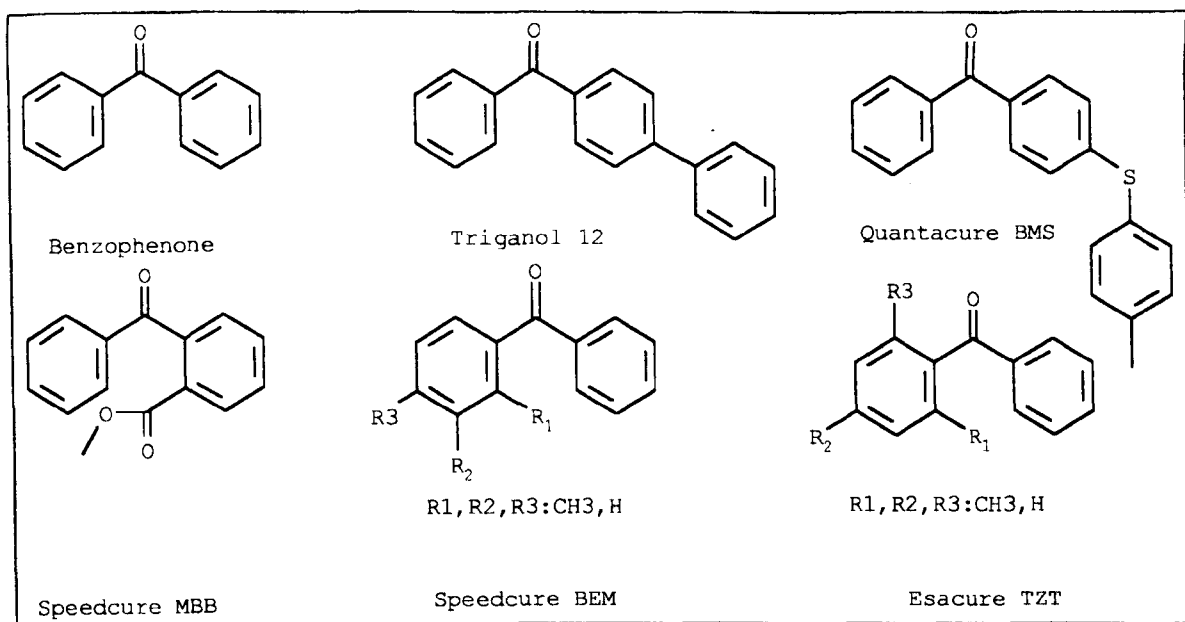


Figure A.2 Commercial benzophenone derivatives photoinitiators

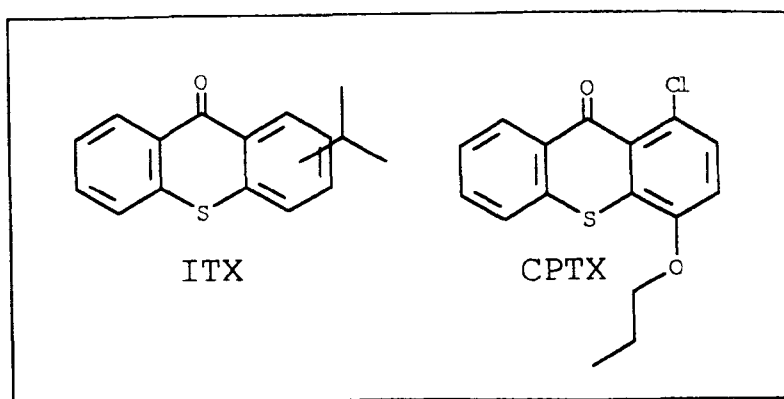


Figure A.3 Commercial thioxanthone photoinitiators.

Commercial name	Supplier	Chemical name	Functionality
Actilane 441	AKCROS	DITMPTA Ditrimethylolpropane tetracrylate.	4
Actilane 440	AKCROS	PPTTA Alkoxylated tetrafunctional acrylate monomer	4
Lucirin LR8889	BASF	Amine modified polyether acrylate	-
Actilane 421	AKCROS	Aliphatic difunctional acrylate ester	2
Actilane 422	AKCROS	DPGDA Dipropylene glycol diacrylate	2
Actilane 432	AKCROS	GPTA Glyceryl propoxylated triacrylate	4
TMPTA DEO	UCB	Trimethylolpropane triacrylate	3
Laromer TPGDA	BASF	Tripropylene glycol diacrylate	2
Ebecryl 53	UCB	Purified OTA480, equivalent to GPTA	3

Table A.2 List of UV reactive diluents.

Commercial name	Supplier	Chemical name	F
EB 657	UCB	Fatty acid modified polyester acrylate oligomer $M_w \approx 1500$	4
EB 870	UCB	Fatty acid modified polyester acrylate oligomer $M_w \approx 1500$	6
EB 1608	UCB	80%EB1600 diacrylate ester of Bisphenol A diglycidyl ether ($M_w \approx 500$) at 20%OTA480	2
ACTILANE 165	AKCROS	Aromatic urethane acrylate based on aliphatic polyester	4
CRODA U2/297	CRODA	Acrylated urethane alkyd resin in 20%GPTA	-
ACTILANE 300	AKCROS	High M_w acrylated epoxidised soya bean oil	4
ACTILANE 330	AKCROS	Acrylated aliphatic epoxy resin	3
UVECRYL E1354	UCB	Low M_w urethane acrylate based on pentaerythritol	6
ACTILANE 167	AKCROS	Low M_w aromatic urethane acrylate/polyester backbone	2
ACTILANE 515	AKCROS	Aliphatic polyester acrylate	4
CRODAMER UVM 104	CRODA	80% epoxy diacrylate based on Bisphenol A and 20% GPTA	2

Table A.3 List of UV resins.