New Liquid Photoinitiators for Light and Dark Pigmented Ink Systems

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Abstract: *Two new liquid photoinitiators designed specifically for pigmented UV inks are described in this presentation. Both of the photoinitiators are TSCA listed and commercially available. Liquid blend packages of the photoinitiators are also prepared based on these two new inventions to provide excellent cost performance. The blends are comparable in photo speed to the best in the market, and have many additional advantages. The impacts of pigment type, pigment loading, photoinitiator dosage, and substrate are discussed in this presentation.*

INTRODUCTION

Liquid form photoinitiators provide many advantages over their powder form counterparts. First, liquids are easy to handle. The hazards associated with the fine dust in using solid photoinitiators can be totally eliminated. Due to their intrinsic physical properties, liquid photoinitiators also have high resin and pigment compatibility, which make the final ink formulations more stable with a longer shelf life. Liquid photoinitiators also do not crystallize out from their formulations. Consequently, more consistent ink shelf performance can be achieved. Painstaking grinding of some solid photoinitiators to dissolve them in resins can be replaced by simple blending, and thus higher productivity can be obtained.

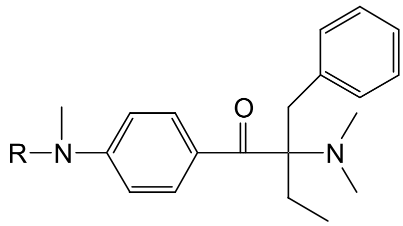
In this presentation, two newly developed liquid photoinitiators are introduced. They are specially designed for pigmented systems and have high resin and pigment compatibility, as well as photoactivity. The photoinitiators have very low toxicity and are TSCA listed. They are free or have very low odor and their cured products have very low extractibles. Both properties provide a safer and more acceptable application environment.

Low viscosity and stable liquid blend packages are also prepared from these two inventions. The blends have great photo speed as well as compatibility toward various pigments and are highly soluble in resins. The impacts of pigment loading, pigment type, and photoinitiator dosage are also described here.

THE NEW LIQUID PHOTOINITIATORS

BDMD-3: The new liquid photoinitiator designed specifically for dark pigmented systems has the structure showed in Scheme 1 below:

Scheme 1: BDMD-3 Structure



R= Polymeric tail

where R is an oligomer of ε -caprolactone and have an average repeating unit of 3. The UV absorption spectrum of BDMD-3 is shown below in Figure 1.

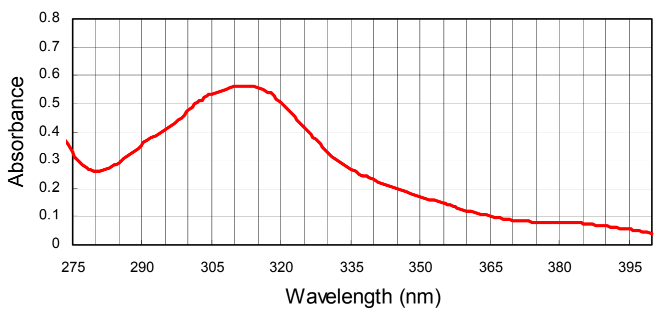


Figure 1: UV Absorption of BDMD-3

Note that BDMD-3 has strong absorption at most commonly used UV curing light wavelength range. This intrinsic property gives BDMD-3 good UV activities. The typical physical properties of BDMD-3 are listed in Table 1.

Table 1: Physical Properties of BDMD-3

Item	Description
Appearance	Yellow to light amber liquid
Viscosity	100,000 cps max.
Color (Gardner)	20 max. (10% in Toluene)
Freezing point	< -10 °C
Density	1.10 g/cm^3 @ 20 °C

Due to the specially designed ε-caprolactone tail, BDMD-3 is a liquid and has great solvency. *It is readily mixable with all commonly used UV curing monomers and oligomers. It also disperses well with pigments, which increases the overall formulation stability significantly*.

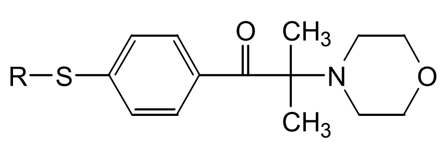
The toxicity data of BDMD-3 are listed in Table 2. Since BDMD-3 does not contain any environmentally harsh functional group or element, and the ε-caprolactone tail is biodegradable, thus it is a very environmentally friendly photoinitiator to use.

Table 2:Toxicity Data of BDMD-3

Item	Level
Acute oral toxicity LD_{50}	>2,000 mg/kg
Acute dermal irritation (rabbit)	Non-irritant
Acute eye irritation (rabbit)	Slight irritant

MMMP-3: This liquid photoinitiator which is designed specifically for light pigmented systems has the structure showed in Scheme 2 below and has been reported previously[1]:

Scheme 2: MMMP-3 Structure



R= Polymeric tail

where R is an oligomer of ε-caprolactone. Similar to BDMD-3, the tail of this liquid photoinitiator also has an average repeating unit of 3. The UV absorption spectrum of MMMP-3 is shown below in Figure 2.

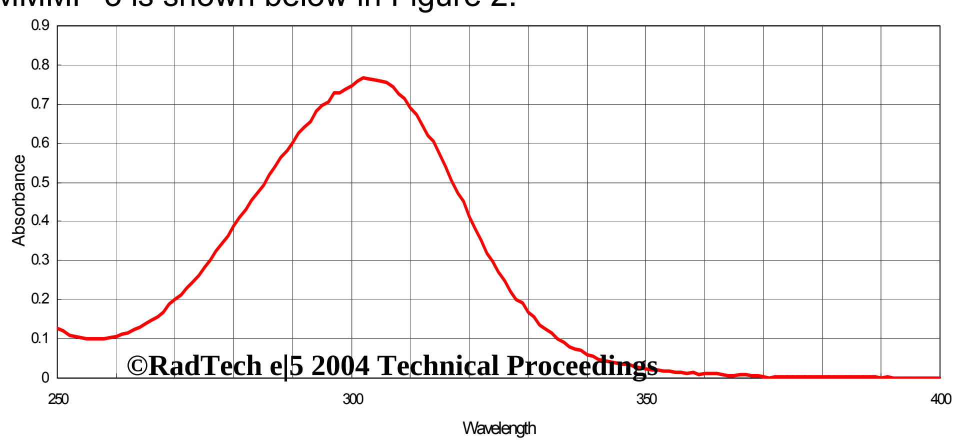


Figure 2: UV Absorption of MMMP-3

Again, MMMP-3 also has strong absorption at most commonly used UV curing light wavelength range and is blue shift by around 10 nm comparing to BDBM-3. The typical physical properties of MMMP-3 are listed in Table 3.

Table 3: Physical Properties of MMMP-3

Appearance	Yellow to light amber liquid
Viscosity	3,000 cps max.
Color (Gardner)	7 max. (10% in Toluene)
Freezing point	< 5 °C (14 °F)
Density	1.20 g/cm^3 @ 20 °C

Due to the specially designed ε-caprolactone tail, MMMP-3 is also a liquid and has great resin compatibility. It is readily mixable with all commonly used UV curing monomers, oligomers, and pigments. Formulations used MMMP-3 also shows a very satisfying long-term stability and performance consistency.

The toxicity data of MMMP-3 are listed in Table 4. Since the MMMP-3 also does not contain any environmentally harsh functional group or element, and also has the biodegradable ε-caprolactone tail, MMMP-3 is also a very environmentally friendly photoinitiator.

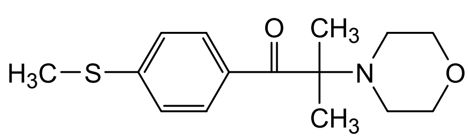
Table 4:Toxicity Data of MMMP-3

Acute oral toxicity LD_{50}	>2,000 mg/kg
Acute dermal irritation (rabbit)	Non-irritant
Acute eye irritation (rabbit)	Slight irritant

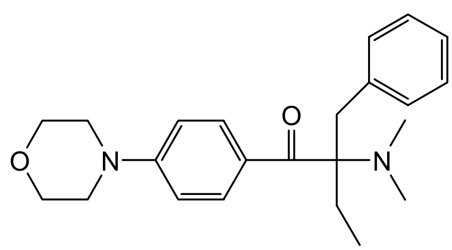
<u>Resin compatibility</u>: Both BDMD-3 and MMMP-3 have high resin stability as illustrated by the following solubility data in Table 5. The high solubility of BDMD-3 and MMMP-3 can be contributed to the ε-caprolactone tail in their structure.

Table 5: Resin Solubility

Solubility (g in 100 ml solvent @ 20 °C)	BDBM	BDMD-3	MMMP	MMMP-3
TMPTA	NA	>50	20	>50
TPDGA	NA	>50	NA	>50
HDDA	5	>50	25	>50



Scheme 3: MMMP Structure



Scheme 4: BDMD Structure

PHOTOACTIVITIES OF BDBM-3 AND MMMP-3

The photoactivity of MMMP-3 is comparable to 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one (MMMP, see Scheme 3), as reported previously[1]. Table 6 compares the photoactivities and ease of incorporation to resin of MMMP-3 and BDMD-3, to BDMD, which is commonly used in the industry. The chemical structure of BDBM is shown in Scheme 4 above.

Table 6: Photoactivity Comparison – MMMP-3, BDMD-3, and BDMD

Composition*1	Ink 1	Ink 2	Ink 3
BDMD*2	5	-	-
MMMP-3*3	-	10*4	-
BDMD-3*5	-	-	10*4
EMK*6	0.5	0.5	0.5
ITX*7	1.0	1.0	1.0
TMPTA	25	25	25
Ebecyl 3702	60	60	60
Carbon black	3	3	3
Times for grinding	**3**	***8**	***8**
Viscosity (cps, initial)	6,670	3,740	4,600
Photospeed (ft/min)	**550**	**530**	**560**

*1: By part.

*2: Available from Ciba Specialty Chemicals as Irgacure 369.

*3: Available from Chitec Technology Co. as Chivacure 3482.

*4: Based on same equivalent chromophore weight.

*5: Available from Chitec Technology Co. as Chivacure 3690.

*6: Available from Chitec Technology Co. as Chivacure EMK.

*7: Available from Chitec Technology Co. as Chivacure ITX.

*8: Blending is applied instead of grinding to dissolve the photoinitiator.

It is obvious from this table that MMMP-3 and BDMD-3 both have phtoactivities similar to BDMD. The new liquid photoinitiators do not need to be ground into the resin system due to their excellent compatibility. At the same time, formulations employing MMMP-3 and BDMD-3 have significantly lower viscosities, which provide easier handling of the final products.

LIQUID PHOTOINITIATOR BLEND FOR DARK COLOR PIGMENTED SYSTEMS

To achieve optimum cost performance, BDMD-3 can be blended with various commercially available photoinitiators to obtain lower cost and to achieve photoactivity synergy. For example, BDMD-3 can be blended with ITX, EMK, BDK, EPD to offer a liquid blend, Quadracure DC. This liquid blend has physical properties listed in Table 7.

Table 7: Physical Properties of Quadracure DC

Appearance	Yellow to light amber liquid
Viscosity	5,000 cps max.
Color (Gardner)	15 max. (10% in Toluene)
Freezing point	< -10 °C (14 °F)
Density	1.13 g/cm^3 @ 20 °C

This free flowing and very stable liquid blend has a UV absorption spectrum, which also shows strong absorption in commonly used UV light range, as shown in Figure 3.

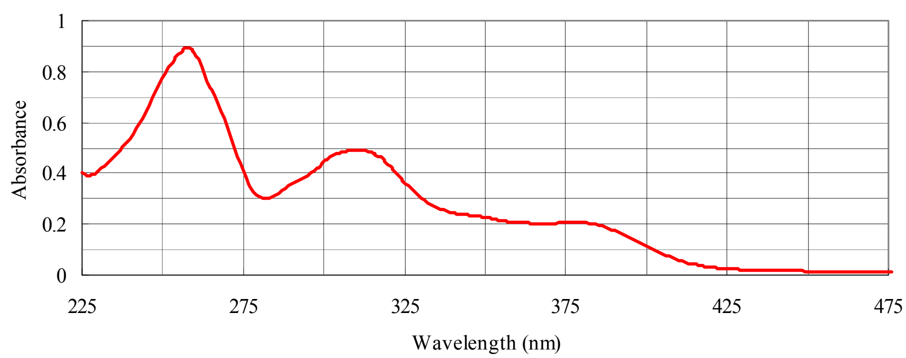


Figure 3: UV Absorption of Quadracure DC

The photoactivity of Quadracure DC is evaluated with different pigments at various loadings. The results are shown in Table 8.

Table 8: Photoactivities of Quadracure DC

	Photospeed, ft/min	
Pigment loading, part	Black	Blue
0	484	484
3	435	476
10	287	459
15	139	451
25	16	443

1. Resin system: 20 parts EB 657, 25 parts EB 220, 10 parts EB 3702, 15 parts EB 436
2. Black pigment: S-250 from Degussa
3. Blue pigment: C. I. B. –15:3 from Dainippon Ink
4. With 10 parts Quadracure DC

It is obvious from the table that Quadracure DC, a blend based on BDMD-3, can offer high photospeed for dark color pigmented system even up to 25 parts blue pigment loading. For black pigment loading, the blend can provides a good photospeed even up to 10 parts level.

In practice, often times pigment loadings have to be high to achieve desired graphic effects. However, as shown in Table 8, it is unavoidable that the photospeed of high pigment inks or coatings could be slowed down. To compensate this photospeed loss at high pigment loadings, usually a higher potoinitiator dosage need to be utilized. Unfortunately, photoinitiators like BDMD do not have good solubility in resins. Therefore, a high enough dosage of photoinitiator cannot be achieved. This difficulty is now completely solved by the invention of BDMD-3 due to its great solubility. ***The formulated inks using BDMD-3 can have dosage higher than 15 parts and still are stable for long-term storage and do not have solubility issue.*** The effects of dosage of Quadracure DC on the ink formulations with high pigment loadings can be explained in Table 9 below.

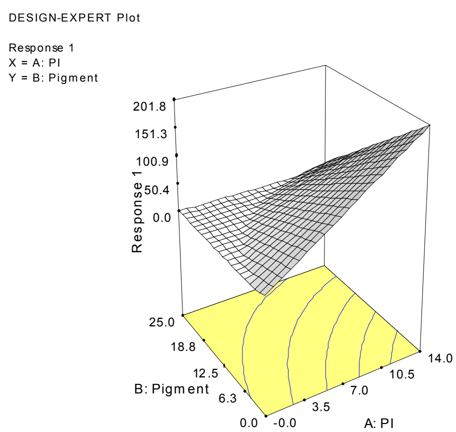
Table 9: Impacts of Quadracure DC Dosage

	Photospeed, ft/min	
Photoinitiator dosage, part	Black	Blue
2	16	74
6	156	205
10	287	451
14	410	484

1. Resin system: the same as Table 8
2. Black pigment, 10 parts; Blue pigment, 15 parts.

To provide further insight on the correlation between Quadracure DC dosage, pigment loadings, and photospeeds, three-dimensional figures are constructed as shown in Figure 4 for black and blue pigments.

Black Ink



Blue Ink

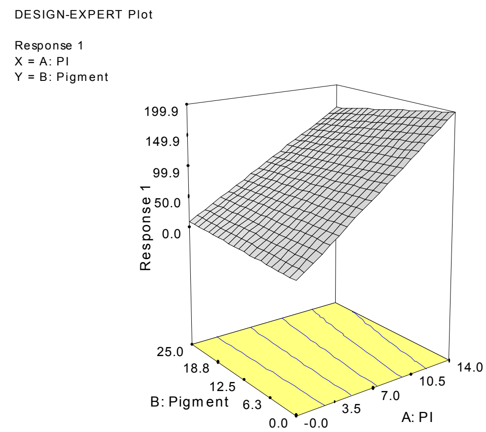


Figure 4: Three-Dimensional Correlation of Quadracure DC

Note that the photospeeds for both blue and black pigment systems are both proportional to the Quadracure DC dosage. The effects do not level out even at as high as 14% parts photoinitiator dosage.

LIQUID PHOTOINITIATOR BLEND FOR LIGHT COLOR PIGMENTED SYSTEMS

Similar to BDMD-3, MMMP-3 can also be blended with various readily available photoinitiators to achieve potoactivity synergy and to achieve an optimum cost performance,. For an example, MMMP-3 can be blended with ITX, EPD, BDK to offer a liquid blend, Quadracure LC. This liquid blend has physical properties listed in Table 10.

Table 10: Physical Properties of Quadracure LC

Appearance	Yellow to light amber liquid
Viscosity	3,000 cps max.
Color (Gardner)	15 max. (10% in Toluene)
Freezing point	< -10 °C (14 °F)
Density	1.13 g/cm^3 @ 20 °C

This free flowing and stable liquid blend has a UV absorption spectrum, which also shows strong absorption in commonly used UV light range, as shown in Figure 5.

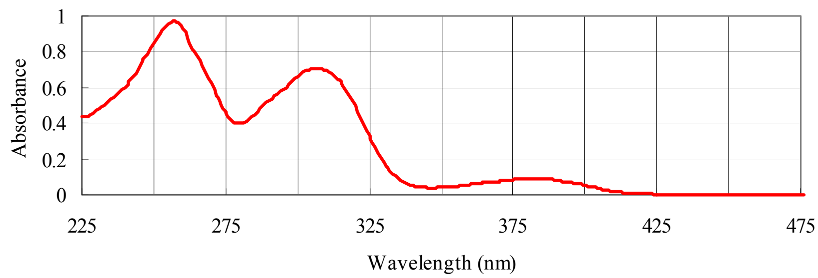


Figure 5: UV Absorption of Quadracure LC

The photoactivity of Quadracure LC is evaluated with various pigments at different loadings. The results are shown in Table 11.

Table 11: Photoactivities of Quadracure LC

	Photospeed, ft/min		
Pigment loading, part	Yellow	Green	Red
0	451	451	451
3	443	443	443
10	418	427	427
15	394	394	410
25	369	361	386

1. Resin system: 27.3 parts EB 657, 20 parts EB 220, 17 parts EB 600, 8 parts OTA 480, 2 parts $CaCO_3$, 0.7 part UV-2
2. Yellow pigment: 304 from Fu Da Co., Taiwan
3. Green pigment: C. I. G.-7 – 15:3 from Dainippon Ink
4. Red pigment: C. I. R. – 57:1 from Dainippon Ink
5. Photoinitiator dosage: 6 parts.

It is obvious from Table 11 that Quadracure LC, a blend based on MMMP-3, can offer high photospeed for light color pigmented systems even up to 25 parts loading without much loss on photospeed. Just like Quadracure DC, ***the formulated inks using Quadracure LC can have dosage higher than 15 parts and still are stable for long-term storage and do not have solubility issues.*** The dosage influences of Quadracure LC on ink formulations with high pigment loadings can be explained in Table 12 below.

Table 12: Impact of Quadracure LC Dosage

	Photospeed, ft/min		
Photoinitiator dosage, parts	Yellow	Green	Red
2	74	66	82
6	295	279	287
10	394	394	410
14	468	459	443

1. Resin system: the same as Table 11
2. Pigment loading: 15 parts.

To provide further insight on the correlation between Quadracure LC dosage, pigment loadings, and photospeeds, three-dimensional figure are constructed as shown in Figure 6 for yellow, green, and red pigments. Note that the photospeeds for yellow, green, and red pigment systems are all proportional to the Quadracure LC dosage. The effects do not level out even at as high as 14% parts photoinitiator dosage.

Yellow Ink Green Ink Red Ink

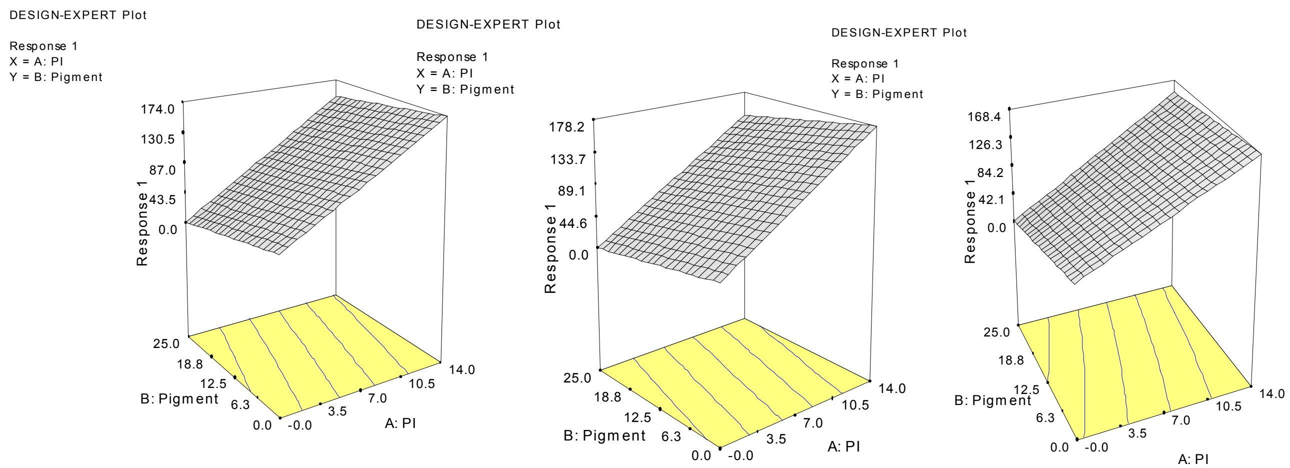


Figure 6: Three-Dimensional Correlation of Quadracure DC

APPLICATION ON PVC

The excellent performance of the new photoinitiator, BDMD-3, and the synergistic effects when it is used with other photoinitiators/photosensitizers are further demonstrated using a black offset ink on PVC substrate. The results are shown in Table 13 below.

Table 13: BDMD-3 Performance on PVC

Photoinitiator	Formula 1	Formula 2	Formula 3	Formula 4
BDMD-3	10	-	4	4
BDMD	-	5[4]	-	-
ITX	3	3	2	2
EMK	-	-	1.5	-
EPD	-	-	2	2
BDK	-	-	-	1
Phtospeed	115 ft/min	131 ft/min	180 ft/min	180 ft/min

1. Resin system: 25.8 parts EB 657, 20 parts EB 220, 15.5 parts EB 600, 18 parts S-250 black

pigment from Degussa, 10.7 parts other additives.

2. Ninety parts of resin are used for each formula. Dosages of photoinitiators are in parts.
3. ITX, EMK, EPD, and BDK are available from Chitec Technology Co. as Chivacure ITX, Chivacure EMK., Chivacure EPD, and Chivacure BDK, respectively.
4. Equal molar dosage comparing to BDMD-3.

Based on the same effective moiety dosage, the photospeed of BDMD-3 is comparable to that of BDMD on PVC surface. The excellent synergistic effects of adding other photoinitiators are also observed on PVC. In these cases, the dosage of BDBM-3 can be reduced by 60% and yet far superior photocuring speed can be obtained.

CONCLUSION

Two new liquid photoinitiators are introduced here. The photoinitiators have great solvency properties and hence shows excellent resin solubility and pigment compatibility. This unique property makes higher dosage possible, and higher photospeed applications can be achieved. The new photoinitiators are also odor-free and are very low in toxicity. Combining these attributes and their liquid properties, safer, more convenient, and less labor required formulation preparation is possible. Two blends are derived from the new invention. They inherit the same convenient liquid forms and have much improved cost performance due to photoactivity synergy. The correlation between pigment loadings, photoinitiator dosage, and photospeed are also presented. Both liquid phtoinitiator blends shows activity proportional to their dosages in the range of our study.

REFERENCES

(1) Gacek, J; Chiu, C; Yang, *Proceedings, RadTech 2002,* p. 397