Low color liquid acylphosphine oxide photoinitiators blends for UV coating applications

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Abstract
Two highly effective photoinitiator liquid blends are introduced for UV coating applications. They are based on acylphosphine oxide technologies and have been designed for: 1) ease of incorporation and compatibility, 2) fast photoresponse, and 3) low yellowing characteristics. Examples are given using the blends in pigmented coatings, clear coatings, UV stabilized coatings, gel coats and composites.

1. Introduction

Acylphosphine oxides are an important class of photoinitiators that are critical to the success of many light curable applications [1-3]. They provide a host of benefits among which are improved through-cure and higher photocure efficiencies. They have been used to photocure inks [4-12], coatings [13-16], pigmented coatings [17,18] and adhesives [19,20]. They are also the key photoinitiators for state-of-the-art manufacturing of optical fiber coatings [21-28], for UV powder coatings [29-33], thick composites [34-45] and highly pigmented gel coats [36,37,45]. For weather resistant coatings and varnishes, which employ UV absorbers, the acylphosphine oxide photoinitiators are essential to provide completeness of cure and low final color [46,47].

The photochemistry of monoacylphosphine oxide (MAPO) and bisacylphosphine oxide (BAPO) photoinitiators is well known, and follows Type I photocleavage from the short lived triplet excited state [48-54]. The radicals produced are very reactive and are used to initiate polymerization [48]. The photoexcitation process is driven by matching the absorption of the photoinitiator with a light source, which typically is in the mid-UV to visible spectral range (300 nm to 430 nm). Upon photocleavage, the long wavelength absorbing chromophore is consumed, which leads to a net photobleaching, and thus lower final color.

It is this photobleaching combined with the efficient production of energetic radicals that make these photoinitiators so powerful and provides new strategies to optimize photocuring. For example, in a typical coating application, an effective strategy is to use an acylphosphine oxide photoinitiator in combination with an α-hydroxy ketone (αHK) [55]. The αHK generally absorbs at shorter wavelengths compared to the acylphosphine oxide photoinitiator, and this fact leads to targeting specific spatial regions. The αHK is found to principally photocure the top of the coating, which is exposed to air, and the acylphosphine oxide targets the bottom region of the coating [2,3]. Since the acylphosphine oxide undergoes photobleaching, an optical hole is generated during light exposure, which consequently further enhances optical penetration and thus through-cure.

BAPO and MAPO photoinitiators may be further differentiated. For example, BAPO derivatives are generally more red shifted than MAPO derivatives [2,3]. The through-cure capability and ultimate photoactivity of BAPO are generally higher than of MAPO as well [2, 22, 35, 39].

With the increasing demands of new applications there is a need for “smarter” formulations. For example, there is a need to deliver faster formulations that are easier to produce, faster to cure, and exhibit lower final (or stable) color over a variety of process conditions. In this paper we wish to describe two new patent pending photoinitiator blends, based on acylphosphine oxides, that play a pivotal role in meeting these challenges. Specifically, the I-2022 photoinitiator and the I-2100 photoinitiator are both liquid blends, and are engineered to deliver high photocure response, lower color, higher miscibility in formulations, and better value-in-use compared to other commercially available photoinitiators in their class.

2. Experimental Methods

2.1. Photoinitiators

The structures and description of the photoinitiators described in this work are given in Table 1 and 2.

Table 1. Description of photoinitiators

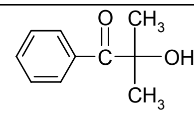
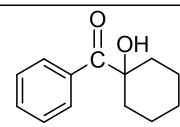
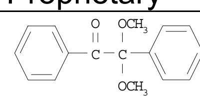
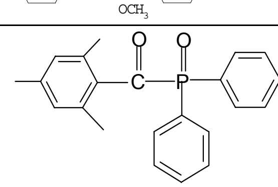
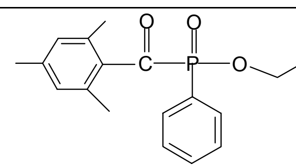
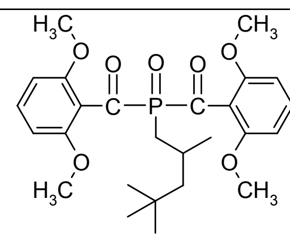
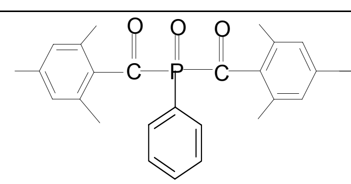
Type	Name [56,57]	Structure
αHK	D-1173	
αHK	I-184	
Phenyl Glyoxylate	I-754	Proprietary
BDK	I-651	
MAPO	TPO	
MAPO	TPO-L	
BAPO	I-403	
BAPO	I-819	

Table 2. Photoinitiator Blends

Type	Name [58]	Composition
Acylphosphine Oxide	I-2100	Proprietary, 100% acyl-phosphine oxide
αHK / Acylphosphine Oxide Blend	I-2022	Proprietary, and contains 22% acylphosphine oxide
αHK / Acylphosphine Oxide Blend	I-2020	D-1173 and 20% acylphosphine oxide
αHK / BAPO Blend	I-1850	I-184 + I-403 (1:1)
αHK / BAPO Blend	I-1700	D-1173 + I-403 (75/25)
αHK / MAPO Blend	D-4265	D-1173 + TPO (1:1)

2.2. Resins

Two white pigmented formulations were selected for evaluation. The first one is based on an aromatic urethane triacrylate from Bayer with 25 % Rutile-TiO_2. The second formulation is the standard screening formulation based on polyester hexaacrylate.

For evaluation of the reactivity the coatings were applied with a 100µm slit coater to coil coated aluminum sheets. They were cured with one 80 W/cm medium pressure mercury lamp at the maximum cure speed which is possible to obtain a through cure and tack-free surface. The coatings were applied to chipboard (100 µm) and cured at a belt speed of 3 m/min to determine the pendulum hardness, yellowing and gloss. After exposure time of 15 minutes and 16 hours under a fluorescent lamp (TL 40W/03) the measurements were remeasured.

Table 3: White aromatic urethane triacrylate formulation

Component [59]	Parts
Roskydal 2298 (aromatic urethane triacrylate, Bayer)	50
HDDA (1,6-Hexanedioldiacrylate, UCB)	15
SR 399 (Dipentaerythritol pentaacrylate, Sartomer)	10
Titaniumdioxide R-TC2 (rutile-type)	25

Table 4: White polyester hexaacrylate formulation

Component [59]	Parts
Ebecryl 830 (polyesterhexaacrylate, UCB)	67.5
HDDA (1,6-Hexanedioldiacrylate)	5.0
TMPTA (Trimethylolpropanetriacrylate)	2.5
Titaniumdioxide R-TC2 (rutile-type)	25.0

The aliphatic urethane clear coat resin used is given in Table 5. All components were mixed together with gentle heating to 50 to 80 ºC for 1 hour, then continued mixing at room temperature for an additional 1 hour.

Table 5: Aliphatic urethane clear coat formulation

Component	Parts
BR 5824 (Urethane acrylate oligomer, Bomar)	20
SR 601 (Ethoxylated bisphenol A diacrylate)	20
TMPTA	32
Di-trimethylolpropane tetraacrylate	25

3. Features and Benefits

3.1. Features and Benefits of I-2022

The main characteristics of I-2022 are summarized as:

- Liquid photoinitiator for free radical polymerization
- Photoinitiator absorbing in the range of 350-420 nm
- Containing BAPO (I-819) and αHK (D-1173) as key components
- Significantly better resistance to low temperature crystallization, compared to other αHK/BAPO blends

I-2022 addresses the limitations of the commercially available photoinitiator products, including those currently used in the fast-growing application areas of pigmented coatings and varnishes containing UV-absorbers. It offers several outstanding features and has a very wide "balance" of performance properties, as described in Table 6.

Table 6. Benefits of I-2022 photoinitiator

- Easy-to-use low viscosity liquid, providing significant savings in production over other solid acylphosphine oxide photoinitiators
- Shows excellent balance between through cure and surface cure in a wide range of systems including acrylates and unsaturated polyesters
- Offers versatility, i.e., can be used in a large range of colors, film thickness and pigment volume concentrations
- Offers the possibility to cure pigmented system without pre-gelation with Ga doped lamp

3.2. Features and Benefits of I-2100

The main characteristics of I-2100 are:

- Liquid photoinitiator for free radical polymerization
- Photoinitiator absorbing in the range of 350-420 nm
- 100% acylphosphine oxide composition

I-2100 addresses several of the shortcomings of the commercial MAPO photoinitiators (TPO or TPO-L) used in pigmented coatings and inks. Its main features are summarized in Table 7.

Table 7. Benefits of I-2100 photoinitiator

- Offers as an easy-to-use low viscosity liquid significant savings in production over other solid phosphine oxide photoinitiators
- Reactivity is improved over TPO-L and slightly better than with TPO
- Through cure is improved over TPO and TPO-L
- Permits the formulation of VOC free coatings

4. Physical Properties
4.1. Absorption Spectra: Broad Spectral Response

The absorption spectra of I-2022 and of I-2100 are given in Figures 1 and 2. Both show long wavelength absorption above 400 nm, which photobleaches upon photoexcitation.

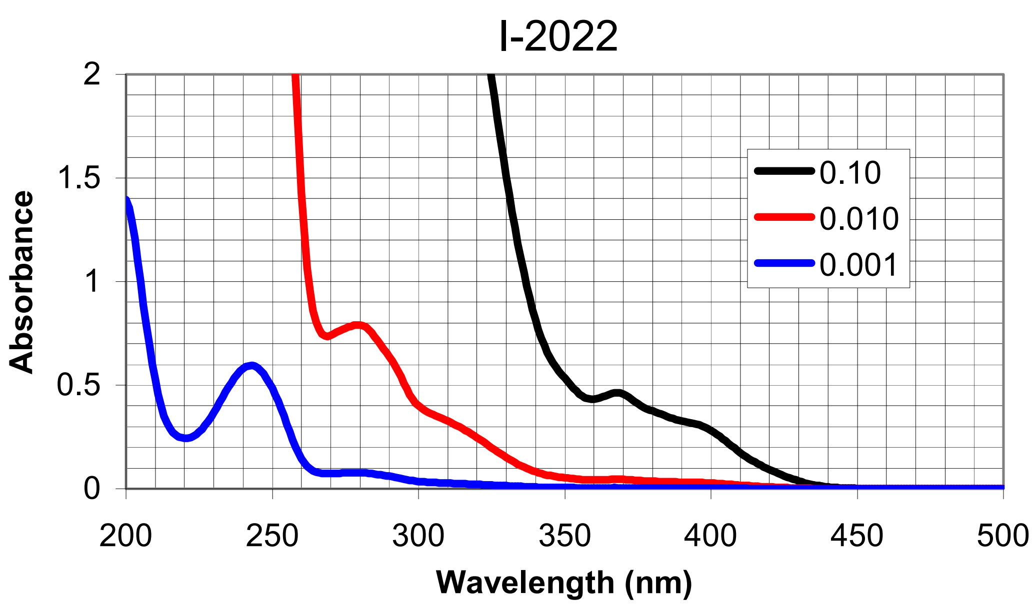


Figure 1. Absorption spectra of I-2022 in acetonitrile

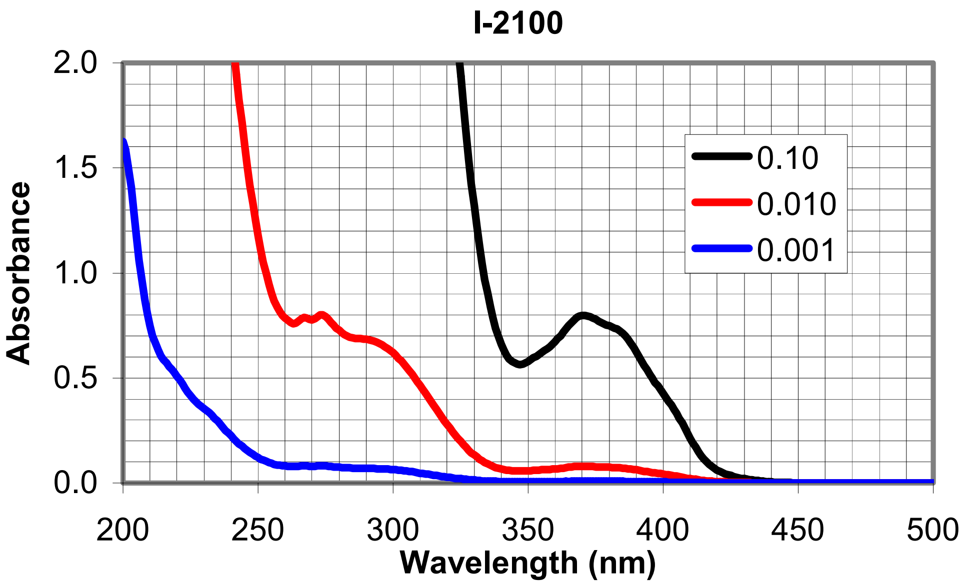


Figure 2. Absorption spectrum of I-2100 in acetonitrile

4.2. Low Volatility

The I-2022 and I-2100 have low volatility, as demonstrated by Figures 3 and 4. In the case of I-2022, the D-1173 is responsible for weight loss below 180 ºC. In contrast the I-2100 has much lower volatility, where significant weight loss occurs only at temperatures greater than 200 ºC.

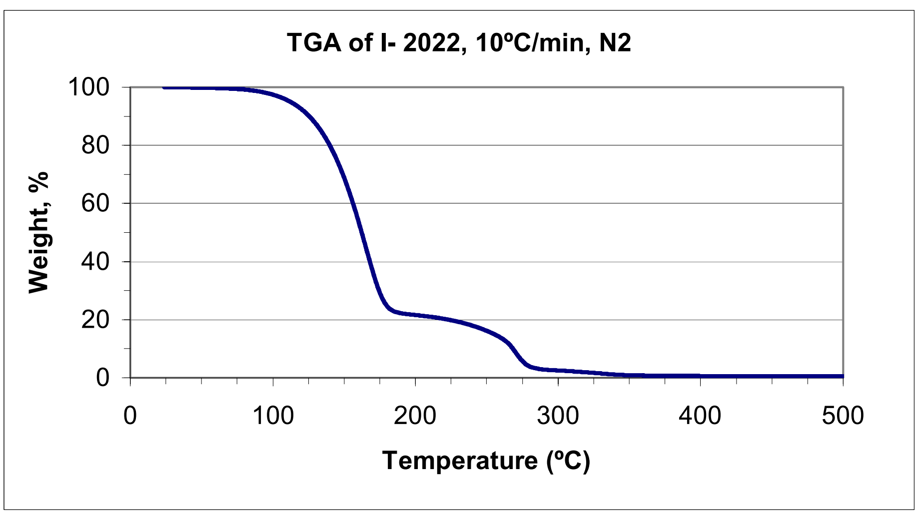


Figure 3. TGA of I-2022, at 10ºC/min under nitrogen.

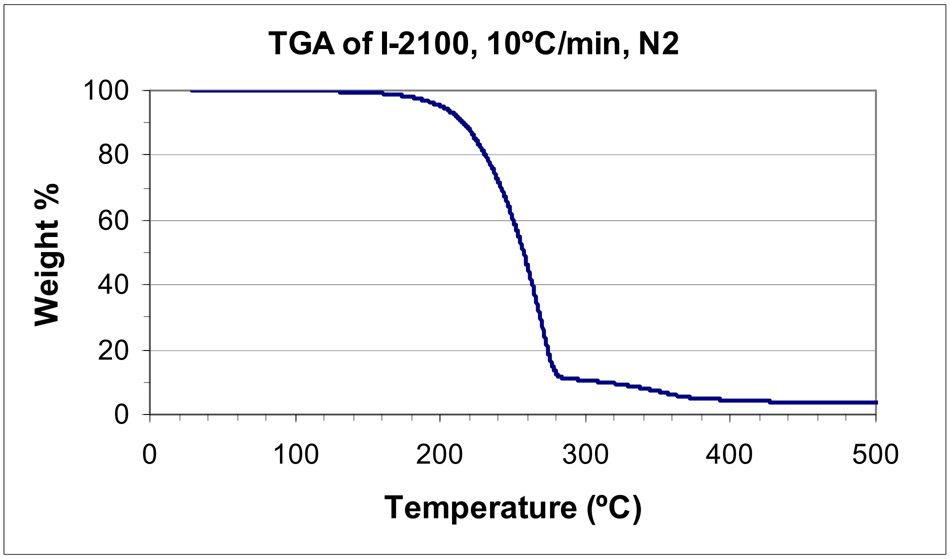


Figure 4. TGA of I-2100, at 10ºC/min under nitrogen.

4.3. Storage Stability

I-2022 is to be considered as a one-to-one replacement for I-2020. Compared to I-2020 this new blend shows significantly improved long-term storage stability. I-2022 may nonetheless freeze upon exposure to low temperatures for extended periods of time. Under such circumstances and also upon storage for extended periods below 6 ºC it cannot be completely excluded that some crystallization of the acylphosphine oxide might occur. In both cases the product is readily returned into its original form by gentle heating (30 ºC to 50 ºC) and stirring for a short period of time.

I-2100 freezes into a glass at low temperatures (< -20 ºC). Although no crystallization has yet been observed in storage stability tests, the possibility cannot be completely excluded that some crystallization may occur when stored for extended periods below 6 ºC. In both cases the product is readily returned into its original form by stirring for a short period of time at room temperature.

4.4. Compatibility / Miscibility in Monomers

Both I-2022 and I-2100 liquid photoinitiators were designed for ease of incorporation into resins as well as high photoactivity. These blends show superior solubility and faster incorporation rates into resins compared to the solid BAPO/MAPO photoinitiators. As shown in Figure 5, the solubility of either I-2022 or I-2100 is vastly superior compared to I-819 or TPO.

Because of their ease of incorporation, I-2022 or I-2100 can be added into the formulation at essentially any point in the resin preparation process. Their addition also requires little or no heating.

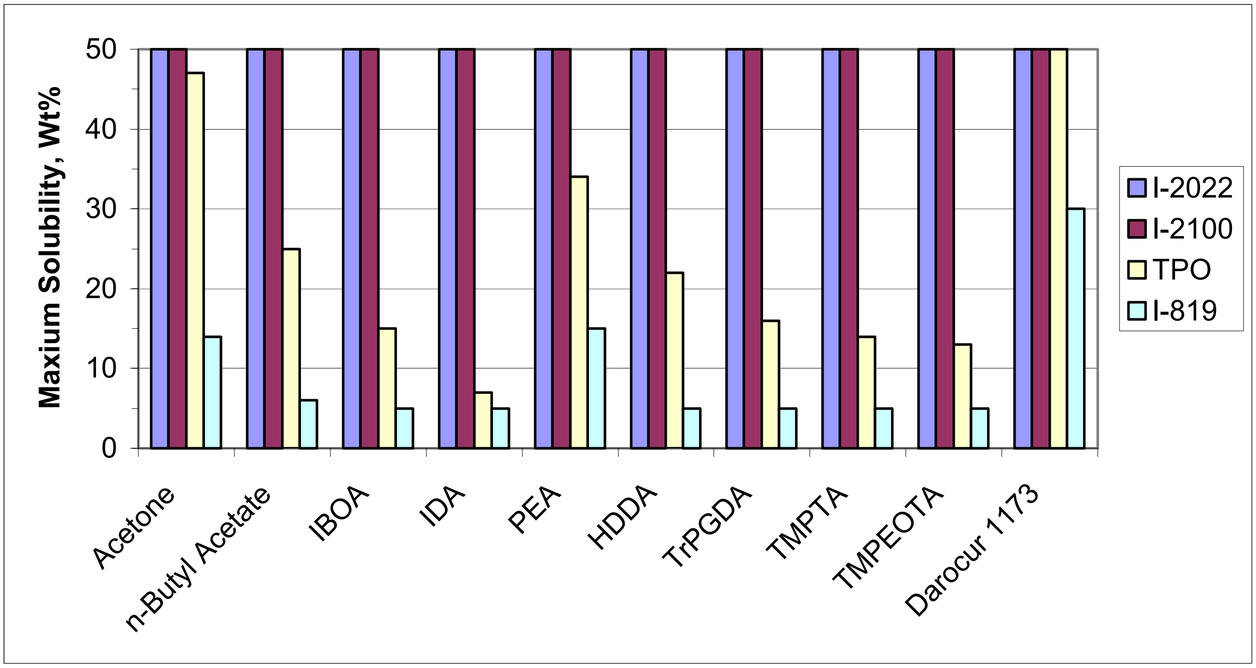


Figure 5. Demonstration of high solubility of I-2022 and I-2100. Note: the solubility of both I-2100 and I-2022 are greater than 50 wt% at 22ºC in the solvents/monomers examined.

5. Photocuring Applications

5.1. Performance of I- 2022

The I-2022 photoinitiator is based on the strategy of combining acylphosphine oxides with αHK photoinitiators. This marriage provides a convenient and powerful way to photocure a broad range of coatings with a variety of light sources. Table 8 lists the suggested starting point concentrations for I-2022 in a variety of important coating applications.

Table 8. Starting point concentrations of I-2022 as used in typical coating applications

Application	Recommended concentrations of I-2022
Clear acrylate coatings:	**1.0 – 2.0 %**
White acrylate furniture coatings:	**1.5 – 3.5 %**
White screen printing inks:	**2.0 – 4.0 %**
Glass reinforced UPES/styrene prepregs and composites:	**1.0 – 2.0 %**

As shown in Figure 6, I-2022 shows very high reactivity. In this example, the I-2022 was used as the photoinitiator in a white unsaturated polyester resin. The final pendulum hardness is similar to the pure acylphosphine oxide TPO, while yellowing is kept at an acceptable level.

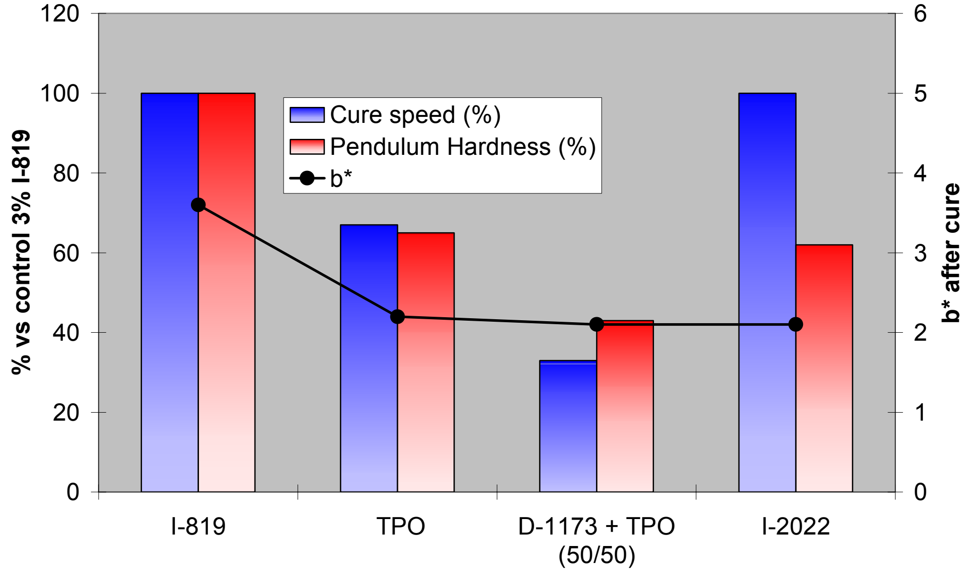


Figure 6. White Unsaturated Polyester, 25% TiO2, 3% Photoinitiator
Wet Film Thickness 100mm, Curing Ga+Hg lamp 80 W/cm, 3 m/min

In another comparative experiment it was found that the I-2022 was the most reactive photoinitiator, as shown in Figure 7. Performance in terms of through cure is slightly inferior to the pure acylphosphine I- 819 but significantly better than with TPO.

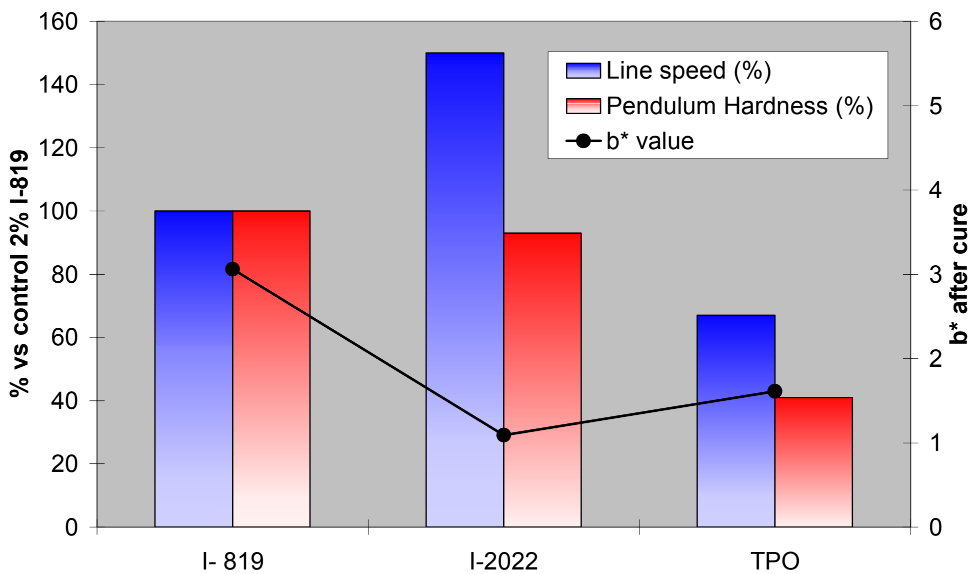


Figure 7. White Polyester Hexaacrylate, 25% TiO_2, 2% Photoinitiator
Wet Film Thickness 100 mm-Curing Hg lamp 80 W/cm, 3 m/min

I-2022 allows photocuring of varnishes containing UV absorber without hindering curing performance. As shown in Figure 8, very high conversion (which results in both surface cure and through cure) was observed when using the I-2022 photoinitiator.

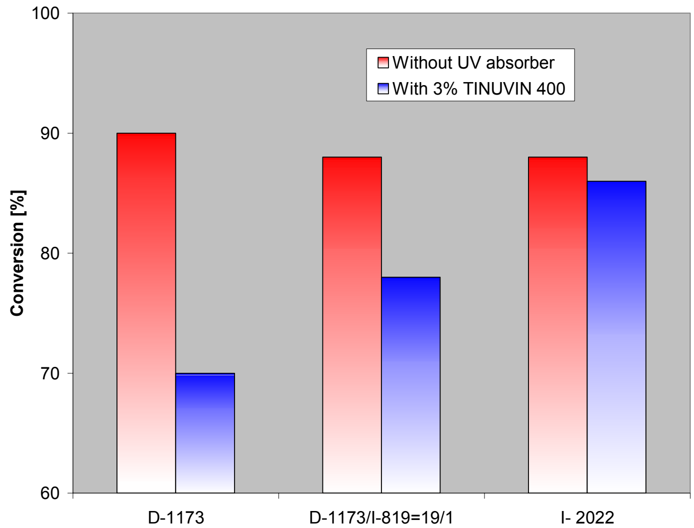


Figure 8. Influence of Photoinitiator and UV-Absorber [60] on Reactivity of Clearcoats: Aliphatic epoxyacrylate/aliphatic urethane acrylate/TPGDA/TMPTA photoinitiator: 3%; cure: 2 x 80 W/cm Hg medium pressure lamp; 20 m/min

5.2. Performance of I-2100

I-2100 is especially suited for white pigmented formulations with minimal yellowing after cure and for coatings with low pigment volume concentration. Suitable UV curable formulations may be based on acrylate resins, acrylate monomer systems and unsaturated polyesters. As a liquid photoinitiator, I-2100 is especially easy to incorporate into formulations.

I-2100 can be used as a sole photoinitiator but in most cases combinations with other photoinitiators, like e.g. α-hydroxyketones or phenylglyoxylates will give improved balance between through-cure and surface curing performance. Starting point concentrations of I-2100 as used in typical coating applications fall in the range of 1-5%, as summarized in Table 9.

Table 9. Starting point concentrations of I-2100 in various applications

Applications	% suggestion	Comments
Opaque White – Offset and Flexo Low Cost	2 to 4	With AHK or benzophenone
Opaque White – Offset and Flexo High-end Packaging	2 to 4	With I-2959 or I-754
Opaque White – Screen Printing	2 to 5	With AHK; I-819 may be required
Non White pigmented systems	1 to 3	More rare because less efficient than AAK For low residual odor
UV OPV – Low Cost	0.3 to 0.8	Cure Booster with AHK or Benzophenone
UV OPV – High-end packaging	0.3 to 0.8	Cure Booster with I-2959 or I-754

With I-2100, fast photopolymerization is possible, as shown in Figure 9. The relative values shown in Figure 9 were made relative to the control, which contained 2% I-819. Pendulum Hardness and cure speed are expressed as % versus control.

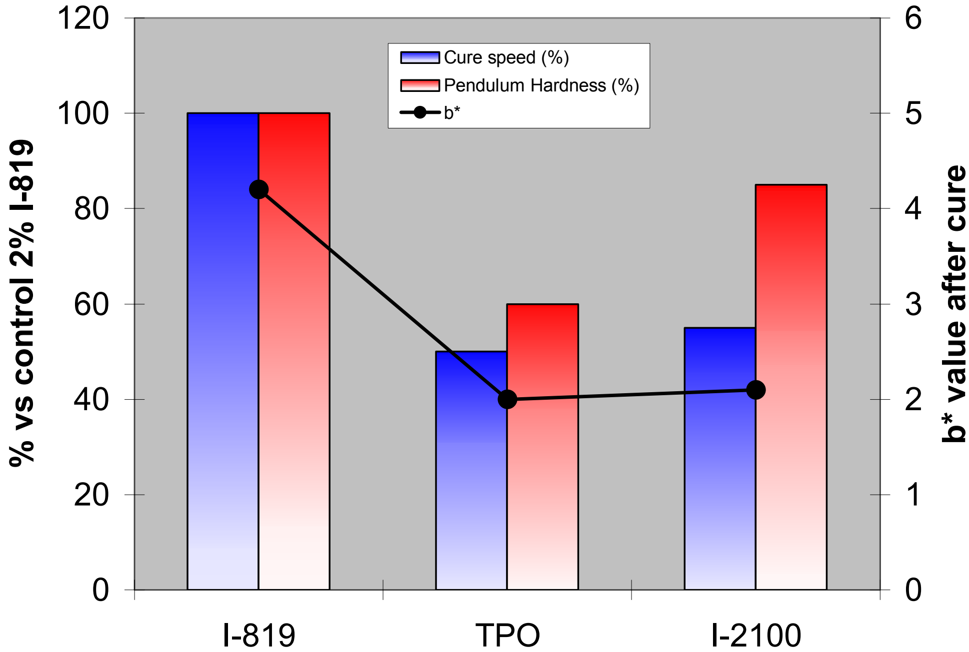


Figure 9. White Polyester Hexaacrylate, 25% TiO_2, 2% Photoinitiator Wet Film Thickness 100 mm-Curing Hg lamp 80 W/cm, 3 m/min

Yellowing after cure in this system is less dependent from photoinitiators than in previous systems. However in this system I-2100 shows superior performance in term of through cure, while maintaining similar b* value to TPO.

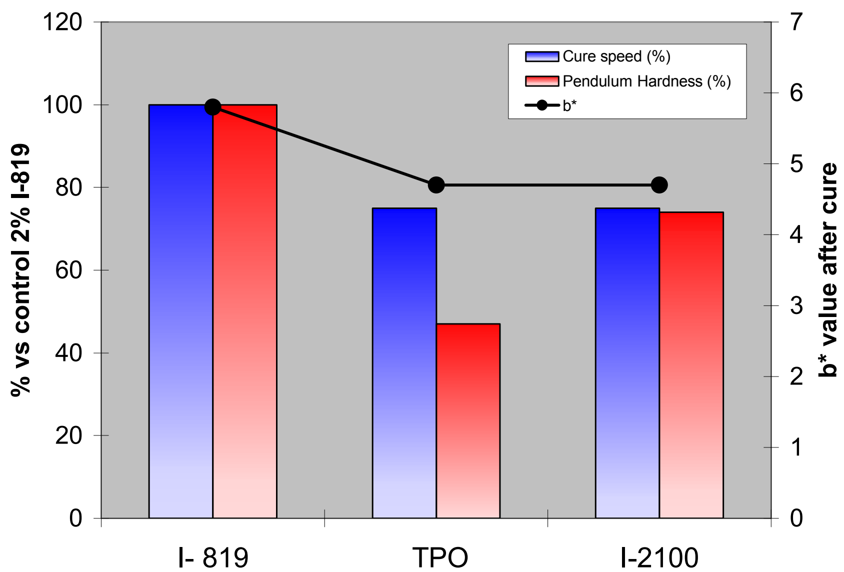


Figure 10. White aromatic Urethane Tri-Acrylate, 25% TiO_2, 2% Photoinitiator Wet Film Thickness 100 mm-Curing Hg lamp 80 W/cm, 3 m/min

The good performance in terms of reduced yellowing after cure is confirmed, as shown in Figure 11. Among the photoinitiators tested I-2100 is the one showing the lowest residual yellowing. Yellowing is improved compared to I-819 at all doses. Indeed, it is lower (better) than that obtained when using TPO above 300 mJ/cm² and before almost equal.

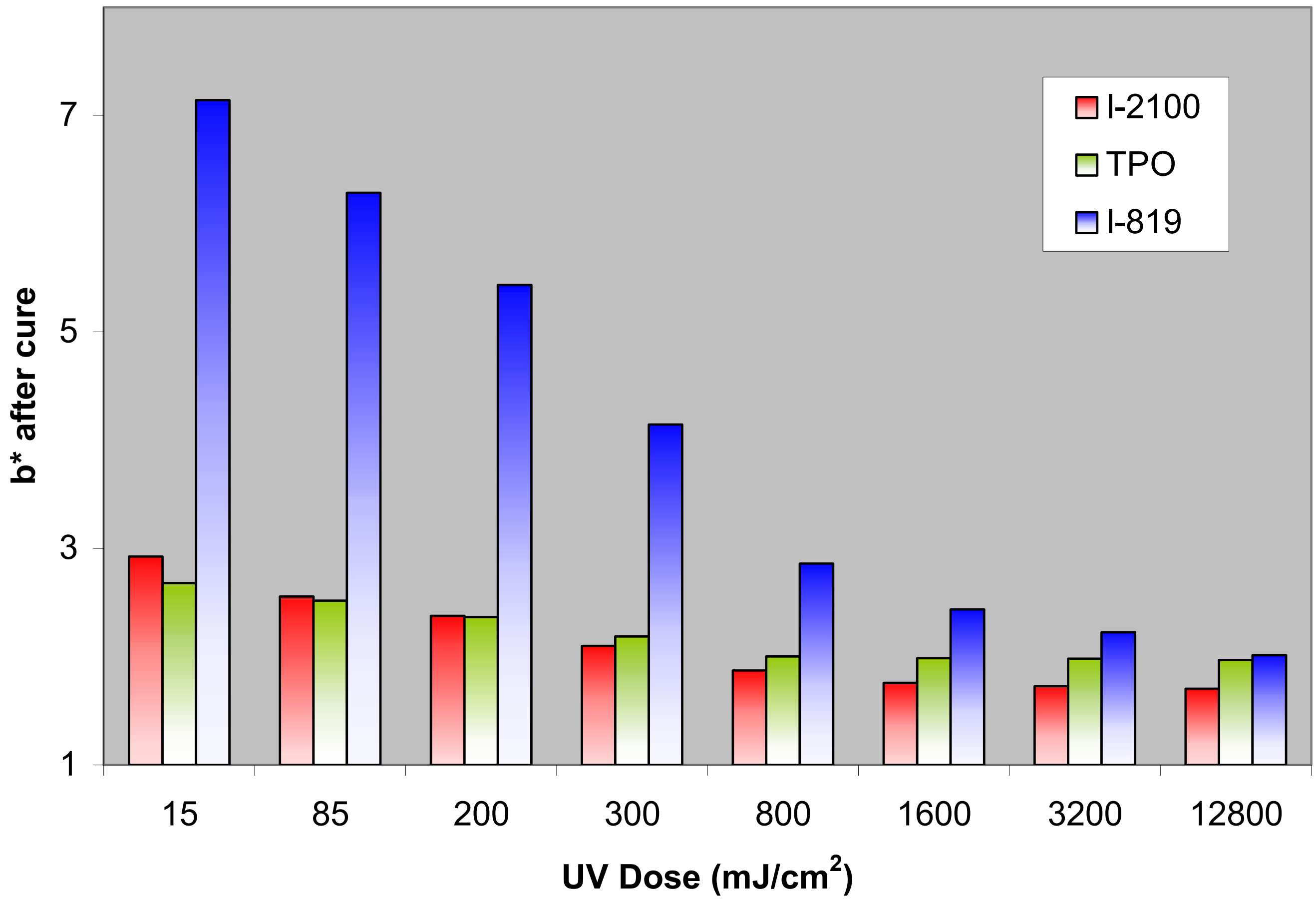


Figure 11. b* after cure of various photoinitiators 3% Photoinitiator in Urethane Acrylate Clear Coat D bulb, DFT 50mm, 15 m/min under N_2

6. Comparison of performance among various photoinitiators

It is useful to compare the performance of I-2022 and I-2100 to other photoinitiators in their respective classes. As given in Table 10, I-2100 shows good photospeed and low yellowing. These properties combined with the fact that it is a liquid, makes I-2100 extremely attractive.

The I-2022 is a blended αHK/acylphosphine oxide system. It shows higher versatility and performance compared to others in its class.

Table 10. Performance of I-2100 and I-2022 as compared to other photoinitiators within their class.

	Pure Acylphosphine Oxide				Combination of Phosphine Oxide and α-Hydroxy Ketone Blends			
Photoinitiators	TPO	TPO-L	I-819	I-2100	D-4265	I-2022	I-1700	I-1800
Chemistry description	MAPO	MAPO	BAPO	Proprietary	αHK +MAPO	αHK +BAPO	αHK +BAPO	αHK +BAPO
Reactivity	mid	mid-low	very good	good	mid	very good	good	good
Pendulum Hard-ness	mid	mid	very good	good	mid	Very good	good	good
Surface cure	-	-	-	-	Very good	Very good	Very good	Very good
Color after cure	Very good	Very good	mid	Very good	Very good	mid	mid	mid
Odor after cure	Very Good	Very Good	Very Good	Very Good	mid	mid	mid	good
Volatility	Very Good	Very Good	Very Good	Very Good	Mid	Mid	Mid	Mid
Handling° (product form)	mid (S)	good (L)	bad (S)	good (L)	mid (L)	mid (L)	mid (L)	mid (S)
Labeling	Poor (R62)	Very good	Mid (R43)	Mid (R43)	Poor (R62)	Mid (R43)	Mid (R43)	Mid (R43)

7. Recommended Uses

Different applications require specific needs that the photoinitiator must meet. In Figure 12, we show the generalized limits where I-2100 and I-2022 provide the best value in pigmented and clear coatings.

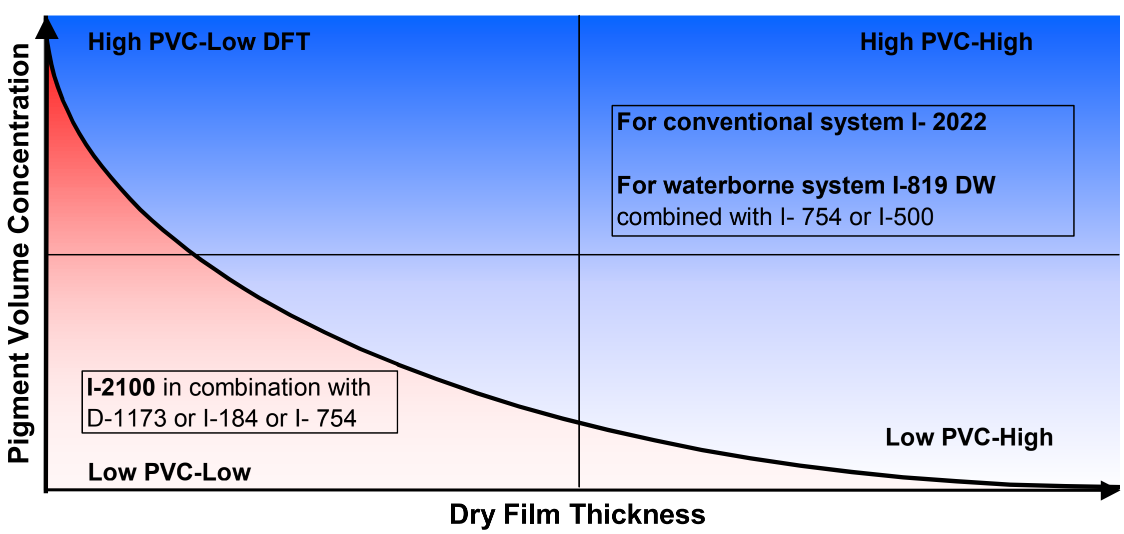


Figure 12. Criteria for matching the photoinitiator in pigmented coating applications

In Table 11, we summarize where I-2022 and I-2100 has been or could be successfully used. Applications that require both good surface curing and through cure are best served with I-2022. For low color and low volatility applications, the I-2100 is to be considered.

Table 11. Summary of various applications that employ I-2022 and I-2100

UV Cure Applications	I-2022	I-2100
UPES Pigmented Wood Top and Intermediate Coat	■	■ combined with I-651 or I-184
Acrylated Pigmented Wood Top and Intermediate Coat	■	□ combined with D-1173 or I-184
Wood Fillers	□	■ combined with I-651 or I-184
Pigmented Top Coats on Plastic and Metal	■	■ combined with D-1173 or I-184
Outdoor, weather resistant coatings, containing UV absorbers	■	□ combined with D-1173 or I-184
Optical fiber coatings and ribbon assembly coatings	□	■ combined with I-754 or I-184
Adhesives	□	■
Glass Fiber Reinforced Composites	■	□
Gel Coats	■	□
Thick Section Polymerization	■	□
Coatings that are processed at high temperatures (before or during photocuring)		■ combined with I-754

■ recommended use
□ possible use

6. Conclusions

The I-2022 and 2100 photoinitiators were found to provide high photoactivity, excellent ease of incorporation into resin formulations. They also are well suited for general coating applications. They work very well in colored coatings and also for low color applications.

References

[1] E. Sitzmann, A. Fuchs, T. Jung, D. Wostratzky. **Handbook of Coating Additives**, ed. L. J. Calbo. Marcel Dekker, Inc. NY (*in press, 2003*).

[2] K. Dietliker. Radiation Curing in Polymer Science and Technology, 2: 155-237, 1993.

[3] A. F. Cunningham, V. Desobry, K. Dietliker, R. Huesler, D. G. Leppard. Chimia , 48: 423-426, 1994.

[4] J.-P. Wolf, G.Hug. WO 2003044030.

[5] L. Xing, C. Ho. WO 2002094574

[6] P. Weissman. EP 1253155, 2002.

[7] J. S. Deeken, R. E. Johnson, L.-M. Wu, K. M. Moussa. US 6114404, 2000.

[8] L. Misev, K. Dietliker, G. Hug, M. Köhler, D. Leppard, A. Litzler, W. Rutsch. Aspects of Photoinitiation: Radcure Coatings and Inks (Egham, UK, Oct. 19-20, 1993) 299, 301-16, 1993.

[9] S. Jönsson, P. E. Sundell, A. Hult. RadTech '90 North Am., Conf. Proc., 1: 417-23, 1990.

[10] A. Carroy, S. Ilg, T. Bolle. Farbe + Lack, 107: 90-96, 2001.

[11] P. G. Garratt. Farbe + Lack, 94: 601-605, 1988.

[12] J. Bieleman. Lackadditive, Wiley-VCH, 1998, pp 366-370.

[13] M. Köhler, B. M. Aebli, M. Holer, E. Eckstein. WO 01029093 A1 (1999)

[14] M. Burglin, M.Köhler, K. Dietliker, J.-P Wolf, I. Gatlik, G. Gescheidt, D. Neshchadin, G. Rist. RadTech 2000, Baltimore, Conf. Proc., 2000, pp 577.

[15] S. R. Kaspers, C. Szewczyk, S. Megert, W. Peter, L. Cressy, D. Rogez, and E. V. Sitzmann: Radtech 2002 North Am. UV/EB Conference Proceedings (2002).

[16] W. Peter, S. Megert, D. Rogez , L. Cressy, E. Sitzmann: European Coatings Conference on Polyurethanes in Berlin (2002).

[17] R. Jahn, T.Jung. Progress in Org. Coating 43: 50-55, 2001.

[18] K. Ellrich, C. Herzig. European patent EP 184095, Nov., 25, 1985.

[19] C. Peinado, E. F. Salvador, A. Alonso, T. Corrales, J. Baselga, F. Catalina. J. Polym. Sci., Part A: Polymer Chemistry. 40, 4236-4244, 2002.

[20] K. Saito, M. Kumakura. JP 2000-10623, 2001.

[21] F. Masson, C. Decker, S. Andre, X. Andrieu. Prog. Org. Coatings. 49, 1-12, 2004

[22] L. S. Baker, J. S. Peanasky. WO 2003008356

[23] D. N. Schissel, M. J. Winningham. WO 2002094731.

[24] T. E. Bishop, F. J. M. Derks, A. J. Tortorello. WO 2002055574

[25] M. J. Winningham. WO 01/49625, WO 01/49629.

[26] P. J. Shustack, D. A. Wilson. WO 99/31161.

[27] P. E. Snowwhite, T. E. Bishop, D. M. Szum, Z. Komiya, M. Ishikawa, T. Ukachi. WO 9847954 , 1998.

[28] B. J. Overton, P. R. Stupak, M. B. Purvis, R. W. Greer, H. M. Yang. WO 2001033275.

[29] Z. Jovanovic, J. Lahaye, H. Laver, S. Megert, C. te Walvaart. RadTech 2000 Proceedings (Baltimore, Apr. 9-12, 2000), 687-697, 2000.

[30] Z. Jovanovic, J. Lahaye, H. Laver, S. Megert, C. te Walvaat. Verfkroniek, 74: 29-32, 2001.

[31] L. Misev, O. Schmid, E. Sjoerd de Jong, R. Bayards. J. Coat. Technol., 71: 37-44, 1999.

[32] J. Bender, Farbe + Lack. 4: 253 – 257, 1994.

[33] R. Jahn, H. Laver, C. te Walvaart. PPCJ, Polym. Paint Colour J., 190: 16-18, 2000.

[34] W. Rutsch, K. Dietliker, D. Leppard, M. Köhler, L. Misev, U. Kolczak, G. Rist. Prog. Org. Coatings, 27: 227-239, 1996.

[35] K. Dietliker, G. Hug, R. Kaeser, M. Köhler, U. Kolczak, D. Leppard, L. Misev, G. Rist, W. Rutsch. RadTech '94 North Am. UV/EB Conf. Exhib. Proc, 2: 693-707, 1994.

[36] T. Jung, M. Köhler, D. Trovato. RadTech Europe 99, Conf. Proc., Berlin, 1999, pp 649-656.

[37] M. Köhler, T. Jung, D. Trovato, W. Al-Akhdar, D. Wostratzky. Composites ’99 Conf. Proc., Composites Fabricators Assoc. (Chicago, 1999), pp 141-151.

[38] E.V. Sitzmann, D. A. Wostratzky, D. A. Bramer, W. Al-Akhdar, J. Jankauskas, T. Jung, and S. Megert, Radtech Europe, 597-602, 2001.

[39] E.V. Sitzmann, D. A. Wostratzky, D. A. Bramer, J. Jankauskas, W. Al-Akhdar, H. Evers, T. Jung, S. Megert and M. Amone, Composites 2001 Conf. Proc., Composites Fabricators Assoc., (2001).

[40] S. Crump, T. Feess, and J. Mazajczk. Composites 2001 Conf. Proc., Composites Fabricators Assoc., 2001.

[41] L. S. Coons, B. Rangarajan, D. Godsehall, A. B. Scranton. ACS Symp. Ser. 673, Photopolymerization Fundamentals and Applications, Ch. 15, A. B. Scranton, C. N. Bowman, R. W. Peiffer, eds., 1997, pp 203 – 218.

[42] V. Narayanan, A. B. Scranton. RadTech Report, 11: 25-30, 1997.

[43] E. V. Sitzmann, D. A. Wostratzky, D. A. Bramer, W. Al-Akhdar, Radtech Report, 14: 28-40, 2000.

[44] H. C. Miller. CFA Conference 2000, Las Vegas, NV, Sept. 27-30th, 2000.

[45] W. Peter, T. Jung, M. Amone, E. V. Sitzmann, D. A. Wostratzky, COMPOSITES 2002, Composites Fabricators Association (Atlanta, September 25-27, 2002)

[46] A. Valet, Light Stabilizers for Paints, 46, Vincentz Verlag, Hannover, 1997

[47] A. Jurgetz, H. Rothbächer, C. Bliefert. Farbe + Lack, 91: 921-927, 1985.

[48] C. S. Colley, D. C. Grills, N. A. Besley, St. Jockusch, P. Matousek, A. W. Parker, M. Towrie, N. J. Turro, P. M. W. Gill, M. W. George. J. Am. Chem. Soc. 124: 14952-14958, 2002.

[49] T. Sumiyoshi, W. Schnabel, A. Henne. Polymer 26:141-146, 1985.

[50] J. E. Baxter, R. S. Davidson, H. J. Hagemann, K. A. McLauchlan, D. G. Stevens. J. Chem. Soc., Chem. Commun, 2:73-75, 1987.

[51] M. Kamachi, K. Kuwata, T. Sumiyoshi, W. Schnabel. J. Chem. Soc., Perkin Trans. 2: 961, 1988.

[52] N. J. Turro, I. V. Khudyakov. Chem. Phys. Lett. 193: 546-552, 1992.

[53] J. E. Baxter, R. S. Davidson, H. J. Hagemann, T. Overeem. Makromol. Chem. 189: 2769-2780, 1988.

[54] A. Kajiwara, Y. Konishi, Y. Morishima, W. Schnabel, K. Kuwata, M. Kamachi. Macromolecules, 26: 1656-8, 1993.

[55] T. Jung, A. Valet. Macromolecular Symp., 187: 531-542, 2002.

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