

# Novel Iodonium Imidazolide Photocatalysts

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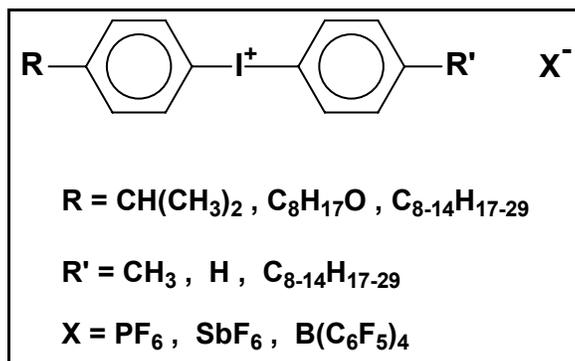
## Introduction

The technology of cationic radiation curable coatings is an established niche of the radiation curable materials industry. Monomers, oligomers, and reactive polymers have been developed that are efficiently crosslinked by 'superacid' species generated upon radiation-induced decomposition of certain 'onium type catalysts. Formulators of cationic radcure compositions were long limited to sulfonium fluorophosphate and fluoroantimonate catalysts. These materials are widely used as they are cost effective in many cationic matrices<sup>1</sup>, but their polar nature (they are ionic salts) renders them immiscible in and unsuitable for photocatalysis of non-polar cationic materials including cyclohexylepoxy-functional silicone release coatings. Sulfonium catalysts also yield benzene and sulfide photolysis byproducts that are objectionable. Iodonium salts are less polar than analogous sulfonium salts, as the positive charge is more delocalized and less centered on the cation. Symmetrical and asymmetrical bis-4-substituted phenyl iodonium salts  $[4-R-C_6H_4]_2I^+ X^-$  where 'R' can be hydrocarbon groups, alkoxy groups, H, or linear and branched alkyl chains, where  $X = SbF_6$  or  $PF_6$ , were developed for use in the aforementioned epoxy silicone release coatings and non-silicone cationic matrices<sup>2-4</sup>.

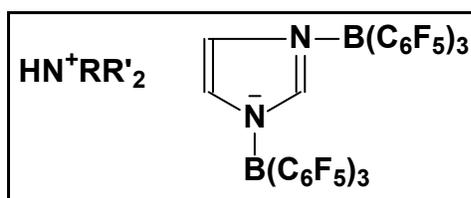
Alkyl substituents on the aromatic rings of diphenyl iodonium salts modify catalyst compatibility, but the extent to which charge delocalization (and resultant photogenerated acid strength) is enhanced in this fashion is limited when the anion is a relatively small  $PF_6$ ,  $AsF_6$ , and  $SbF_6$ . A weakly coordinating, very large anion, tetrakis(perfluorophenyl)borate,  $B[C_6F_5]_4^-$ , was developed to take advantage of the weak nucleophilicity of fluorine atoms and the strong electron-withdrawing properties of the perfluorophenyl group; iodonium salts of this anion are particularly efficacious for photocure of epoxysilicones<sup>5,6</sup>. Analogous salts of tetrakis(perfluorophenyl)gallate,  $Ga[C_6F_5]_4^-$ , have similar properties<sup>7,8</sup>. Commercial iodonium salts used in a wide range of cationic curable coating materials are depicted in **Figure 1**.

There is considerable interest in weakly coordinating anions besides cationic photocatalysis. Useful anions for olefin polymerization reactions are based on perfluorophenyl borates, for example<sup>9</sup>. Investigation of such novel systems led to the discovery of borate anions where two or more perfluorophenylboranes are bridged by linking groups including imidazole<sup>10</sup>. An ammonium bis[tris(perfluorophenyl)borane]imidazolide salt is shown in **Figure 2**. Shortly after initial reports of these anions were published, iodonium salts of the imidazolides were prepared and their efficacy as cationic photocatalysts demonstrated<sup>11, 12</sup>. We now report on results of a follow-up program initiated to study syntheses and photocatalytic properties of 'onium

imidazolides, with particular emphasis on potential commercial application for industrial coating markets.



*Figure 1:* Examples of iodonium salt photocatalysts



*Figure 2:* Ammonium salt of di[tris(perfluorophenyl)borane] imidazolidine.

## Experimental

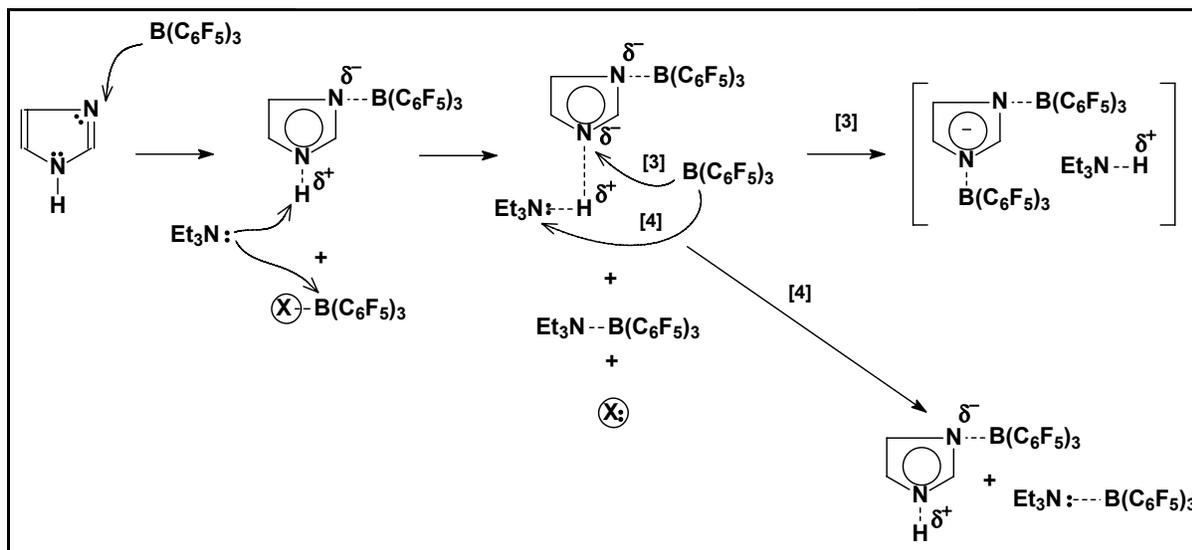
### Analysis, Reagents and General Methodology.

Reagents used in syntheses of ‘onium imidazolidine compounds were purchased from commercial vendors, purified (sublimation or distillation) if necessary, and dried before use as described in literature. Tris (perfluorophenyl)borane was obtained as a 3% solution in Isopar aliphatic hydrocarbon solvent from Boulder Scientific and used as furnished. Commercial grades of epoxy functional silicone release agents and of UV9380C photocatalyst were obtained from GE Silicones, and are identified as such. Other cationic photocatalysts were obtained from commercial sources.

The experiments with  $Et_3NH^+C_3H_3N_2[B(C_6F_5)_3]_2$  and its ‘onium salts were carried under argon in Schlenk apparatus, flame dried under vacuum prior to use.  $^1H$  NMR and  $^{19}F$  NMR spectra were recorded in  $CDCl_3$  on Bruker AC-200 MHz spectrometer.

Release coatings were applied to film and film-laminate substrates using the 12 inch width pilot coater at GE Silicones in Waterford, NY, or the 18 inch width pilot coater at Black Clawson Converting Equipment, Inc., in Fulton, NY. TESA test tapes were affixed to cured silicone coatings and tested for release force required to separate them from the silicone liner by means of a TMI peel tester.

## Synthetic route to ammonium bis(perfluorophenyl)borane imidazolides



### Synthesis of $C_3N_2H_3[B(C_6F_5)_3]_2Et_3NH$ :

A solution of  $B(C_6F_5)_3$  in Isopar was placed in a 3-necked flask equipped with a magnetic stirrer, a condenser and a dropping funnel. Solvent was removed at RT under reduced pressure to leave 46.11 g, 0.09 mol, of  $B(C_6F_5)_3$ . Borane was dissolved in toluene (360 ml). Imidazole (6.11 g, 0.0898 mol) was incrementally added to this solution (the solution warmed up slightly). Imidazole readily dissolved to form a clear brownish solution. The mixture was stirred for 1 h at room temperature and  $^{19}F$  NMR analysis was run:  $^{19}F$  NMR:  $C_3N_2H_3B(C_6F_5)_3$  (85%),  $B(C_6F_5)_3$  (9%),  $C_6F_5H$  (6%). The flask was placed at 40°C in an oil bath. The mixture was stirred at 40°C overnight.  $^{19}F$  analysis did not show any difference and the mixture was cooled down to RT.  $^{19}F$  NMR:  $C_3N_2H_3B(C_6F_5)_3$  (81%),  $B(C_6F_5)_3$  (7%),  $C_6F_5H$  (12%) A solution of  $Et_3N$  (12.4 ml, 0.09 mol) in toluene (200 ml) was added to the reaction mixture and the system was stirred at RT for 1h. The mixture was analyzed by  $^{19}F$  NMR spectroscopy.  $^{19}F$  NMR:  $C_3N_2H_3B(C_6F_5)_3Et_3N$  (79%),  $C_6F_5H$  (21%).  $B(C_6F_5)_3$  [51.01 g, 0.1 mol obtained by solvent removal from Boulder solution of  $B(C_6F_5)_3$ ] in 300 ml of toluene was added slowly to the reaction mixture at RT, stirring was continued and progress of reaction was controlled by  $^{19}F$  NMR. After 1h at RT the mixture was composed of:  $^{19}F$  NMR:  $C_3N_2H_3[B(C_6F_5)_3]_2Et_3NH$  (3%),  $C_3N_2H_3B(C_6F_5)_3$  (45%),  $C_6F_5H$  (43%),  $B(C_6F_5)_3$  (9%). The temperature was increased to 70°C (oil bath). After 6 days at 70°C the mixture was composed of:  $^{19}F$  NMR:  $C_3N_2H_3[B(C_6F_5)_3]_2Et_3NH$  (58%),  $C_3N_2H_3B(C_6F_5)_3$  (22%),  $C_6F_5H$  (20%). A new batch of  $B(C_6F_5)_3$  (35.0 g, 0.068 mol) in 270 ml of toluene was added to the reaction mixture and stirring at 70°C was continued with NMR control of mixture composition: After 5 days the reaction was completed  $^{19}F$  NMR:  $C_3N_2H_3[B(C_6F_5)_3]_2Et_3NH$  (78%),  $C_3N_2H_3B(C_6F_5)_3$  (7%),  $C_6F_5H$  (15%). Toluene was distilled off under vacuum to leave about 100 ml of the reaction mixture and 400 ml of  $CH_2Cl_2$  was added.  $C_3N_2H_3[B(C_6F_5)_3]_2Et_3NH$  was precipitated from toluene/ $CH_2Cl_2$  solution with hexane (1500 ml). The precipitate was filtered off and crystallization from  $CH_2Cl_2$ /hexane was repeated twice. The

precipitate was filtered off, washed with hexane and dried under vacuum to leave 88.69 g of  $C_3N_2H_3[B(C_6F_5)_3]_2Et_3NH$  ( $Y=83\%$ ,  $^{19}F$  NMR purity 93%).

**General Observations:** 3-step procedure carried out at elevated temperatures, in a mixture of solvents of suitable polarity, and with controlled addition of excess of  $B(C_6F_5)_3$  at the 3rd step of reaction, seems to be the best way for synthesis of  $IMI[B(C_6F_5)_3]_2Et_3NH$ .

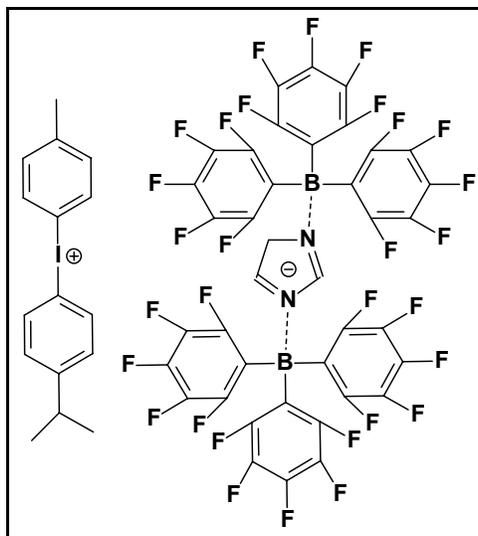
#### Synthesis of tolyl-cumyl-iodonium imidazolide:

$C_3H_3N_2[B(C_6F_5)_3]_2Et_3NH$  (86.17 g, 0.072 mol) was dissolved in 1000 ml of dry  $CH_2Cl_2$  and  $(CH_3)C_6H_4-I-C_6H_4[CH(CH_3)_2]Br$  previously prepared by an established procedure (30.04 g, 0.072 mol), dissolved in 400 ml of  $CH_2Cl_2$ , was added drop-wise (the flask was wrapped in aluminum paper to protect the mixture against light). The mixture was stirred for 24h (protected against light) and then  $\frac{1}{2}$  of  $CH_2Cl_2$  was removed under reduced pressure at RT, 700 ml of hexane was added and the solution was passed through a column filled with silica gel ( $57\text{ cm}^3$ ) and eluted with 1000 ml of  $CH_2Cl_2$ /hexane (1:1 volume ratio). 3 fractions were collected and analyzed by  $^{19}F$  NMR. They contained still some  $Et_3NHBr$  and thus the mixtures were passed again through a column filled with fresh silica gel ( $126\text{ cm}^3$ ). 3 fractions collected were free from  $Et_3NHBr$ , they contained 67.1 g of  $(CH_3)C_6H_4-I-C_6H_4[CH(CH_3)_2]^+ C_3N_2H_3[B(C_6F_5)_3]_2$ . The rest of the sample had to be filtered 2 times through silica gel (new layer). After purification 81.5 g of pure tolyl-cumyl-iodonium imidazolide was collected ( $Y=79.2\%$ ).  $^1H$  NMR  $\delta$  [ppm]: 1.24, 1.27  $CH_3$  (6H, d); 2.46  $CH_3$  (3H, s); 2.98 CH (1H, m); 6.76 [2H, s (IMI)]; 7.2 -7.5 [8H, m (aromatic)], 7.48 [1H, s (IMI)].  $^{19}F$  NMR  $\delta$  [ppm]: -131.95 (m, 12F-o); -158.0 (t, 6F-p); -163.9 (m, 12F-m). The material described above was used for subsequent experiments and evaluations described herein. A depiction of the iodonium imidazolide is provided in **Figure 3** below, and its UV absorption spectrum is displayed in **Figure 4**.

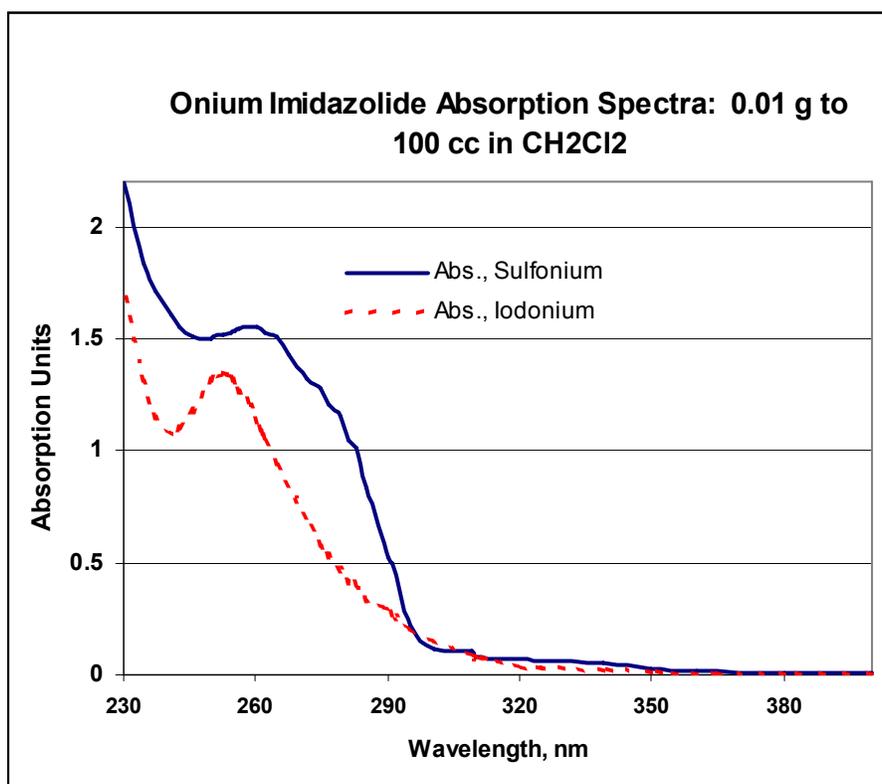
#### Synthesis of di-tolyl-p-octaneoxyphenylsulfonium imidazolide:

$\{C_3H_3N_2[B(C_6F_5)_3]_2\}^+ \{Et_3NH\}^-$  (6.42g, 0.00538 mol) was dissolved in 220 ml of dry  $CH_2Cl_2$  and mixed in the dark with di-tolyl-p-octaneoxyphenylsulfonium hexafluorophosphate, previously prepared from ditolylsulfoxide, octanoxyphenyl ether, and  $P_2O_5$  (3.02g, 0.00535 mol) and dissolved in 100 ml of  $CH_2Cl_2$ . The mixture was stirred for 24h (protected against light) and then all  $CH_2Cl_2$  was removed from the solution at RT under reduced pressure. 30 ml of wet acetone was added and the product was precipitated on addition of water (10 ml). Precipitation from acetone/ $H_2O$  was repeated 4 times to give finally 4.35 g of di-tolyl-p-octaneoxyphenyl sulfonium imidazolide ( $Y=54\%$ ).  $^1H$  NMR  $\delta$  [ppm]: 0.87 (3H, t); 1.2 - 1.5 (10H, m); 1.8 (2H, m); 2.47 (6H, s); 4.01 (2H, t); 6.75 [2H, s (IMI)]; 7.1 -7.45 [12H, m (aromatic)], 7.49 [1H, s (IMI)]  $^{19}F$  NMR  $\delta$  [ppm]: -131.9 (m, 12F-o); -158.7 (t, 6F-p); -164.2 (m, 12F-m).

The sulfonium imidazolide is shown in **Figure 5** and its UV absorption spectrum is included in **Figure 4**. I-imid proved to be compatible with all epoxysilicone polymers tested and dissolved in DY-025 alkyl glycidyl ether. We found that the S-imid compound was only partially miscible with commercial epoxysilicone polymers despite the long chain alkyloxy phenyl group bonded to sulfur in the cation, but dissolved nicely in propylene carbonate to form a 25% solution designated Catalyst Solution S.



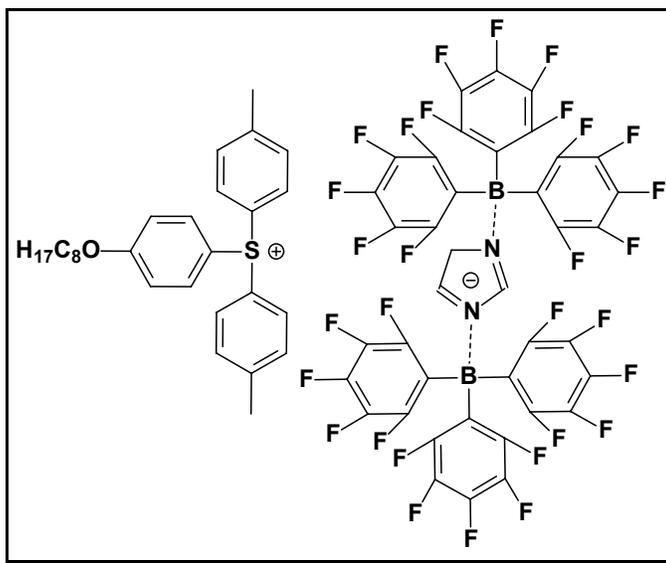
**Figure 3:** Iodonium di[tris(perfluorophenyl)borane]imidazolid (I-imid). MW = 1427



**Figure 4:** Onium imidazolid UV absorption spectra

## Experimental Evaluations and Results

The excellent solubility of I-imid in epoxysilicone polymers suggested that an application fit for this and other imidazolide catalysts is in UV cure silicone release coatings. A solution of I-imid in Ciba DY-025™ alkyl glycidyl ether reactive diluent was prepared and designated catalyst solution I. A second 25% solution + 2-isopropylthioxanthone (ITX) sensitizer in DY-025 was also prepared and designated catalyst solution II.



**Figure 5:** Sulfonium di[tris(perfluorophenyl)borane]imidazolide (S-imid). MW 1474.

Catalyst solution II included ~ 26 mole% ITX as a function of I-imid. A series of coating trials were carried out in which experimental imidazolide catalyst solutions were mixed with various combinations of commercial epoxysilicone polymers, the coating baths then applied to film and film laminate liners and cured by exposure to deep UV irradiation from Fusion Systems™ ‘H’ type lamps. In each case, ‘control’ coating baths were catalyzed with UV9380C, a commercial catalyst package with ~ 46% bis(4-alkylphenyl)iodonium  $\text{SbF}_6$  + 2% ITX dissolved in DY025. TESA™ 7475 solvent-borne acrylic PSA test tape or TESA™ 4651 rubber based PSA test tape was laminated to cured silicone release coatings immediately on cure or at intervals following coating. The force required to peel the tape from the silicone coating was recorded as a function of time and aging conditions. The Release Ratio method of evaluating degree of cure of cationic type UV cure release coatings was used. In brief, TESA7475 acrylic test tape laminates on cured epoxysilicone coated on film liner are aged for 24 hours at ambient conditions and at 70C. The oven-aged taped samples are cooled to room temperature for an hour, then release force required to separate the liner from the tape is measured at a given peel speed. Interaction of free epoxy groups in the coating with the aggressive TESA7475 acrylic adhesive leads to release build on aging, particularly at elevated temperature. The ratio of release from the 70C aged laminates divided by release from the RT aged laminates = release ratio: the higher the ratio, the less the degree of cure of the coating. A release ratio < 1.5 indicates that stable release can be expected as the release liner is aged under normal storage conditions.

## Release Coating Experiments 1 & 2

Many industrial users of UV cure epoxysilicone release agents are small converters of specialty film liners who run on narrow web equipment at relatively slow line speeds. To mimic such coating and curing conditions, a series of coating runs was carried out on a 12 inch pilot line at GE Silicones using Mitsubishi 2 mil PET or Thilmany polykraft liners. One bank of Fusion™ 300 watt/in H lamps was used for irradiation of ~ 1 g/m<sup>2</sup> coating applied via 3 roll offset gravure technique at different machine line speeds. Coating baths were prepared from combinations of commercial epoxysilicone polymers. Control and experimental baths were prepared as described above. In-line corona treatment of film liners aided coating anchorage. TESA 7475 test tape was laminated to all cured coating samples immediately off line, laminates then aged at 70C and RT as described above.

**Table 1: Coating Experiment 1 Formulations & Conditions: PET liner, variable line speed**

Bath	Polymer	Catalyst	Wt % I <sup>+</sup>	Mole Cat/100g
Control	9/1 UV9500/UV9430	2.5% UV9380C	~ 1.15	.00175
Exp	“	3% Solution II	0.75	.00053

Release results and release ratio are displayed in **Table 2** and **Figure 6**, respectively.

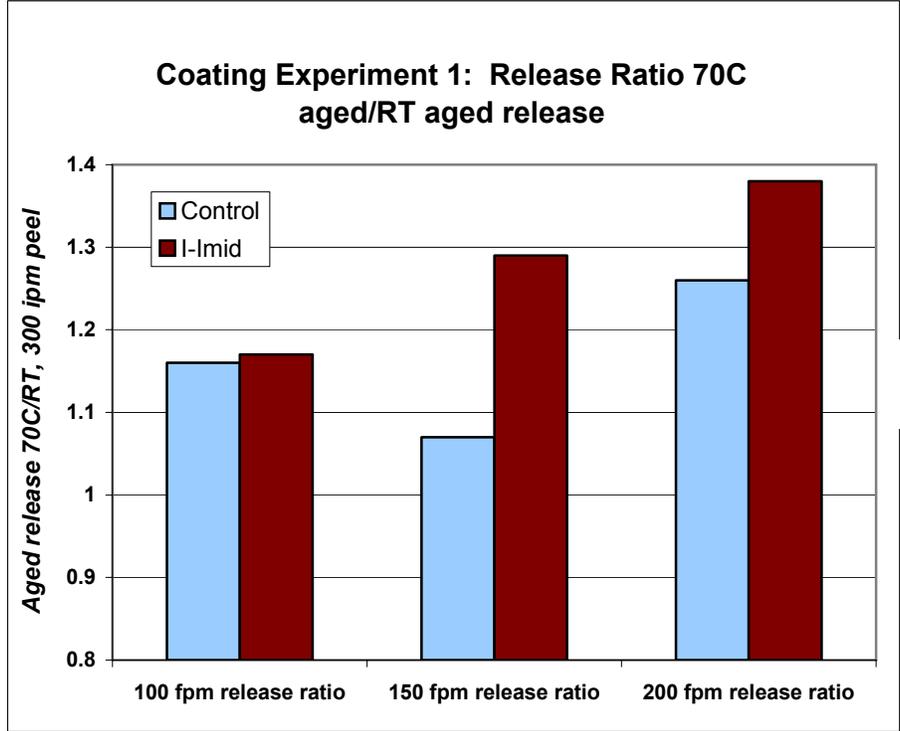
**Table 2: Release, 300 ipm peel, 180 degree, g/in from TESA 7475 Experiment 1**

Coating	Speed, fpm	1 day RT	1 day 70C
Control	100	15.4	17.8
“	150	15.9	17
“	200	16	20.1
Exp	100	15.9	18.5
“	150	15.9	20.5
“	200	15.9	21.9

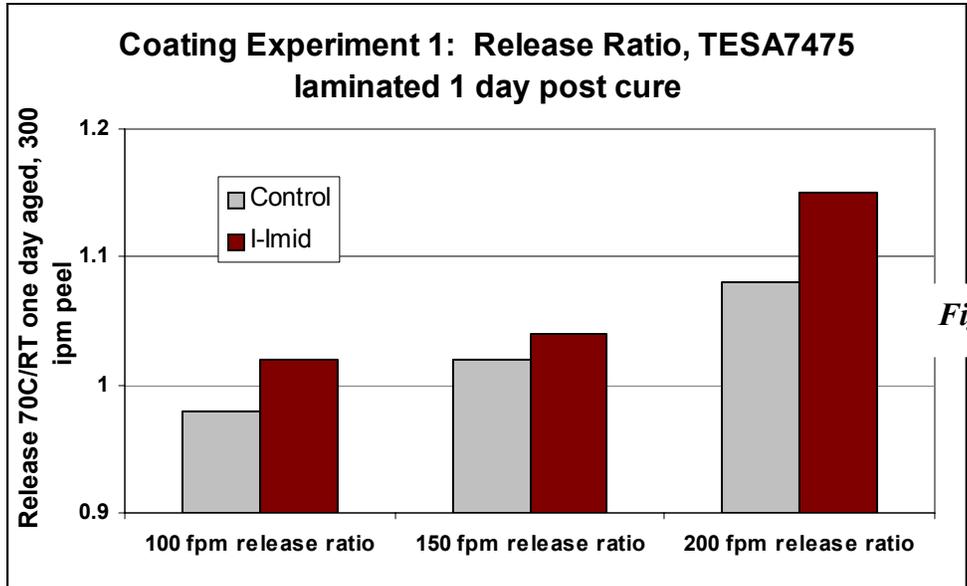
While all ratios from Coating Experiment 1 are < 1.5, the I-imid catalyzed coatings age up slightly more on 70C oven laminate aging than the control coatings. We applied new TESA7475 tape strips to 1 day old cured coatings and repeated the release ratio determination to see the effect of 1 day post cure on release stability; results are shown in **Figure 7**. It is apparent that I-imid catalyzed coatings undergo a rapid post-cure that improves oven aged release of TESA7475 test tape soon after initial cure. Differences in post-cure behavior are attributed to the higher MW of the I-imid salt versus the bis(4-alkyl)phenyl iodonium antimonate salt coupled with its lower wt% concentration. We then ran Coating Experiment 2 on Thilmany Polykraft liner (LDPE laminated to MF paper) at constant 300 fpm line speed, varying the I-Imid concentration as shown in **Table 3**.

**Table 3: Experiment 2 formulations (Premium release epoxysilicone base blend)**

Formula	Catalyst	Actual Iodonium Salt Concentration
Control A	2% UV9380C	0.92% (.0014 mole/100g)
Exp B	1% CatI Soln II	0.25% (.00018 mole/100g)
Exp C	2% CatI Soln II	0.5% (.00035 mole/100g)
Exp D	3% CatI Soln II	0.75% (.00053 mole/100g)



*Figure 6*



*Figure 7*

TESA7475 acrylic test tapes were affixed to each cured coating right after cure for RT and 70C laminate aging and peel release determination as described above. A post cure release ratio determination was carried out 2 weeks after coating and cure to mimic a typical inventory situation where release liner is shipped days or weeks after coating/curing of the release coating. 70C/RT aged release ratio results were recorded and are displayed in **Table 4**.

**Table 4: Experiment 2 release ratios**

Coating	Release ratio, immediate lamination	Release ratio, 2 wk postcure lamination
Control A	1.43	0.94
Exp B	10.6	0.89
Exp C	4.02	0.92
Exp D	1.78	0.83

Post cure as a function of catalyst concentration is apparent for the I-imid catalysed coatings but 2 weeks aging post-coating eliminates performance distinctions between the I-imid and control photocatalyst. Besides the TESA7475 release ratio testing, conventional RT aged release of TESA7475 and TESA4651 test tape laminates was recorded over a 4 week period, with results depicted in **Figure 8**. Higher levels of I-imid catalyst provided better long term release stability, consistent with the release ratio test results.

### Release Coating Experiment 3

A third coating & cure trial was carried out on the 18 inch 5 roll pilot coater at Black Clawson Converting Equipment, Inc. at their Fulton, NY facility to mimic high speed processing. A premium release blend of epoxysilicone + di-carbinol-stopped linear silicone<sup>13</sup> additive was treated with 5 different photocatalyst solutions as shown in **Table 5** below:

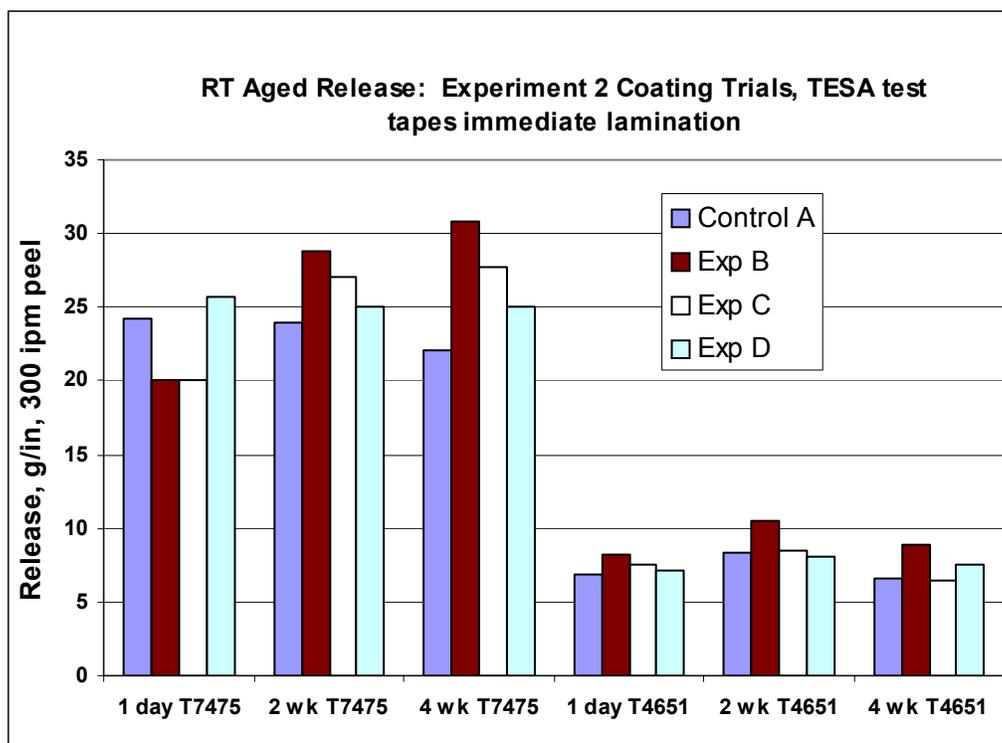
**Table 5:**

Formula	Catalyst	Catalyst Concentration	Iodonium Salt Concentration
Control	UV9380C	2 %	0.92 wt% (~.0014 mole/100g)
Exp E	Catalyst Sol I	2 %	0.5 wt % (~.00035 mole/100g)
Exp F	Catalyst Sol II	2 %	0.5 wt % (~.00035 mole/100g)
Exp G	Catalyst Sol II	3 %	0.75 wt % (~.00053 mole/100g)
Exp H*	Catalyst Sol II	2 %	0.5 wt % (~.00035 mole/100g)

Coating bath H\* consisted of 95 pts of the silicone polymer mix of the other formulas + 5 pts of a 1/1 mix of dodecylphenyl (DDP)/dodecylvinyl ether (DDVE) that was previously found to improve post-cure performance of cationic photocured silicone coatings<sup>3,14</sup>. Each formula was applied to polykraft liner at 800 fpm line speed and ~ 1.1 g/m<sup>2</sup> deposition and cured by exposure to one bank of Fusion Systems<sup>TM</sup> 600 watt/in H lamps. TESA 7475 acrylic test tape was laminated to the cured silicone coatings off-line and 1 day later; laminates were aged 24 hours at RT and 70C to determine release ratio as described above. Results are displayed in **Table 6**.

**Table 6: Experiment 3 Release Ratios**

Coating	Release Ratio, immediate lamination	Release Ratio 1 Day postcure lamination
Control	1.31	1.32
Exp E	2.72	1.40
Exp F	2.70	1.13
Exp G	1.72	1.26
Exp H*	1.32	1.26

**Figure 8**

The presence of ITX sensitizer has little effect on I-imid photocure; concentration of the catalyst was more important. 5% of the DDP/DDVE additive mixture markedly improved Release Ratio; post cure for all the I-imid catalyzed formulations was complete in < 1 day. Comparison of release ratio data from Release Coating Experiments 2 & 3 suggests that increasing the power of UV irradiation sources aided photocure of I-imid catalyzed coatings even at higher line speed.

### Non-Silicone Photocurable Coatings

Cure studies of different ‘onium imidazolides in a 60/30/10 UVR6105 / UVR6000 / DGEBA (diglycidyl ether of BPA) matrix were conducted to assess their performance in a conventional non-silicone coating based on the common dicyclohexyl epoxy resin. Low levels of silicone-polyether flow agents and polyfluoroether slip agents were added to the matrix, then sufficient amounts of commercial and experimental ‘onium photocatalyst and sensitizers to furnish 0.75 wt% active iodonium or sulfonium salt, per **Table 7** below:

**Table 7: Catalyst Additives in Cationic Cure Matrix**

<b>Coating</b>	<b>Catalyst</b>	<b>'onium salt</b>	<b>Mole cat/100 g</b>
J	1.5% UVI6992	Sulfonium PF <sub>6</sub>	~0.0015
K	1.0% Ciba Irgacure 250	Iodonium PF <sub>6</sub>	0.0016
L	3.0% Catalyst Solution I	I-Imid	0.00053
M	3.0% Catalyst Solution II	I-Imid (+ ITX)	0.00053
N	3.0% Catalyst Solution I	I-Imid (+ Irgacure 2959*)	0.00053
P	1.6% UV9380C	Iodonium SbF <sub>6</sub> (w/ ITX)	0.0009
Q	3.0% Catalyst Solution S	S-Imid	0.00051

(\* Irgacure 2959 (Ciba) is a useful sensitizer for iodonium photocatalysis)

The above formulations were spin-coated on Noryl™ blank optical media discs to ~ 80 micron thickness, then exposed to pulsed UV light from a focused Xenon RC747 D lamp source. The number of 'D lamp' pulses required to effect a tack-free through-cured coating was determined for each coating. The Xenon D lamp emits a continuum spectrum > 190 nm wavelength, 10 pulse/sec, 1811 Watt/cm<sup>2</sup> peak power. Qualitative Results are tabulated below.

<b>Coating</b>	<b>Pulse to Cure</b>
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J	5
K	20
L	25
M	20
N	20
P	15
Q	30

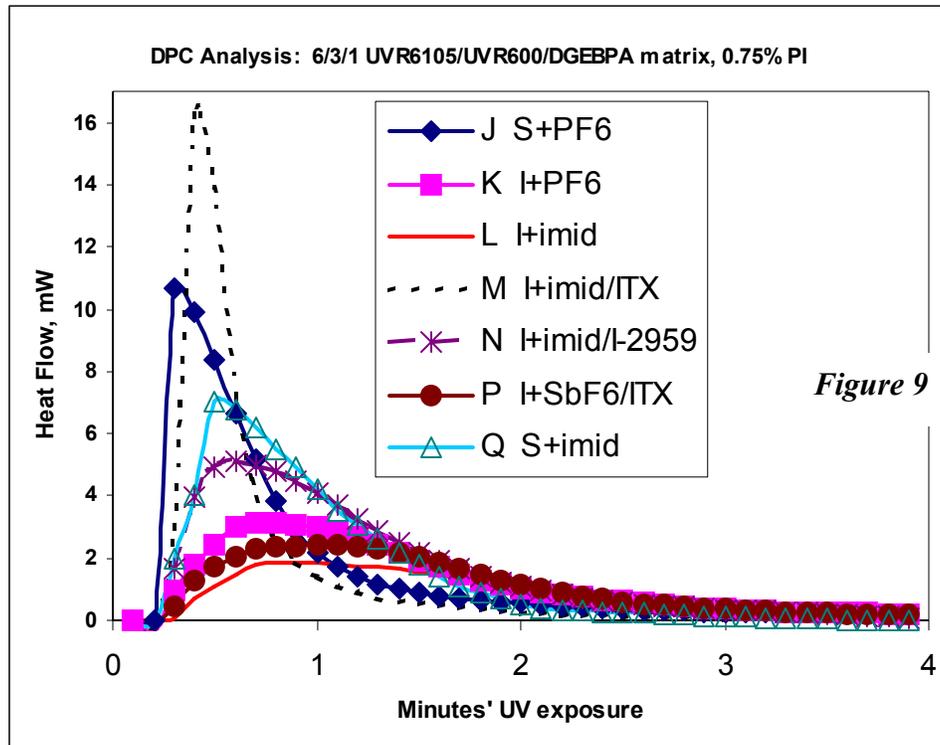
All catalysts tested proved effective for photocure of the UVR6105-based coatings in this study; the commercial Sulfonium PF<sub>6</sub> product was the most efficient. As noted in release coating evaluations, sensitizers somewhat enhanced photoresponse of I-imid catalyst in the non-silicone matrix per the qualitative criterium.

DPC analyses of the same coating mixtures were carried out using a TA Instruments Q series PCA device equipped with a 100 Watt Novacure 2100 mercury vapor arc lamp UV source. Light was furnished to ~ 5mg samples through a 250-450 bandpass filter. Results of the DPC study unexpectedly varied from the simple cure study. DPC traces are displayed in **Figure 9**.

The DPC experiment indicated that the photoresponse of the catalyst/sensitizer combinations studied were in the approximate order S<sup>+</sup>PF<sub>6</sub>>I<sup>+</sup>imid w/ITX>S<sup>+</sup>imid>I<sup>+</sup>imid w/I-2959> I<sup>+</sup>PF<sub>6</sub> ~ I<sup>+</sup>SbF<sub>6</sub> w/ITX ~ I<sup>+</sup>imid. The presence of ITX sensitizer caused a big jump in speed of photoresponse of the I<sup>+</sup>imid catalyst in the DPC experiment, probably due to the bandwidth filter excluding light <250 nm wavelength. Sulfonium catalysts absorb in the 250 –350 nm region, so the light source may have skewed these results some.

### Summary and Prospectus

A novel class of 'onium salt cationic photocatalysts based on the weakly coordinating anion bis[tis(perfluorophenyl)borane] imidazolide has been described. Evidence compiled to date shows that the iodonium imidazolide compound is well suited for use in radiation curable epoxysilicone release coatings, and that both iodonium and sulfonium imidazolides are active catalysts in non-silicone cycloaliphatic epoxy based matrices.



Work in progress is focused on further evaluations of catalysis in related coating systems, and on feasibility of commercial production and marketing of the new materials.

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### References

1. A. Carroy, *RadTech 1994 North America Conference Proceedings*, Orlando 1994, 462.
2. R. Eckberg and R. LaRochelle, US Patent 4,279,717 (1981).
3. R. Eckberg and S. Rubinsztajn, *RadTech North America 2002 Conference Proceedings*, Indianapolis 2002, 41.
4. J. Crivello, *RadTech 90 North America Conference Proceedings*, Chicago 1990, 424.
5. C. Priou, J. Cavezzan, A. Soldat-Rhone, *RadTech 1994 North America Conference Proceedings*, Orlando 1994, 187.
6. C. Priou, FR 272416 A1 (1994).
7. K. Ren, P. Serquievski, H. Gu, O. Grinevich, J. Malpert, and D. Neckers, *Macromolecules* 2002, 35, 898.
8. H. Gu, K. Ren, D. Martin, T. Marino, and D. Neckers, *J. Coatings Technology* 2002, 74, 49.
9. E. Chen and T. Marks, *Chem. Rev.* 2000, 100, 1391.
10. R. LaPointe, G. Roof, K. Abboud, and J. Klosin, *J. Amer. Chem. Soc.* 2000, 122, 9560.
11. R. Eckberg, S. Rubinsztajn, D. Neckers, J. Malpert, and K. Ren, WO 03/062208 A1 (2003).
12. K. Ren, J. Malpert, H. Li, H. Gu, and D. Neckers, *Macromolecules* 2002, 35, 1632
13. R. Eckberg and R. Agars, US Patent 5,814,679 (1998)
14. R. Eckberg, US Patent 6,492,433 (2002).