Heraeus

CURING WITH MULTI-WAVELENGTH LEDS

Radtech NA, 3/9/2020, Orlando, FL

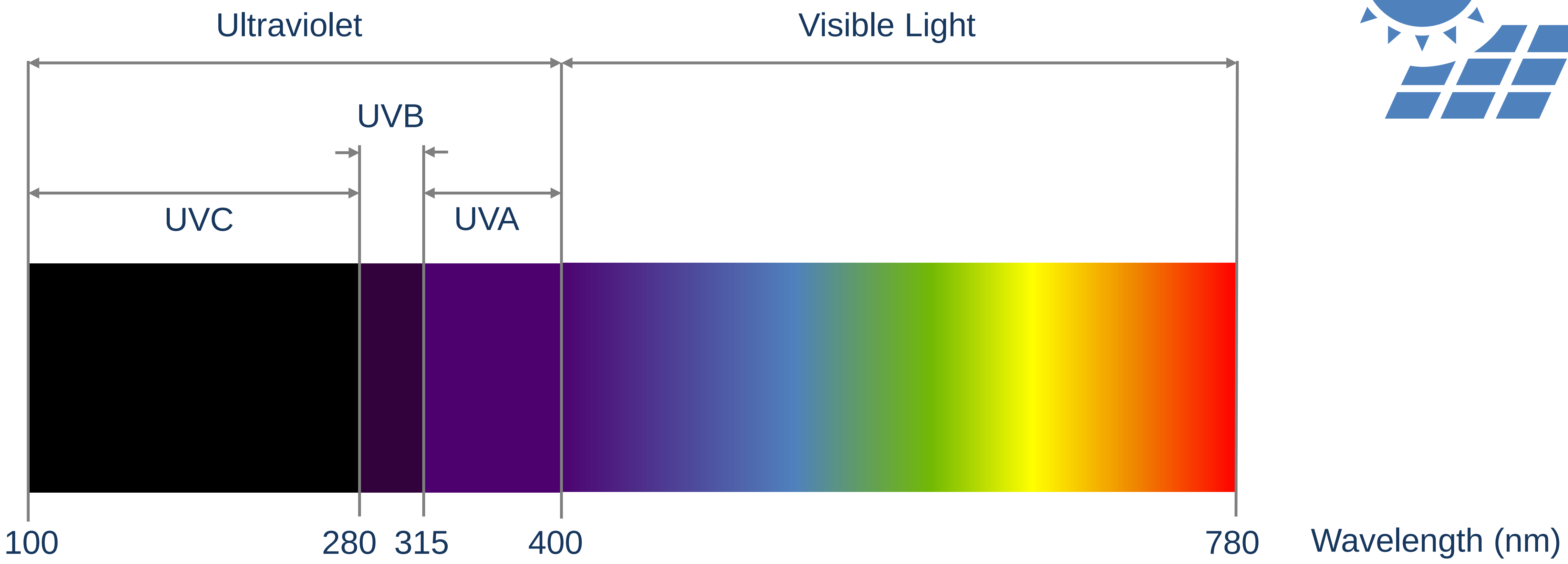
Brett Skinner, Senior Research Scientist, Heraeus Noblelight America

AGENDA

AGENDA

OVERVIEW

OVERVIEW- UV SPECTRUM



OVERVIEW- TECHNOLOGY

Microwave-Powered Hg

Advantages

- Mature technology
- Fast process speed
- Low cost of ownership
- Working distance >50mm

Drawbacks

- High electrical power consumption
- Requires large blowers
- Ozone formation
- Presence of Hg

LED Technology

Advantages

- Instant on-off
- Hg free
- Long life
- No blowers

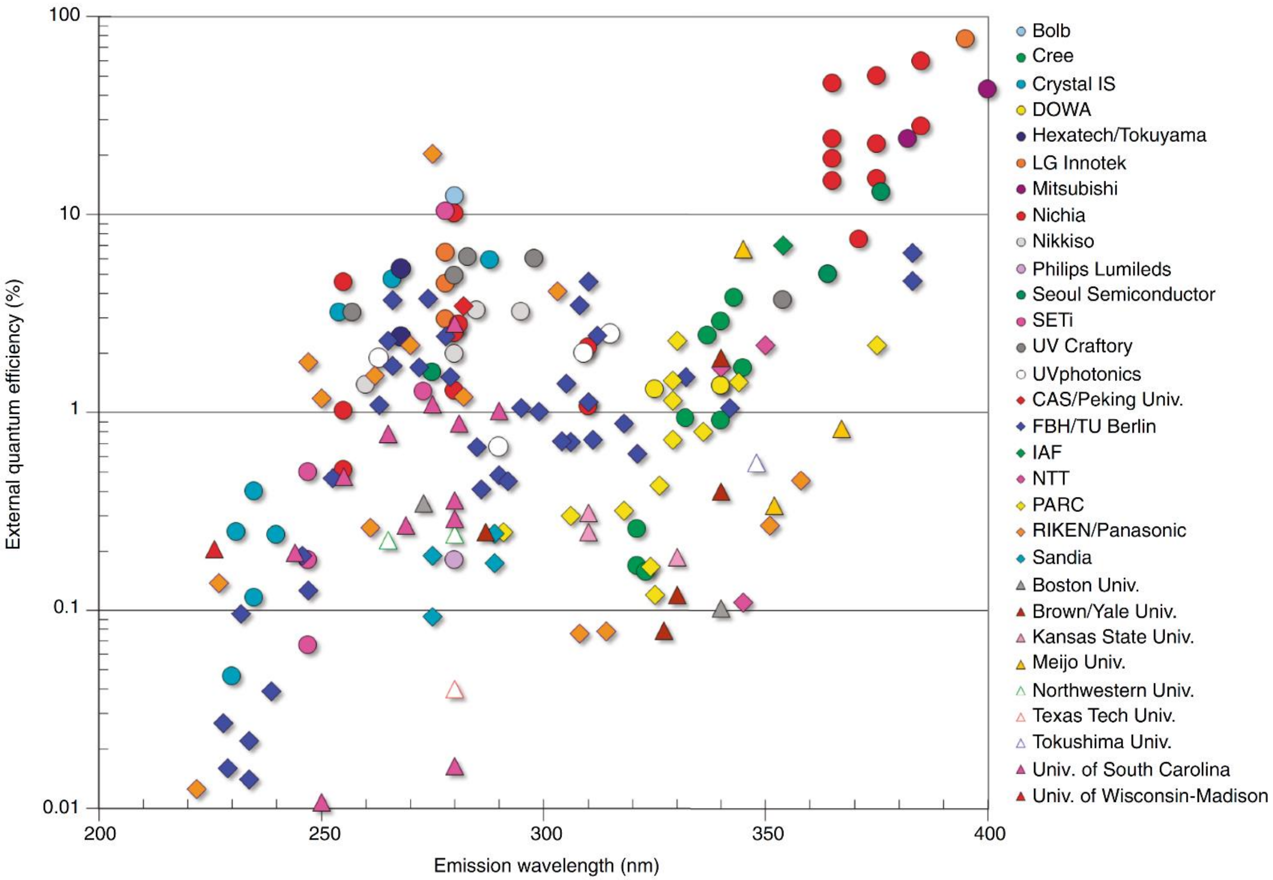
Drawbacks

- Newer technology
- Limited wavelength choices
- Low efficiencies at shorter λs
- Generally need close working distance of a few mm

Heraeus

OVERVIEW- CURRENT STATE OF DUV LEDS

EQEs for group-III-nitride-based LEDs



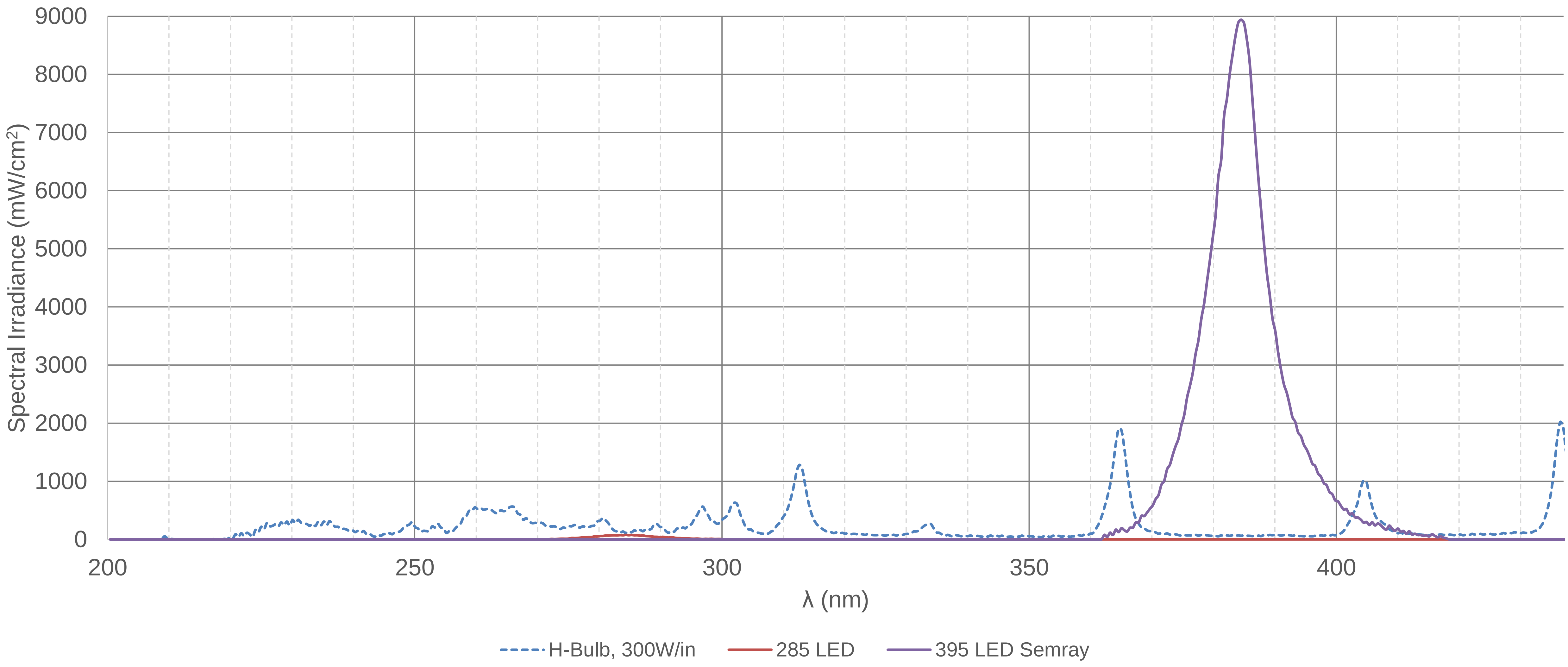
Kneissl, M., Seong, T., Han, J. et al. The emergence and prospects of deep-ultraviolet light-emitting diode technologies. Nat. Photonics 13, 233–244 (2019). https://doi.org/10.1038/s41566-019-0359-9

External Quantum Efficiency

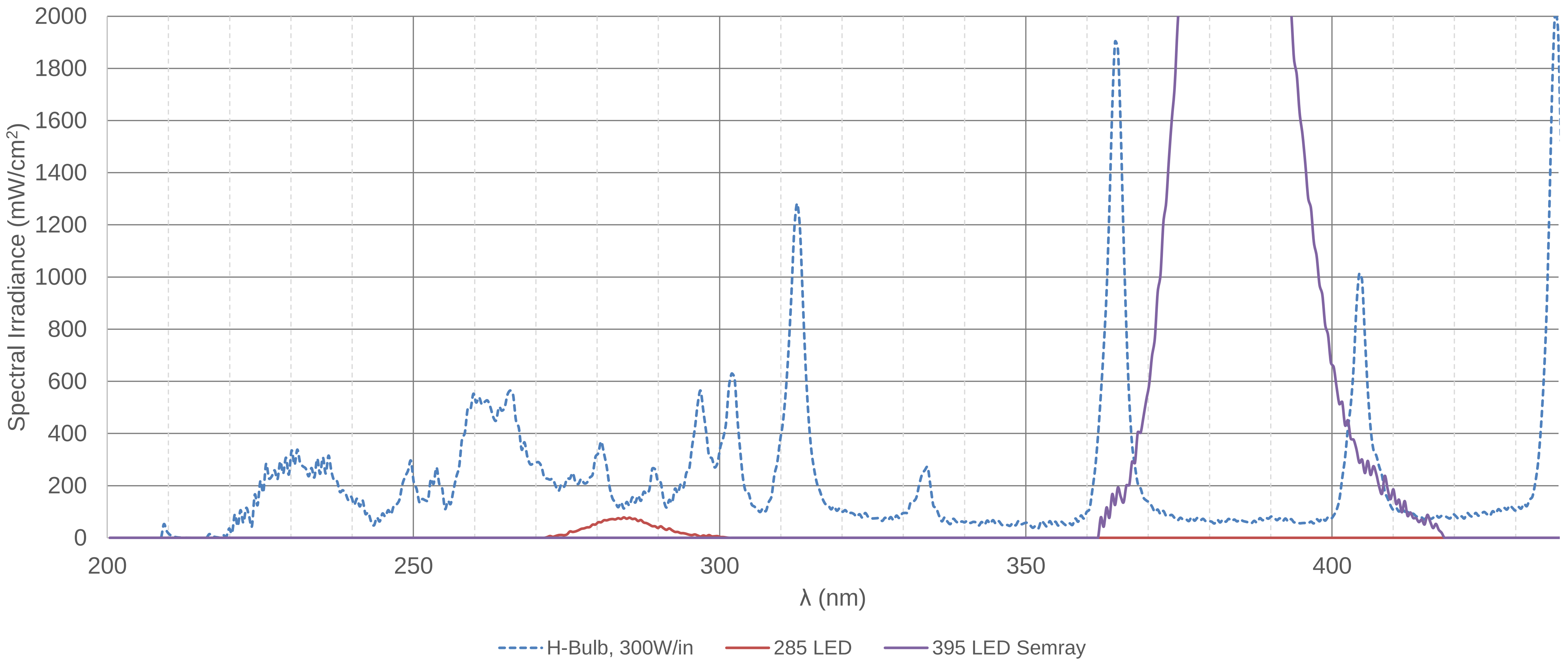
- EQE of UVA LEDs (InGaN-based) is 46-76%
- EQE of DUV LEDs (AlGaN-based) is 20% max at 275nm
- Sharp drop in EQEs at wavelengths shorter than 250nm
- Significant dip across UVB band
- EQE and WPE for commercially available UVC LEDs is only 6.4% and 4.1%, respectively

EXPERIMENTAL SETUP

EXPERIMENTAL SETUP- SPECTRAL IRRADIANCE OF SOURCES



EXPERIMENTAL SETUP- SPECTRAL IRRADIANCE OF SOURCES



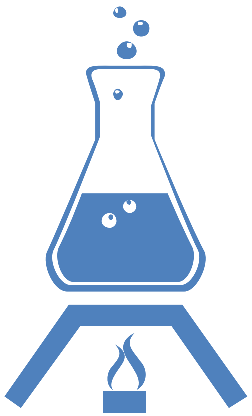
EXPERIMENTAL SETUP- FORMULATIONS

Coating A- Direct-to-metal (DTM), clear, 26µm DFT

10.0%	SC 5242 (acrylic oligomer - Miwon)
24.0%	PE 2120B (80% epoxy acrylate, 20% TPGDA - Miwon)
7.0%	Ebecryl 4827 (aromatic urethane acrylate - Allnex)
15.0%	IBOA (monomer)
32.5%	TPGDA (monomer)
3.0%	SC 1400 (acidic adhesion promoter - phosphate methacrylate - Miwon)
0.25%	Byk 333 (wetting agent - Byk)
0.25%	Byk UV 3500 (surface slip additive - Byk)
2.5%	CPK/Irgacure 184 (photoinitiator - Rahn)
2.5%	DMHA/Darocure 1173 (photoinitiator - Rahn)
2.5%	MBF (photoinitiator - Rahn)
0.5%	TPO (photoinitiator - Rahn)

Coating B- Direct-to-metal (DTM), pigmented, 26µm DFT

43.3%	S5257 (Miwon)
27.9%	IBOA (Genomer 1121 Rahn)
9.6%	EOTMPTA (M3130 Miwon)
7.7%	SR 9051 (Sartomer)
4.8%	TPO (Rahn)
2.9%	Irgacure 500 (IGM)
3.8%	Plasticolors 73-02339 Black Dispersion



Coating C- Clear, on Leneta cards, 14µm

45%	Ebecryl 221
40%	Ebecryl 85
10%	Ebecryl P115
2.5%	TPO
2.5%	Irgacure 184

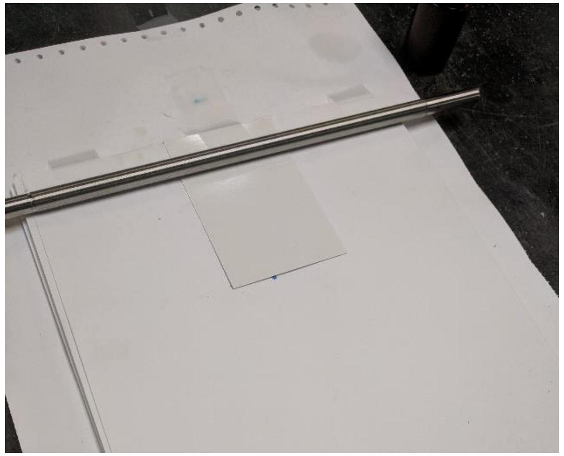
Coating D- Clear, on Leneta cards, 14µm

75%	Ebecryl 5781
20%	Ebecryl LED 02
2.5%	TPO
2.5%	Irgacure 184

EXPERIMENTAL SETUP

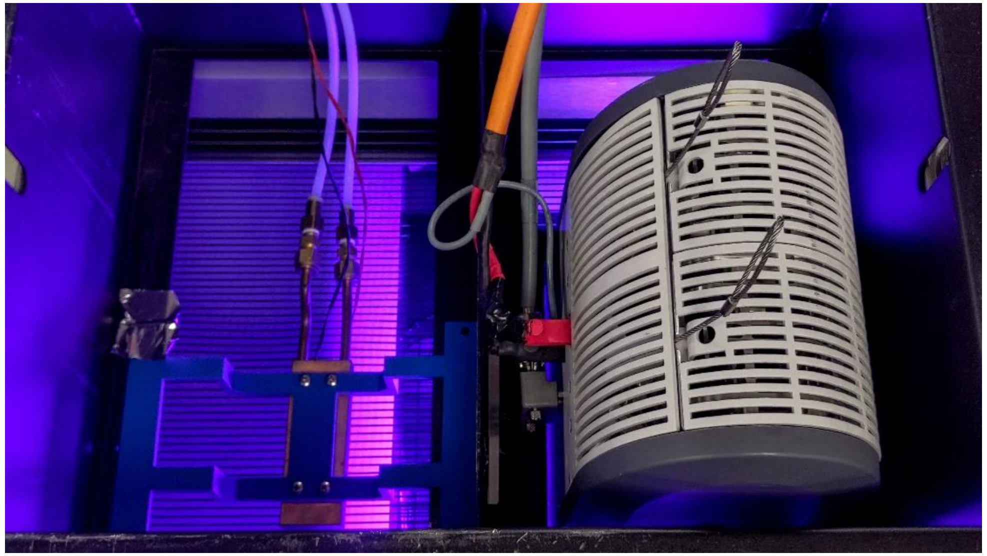
Drawdown

- Drawdown rod was used to apply a uniform thickness to the substrate



Exposure

- Nitrogen inerting was used for many samples (<100ppmO_2)
- All samples were first exposed to 395nm then 285nm

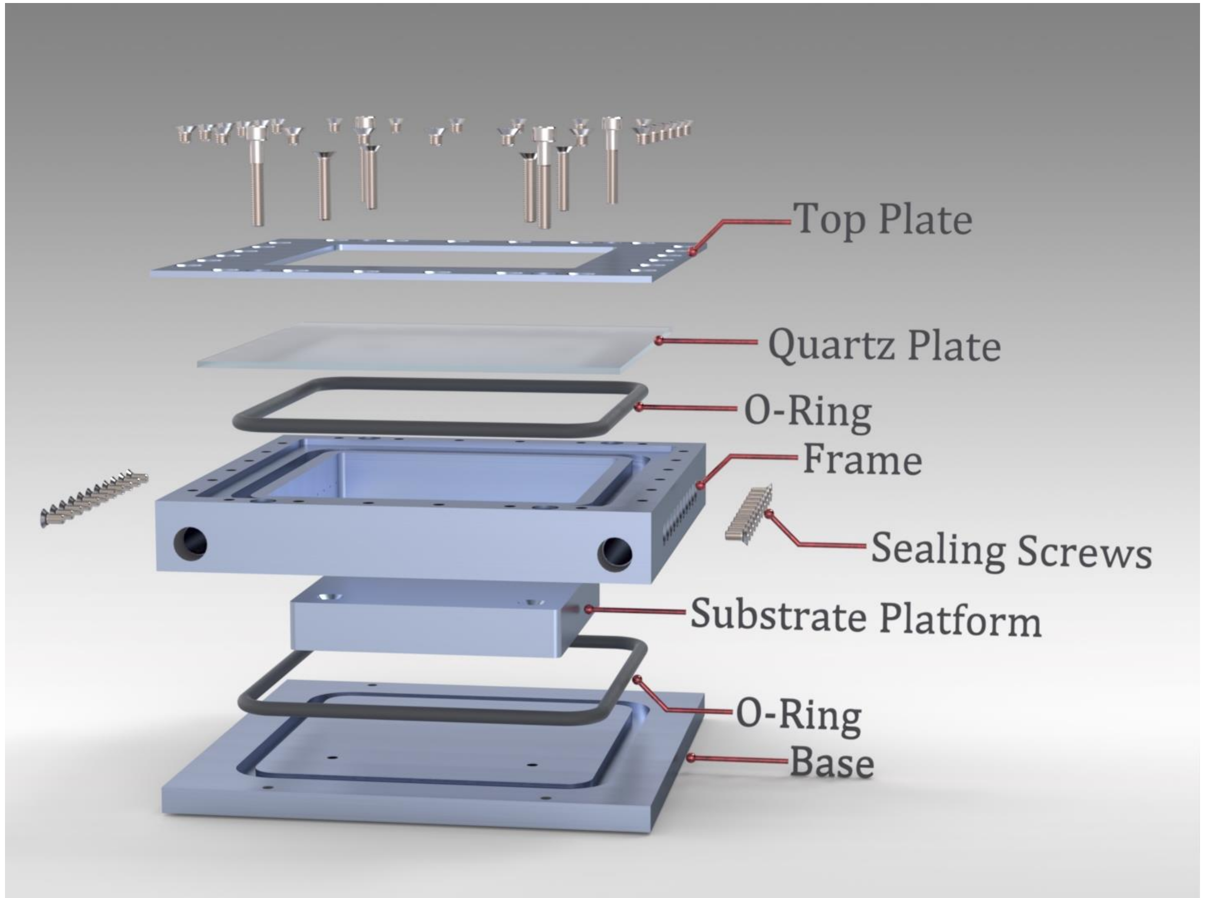


Physical Tests

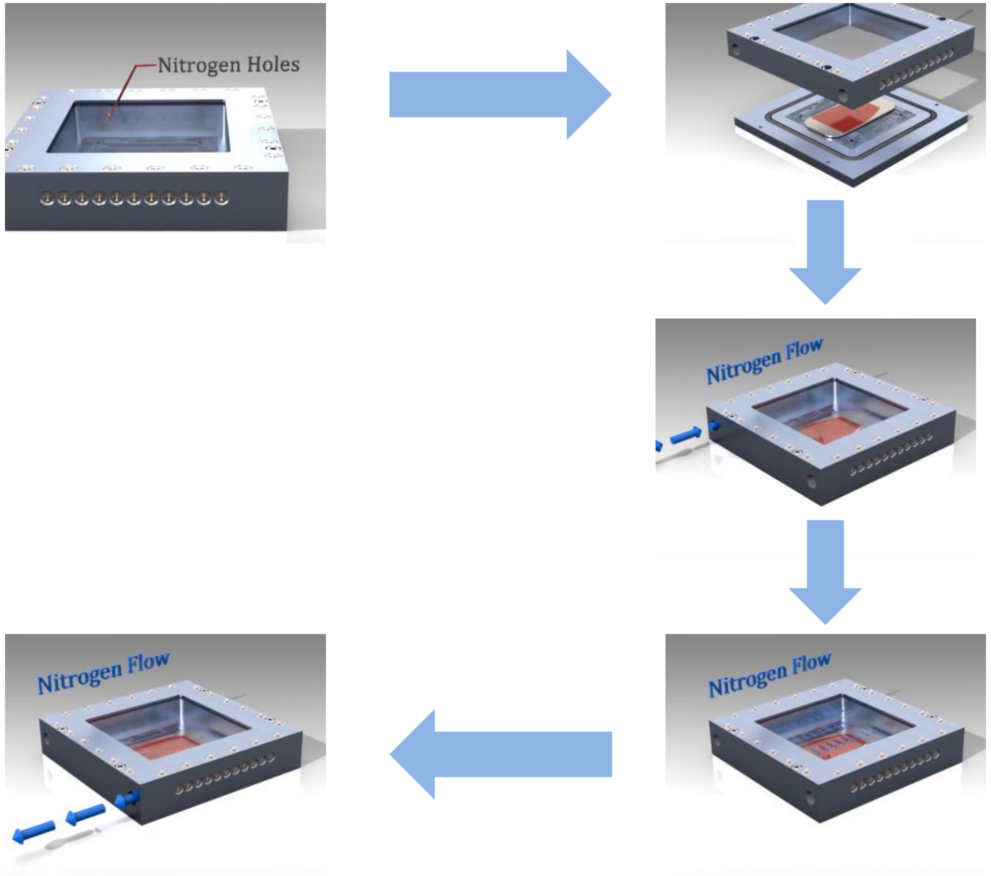
- Thumb twist for “bulk cure”
- MEK double rub for chemical resistance
- Marginal success points (MSP) were found for various levels of UVA and UVB exposures

EXPERIMENTAL SETUP- NITROGEN INERTING BOX

Exploded View



How It Works

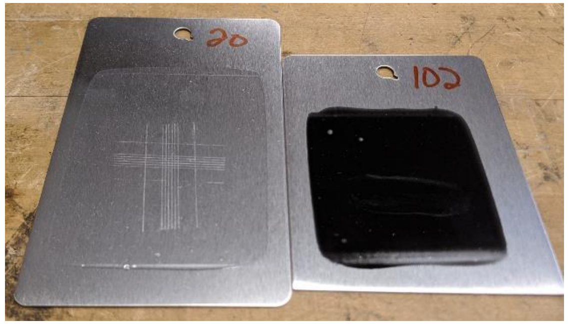


RESULTS

RESULTS- GENERAL

Coatings A and B

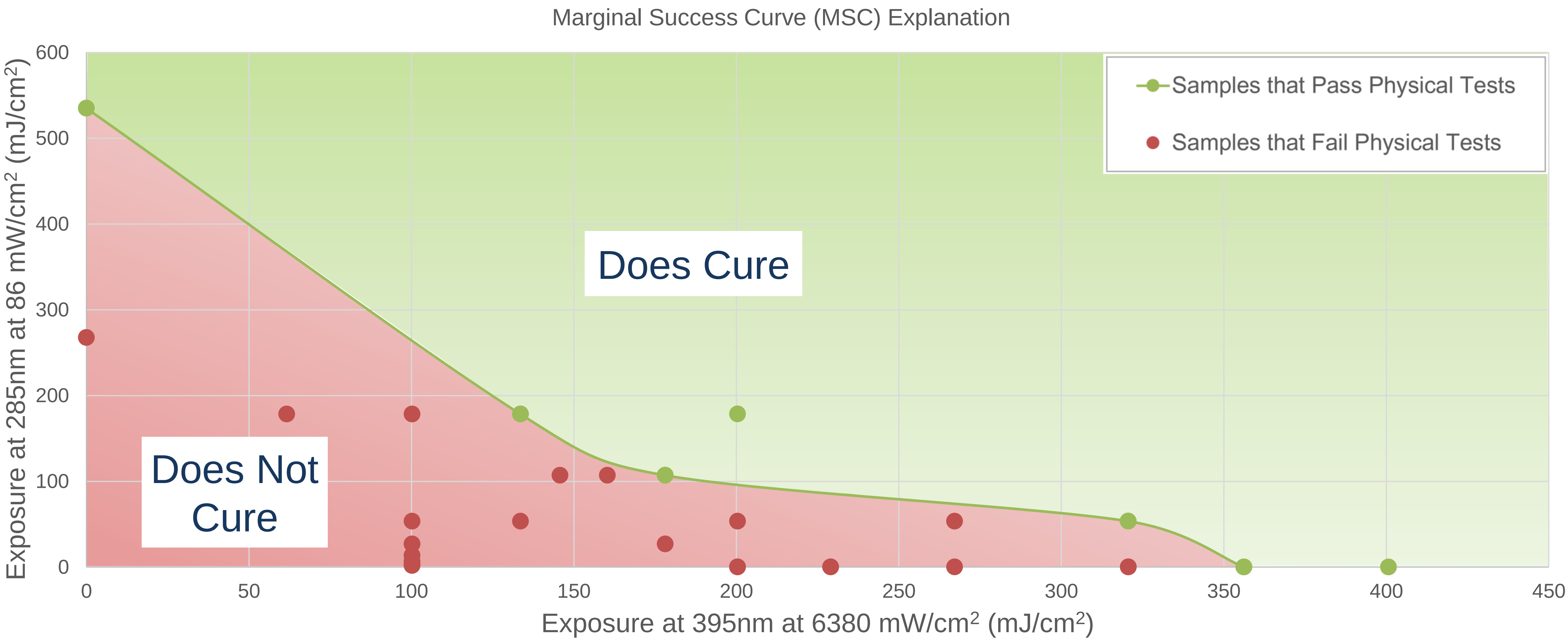
- DTM, Clear (A) and pigmented (B), 26µm (1mil)
- Did not cure in air at minimal belt speeds (up to 500mJ/cm^2 UVB and 6,000mJ/cm^2 UVA)
- Cured in N_2 at fast speeds/low exposures
- Marginal success curve (MSC) plotted for MEK double rub in N_2
- Cured with only UVA or only UVB at high exposures, and cured with a combination of both at lower exposures
- Using more UVA energy means less UVB is necessary to cure, and vice versa



Coatings C and D

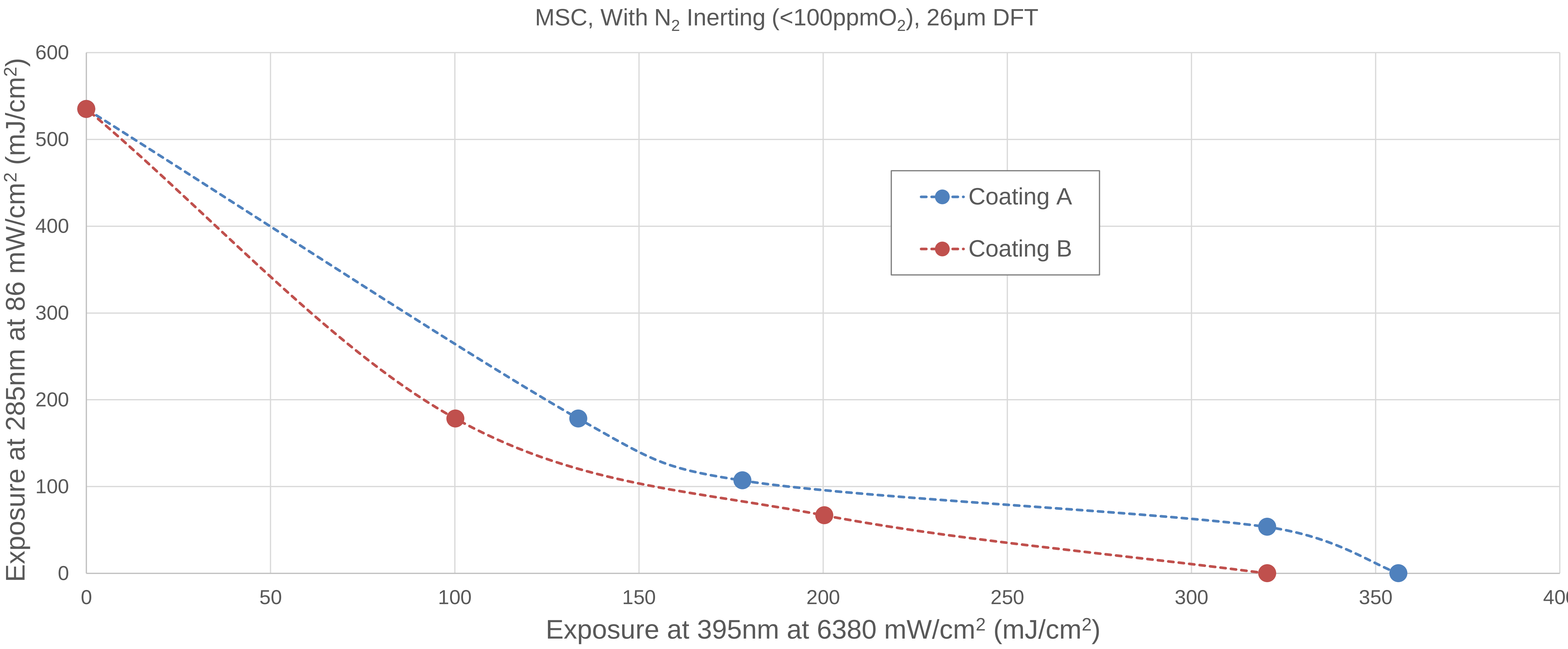
- Clear, 14 µm (0.55mil)
- Cured in air
- Small amount of UVB (30-100 mJ/cm^2) had significant impact on cure speed
- Cured with only UVB (Coating D) at high exposure
- Using more UVA energy means less UVB is necessary to cure, and vice versa

RESULTS

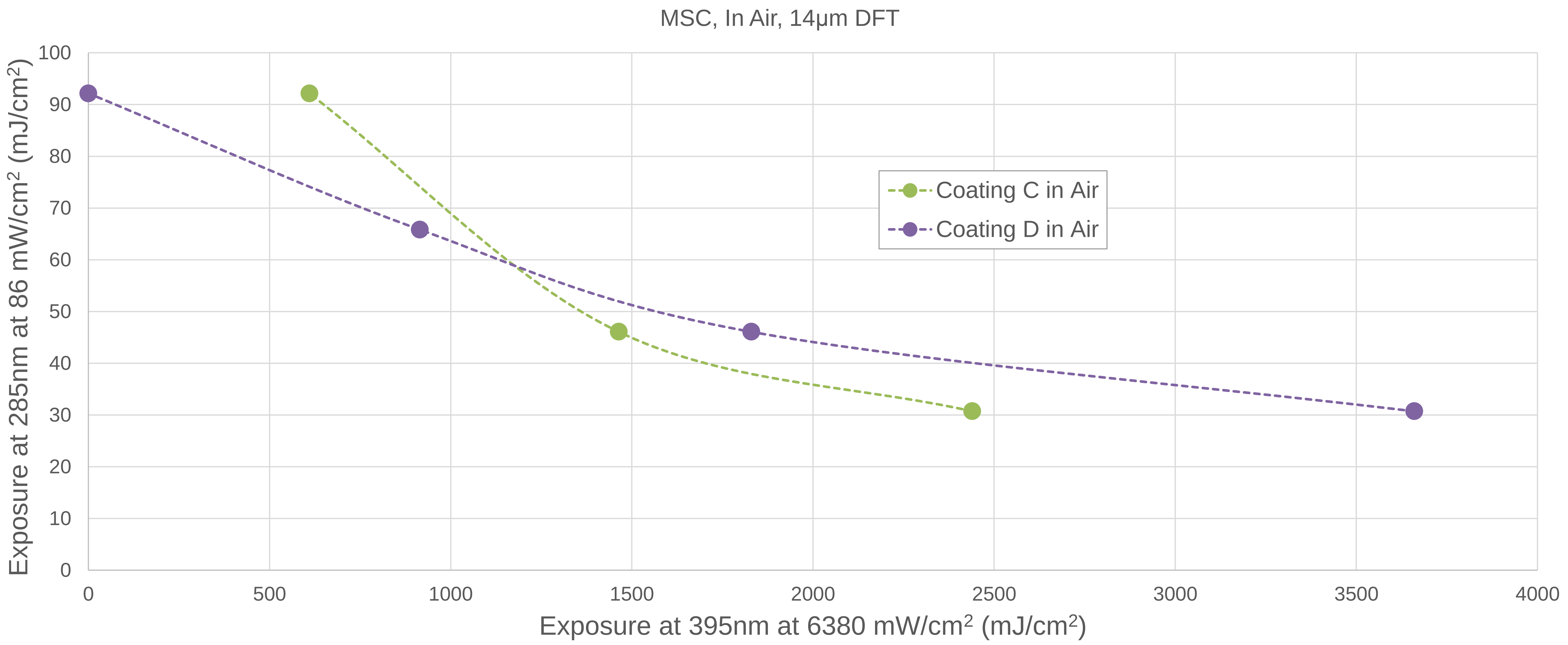


Marginal Success Curve (MSC) Explanation
Samples that Pass Physical Tests
Samples that Fail Physical Tests
Does Cure
Does Not Cure
Exposure at 285nm at 86 mW/cm² (mJ/cm²)
Exposure at 395nm at 6380 mW/cm² (mJ/cm²)
0
100
200
300
400
500
600
0
50
100
150
200
250
300
350
400
450

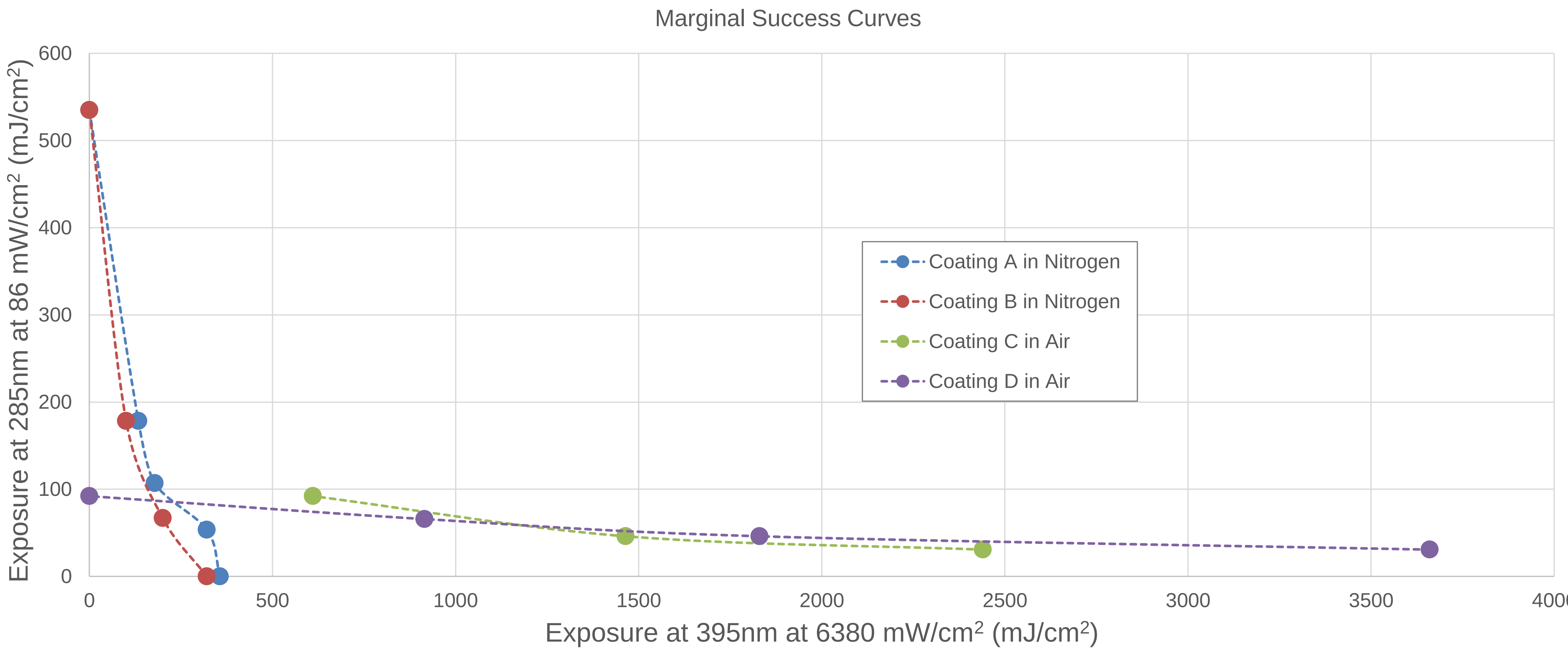
RESULTS- COATINGS A AND B



RESULTS- COATINGS C AND D



RESULTS

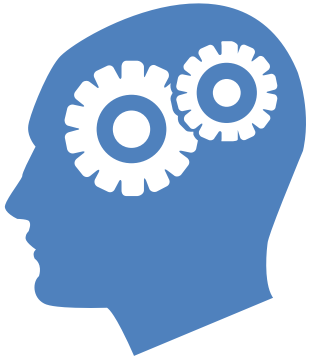


Marginal Success Curves
Exposure at 285nm at 86 mW/cm2 (mJ/cm2)
600
500
400
300
200
100
0
0
500
1000
1500
2000
2500
3000
3500
4000
Exposure at 395nm at 6380 mW/cm2 (mJ/cm2)
Coating A in Nitrogen
Coating B in Nitrogen
Coating C in Air
Coating D in Air

CONCLUSIONS

CONCLUSIONS

- Overcoming oxygen inhibition with LED is challenging while formulating to maintain all other properties that commercial formulations need to have—primarily adhesion and flexibility—without yellowing
- It is difficult to formulate certain coatings to work successfully with UV LED—even combinations of wavelengths, contrasted with H-bulb at 300W/in
- Exponentially more time consuming to characterize MSP and MSC of coating as more sources are added to exposure
- Using nitrogen to overcome the problem is a valid option. It could be used to a lesser degree than here (at, say 5,000-1,000ppm O_2) to have a positive effect

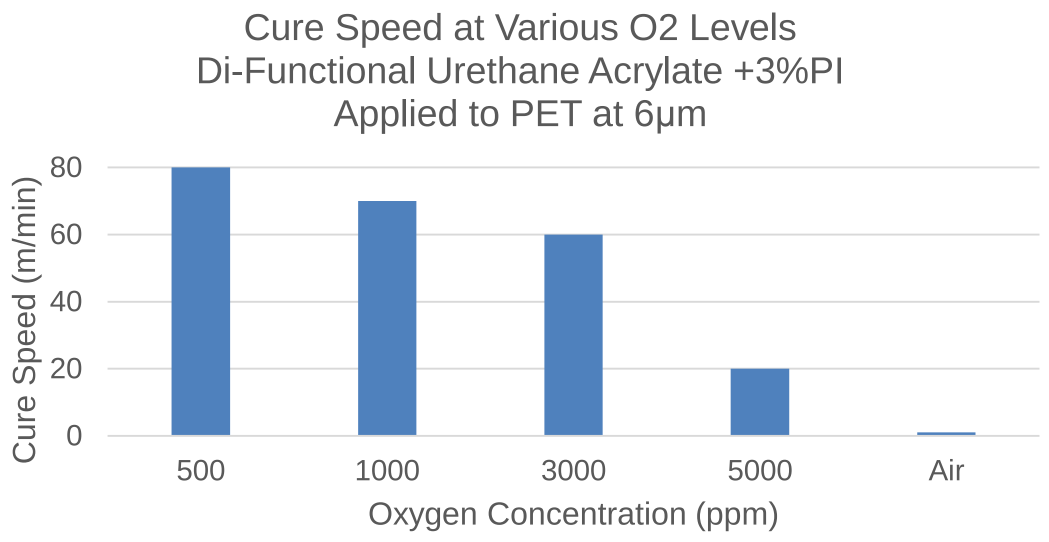


DISCUSSION

DISCUSSION- OVERCOMING OXYGEN INHIBITION

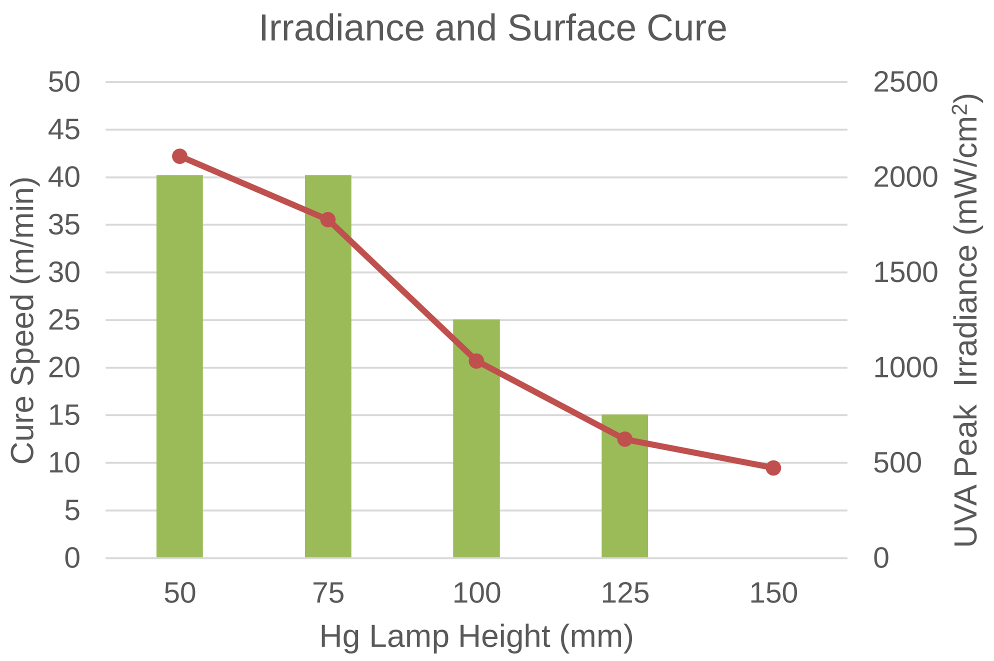
Nitrogen Inerting

- Significant improvements were noted at 1,000 and 3,000ppm oxygen with some coatings
- Enables curing at extremely low film thickness (6µm)



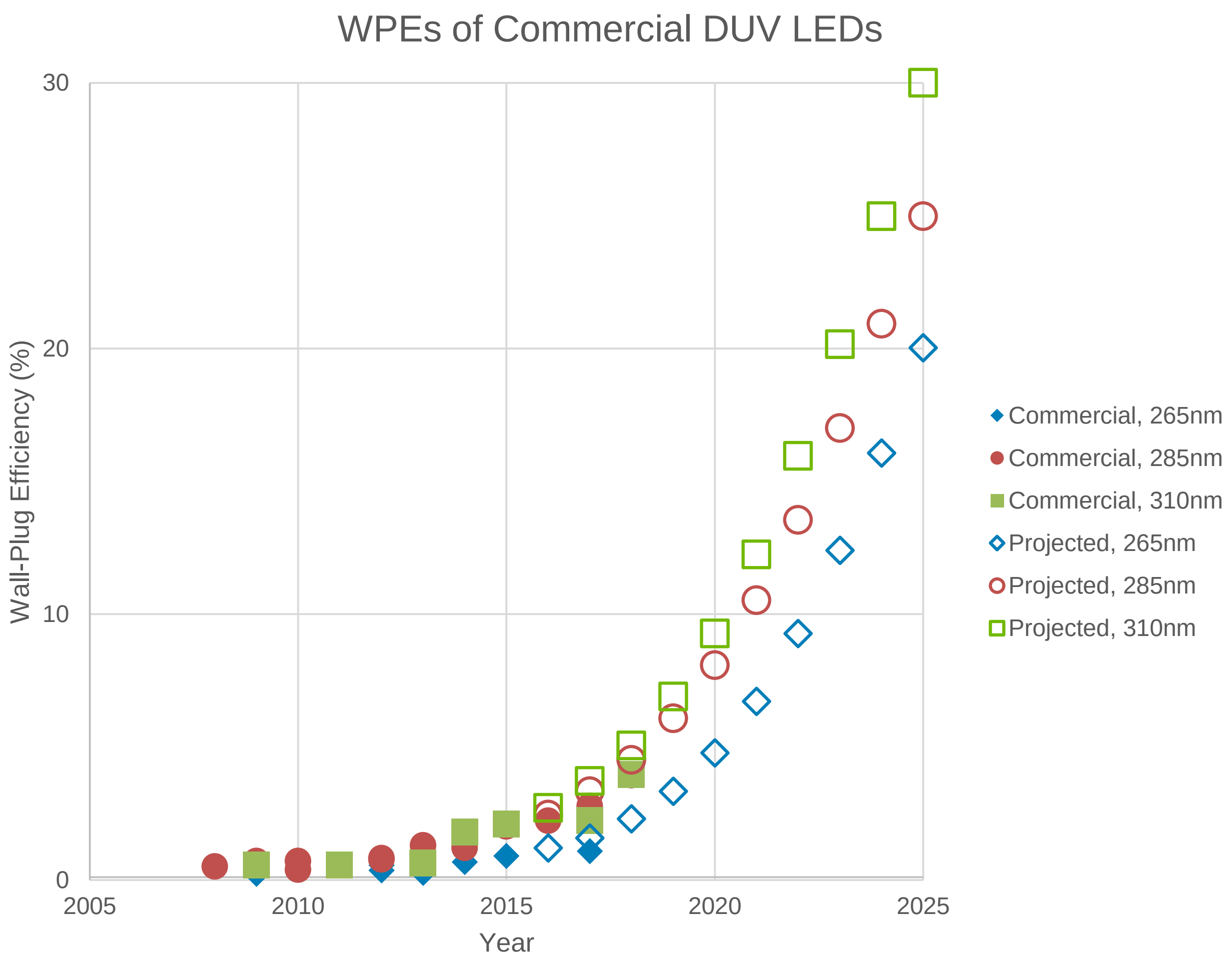
Peak Irradiance

- Increasing UV intensity (mW/cm^2) can improve cure speed at the same energy level (mJ/cm^2)



Skinner, Dawn. “Investigating the Practical Issues of Nitrogen Inerting in UV Curable Processes.” Fusion UV Systems Inc.

DISCUSSION- FUTURE OUTLOOK



Kneissl, M., Seong, T., Han, J. et al. The emergence and prospects of deep-ultraviolet light-emitting diode technologies. Nat. Photonics 13, 233–244 (2019). https://doi.org/10.1038/s41566-019-0359-9

Future Outlook

- 310, 285, and 265nm emission bands are currently the most relevant for high-volume applications, and thus attract focused research and development effort
- There could be a case made for 285nm LEDs overtaking 310nm LEDs in WPE due to high-volume applications in water treatment and disinfection
- We should expect commercially available UVC and UVB LEDs with WPEs exceeding 10% by 2021
- Higher WPEs → higher irradiance, which will help overcome oxygen inhibition and produce faster cure speeds
- In the meantime, nitrogen inerting is an effective option when combined with LEDs
- MSC guides equipment flexibility—Older lamps will not become obsolete quickly

SPECIAL THANKS TO RAPID CURE TECHNOLOGIES

Rapid Cure Technologies

- Provided several formulations for testing via Dan Montoney
- Formulate and manufacture paints, coatings, inks, adhesives, sealants, and resins for new startups, fortune 500 companies, and everything in between
- Have competitive solutions using conventional (water-based, solvent-based, high-solids)
  and radiation curable (UV, E-beam, X-ray) chemistries

RAPID CURE
TECHNOLOGIES
Sustainable Chemistry... Customized

Corporate Headquarters
7030 Fly Road
East Syracuse, NY 13057

TEL: 888-847-3610
FAX: 888-847-3610

R&D
7030 Fly Road
East Syracuse, NY 13057

R&D Manufacturing
4724 Burr Drive
Liverpool, NY 13088

R&D Manufacturing
25 Freedom Way
Saratoga Springs, NY 12866

REFERENCES

1. Kneissl, M. & Rass, J. (eds) III-Nitride Ultraviolet Emitters–Technology and Applications (Springer, 2016).

2. Kneissl, M., Seong, T., Han, J. et al. The emergence and prospects of deep-ultraviolet light-emitting diode technologies. Nat. Photonics 13, 233–244 (2019). https://doi.org/10.1038/s41566-019-0359-9

3. Skinner, Brett. "Curing Traditional Formulations With Multi-Wavelength LEDs." Radtech International UV & EB Technology Expo & Conference. Chicago, IL. 9 May 2018. Speaker Presentation

4. Skinner, Dawn. "Investigating the Practical Issues of Nitrogen Inerting in UV Curable Processes." Fusion UV Systems Inc.

QUESTIONS

THANK YOU FOR YOUR ATTENTION

Acknowledgements: Darrin Leonhardt, Dawn Skinner, Eric Nelson