A Liquid Photoinitiators Blend for Pigmented UV Inks System

- Presentation for Radtech 2020 -

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Status of PI-907 & 369

Substance name (expand / collapse)		EC No.	CAS No.	Date of inclusion	Reason for inclusion	Decision	IUCLID dataset	
2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one	PI-907	400-600-6	71868-10-5	16/01/2020	Toxic for reproduction (Article 57c)	ECHA_01_2020.pdf		
2-benzyl-2-dimethylamino-4'-morpholinobutyrophenone	PI-369	404-360-3	119313-12-1	16/01/2020	Toxic for reproduction (Article 57c)	ECHA_01_2020.pdf		

ECHA website link: https://echa.europa.eu/candidate-list-table

- Both PI-907 and 369 are put into SVHC list in 2020 Jan, due to **reprotox. 1B** toxicity.

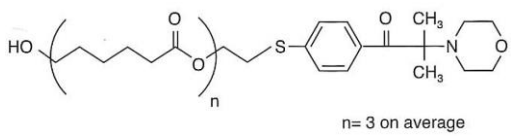
Approaches to Improve the Toxicity of Aminoketone PIs

For decades, Chitec has kept doing researches in developing a new generation aminoketone photoinitiators through approaches of:

1. Oligomerized structure to enlarge the molecular weight
2. Modification of Structure or functional group
3. Functional blend to achieve similar performance

Oligomerized Liquid Aminoketone Photoinitiators

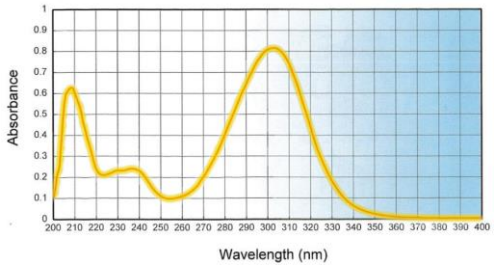
Chivacure® 3482 (2003)



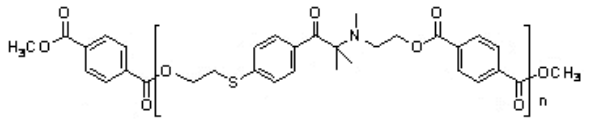
n= 3 on average

- Amber viscous liquid
- Molecular weight: ca. 700
- λmax= 303nm

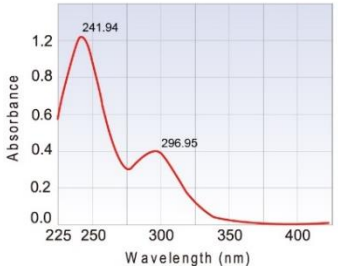
UV Spectrum



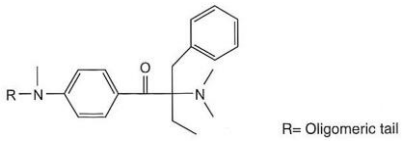
R-gen 2010 (2012)



- Yellow to amber syrup
- Molecular weight: ca. 1500
- λmax= 296nm



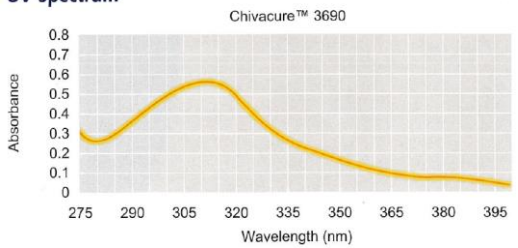
Chivacure® 3690 (2006)



R= Oligomeric tail

- brownish viscous liquid
- Molecular weight: ca. 750
- λmax= 312nm

UV Spectrum

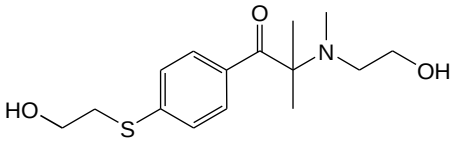


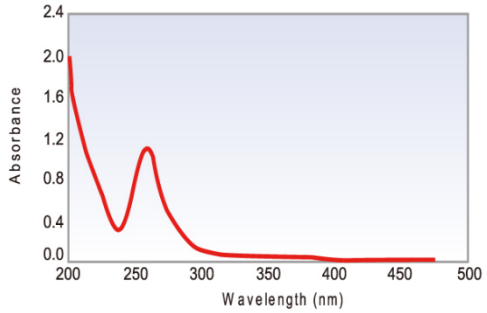
But they never became accepted in the industry……

- Oligomeric structures are proven to reduce aminoketone PI's photo-speed significantly which requires a higher dosage requirement and higher cost.

New Molecular Designs of Aminoketone Photoinitiator

R-gen® 7W (2010)

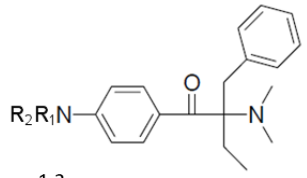


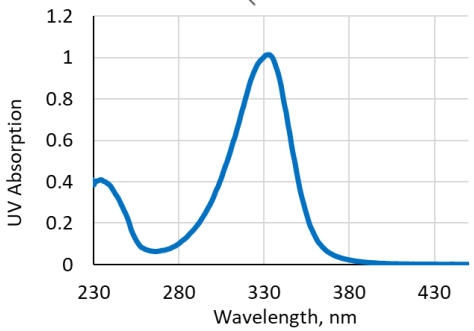


- White crystalline powder
- Molecular weight: 297.41
- λmax= 257nm

Mass production issue…..

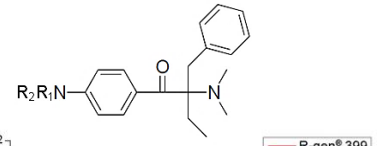
R-gen® 919 (2014)

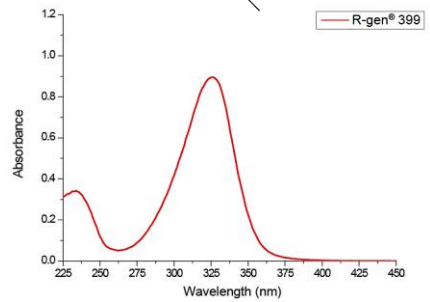




- Brownish viscous liquid
- λmax= 332nm

R-gen® 399 (2013)





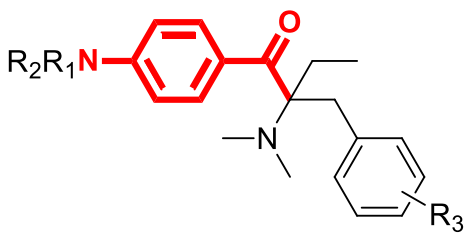
- Brownish viscous liquid
- λmax= 326nm

Odor after curing…
Dark color

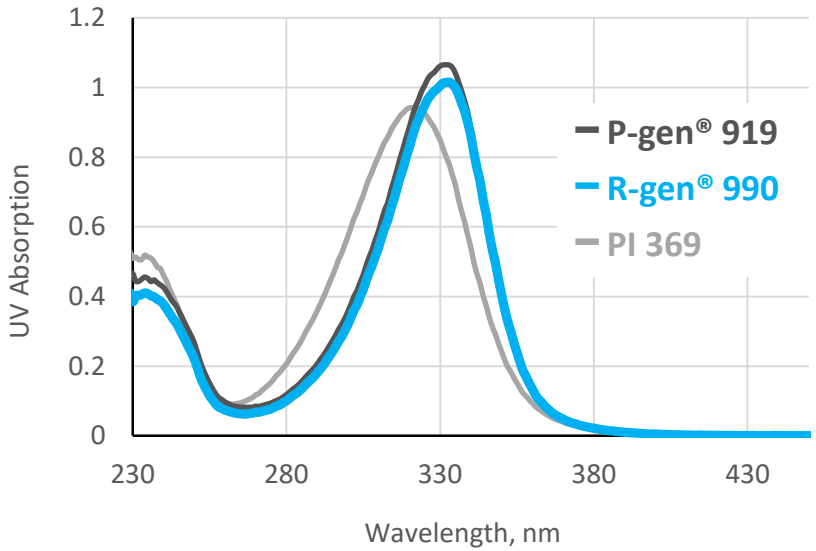
- In 2014, Chitec introduced R-gen® 919, which has excellent photo-curing performances, and no odor after curing, but suffered from dark color and higher acute toxicity issue.
- Though existed above two drawbacks, R-gen® 919 is still a good choice in photoresist and inkjet ink applications.

R-gen® 990* – A Novel Liquid Aminoketone PI

R-gen® 990 (2018)



R-gen® 990



Concentration: 10 ppm in CH_2Cl_2

	R-gen® 990	R-gen® 919
Appearance	**Light yellow** viscus liquid	Dark brown viscus liquid
Photoactivity	High	High
Purity, %	**~98%**	~92%
Acute toxicity	**LD_{50} > 5,000 mg/kg**	LD_{50} = 1,000 mg/kg
Odor	**Odorless**	Slight ester odor

****WO patent pending***

Photoactivity Evaluation of R-gen® 990

	LED 365nm (4W)		LED 395nm (8W)	
	Surface Cure	Full Cure	Surface Cure	Full Cure
PI 369	1	2-3	1	2
R-gen® 919	1	2	1	2-3
R-gen® 990	**1**	**2**	1	2-3
TPO	2	3	1-2	3

Times for achieving full curing

Conditions:

- System: Flexo black ink (Epoxy/ PU acrylate)
- PI System: aminoketone PI 4%, DETX 2%
- Carbon black: **10%**, MA-100 grade
- Film thickness: 12 μm
- Substrate: PET
- UV source: LED UV, 365 & 395 nm, 40 m/min

■ Photospeed in High Carbon black Loading Ink

	Dosage	UV Curing Times					
		1	2	3	4	5	6
PI-169	4%	X	X	X	X	Δ	O
	8%	Over-saturation					
R-gen® 990	4%	X	X	X	Δ	O	
	8%	Δ	Δ	O			
	12%	O					

Times for achieving full curing

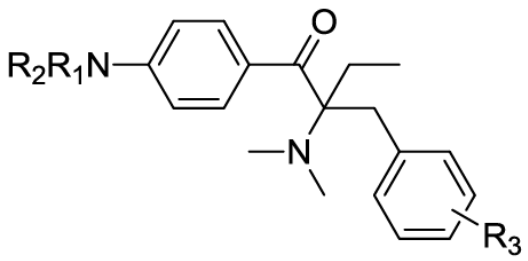
X: tack surface
Δ: surface cure without physical property
O: full cure

Conditions:

- System: Flexo black ink (Epoxy/ polyester acrylate)
- PI System: aminoketone PI with, DETX 2%
- Carbon black: **20%**, high color black
- Film thickness: 6 mm
- Substrate: PET
- UV source: LED UV, 4W, 365, 20 m/min

R-gen® 990 Status

Structure



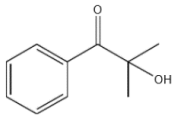
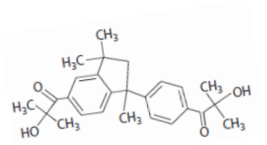
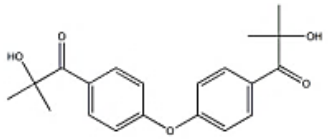
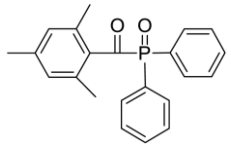
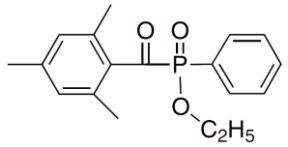
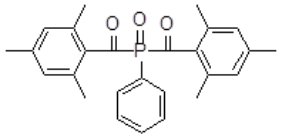
Chemical family	Aminoketone
CAS No.	Proprietary

- The OECD 407 (repeated dose 28-day oral toxicity study) results showed R-gen® 990 performed similar as Irgacure® 369 at the same dosage at 100mg/kg.
- OECD 421 (reproduction and developmental toxicity screening test) or OECD 414 (prenatal developmental toxicity test), are not considered at the priority further as no improvement found during OECD 407 test.

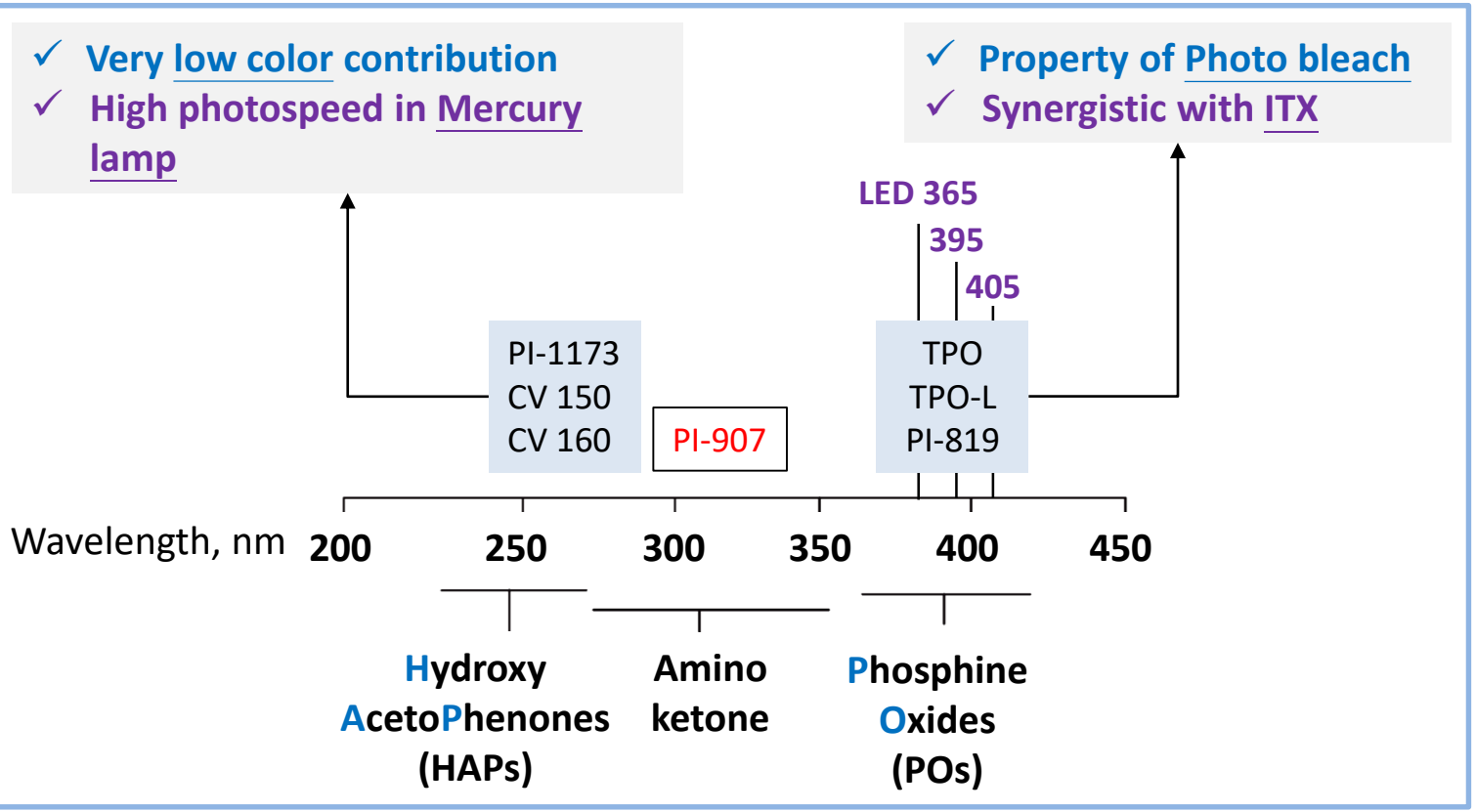
Summary of Pros and Cons of PI-907

PI-907	
Pros	**Cons**
Excellent photospeed	SVHC
Colorless → Suitable for clear coating	Strong odor after curing
Synergistic with ITX → Suitable for pigmented coating	
Good Solubility	
Good Price	

Candidates of Liquid Photoinitiator Blend

Type	PI	Structure
HAP	PI-1173	
HAP Dimer	**Chivacure® 150** (CV150)	
HAP Dimer	**Chivacure® 160** (CV160)	
MAPO*	**Chivacure® TPO**	
MAPO	**Chivacure® TPO-L** (TPOL)	
BAPO**	PI-819	

*MAPO= mono-acyl PO
** BAPO= bis-acyl PO



■ To fulfill the requirements of PI-907 replacement, the combinations of HAP dimer and TPOL have high potential:

✓ Low color contribution
✓ Wide range photoactivity
✓ Consideration of substance regulations

Liquid Photoinitiator Blends

		Liquid functional Blend	Ratio	Concerns
Target system	Aminoketone	PI-907		SVHC
Reference system	HAP+MAPO	PI-1173/ TPO	**1/1**	PIs are in the Nestle exclusion list
Reference system	HAP+MAPO	PI-1173/ TPO-L	**1/1**	1173 is in the Nestle exclusion list
	HAP dimer + MAPO	EXP407	**CV160/ TPO-L** Proprietary	
	HAP dimer + MAPO	EXP507	**CV150/ TPO-L** Proprietary	
Reference system	MAPO + BAPO	TPO-L/ PI-819	**91/9**	Oxygen inhibition

- The ratio of liquid blend are designed depending on compatibilities between photoinitiators.

Photospeed Evaluation on Black Inks – LED UV

■ **Black Ink conditions:**

	Parts
Mixture of epoxy acrylate and urethane acrylate, F=3.5	57
HDDA	38
Carbon black (middle color black)	5
Test PI/ 2-ITX	6%/ 1%

- dry film thickness= 9um
- Substrate: PET
- Height of LED UV= 1cm

	LED UV	Photospeed, M/min	907	1173/TPO= 1/1	1173/TPOL = 1/1	EXP407	EXP507	TPOL/819= 91/9
Energy increase	365 4W	35M						
		30M						
		25M						
		20M						
		15M						
		10M						
Energy increase	395 4W	35M						
		30M						
		25M						
		20M						
		15M						
		10M						

■ Under LED UV curing condition, photospeed of EXP407 and EXP507 are close to PI-907.

Photospeed Evaluation on Black Inks – Mercury Lamp

☐ Black Ink conditions:

	Parts
Mixture of epoxy acrylate and urethane acrylate, F=3.5	57
HDDA	38
Carbon black (middle color black)	5
Test PI/ 2-ITX	6%/ 1%

- dry film thickness= 9um
- Substrate: PET
- Mercury Medium Pressure UV Lamp

		UV dosage, mj/cm2	907	1173/TPO= 1/1	1173/TPOL= 1/1	EXP407	EXP507	TPOL/819= 91/9
Condition A	UVA	52	O	X	X	Δ~O	X	X
	UVB	62						
	UVC	11						
Condition B	UVA	87	O	X	X	O	Δ	X~Δ
	UVB	106						
	UVC	23						

O= full cure
Δ= surface tacky
X= wet film

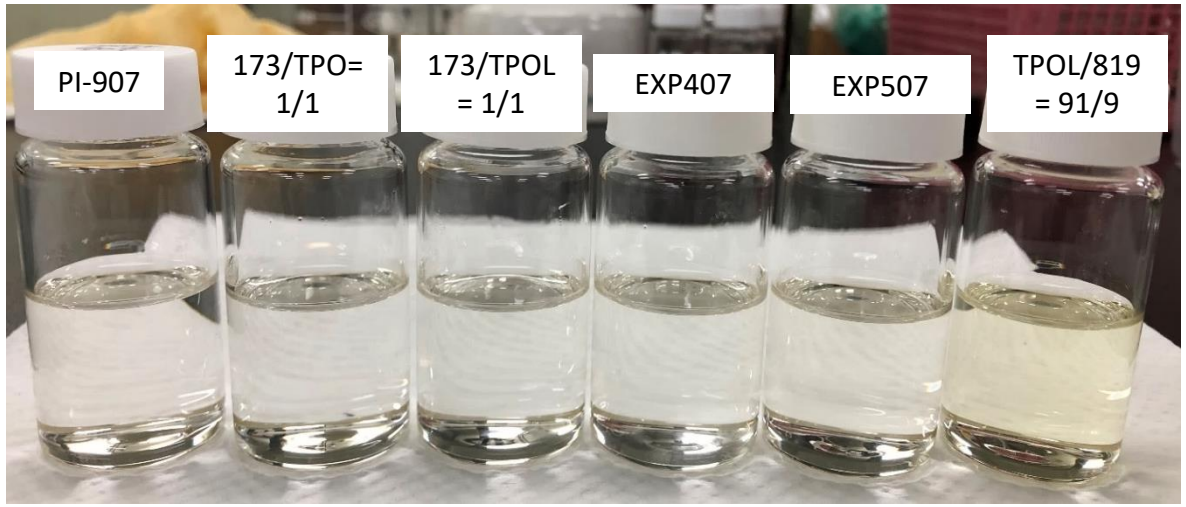
■ Under curing condition of mercury medium pressure UV lamp, the EXP407 shows outstanding photospeed compared to other liquid blend systems.

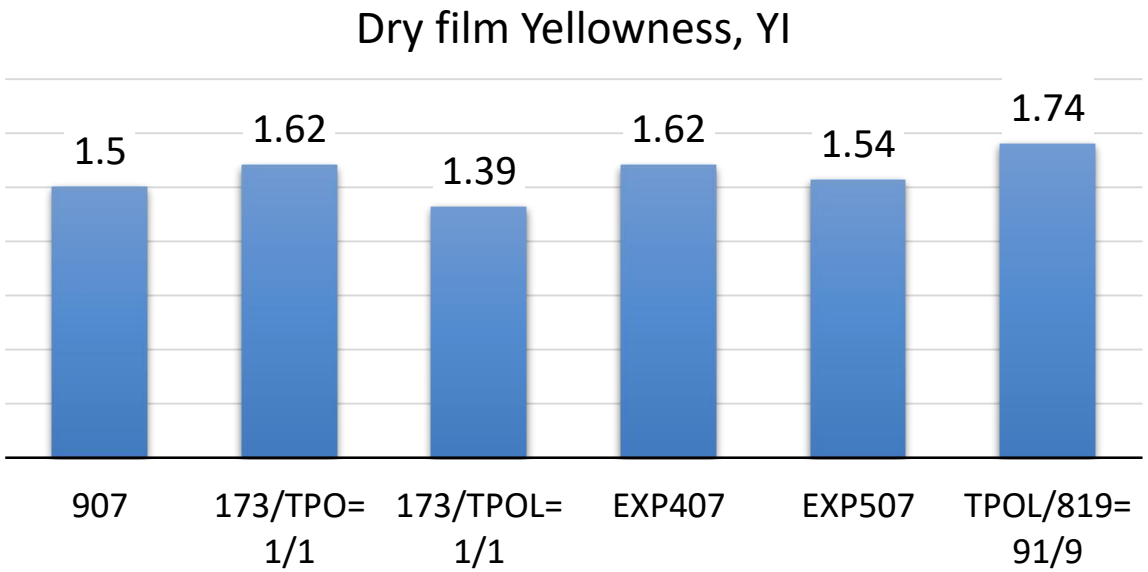
Color of Liquid Photoinitiator Blends

■ **UV Varnish**

	Parts
Mixture of epoxy acrylate and urethane acrylate, F=3.5	96%
Test PI	4%

- dry film thickness= 9um
- Substrate: PET
- LED 365nm





■ Due to photo-bleaching property, all liquid blends showed low initial color contribution as good as PI-907. Only TPO-L/819 blend has slightly higher yellowness.

Two High Potential Liquid Photoinitiator Blends

Liquid Photoinitiators Blends of **EXP407** **EXP507**
✓ Good to Excellent photospeed
✓ Colorless → Suitable for clear coating
✓ Synergistic with ITX → Suitable for pigmented coating
✓ Good Solubility
✓ Non-odor after curing
✓ Compliant with Nestle list

Why Chitec?

Chivacure® TPO-L

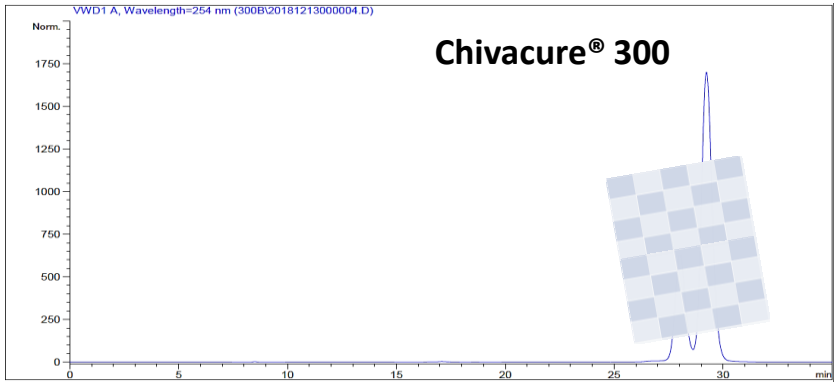
- produced by a proprietary process preventing the release of the ozone-depleting agent chloroethane into the air.

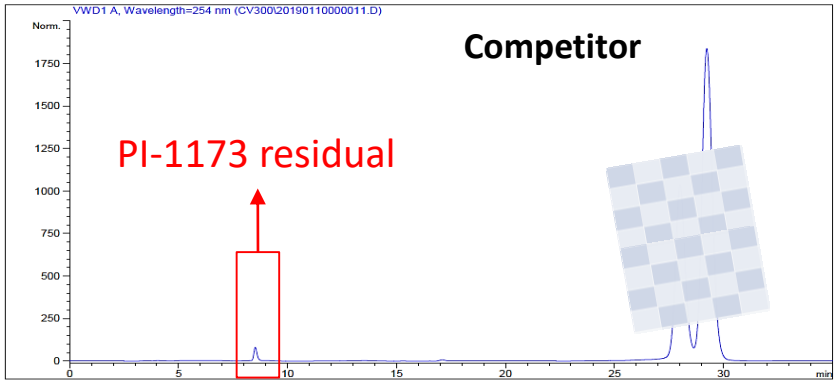
Chivacure® 160

- Excellent initial color

Chivacure® 150/ 300

- No PI-1173 residual





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