

Abstract

The Non-Migration Study of Reactive UV Absorbers

Adding UV absorber (UVA) is a simple but efficient way to upgrade coatings against sunlight exposure. However, the migratory nature of UVA's limits formulators to improve weather resistance by increasing the dosage and besides, various environment factors could be able to remove/ extract UVAs from coating layers, decreasing the effective dosage over time. A reactive UVA could be an ultimate solution.

In this research, a novel benzotriazole (BTZ) UV absorber is introduced. It carries two primary hydroxyl groups, which can react with isocyanates or melamine resins and covalently bond with the polymer backbone. We use various extraction aggravators to simulate migration loss and show the advantage of the non-migration performance of reactive type UVA compared to other additive type UVAs.

For some applications this advanced technology overcomes the migration issue and dramatically improves the coatings performance to levels that were otherwise unattainable.



The Non-Migration Study of Reactable UV Absorbers

- Reactivity and Solvent Extraction Performances -

Chitec Technology

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Dr. George Mauer, Senior Scientist

Coatings Trends & Technologies 2021

Factors of a UVA Performance

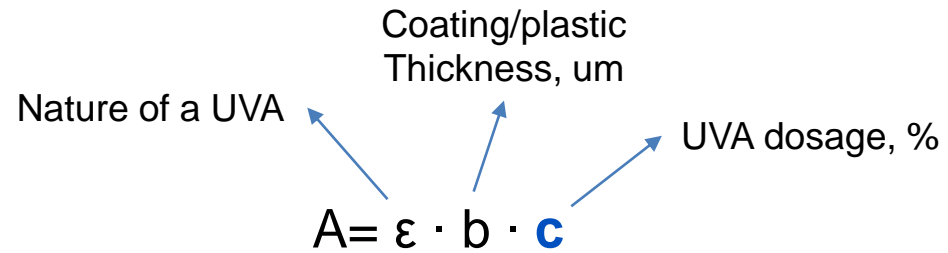
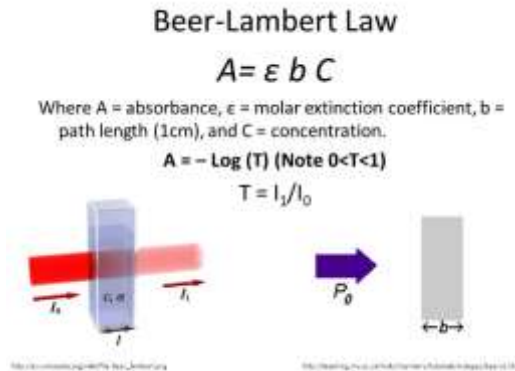


Photo-physical property of UVAs can be described as a UV filter and it obeys beer's Law.

Factors	Description	Beer's Law
Photo-permanence	<ul style="list-style-type: none"> UV resistance of UVA (UVA will be decomposed eventually under UV exposure) Usually Triazine > benzotriazole > benzophenone → Effective content decreases over time 	C
Molar absorption Coefficient	<ul style="list-style-type: none"> Nature of a UVA 	ϵ
Molecular weight	<ul style="list-style-type: none"> Low MW. means higher mole equivalent in the same loading weight. But low MW. usually leads to migration issue. 	C
Migration	<ul style="list-style-type: none"> Low molecular weight → Effective content decreases over time 	C
Heat Resistance	<ul style="list-style-type: none"> A UVA may be thermal decomposed during heat process → Effective content decreases along with thermal decomposition 	C

Migration Mechanism of UV Absorber

Reactive UVA Technology



- Time-dependent behavior



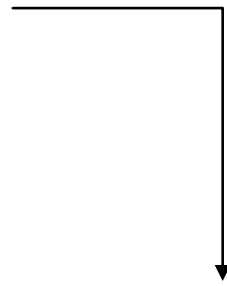
- Rain flush
- Cleaners/ heavy duty cleaner
- Degreaser
- fuels
- Polish



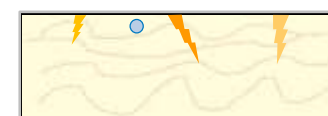
Conventional UVA in PU



- Polish



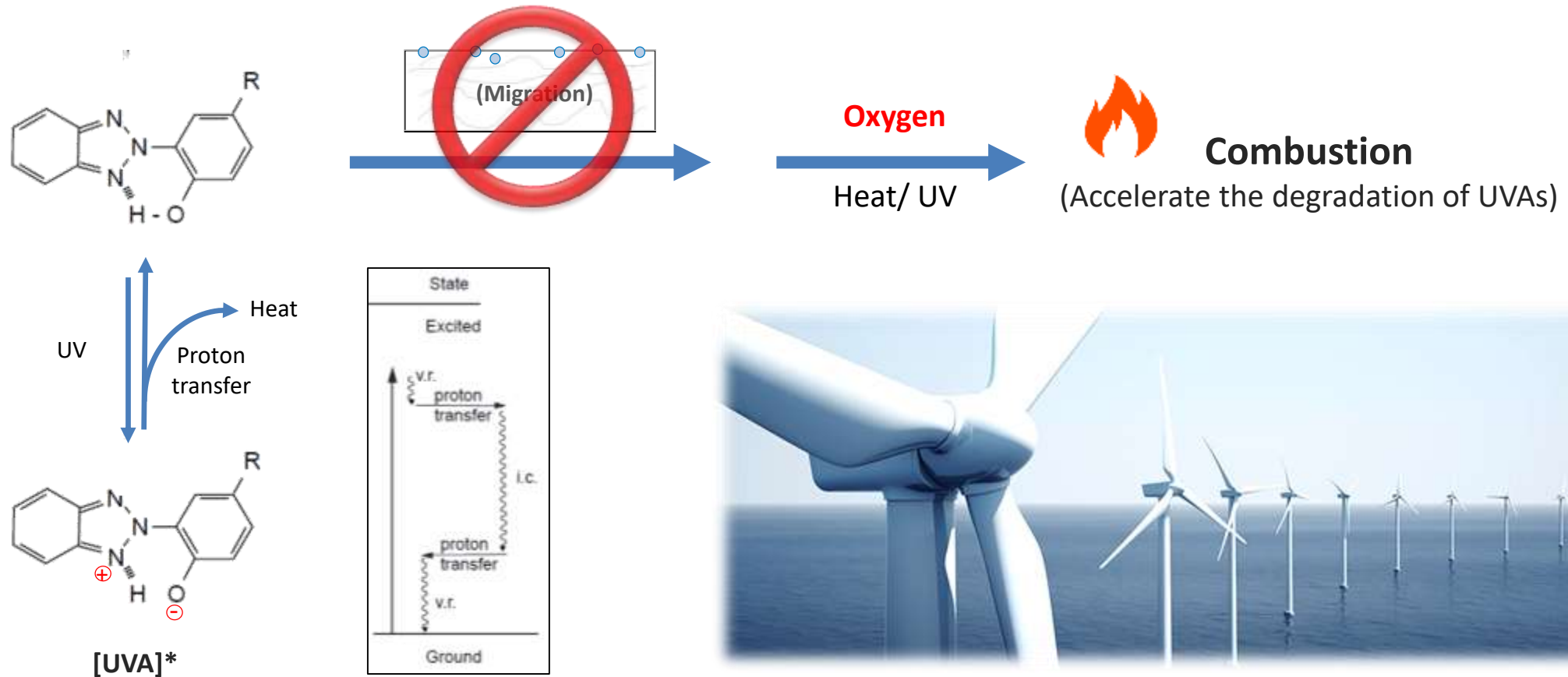
- Rain flush
- Cleaners/ heavy duty cleaner
- Degreaser
- fuels



- Yellowing, loss of glossing, and loss of mechanical properties were observed due to loss of UV absorbers.

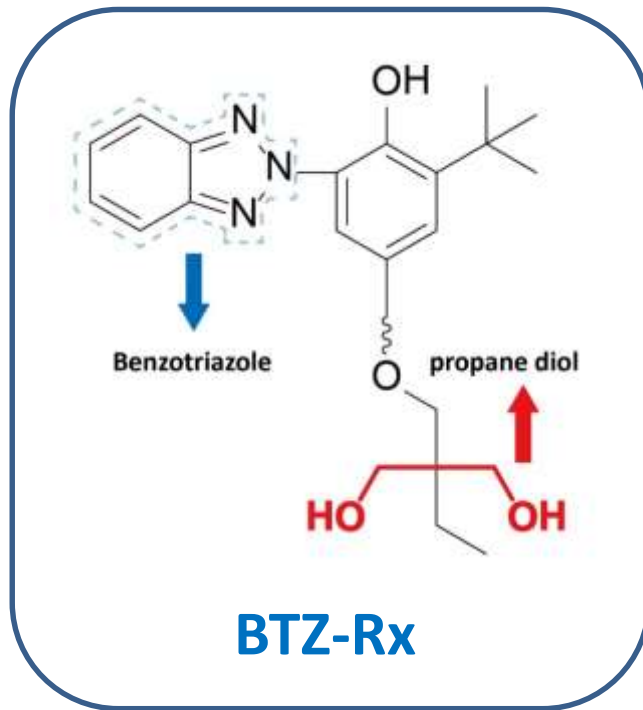
Hypothesis of UVA Degradation

□ Decrease of photopermanence:



The Concept of BTZ-Rx

A novel benzotriazole UV absorber BTZ-Rx carries two primary hydroxyl groups which is able to react with various hardeners such as isocyanates and becomes part of the polymer matrix.



+

Isocyanates

Amino Resin

Siloxane

Functions as a UV Absorbing diol

2K-PUR Coating

Baking Enamel

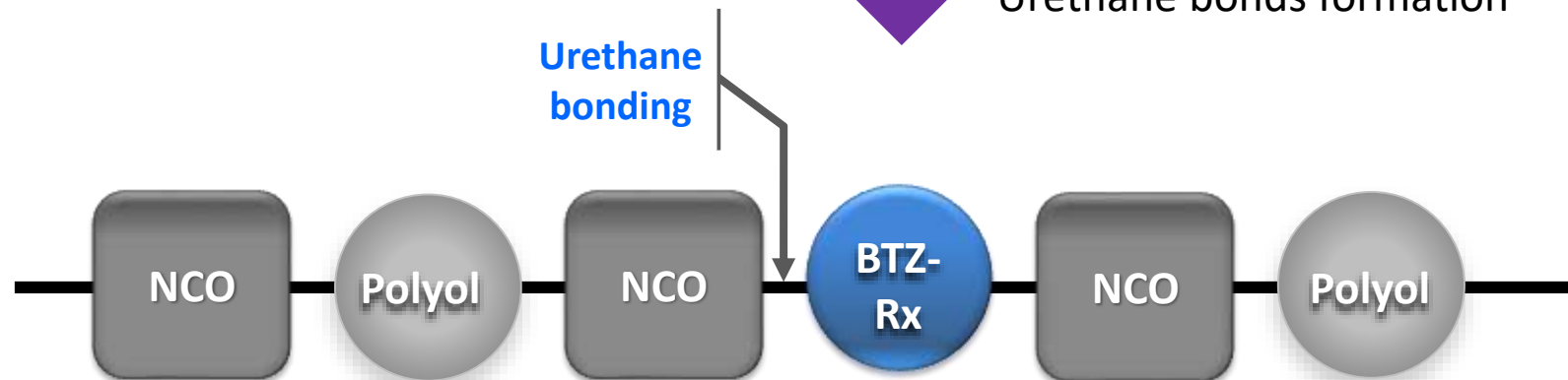
UV Absorbing Pre-polymer

UV Absorbing Resin

UV Absorbing Polyurethane Polymer



Urethane bonds formation



UV Absorbing
Polyurethane Resin/coating

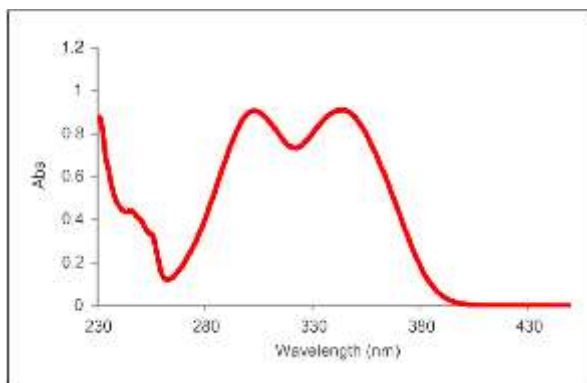
Technical Data of BTZ-Rx

Physical Data

Appearance : Light yellow powder
Odor : Odorless
Assay : 98% min.
Bulk density : 0.308 g/cm³
Hydroxyl Value : 242

Solubility (g in 100 ml solvent @ 25°C)

PM : >10
Methanol : 10
Toluene : 1.5

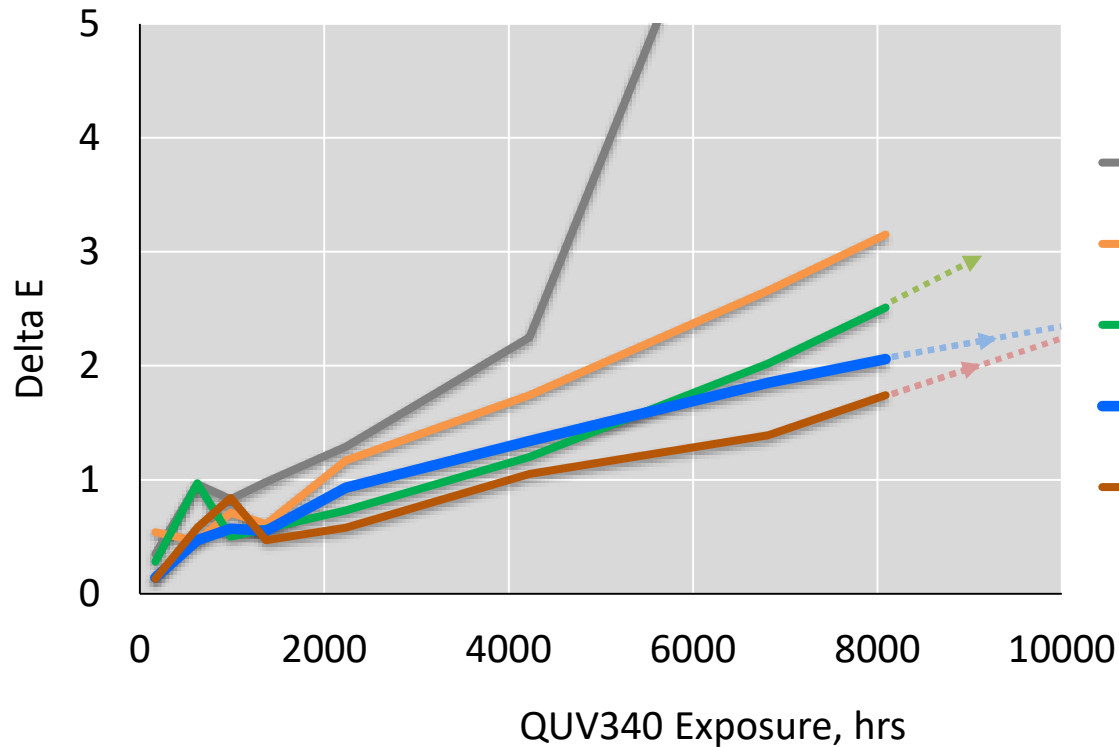



Specification

Appearance : Light yellow powder
Assay : 98% min.
Melting point : 115°C min.
Volatile : 0.5% max.



Long-term Durability of BTZ-Rx



- Blank
- BTZ-30*/ N-R-92*
- BTZ-82WB*/ NO-R-01WB*
- **BTZ-Rx PUD/ NO-R-01WB** 
- TRZ-40WB/ NO-R-01WB

- * BTZ-30, BTZ-82WB= Benzotriazole UVA
- * BTZ-Rx= Reactable benzotriazole UVA
- * TRZ-40WB= Triazine UVA
- * N-R-92= N-R HALS
- * NO-R-01WB= NO-R HALS

- w/b 2K-PUR
- UVA/HALS= 1/1, total 2%wt
- Substrate: Aluminum plate
- Test Condition: ASTM G-154-1

20um Clear coat UVA/HALS
30um Blue base coat



• After 8088hr weathering test of ASTM G-154-1, BTZ-Rx PUD shows a good photo-permanence with consistent yellowing slope.

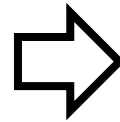
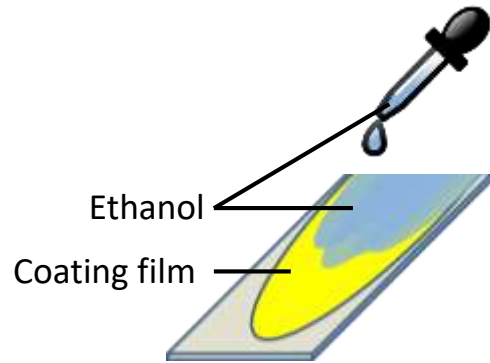
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Study of Reactivity and Solvent Extractions

* Authorized information to Chitec Partners only. Do not forward or cite *

In the Previous Study

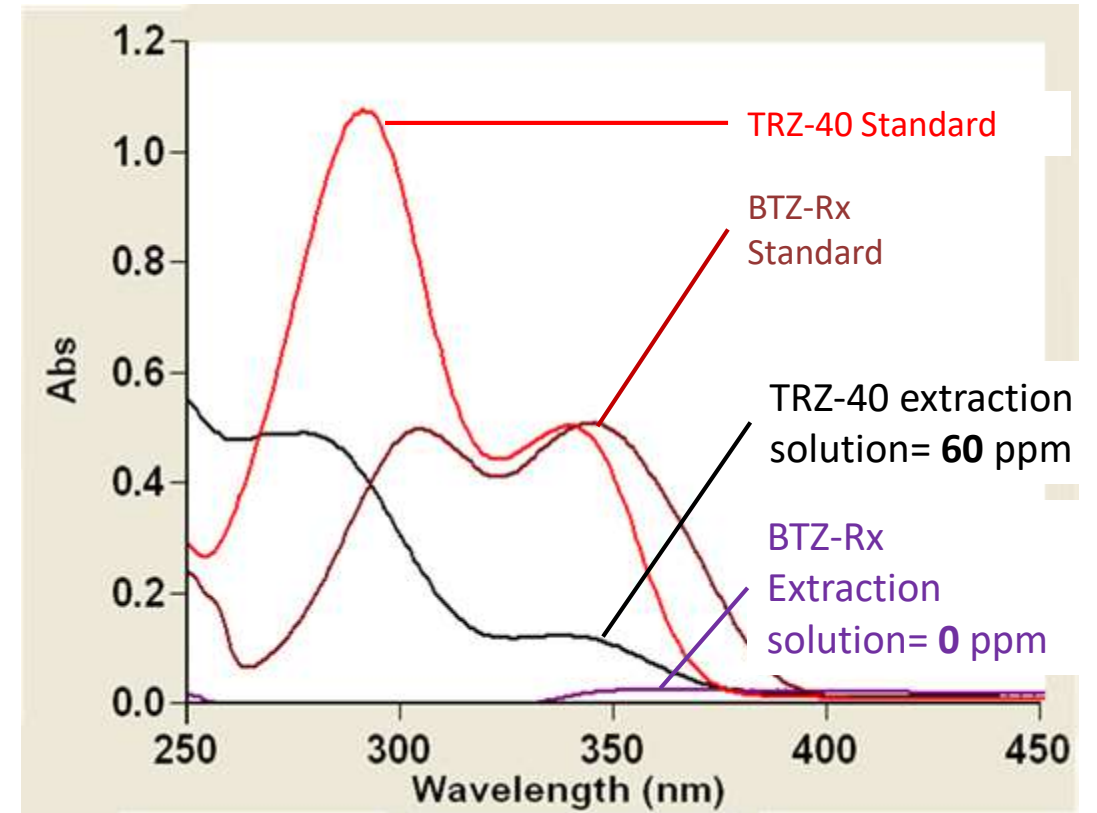
Simulation of 75% Ethanol flush at 2K PU System



Flushed the coating film with 7g 75% ethanol. Collected the extraction solution for UV-VIS .

	TRZ-40	BTZ-Rx	
Acrylate polyol	30	30	NV= 75%
HDI	15.5	15.5	NV=90%
NBAC	8	8	
TRZ-40	0.36		UVA, 1%
BTZ-Rx		0.36	UVA, 1%

Baking Condition: 80 degree C, 30mins
Film thickness: 25um



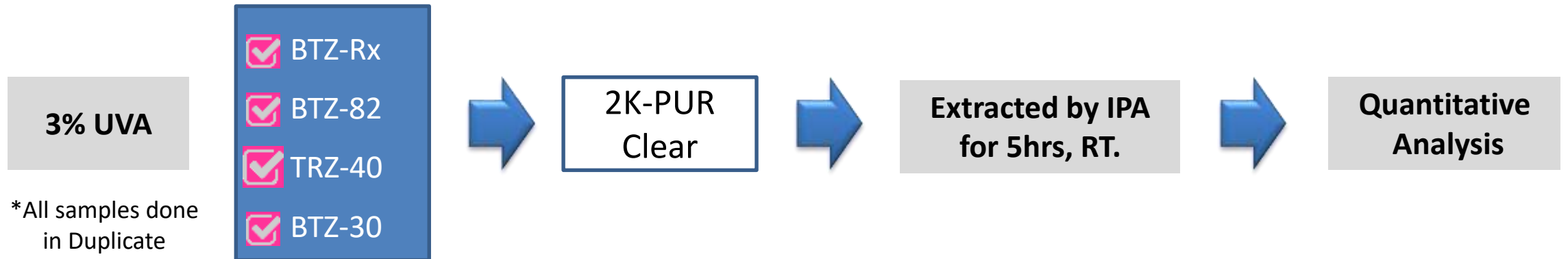
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IPA Extraction Experiment

□ IPA Extraction Protocol*



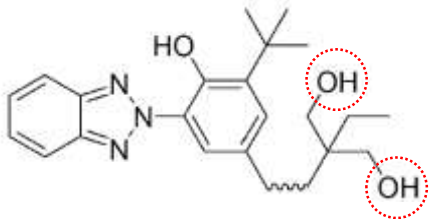
- ◆ Isopropyl alcohol, IPA
- ◆ Common component of degreasers and all-purpose cleaners.



Selections of UV Absorbers

BTZ-Rx

CAS# Proprietary

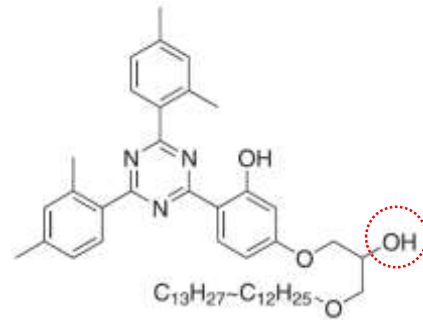


Reactable

Two 1^o -OH

TRZ-40

CAS# 153519-44-9



Reactable

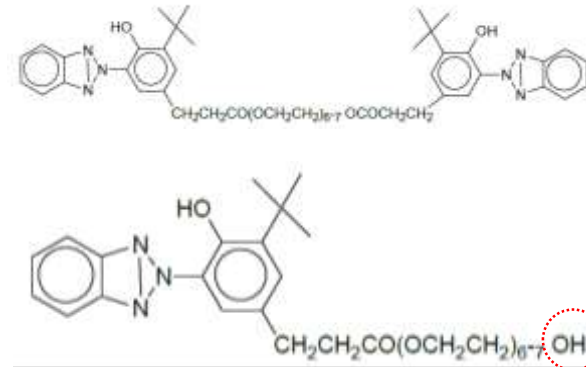
One 2^o -OH

BTZ-30

CAS#

104810-47-1 (37.5%)

104810-48-2 (62.5%)

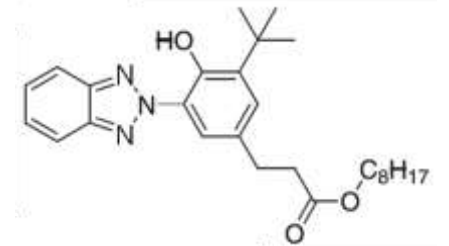


Partially
Reactable

One 1^o -OH

BTZ-82

CAS# 127519-17-9



Additive Type
Not reactable

Coating Formulation

	3% BTZ-Rx	3% TRZ-40	3% BTZ-30	3% BTZ-82
Acrylate polyol	13.1	12.94	12.86	12.58
HDI	21.23	21.43	21.52	21.84
MEK	5	5	5	5
Wetting agent	0.04	0.04	0.04	0.04
BTZ-Rx	0.86			
TRZ-40		0.86		
BTZ-30			0.86	
BTZ-82				0.86
Total	40.22	40.26	40.27	40.33
N.V.	71.13%	71.09%	71.05%	70.94%

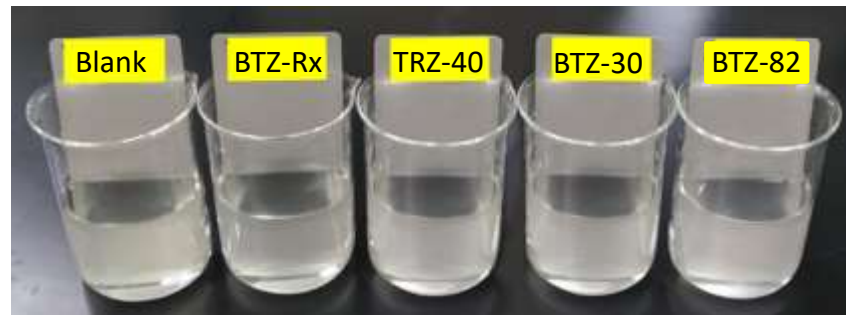
- ◆ NCO/OH= 1.1
- ◆ Hardness: HB-B
- ◆ Film thickness: 55-60um
- ◆ Film Weight: 0.5g

Experiment Details

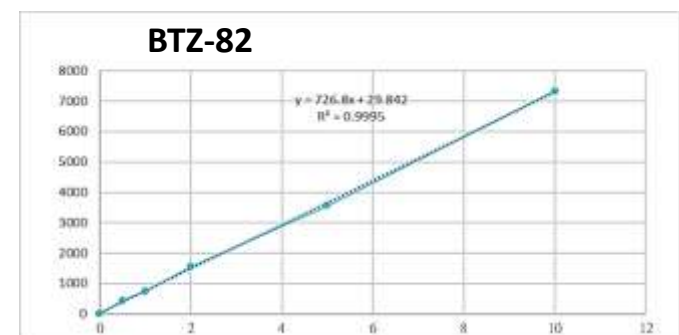
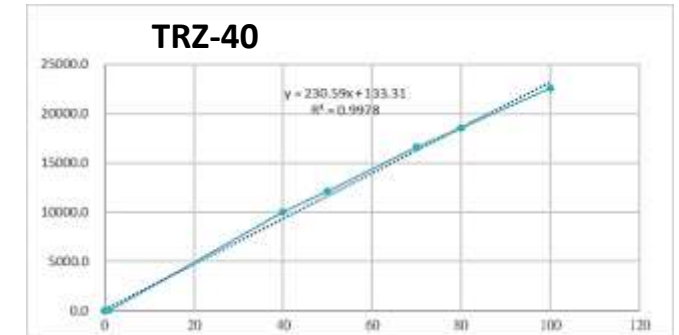
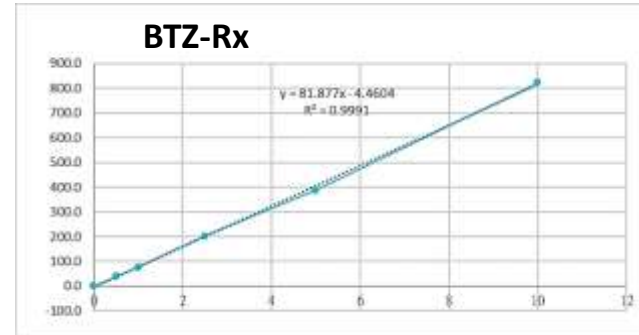
Coating Sheet



Solvent Extraction



HPLC Calibration Curve of UVAs



Curing Conditions vs. Extraction Rates

	1 st extraction rate @ IPA/ 5hrs (% UVA extracted)				
	BTZ-Rx	TRZ-40	BTZ-30	BTZ-82	
80C/ 2hrs, w/o DBTDL	7.9 %	33.5 %			
60C/ 24hrs, w/o DBTDL	0.0 %	0.5 %			
60C/ 30mins, 0.05% DBTDL	11.5 %	24.9 %			
80C/ 30mins, 0.1% DBTDL	0.8 %	4.3 %			
50C/ 2hr, 0.5% DBTDL	0.4 %	1.2 %	3.8 %	17.7 %	Auto-refinish
95C/ 30mins, 0.5% DBTDL	0.0 %	0.0 %	2.9 %	16.7 %	
120C/ 30mins, w/o cat	0.1 %	2.9 %	4 %	13.0 %	OEM Coating

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Skydrol Extraction Experiment

☐ Skydrol* Extraction Protocol

3% UVA

@

2K-PUR

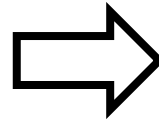
☑ BTZ-Rx

☑ BTZ-82

☑ TRZ-40

☑ BTZ-30

*All done in Duplicate



1st Skydrol
Extraction



1st QUV
7 days



2nd Skydrol
Extraction



2nd QUV
30 days



3rd Skydrol
Extraction



◆ Skydrol



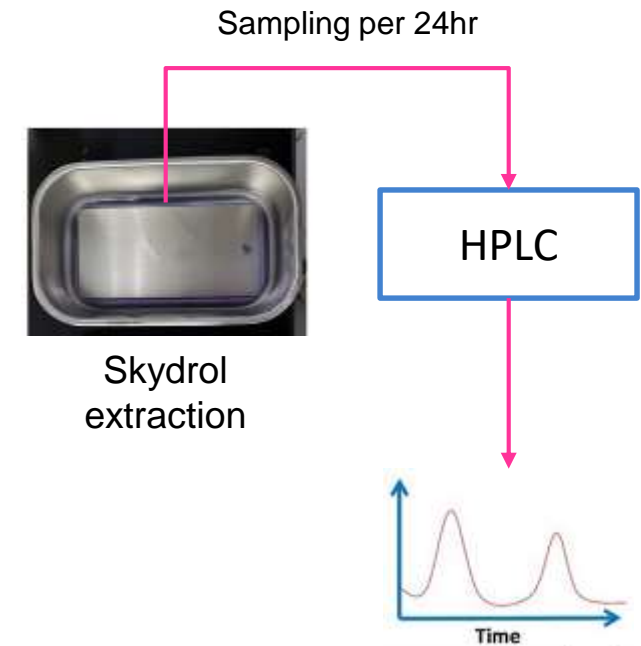
Aviation fire resistant
hydraulic fluid

◆ Chromated Al panels



Results of 1st Skydrol Extraction

120C/ 30mins, w/o cat	Skydrol Extraction			
	BTZ-Rx	TRZ-40	BTZ-30	BTZ-82
Hours				
24	0%	3.62%	0.97%	7.69%
48	0%	6.02%	3.34%	14.02%
72	0%	5.28%	5.03%	23.53%
96	0%	6.41%	5.75%	20.15%
144	0%	5.51%	5.58%	19.72%



1. In Skydrol extraction experiments, BTZ-Rx is proved to has higher reactivity and better solvent extraction resistance than TRZ-40.
2. Compared with additive type BTZ-82, BTZ-Rx shows superior solvent extraction resistance.

UVA Extraction vs. UV Protection

1st Skydrol
Extraction
144 hrs

1st QUV
7 days

2nd Skydrol
Extraction
144 hrs

2nd QUV
30 days

3rd Skydrol
Extraction
144 hrs



UVA	Extraction rate
BTZ-Rx	0%
TRZ-40	5.51%
BTZ-30	5.58%
BTZ-82	19.72%

UVA	ΔYI
BTZ-Rx	-3.3 -1.6
TRZ-40	-0.8 -0.4
BTZ-30	1.8 1.9
BTZ-82	2.6 3.8

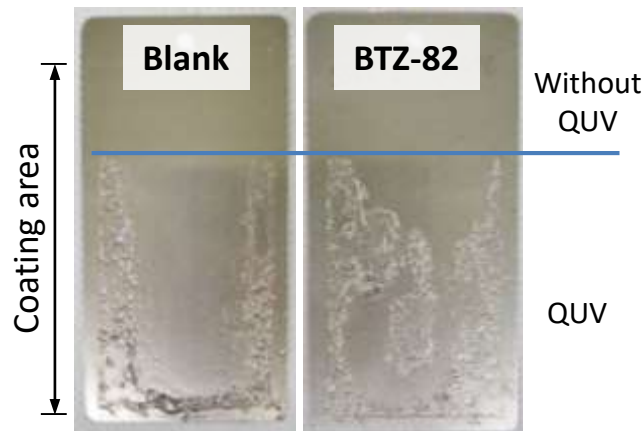
No more extraction

But,

UVA	ΔYI
BTZ-Rx	-2.73 0.94
TRZ-40	3.4 4.41
BTZ-30	6.89 7.57
BTZ-82	

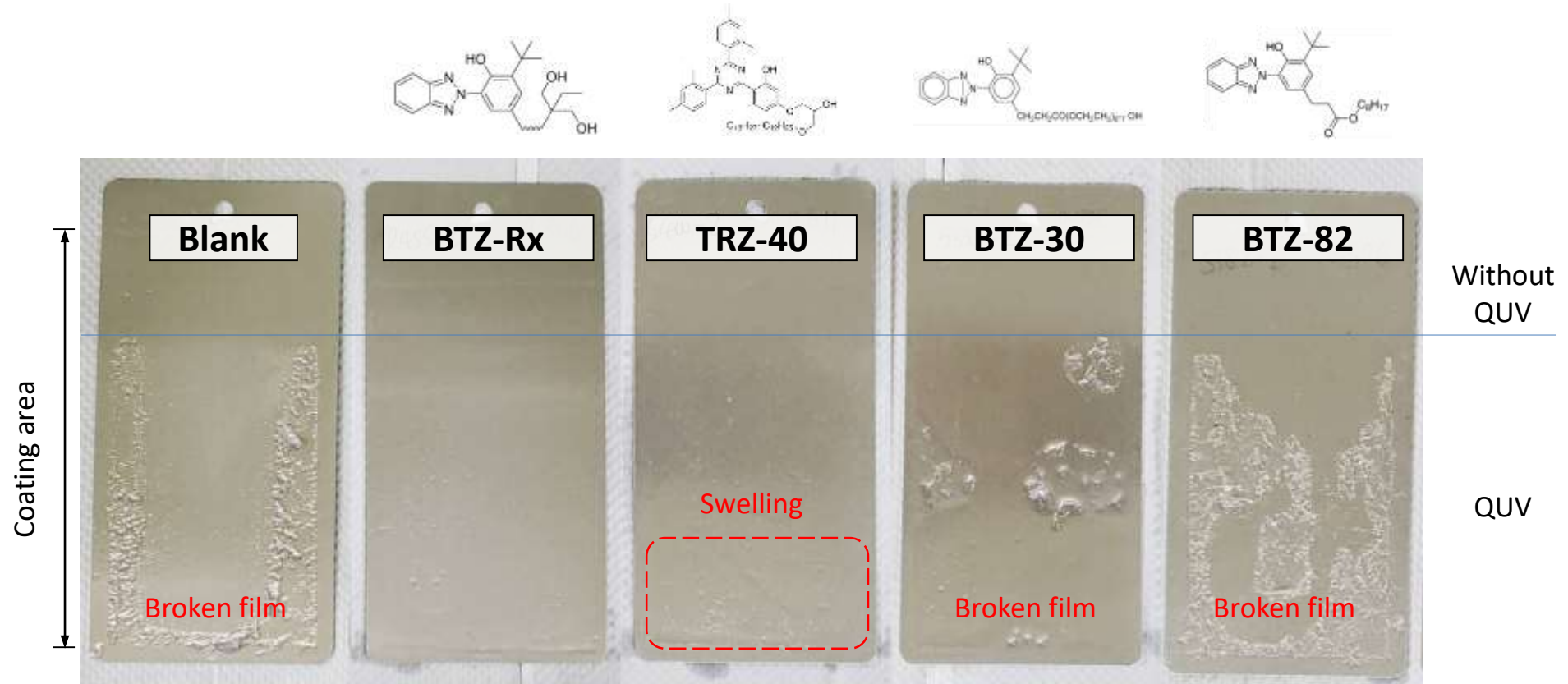
No more extraction

But,



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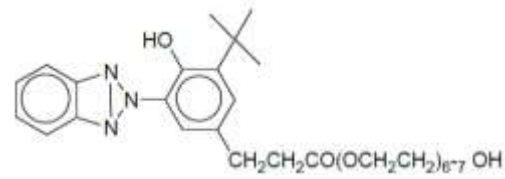
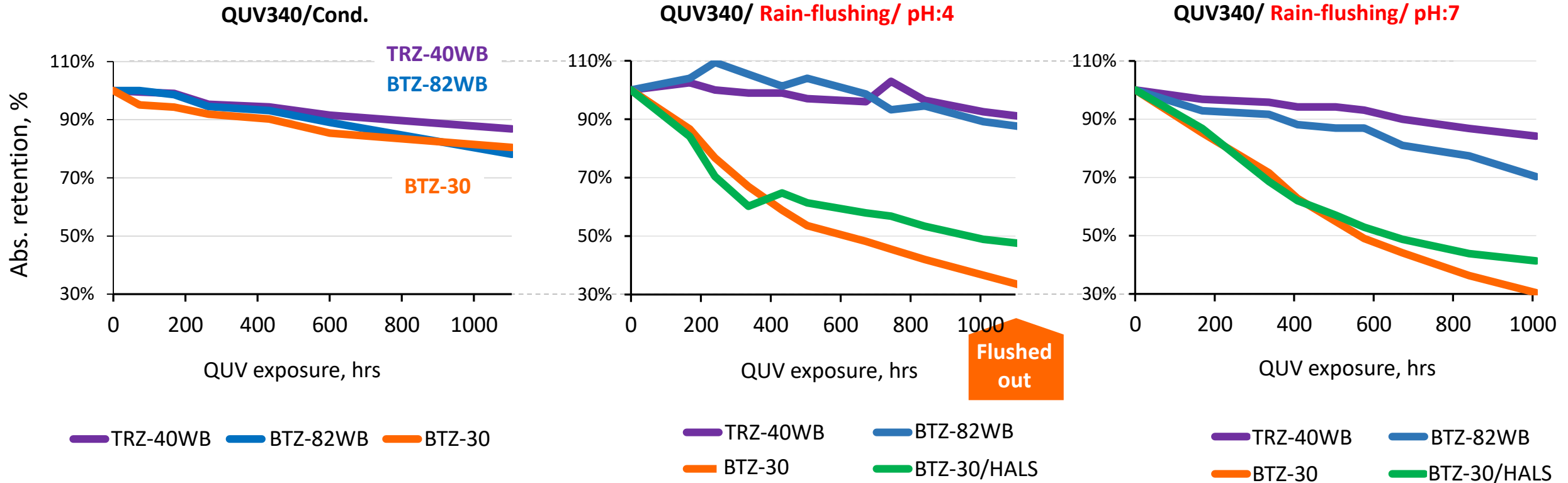
The Final Result of Skydrol Extraction



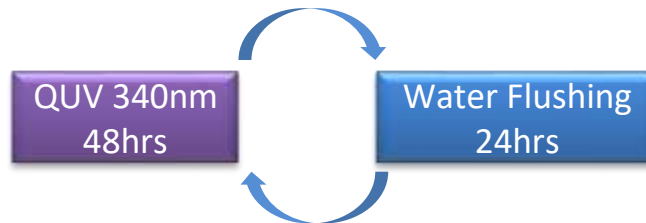
UVA	BTZ-Rx	TRZ-40
ΔYI	0.94	4.41
Gloss (60°)	90	75

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Rain-flushing Test of Miscible UV Stabilizers



BTZ-30

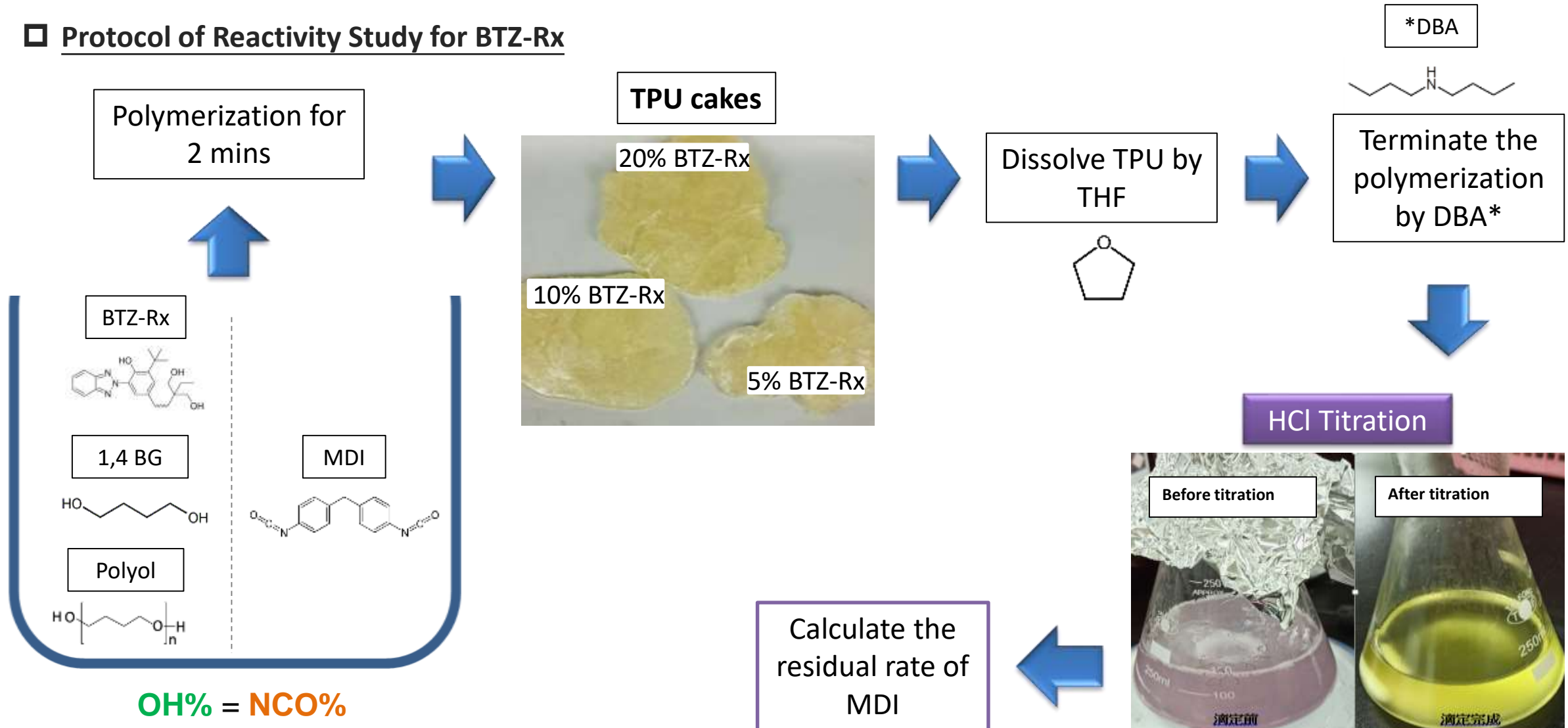


After 15 cycles, nearly 1,100 hours, BTZ-30 lost more than **65%** of its functionality.

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Reactivity Study of BTZ-Rx @ MDI-base TPU

□ Protocol of Reactivity Study for BTZ-Rx



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High Reactivity of BTZ-Rx

HCl Titration

		mw	wt	NCO%wt	2min free NCO%	Residual rate of MDI	MI(200°C 5kg)
OH%	PTMEG1000	1000	100	4.66%	11.24%	1.51%	12.0
	4.99% R-455	455.55	9	0.92%			
	BG	90	11	5.69%			
NCO%	MDI	250	60.3	11.24%			

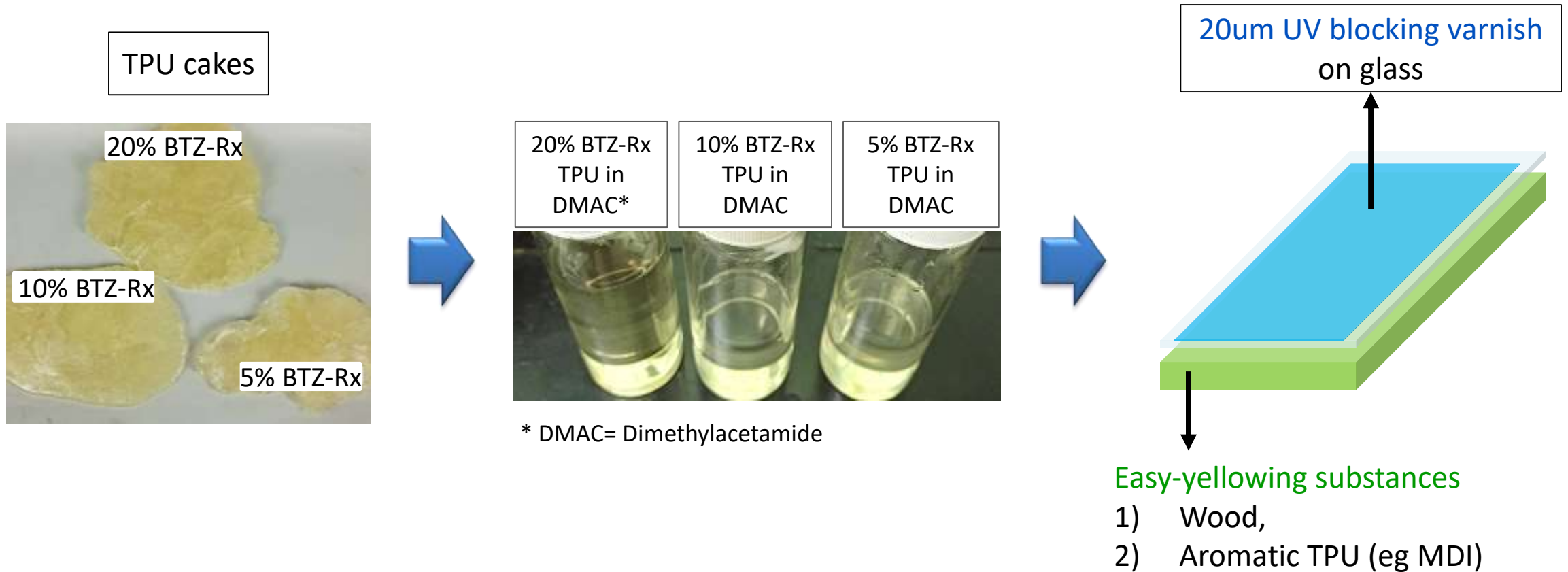
		mw	wt	NCO%	2min free NCO%	Residual rate of MDI	MI(200°C 5kg)
	PTMEG1000	1000	100	4.26%	0.11%	0.97%	12.0
10.00%	R-455	455.55	19.7	1.84%			
	BG	90	11	5.21%			
	MDI	250	66.3	11.31%			

		mw	wt	NCO%	2min free NCO%	Residual rate of MDI	MI(200°C 5kg)
	PTMEG1000	1000	100	3.47%	0.40%	3.51%	12.0
20.0%	R455	455	48.5	3.70%			
	BG	90	11	4.24%			
	MDI	250	82	11.39%			

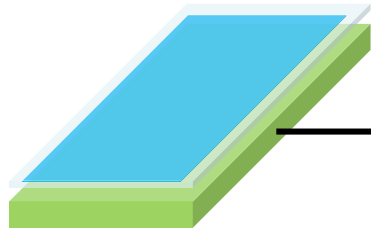
- Under the condition of 20% BTZ-Rx, the system still showed a very low residual rate of MDI, only 3.51%.
- The exp. demonstrates that in the MDI base system, two primary hydroxyl groups of BTZ-Rx both features excellent reactivity, which is significant to chain extension for polymerization.

A highly Efficient UV Blocking Varnish

□ Protocol of Making Highly Efficient UV Blocking Film

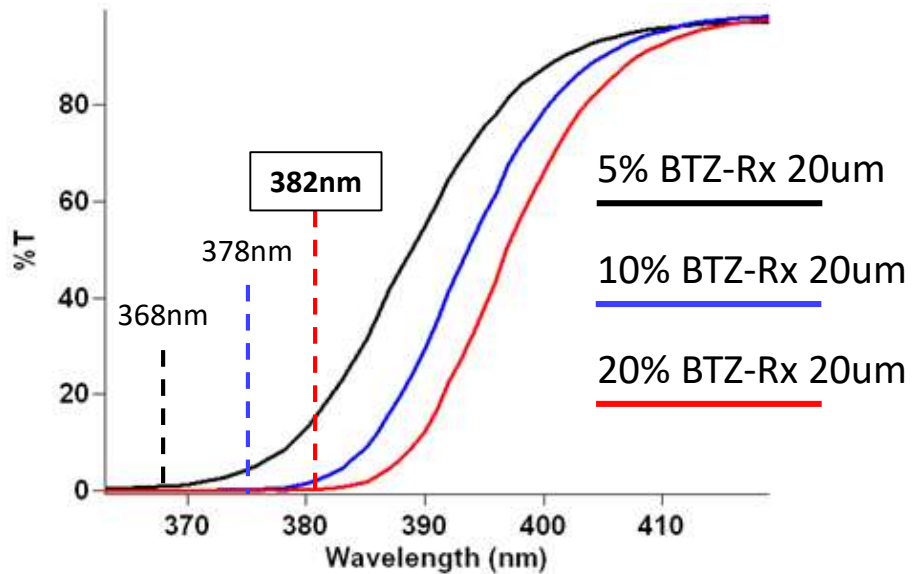


UV Protection of High BTZ-Rx Loading

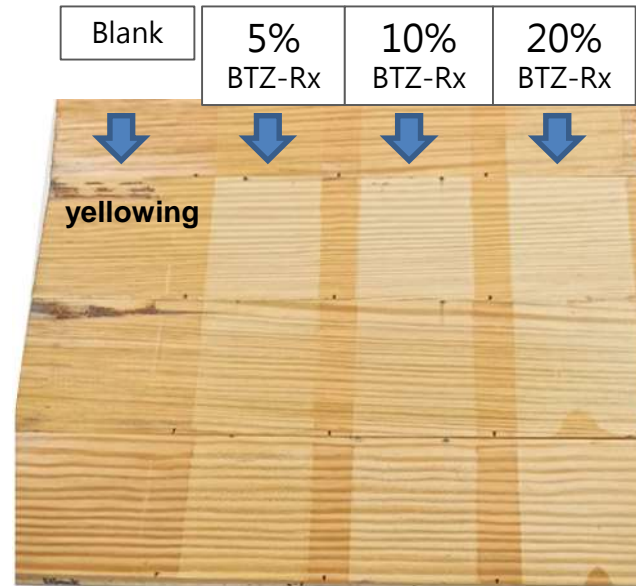


Yellowing test

◆ T% of 20um UV blocking varnish



◆ Southern pine



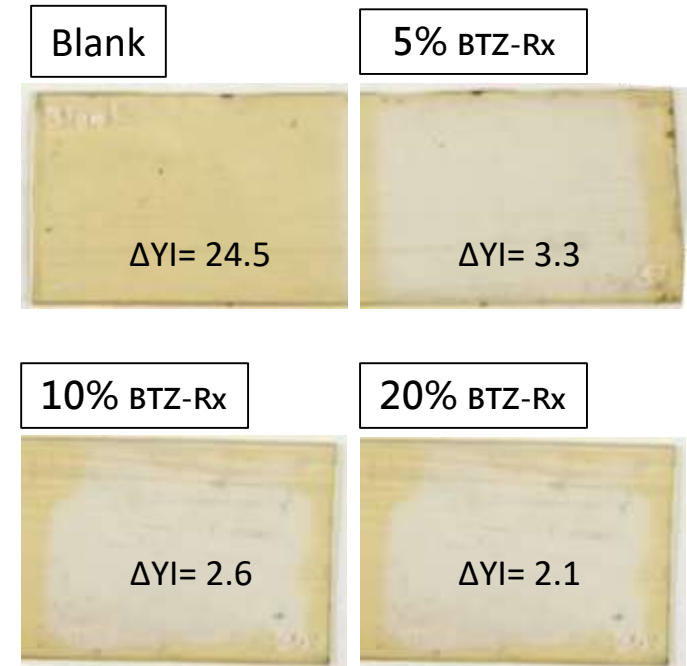
Outdoor 19 weeks

Severe

Yellowing

Slight

◆ Aromatic TPU (MDI)

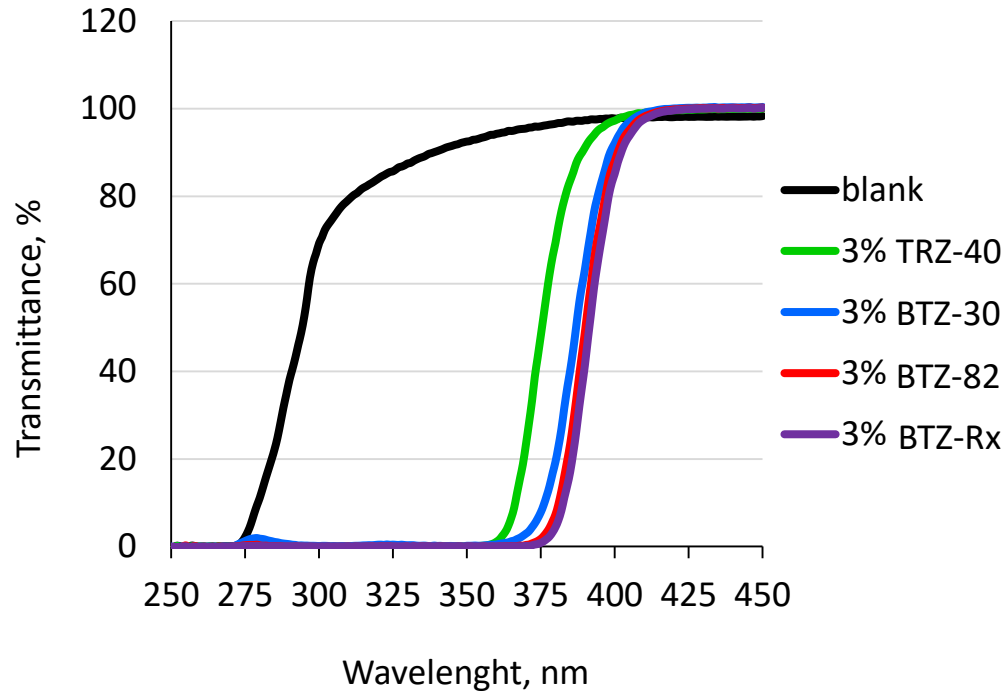


Outdoor 28 weeks

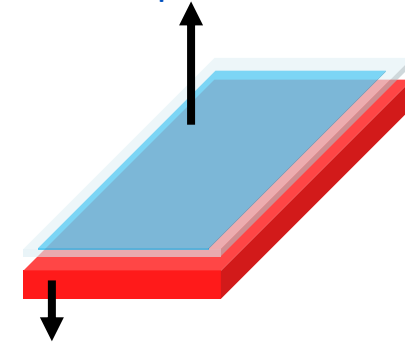
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Follow-up Experiment – Color-shift Test

◆ T% of 20um UV blocking varnish



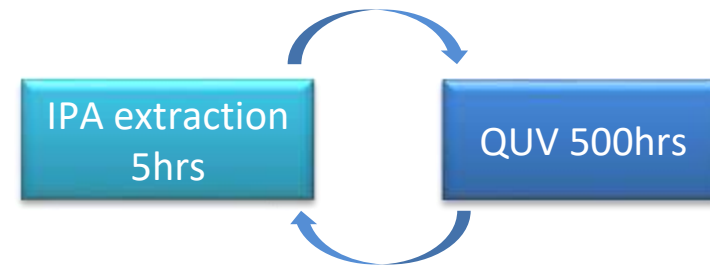
Clear top w/ 3% UVA



Red basecoat, PR# 170



The next research:
UV coverage vs. Color protection



We ain't finished yet...

Application Opportunity

- BTZ-Rx has potential in the following applications:
 - ❑ **Coatings and adhesives:**
 - OEM, Aerospace and Auto-refinish Coating
 - Polyurethane dispersion (PUD)
 - Moisture-cure PU coatings
 - PU sealant and adhesive
 - ❑ **TPU and PU Elastomers:**
 - TPU synthesis
 - TPU fiber/ fabric/ film
 - CPU (PU prepolymer)
 - E-TPU
 - Spandex system (Lycra)
 - Food contact and medical applications

Global Registration Status

- **EU REACH**
<10 mt/a registration
- **TSCA**
Completed
- **CN REACH**
<10 mt/a registration
scatter
- **TW REACH**
<10 mt/a registration
- **Japan REACH**
In preparation of METI SVE (<1mt/a)
- **Korea REACH**
<0.1 mt/a

We pursue difference, not number.

