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AkzoNobel

INVESTIGATION OF DBTL CATALYST ALTERNATIVES IN 2K ACRYLIC CLEARCOAT

SEVDE İLAYDA TOPCUK*
CEMRE KOCAHAKİMOĞLU
HAZAL AKTAŞ

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Organic Coatings

- Resin
- Pigment
- Filler
- Solvent
- Additive

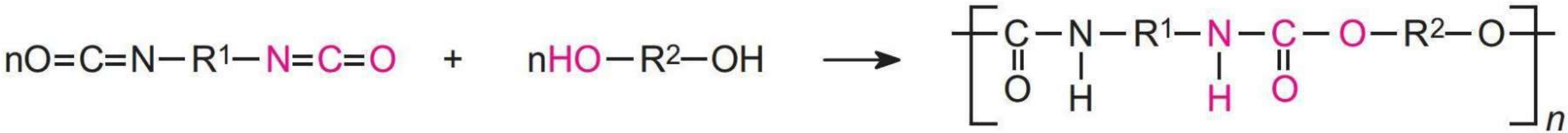
2K System

- The 2K varnish system is a type of coating that consists of two components:

1. Varnish
2. Hardener

- These components are mixed together just before application to create a chemical reaction.

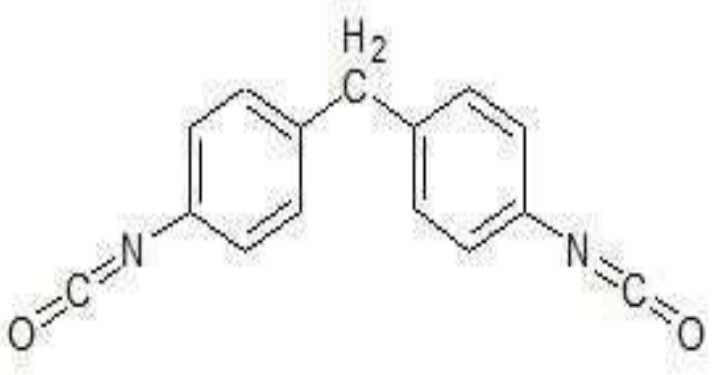
What is polyurethane?



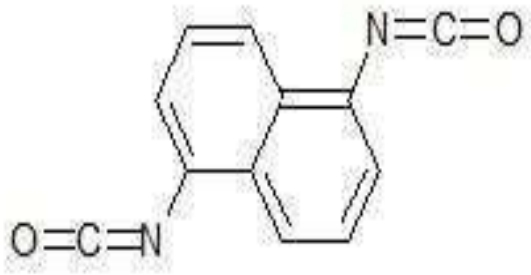
isocyanate **polyol** **Polyurethane**

- Polyurethanes are polymers that can be thermoset and thermoplastic and contain urethane link units in the main polymer chain.
- Automotive, sponge, shoes, cooling, insulation...

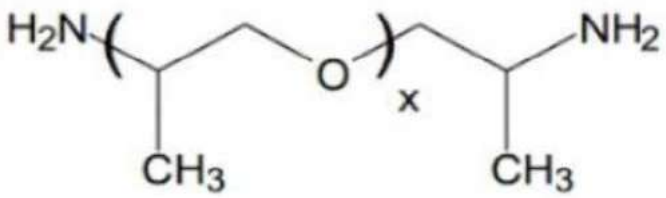
(Poly)isocyanate + (Poly)ol



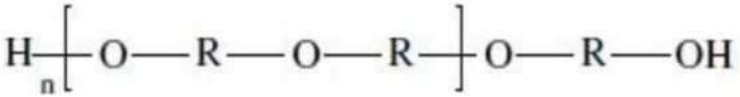
MDI (4,4'-methylene diphenyl diisocyanate)



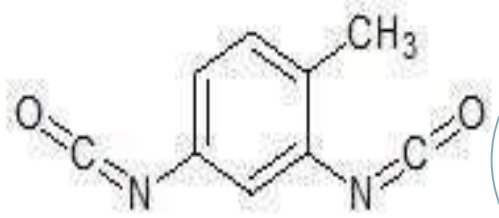
NDI (1,5-naphthylenediisocyanate))



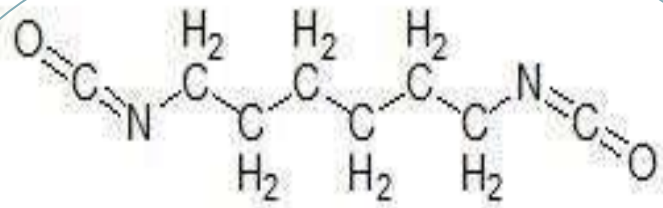
Amine-terminated polyether polyol



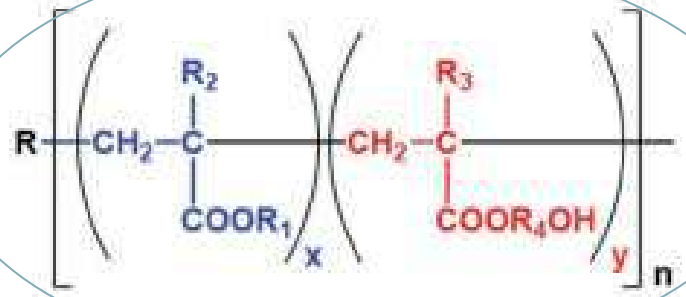
Polyether Polyol



TDI (Toluene diisocyanate)



HDI (Hexamethylene diisocyanate)



Acrylic Polyol

RAW MATERIALS

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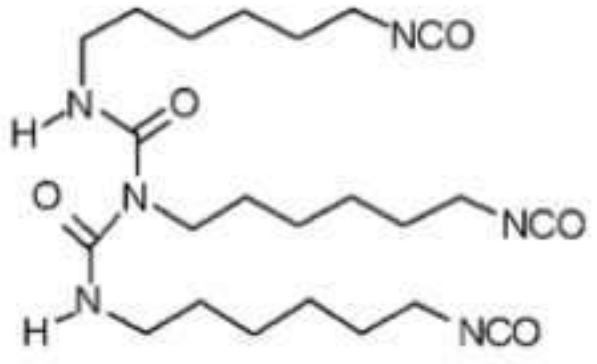
POLYOL PART

- Acrylic Resin
- Surface Additives
- UV additives
- Solvent
- Catalyst

- Acrylic Polymer
- Raw material solid content % 55
- **OH# TDS 118**

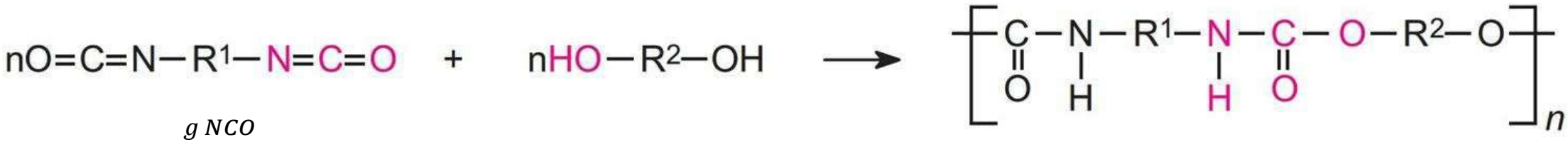
ISOCYANATE-hardener



HDI Biuret

- Raw material solid content % 75
- **NCO TDS 16.5**

NCO/OH ratio



$$\frac{\%NCO}{MW_{NCO}} = \frac{\frac{g\ NCO}{100g}}{42\ g/mol} = \frac{mol}{NCO}/100\ g = 0.19\ \frac{mol}{NCO}/100\ g$$

$$\frac{\%kb*OH\#}{MW_{KOH}*1000} = \frac{\frac{g\ kb}{100g}*OH\#*\frac{mg}{KOH}/g}{56.1\frac{g}{mol}*1000\ mg/g} = \frac{mol}{OH}/100\ g = 0.088\ \frac{mol}{OH}/100\ g$$

- The NCO/OH ratio is defined as the equivalent ratio between materials containing.
- Considering the volume in which it is mixed, the NCO/OH ratio is calculated.

$$\frac{NCO}{OH} = 1.1$$

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THE PURPOSE OF THE PROJECT

1. DBTL-AMINE SYNERGISTIC EFFECT INVESTIGATION
2. EXAMINATION OF ALTERNATIVE CATALYSTS FOR DBTL

RESEARCH AND SELECTION OF PU CATALYST

SELECTION OF SUPPLIERS

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DBTL

- Dibutyltin dilaurate is an organotin compound with the formula $(CH_3(CH_2)_{10}CO_2)_2Sn((CH_2)_3CH_3)_2$. It is a colorless, viscous, and oily liquid used as a catalyst.

- There are numerous applications where DBTL or other organotin catalysts are employed. A few examples include:
  - 2K systems based on aliphatic or aromatic isocyanates
  - 1K systems
  - Blocking of blocked isocyanates
  - Curing of PU powder coatings
  - Formulation of polyurethane dispersions (PUDs)
  - Synthesis of PU prepolymers
  - Among others, the primary application areas include automotive repair, other transportation means, industrial coatings, and wood coatings. [2]

DBTL

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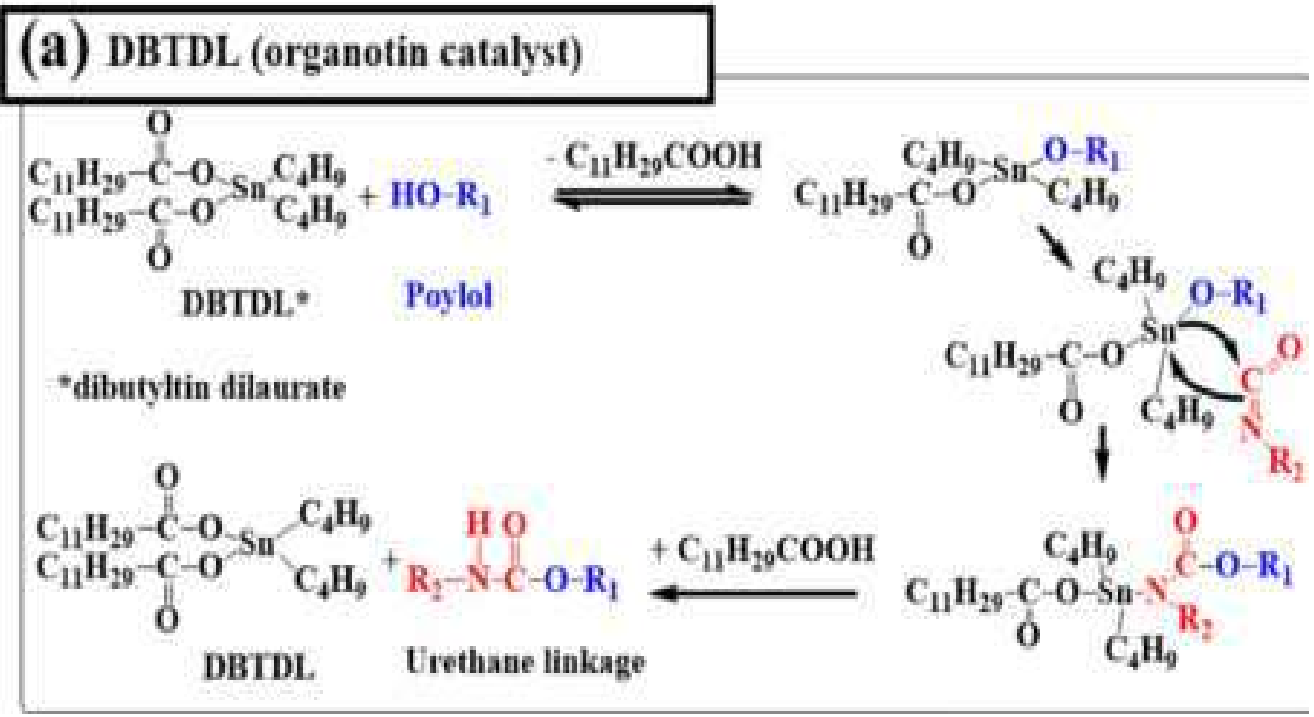
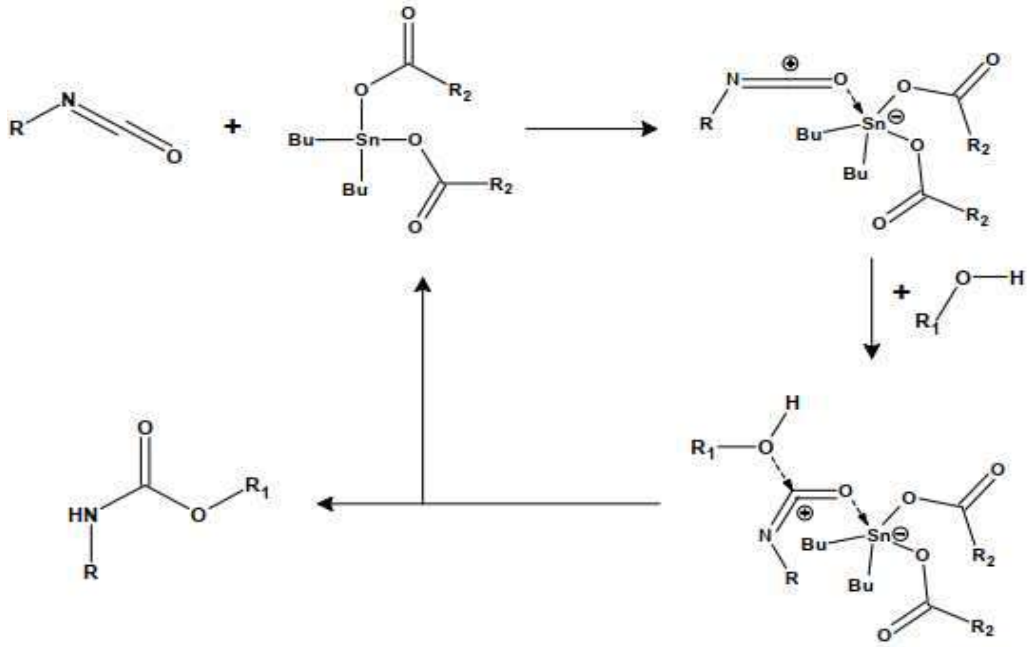
Binding of DBTL to OH

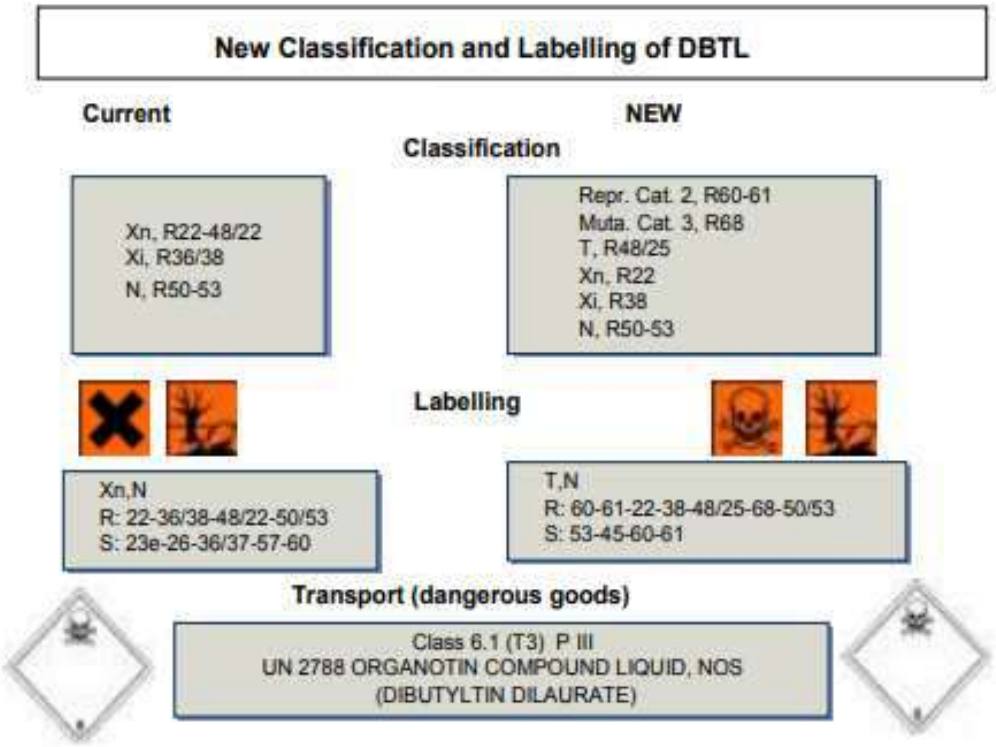


Binding of DBTL to NCO



The excellent catalytic performance of DBTL is based on its Lewis acid properties. The literature indicates that the complexation of the tin center in DBTL with the OH group is a key step in catalyzing the urethane reaction. [2]

THE ENVIRONMENTAL IMPACTS OF DBTL



The European Chemicals Bureau of the European Commision has decided to change the classification of Dibutyltindilaurate and other Dibutyltin based products.

As a result, the labeling of DBTL changes from **"Xn" = harmful** and **"N" = dangerous** for the environment to **"T" = toxic** and **"N.** [2]

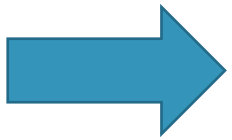
According to Annex XVII of the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) by the European Parliament and Council, **a weight limit of 1%** was imposed in 2010. [3] **(COMMISSION REGULATION (EU) No 276/2010)**

Catalysts	(EC) No 1272/2008	Signal word
DBTL (Dibutyltin Dilaurate)		Danger
		

Catalysts	(EC) No 1272/2008	Signal word
Supplier 1 Bi	Not established.	None.
Supplier 1 Zn + metal		Danger
		
Supplier 1 Zn/Bi		Warning

Catalysts	(EC) No 1272/2008	Signal word
Supplier 1 Zn + amine		Danger
		
		

Catalysts	(EC) No 1272/2008	Signal word
Supplier 2 Bi_2	Not established.	None.
Supplier 2 TEA		Danger
Supplier 2 – Mat 1		Danger
		



	**Corrosion**: Materials causing skin corrosion/burns or eye damage on contact, or that are corrosive to metals.
	**Skull and Crossbones:** Substances, such as poisons and highly concentrated acids, which have an immediate and severe toxic effect (acute toxicity).
	**Exclamation Mark:** An immediate skin, eye or respiratory tract irritant, or narcotic.
	**Health Hazard:** A cancer-causing agent (carcinogen) or substance with respiratory, reproductive or organ toxicity that causes damage over time (a chronic, or long-term, health hazard).
	**Flame:** Flammable materials or substances liable to self ignite when exposed to water or air (pyrophoric), or which emit flammable gas.

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PROJECT PROGRESS

1. MECHANICAL TESTS

2. ANALYTICAL TESTS

IMPACT RESISTANCE AND CONICAL BEND TEST

- 9/19 DKP- 6 Day

SCRATCH RESISTANCE TEST-

- 10x10 DKP- 7 Day

QCT-CORROSION

9/19 DKP -7 DAY (2 Times)

UV-A

- 7.5/15 Aluminum Panel-7 Days

CURING & HARDNESS TEST

On Glass Panels with a 90µ Applicator (2 Times)

ANALYSIS

FTIR- Tinplate Panel - 7 DAYS

ADHESION & STONE CHIP

A4 DKP – 7 DAY

LEVELLING

A4 DKP – 7 DAY

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Panel Preparation

1. SANDING
2. PRIMER
3. SANDING
4. BASE COAT
   - White Yellowing
   - Red Mechanical Tests
   - Black Spreading
5. VARNISH (1 WET COAT + 10 MIN. 2 WET COAT)

At Room Temperature for 7 Days

Prepared Samples

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SAMPLE		CHEMICAL	AMOUNT
1		DBTL	x
2	Supplier 2	DBTL + TEA	x + x
3	Supplier 2	DBTL + TEA	x + 10 x
4	Supplier 2	TEA	10 x
5	Supplier 1	Bi	10 x
6	Supplier 1	Bi	20 x
7	Supplier 1	Zn + metal	10 x
8	Supplier 1	Zn + metal	20 x
9	Supplier 1	Zn/Bi	5 x
10	Supplier 1	Zn/Bi	10 x
11	Supplier 1	Zn/Bi	15 x
12	Supplier 1	Zn + amine	5 x

SAMPLE		CHEMICAL	AMOUNT
13	Supplier 1	Zn + amine	10 x
14	Supplier 1	Zirconium chelate	40 x
15	Supplier 1	Zirconium chelate	30x
16	Supplier 1	Zirconium chelate	10 x
17	Supplier 1	Zirconium chelate	20 x
18	Supplier 2	DBTL+ Mat 1	x + 2 x
19	Supplier 2	DBTL+ Mat 1	x + 5 x
20	Supplier 2	Mat 1	10x
21	Supplier 2	Bi_2	x
22	Supplier 2	Bi_2	5 x
23	Supplier 2	Bi_2	10 x
24		No- Cat	

- The value of X is approximately 0.05 grams.
- TEA = %33 triethylene diamine

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Coating Pot Life

- For the shelf life test, viscosity measurement was conducted using a DIN4 cup.
- The time taken for the viscosity of the mixture to double was recorded.

CATALYSTS	AMOUNT	COATING POT LIFE TEST
DBTL	x	24 HR.
DBTL + TEA	x + x	24 HR.

CATALYSTS	AMOUNT	COATING POT LIFE TEST
DBTL	x	24 HR.
DBTL + TEA	x + x	24 HR.
DBTL + TEA	x + 10 x	24 HR.
TEA	10 x	24 HR.
DBTL+ Mat 1	x + 2 x	24 HR.
DBTL+ Mat 1	x + 5 x	24 HR.
Mat 1	10x	24 HR.

CATALYSTS	AMOUNT	COATING POT LIFE TEST
Bi	10 x	50 dk
Bi	20 x	1 HR. 27 MIN.
Bi_2	2 x	24 HR.
Bi_2	5 x	3 HR. 55 MIN.
Bi_2	10 x	1HR. 48 MIN.

CATALYSTS	AMOUNT	COATING POT LIFE TEST
Zn/Bi	5 x	24 HR.
Zn/Bi	10 x	6 HR. 43 MIN.
Zn/Bi	15 x	7 HR. 18 MIN.

CATALYSTS	AMOUNT	COATING POT LIFE TEST
Zirconium chelate	10 x	48 HR.
Zirconium chelate	20 x	24 HR.
Zirconium chelate	40 x	24 HR.
Zirconium chelate	30x	24 HR.

CATALYSTS	AMOUNT	COATING POT LIFE TEST
Zn + amine	5 x	48 HR.
Zn + amine	10 x	28 HR.
Zn + metal	10 x	24 HR.
Zn + metal	20 x	7 HR. 18 MIN.

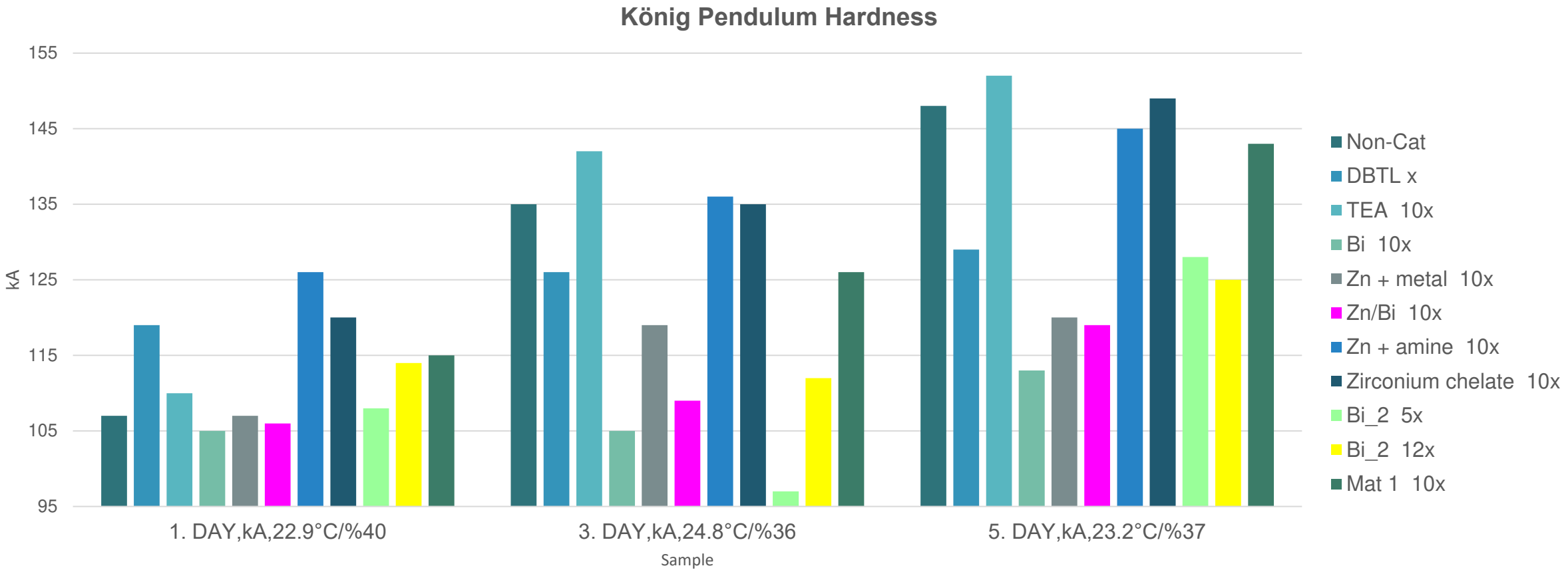
Curing Test

- Touch-free drying (1kg)
- Dust-free drying

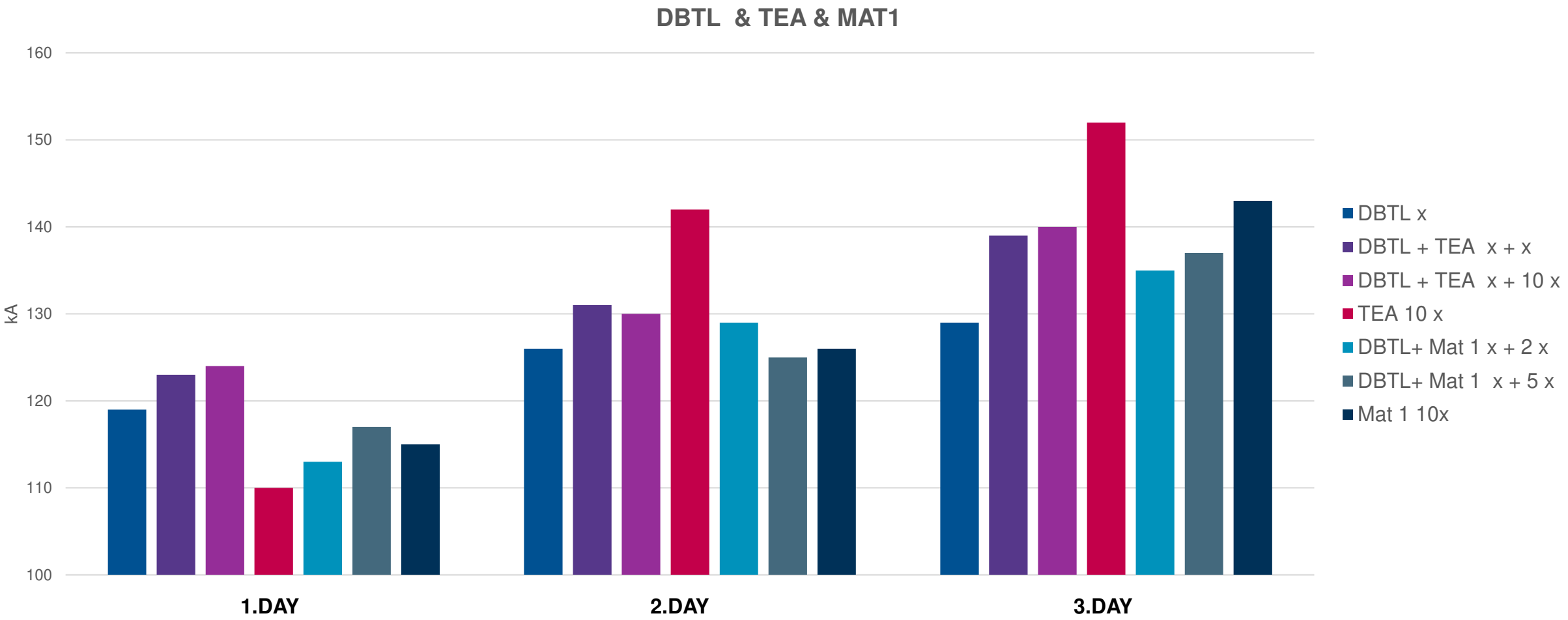
- The touch-free drying of samples **zirconium chelate** and **catalyst-free** took more than 6 hours.
- Catalysts that dry at the same time like DBTL are **Zn/Bi & Zn/Amine & Zn/metal.**
- **Zn/Bi (5X)** catalyst has the closest drying time and shelf life to DBTL.

Hardness Test

- The hardness of the dry paint film is the resistance it exhibits against external physical and atmospheric conditions in terms of the thickness of the paint film.



Pendulum Hardness Test



Impact & Bending Tests

Impact test,

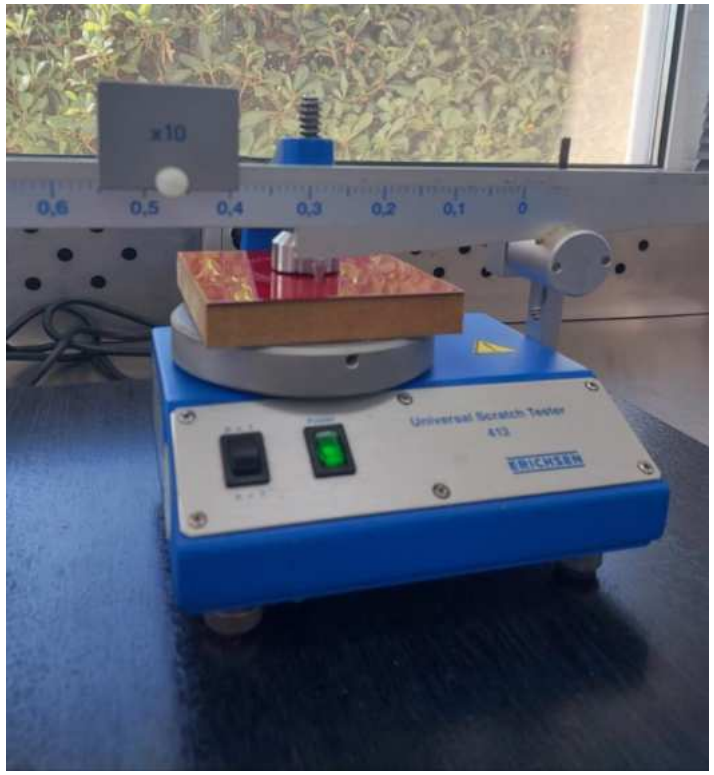
- DBTL >36 kg.cm.
- All catalysts containing Zn yielded less than 36 kg.cm in the impact test.
- The catalyst-free sample resulted in 21 kg.cm.

Conical Bending,

- DBTL + TEA x + 10 x,
- Zn + metal 10 x, 20 x,
- Zirconium chelate 10 x,
- Catalyst-free

Cracking was observed on the samples.

Scratch Resistance Test



Scratch Test results

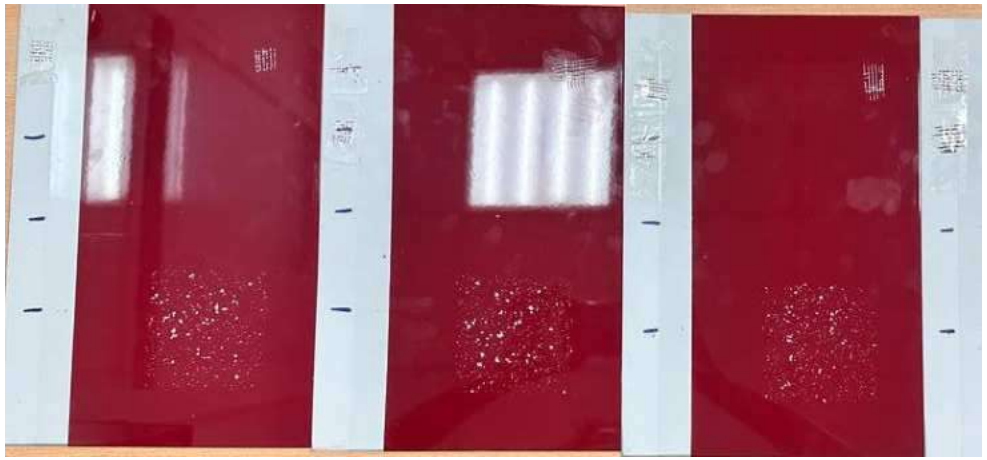
4.5 N **DBTL x**

3.0 N **Zn/Bi 15 x**

3.0 N **Zn + metal 20 x**
6.0 N **DBTL+ Mat 1 x + 5 x**
6.0 N **Mat 1 10x**

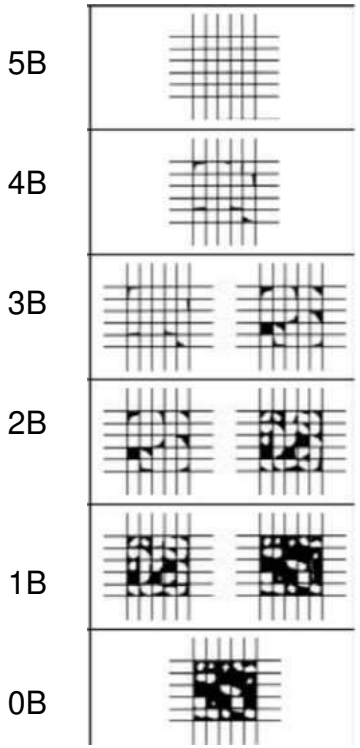
Adhesion

1-2-3 (DBTL &TEA)

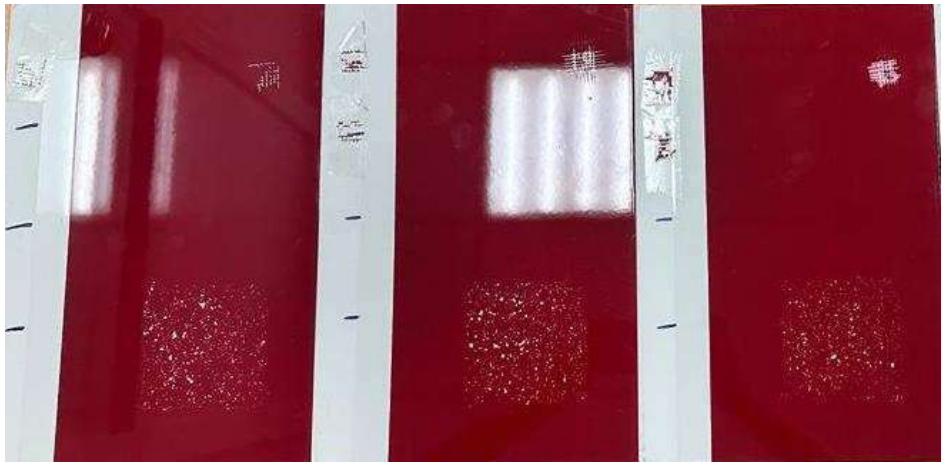


CATALYSTS	AMOUNT	ADHESION
DBTL	x	**BV:5B**
Bi	10 x	**BV:2-3B**
Bi	20 x	**BV:1B**
Zn/Bi	15 x	**BV:3B**
Bi_2	5 x	**BV: 3B**
Bi_2	10 x	**BV: 1B**

Only in these examples different results were obtained from DBTL between Base coat and Varnish.



21-22-23 (Bi_)



No adhesion problem between BV was observed before the stone chip tape.

Those without adhesion problem between BV after the stone chip tape;

DBTL x
DBTL + TEA x + x
DBTL + TEA x + 10 x
TEA 10 x
Bi 10 x
Bi 20 x

Levelling

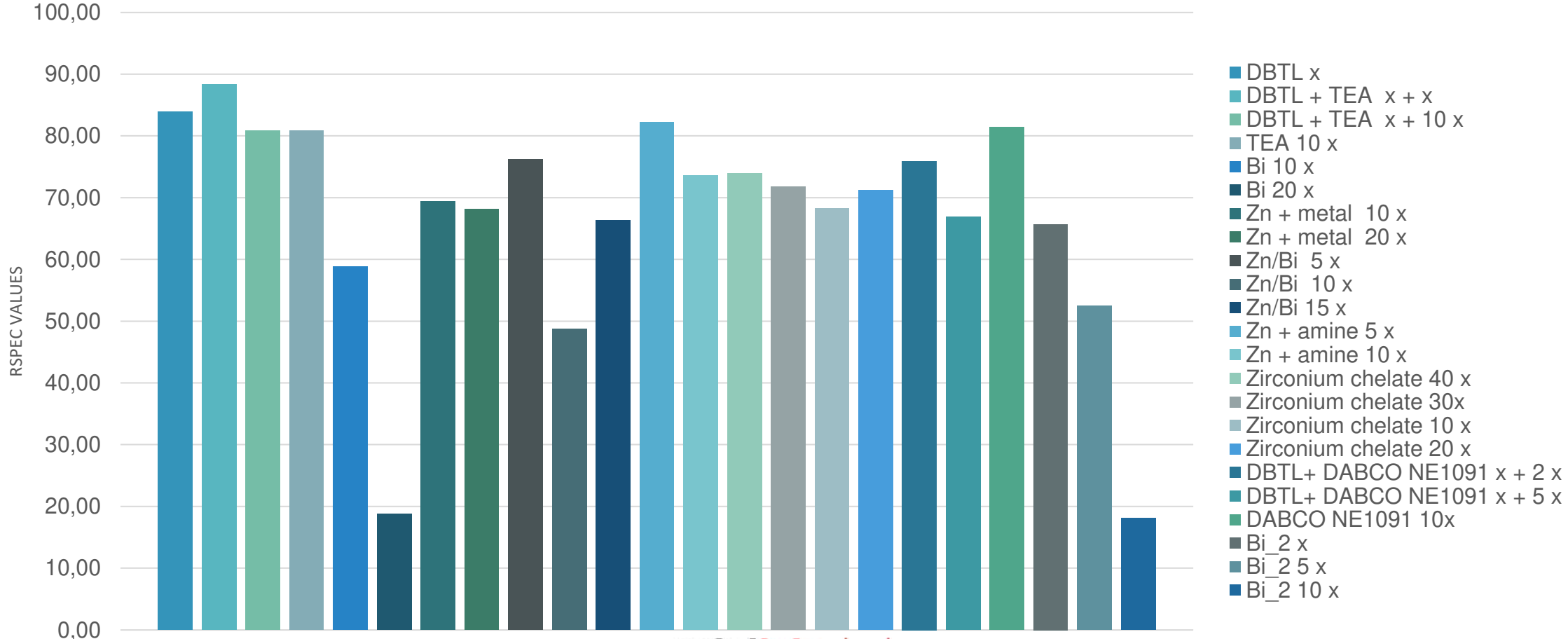
In the DOI results, the values for catalysts containing bismuth were very low.

1- DBTL X
RSPEC 92.9
DOI 98.1

6- Bi 20 X
RSPEC 48.1
DOI 80.6

RSPEC

- Low DOI & RSPEC values; Bi

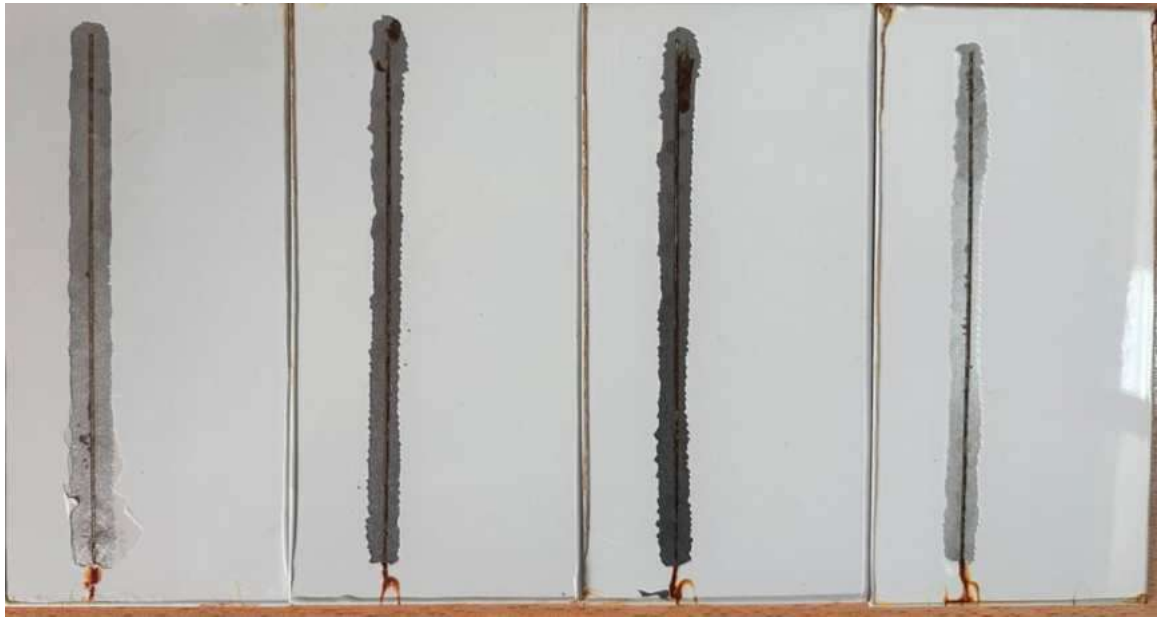


Corrosion Resistance Test

SALT SPRAY TEST 200 HOURS

- No rust or blistering was observed on the panel. Rust and blistering were observed on the stripe.

1-7-8-13



CATALYSTS	AMOUNT	ADHESION LOSS AFTER TAPE REMOVAL
DBTL	x	13-15 mm
Zn + metal	10 x	10 mm
Zn + metal	20 x	10 mm
Zn + amine	10 x	10 mm

CORROSION RESISTANCE TEST- Best Examples

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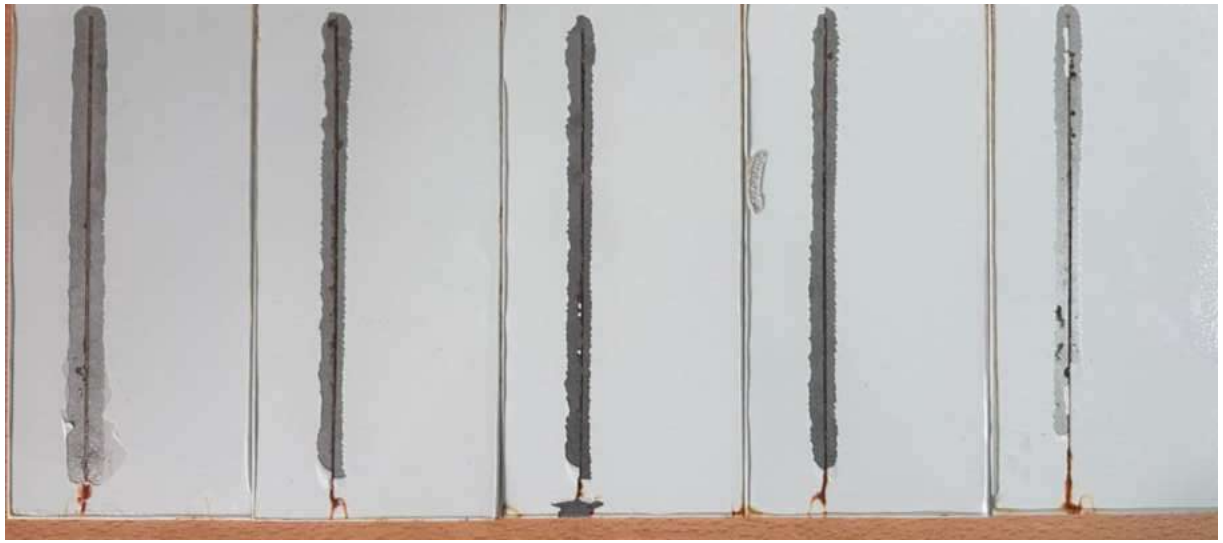
1-9-10-11-23



CATALYSTS	AMOUNT	ADHESION LOSS AFTER TAPE REMOVAL
DBTL	x	**13-15 mm**
Zn/Bi	5 x	**10 mm**
Zn/Bi	10 x	**10 mm**
Zn/Bi	15 x	**10 mm**
Bi_2	10 x	**10 mm**

1-16-17-20

CATALYSTS	AMOUNT	ADHESION LOSS AFTER TAPE REMOVAL
DBTL	x	**13-15 mm**
Zirconium chelate	10 x	**10 mm**
Zirconium chelate	20 x	**10 mm**
Mat1	10x	**10 mm**

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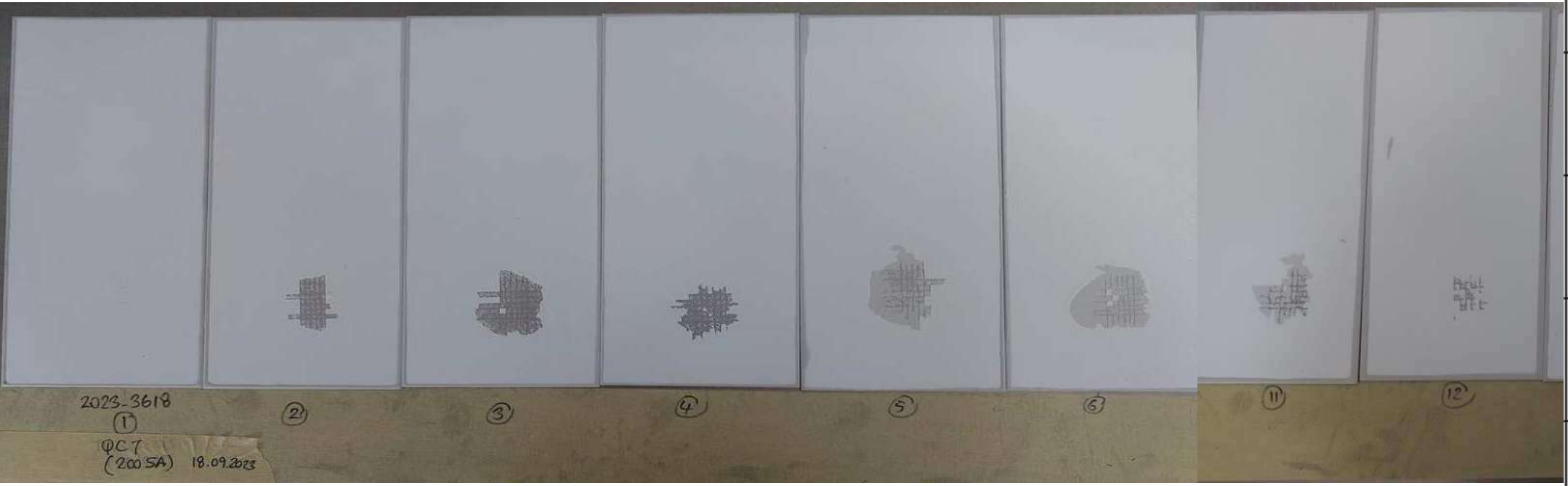
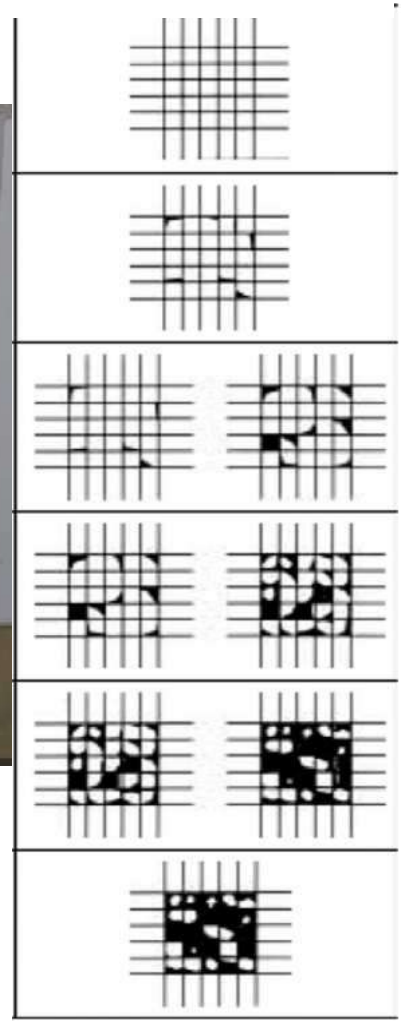
QCT-Humidity Test & Adhesion Test





- The test lasted for 200 hours
- The blister results were consistent with each other.

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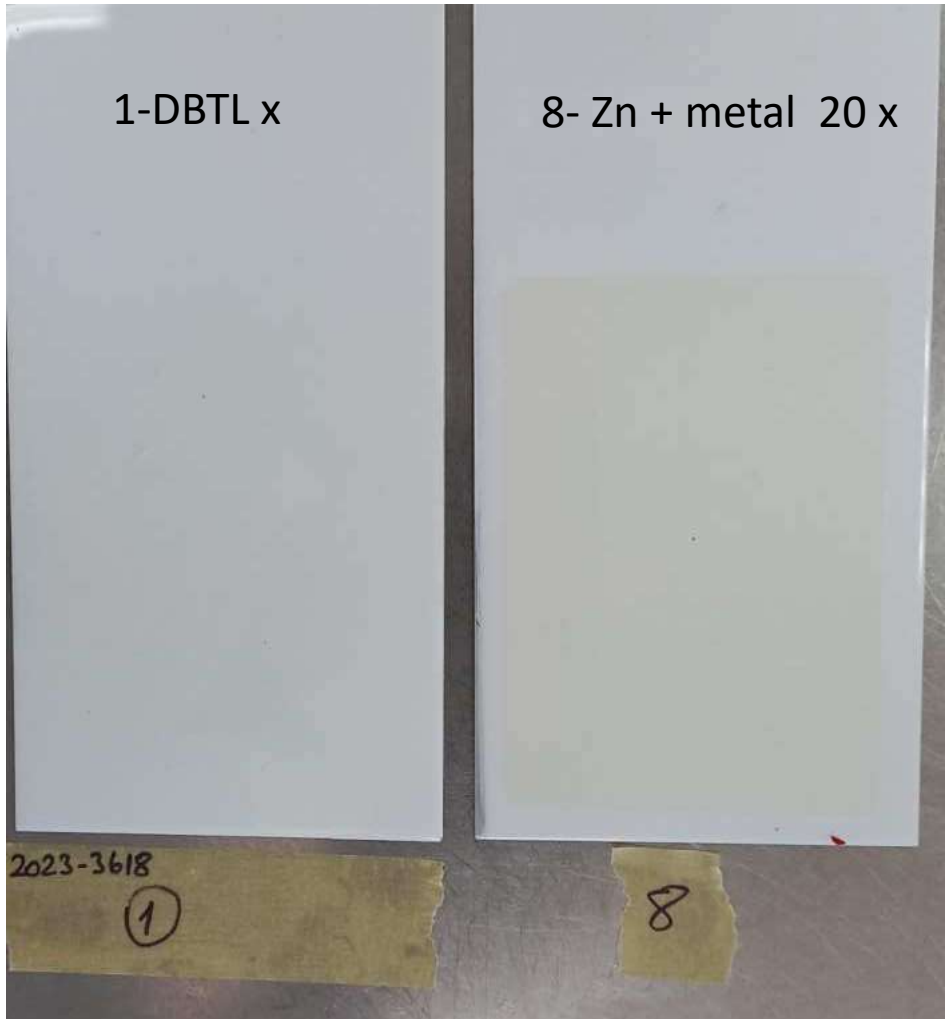
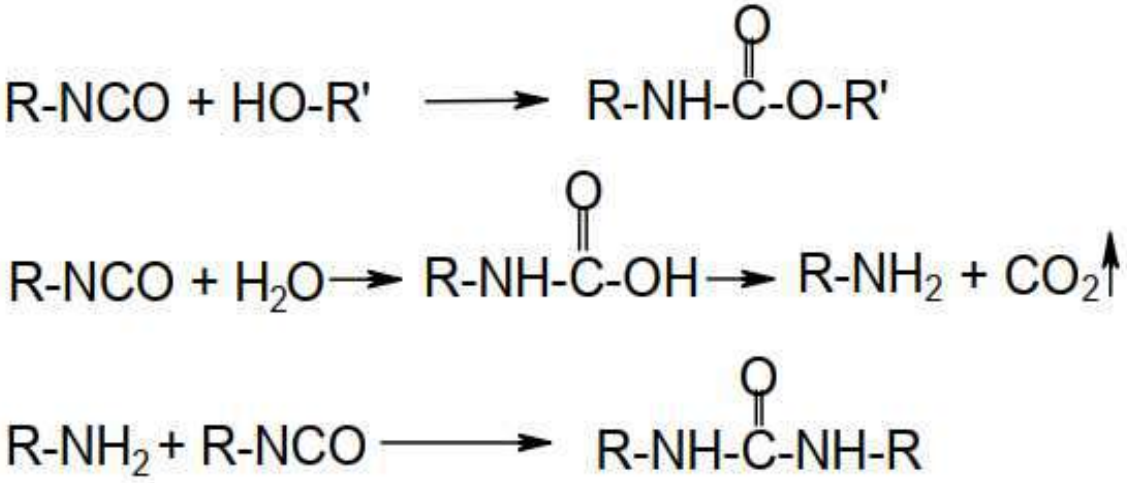
UV-A Test - 200 Hours



It is used to determine the extent of color change in painted surfaces under UV rays.

- According to the 20° gloss values, gloss retention was calculated for both UV pre-exposure and post-exposure. The gloss retention ratios for all samples ranged between 95% and 99% (Std).
- The b-value for all panels containing zinc was found to be very high according to DBTL (Yellowing).
- The DOI values for samples containing bismuth were very low.

Selectivity



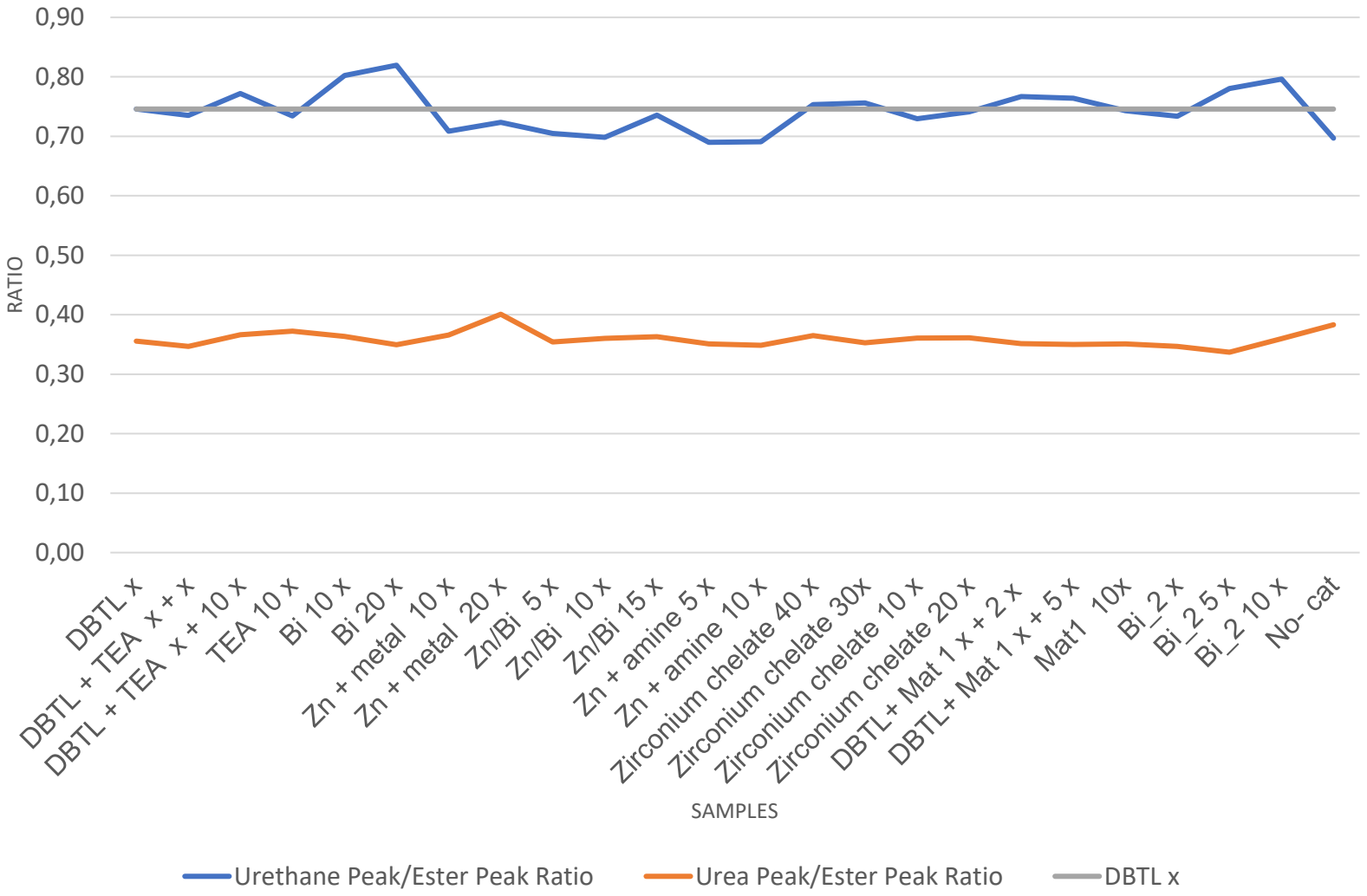
Isocyanate + Polyol ⟶ (Poly)urethane

Carbamic Acid decomposes.

Amine and carbon dioxide are produced.

When amine reacts with isocyanate (NCO), Urea is formed.

FTIR RESULTS



Ester peak (1735 1/cm)

Urethane peak (1690 1/cm)

Urea peak (1630 1/cm)

- Catalysts that provide the urethane bond formation rate closest to DBTL are, **Zn/Bi 15 x, all samples with Zirconium chelate, and DBTL + Mat 1 x + 5 x, Mat 1.**
- Catalysts providing a higher urethane peak ratio than DBTL are, **DBTL + TEA x + 10 x, Bi 10 x, Bi 20 x, DBTL + Mat 1 x + 2 x, Bi_2 5 x, Bi_2 10 x.**

Results - Alternative Catalysts - Containing Bismuth

Catalyst-Amount	COATING POT LIFE TEST	HARDNESS	DRYING	CONICAL BEND TEST	IMPACT	SCRATCH RESISTANCE TEST	ADHESION	DOI	UV-A	CORROSION
DBTL x										
Bi 10 x										
Bi 20 x										
Bi_2 x										
Bi_2 5 x										
Bi_2 10 x										

bad
average
good

Results - Alternative Catalysts- Containing Zinc

Catalyst-Amount	COATING POT LIFE TEST	HARDNESS	DRYING	CONICAL BEND TEST	IMPACT	SCRATCH RESISTANCE TEST	ADHESION	DOI	UV-A	CORROSION
DBTL x										
Zn + metal - 10 x										
Zn + metal - 20 x										
Zn/Bi - 5x										
Zn/Bi -10x										
Zn/Bi -15x										
Zn + amine -5x										
Zn + amine -10x										

bad
average
good

Results - Alternative Catalysts- Zirconium Chelate

Catalyst-Amount	COATING POT LIFE TEST	HARDNESS	DRYING	CONICAL BEND TEST	IMPACT	SCRATCH RESISTANCE TEST	ADHESION	DOI	UV-A	CORROSION
No- cat										
DBTL x										
Zirconium chelate 10 x										
Zirconium chelate 20 x										
Zirconium chelate 30x										
Zirconium chelate 40 x										

bad

average

good

Results - DBTL- Amine & Mat1

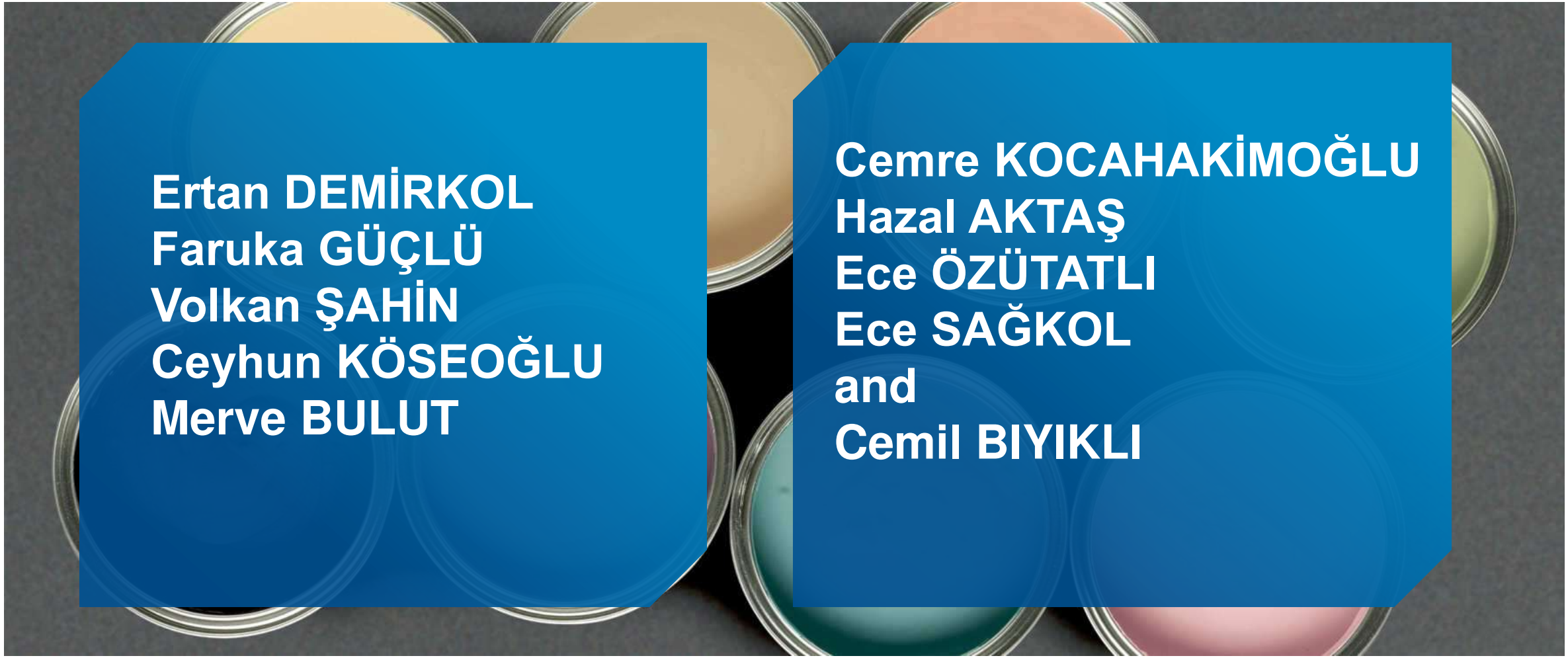
Catalyst-Amount	COATING POT LIFE TEST	HARDNESS	DRYING	CONICAL BEND TEST	IMPACT	SCRATCH RESISTANCE TEST	ADHESION	DOI	UV-A	CORROSION
No- cat	bad	average	bad	bad	bad	good				
DBTL x	good	good	good	good	good	good	good	good	good	average
DBTL + TEA x + x	good	average	average	good	good	good	good	good	good	good
DBTL + TEA x + 10 x	good	average	good	bad	good	good	good	good	good	average
TEA 10 x	good	average	good	good	bad	good	good	good	good	average
DBTL+ Mat1 x + 2 x	good	good	good	good	good	average	good	good	good	average
DBTL+ Mat1 x + 5 x	good	average	good	good	good	average	good	good	good	average
Mat1 10x	good	average	average	good	good	average	good	good	good	average

bad
average
good

The Future of the Project

- The addition of Supplier 1- Zirconium chelate and Supplier 2-TEA to NCO
- The impact of DBTL with different solvents
- Examination of curing at different temperatures
- The experiments combining amines and metal-containing catalysts

THANK YOU!


Ertan DEMİRKOL
Faruka GÜÇLÜ
Volkan ŞAHİN
Ceyhun KÖSEOĞLU
Merve BULUT
Cemre KOCAHAKİMOĞLU
Hazal AKTAŞ
Ece ÖZÜTATLI
Ece SAĞKOL
and
Cemil BIYIKLI

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THANK YOU!

BOSAD BOYA SANAYİCİLERİ DERNEĞİ THE ASSOCIATION OF PAINT INDUSTRY 2003-2023 20

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