



# Askofen R 9600 and can coatings - A sensitive cross-linker with reduced free formaldehyde

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ASK Chemicals GmbH



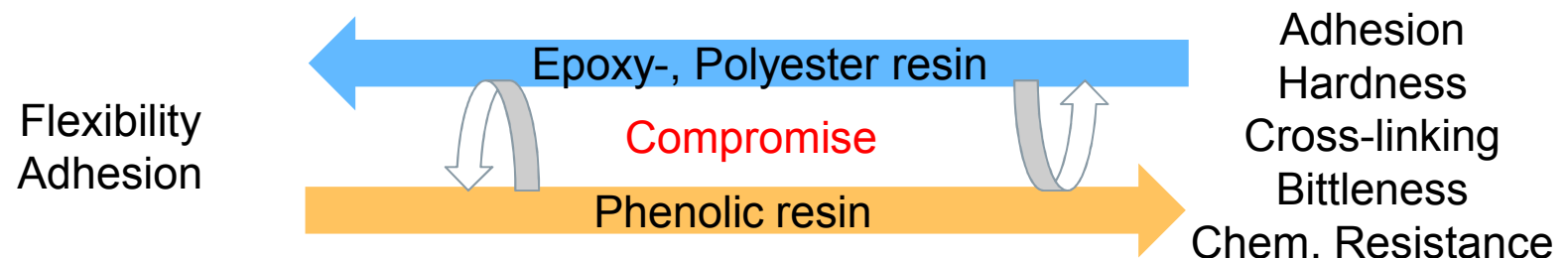
# Content

- ✓ Introduction
- ✓ Motivation
- ✓ Properties
- ✓ Phenolic resins and Formaldehyde
- ✓ Results
- ✓ Summary and Outlook

# Can Coatings – Components and Functionality

Can coatings generally consist of...

- ✓ Epoxy- or Polyester resins (Acryl, Vinyl)
- ✓ Cross-linker
- ✓ Solvent
- ✓ Catalyst
- ✓ Additives



Phenolic resins - Task:

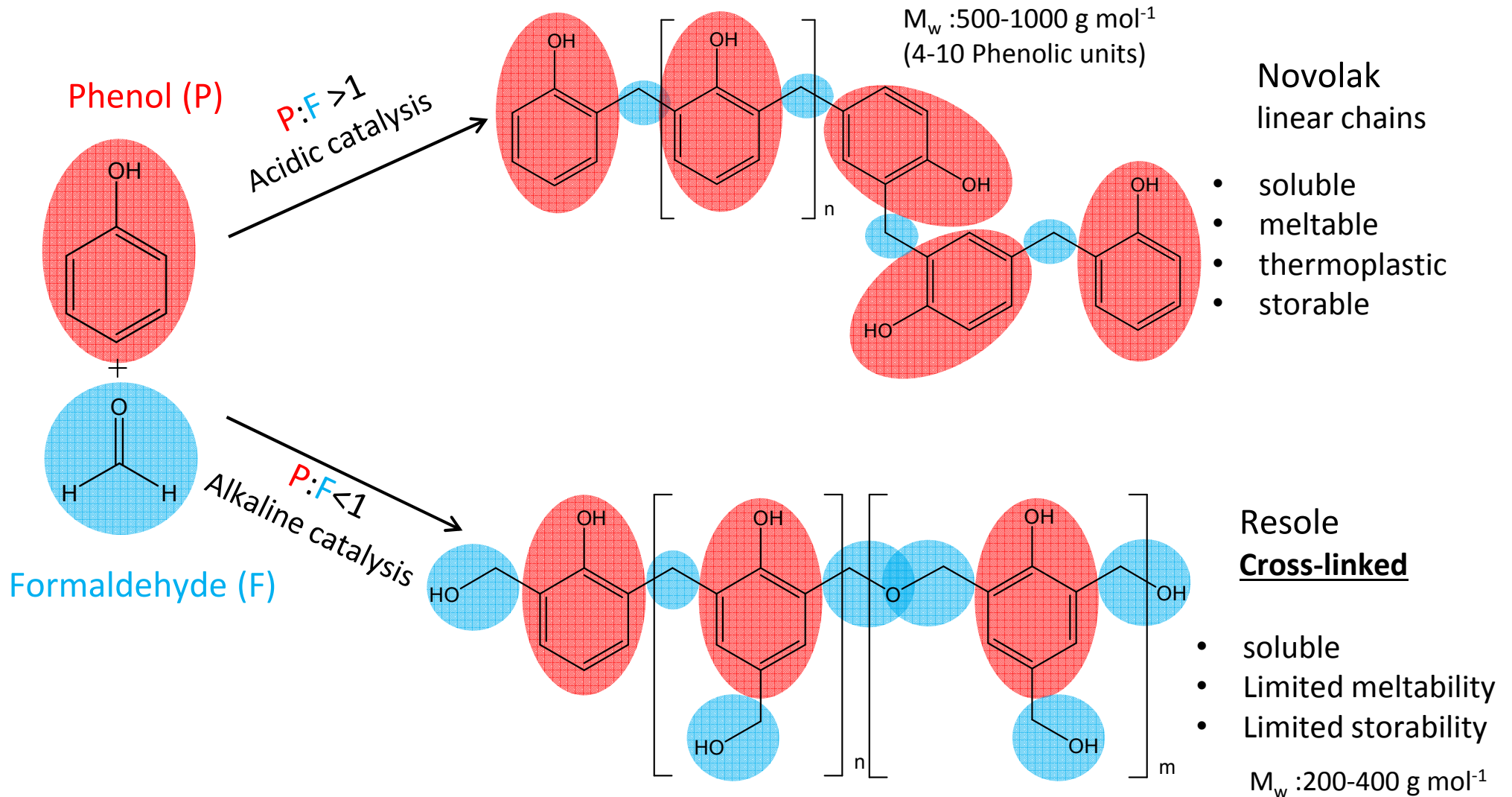
- ✓ Chemical- and Corrosion-resistance
- ✓ Adhesion
- ✓ Hardness



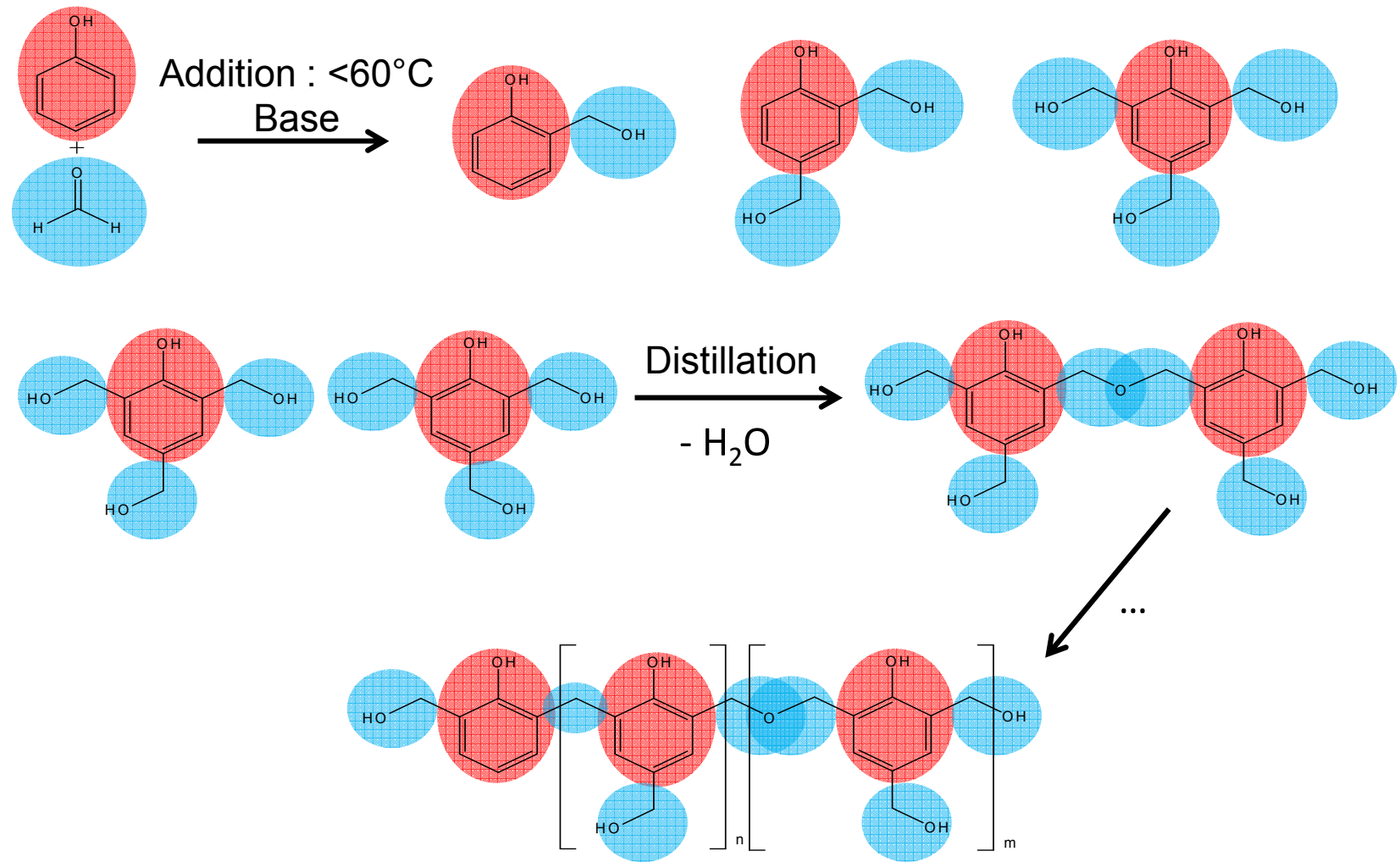
## Requirements of Can Coatings are...

- Chemical resistance against acidic/alkaline food
- Good Sterilization resistance
- Outstanding adhesion to the substrate
- Stability: No migration/contamination of monomers or fragments into the food
- Good reactivity
- Outstanding flexibility

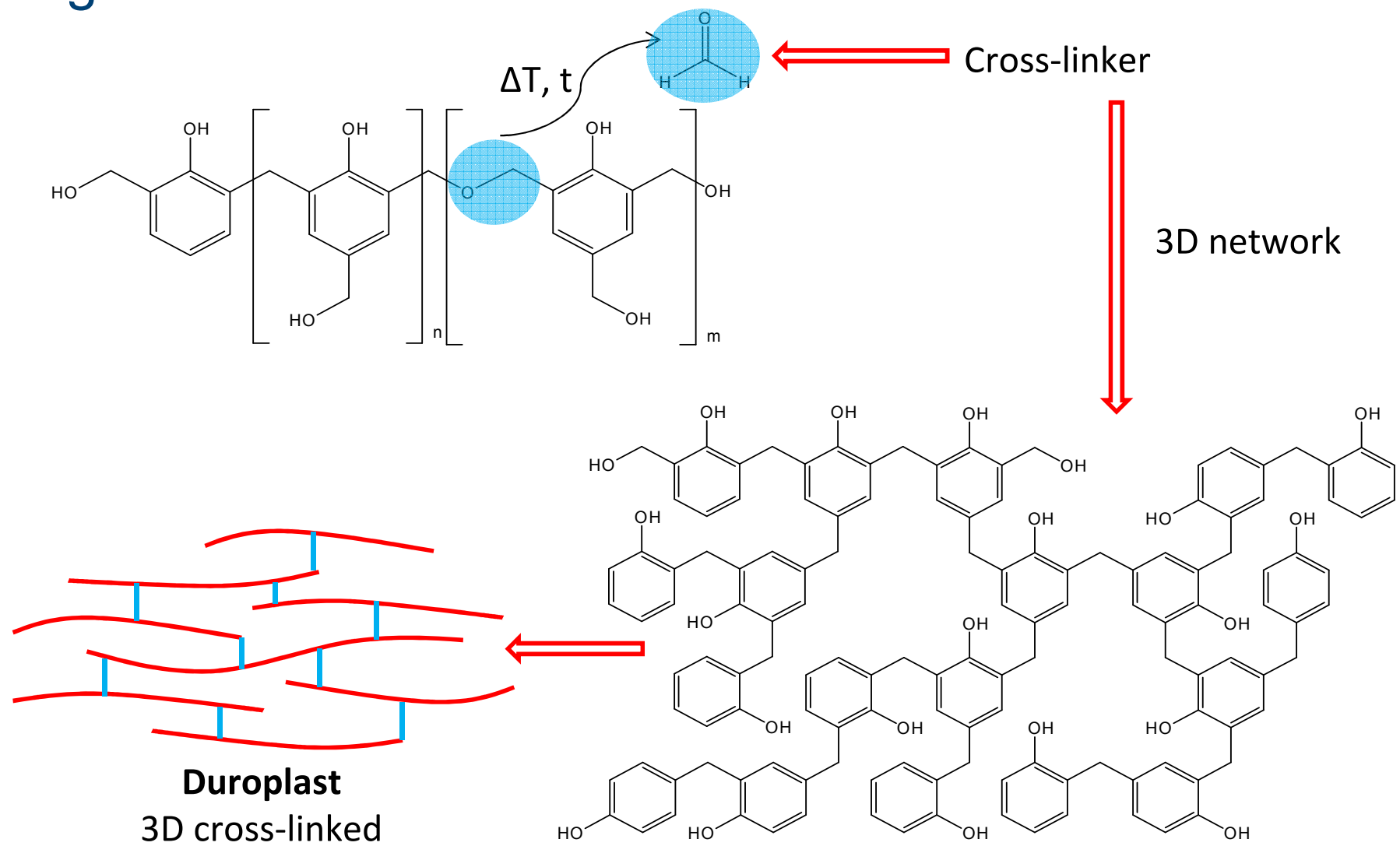
# Phenolic Resins - Novolak vs. Resole



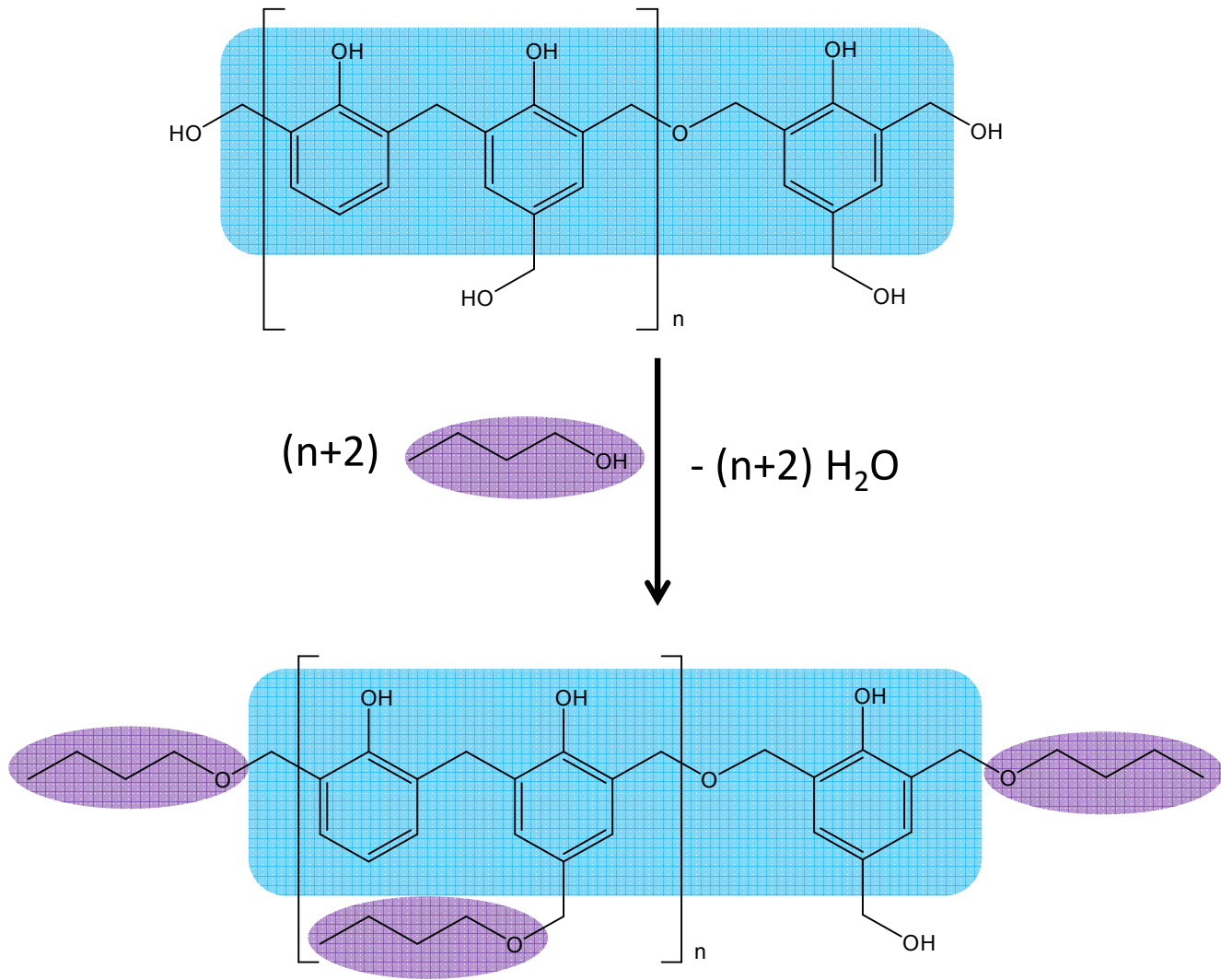
# Resole – Synthesis steps



# Curing of Resoles

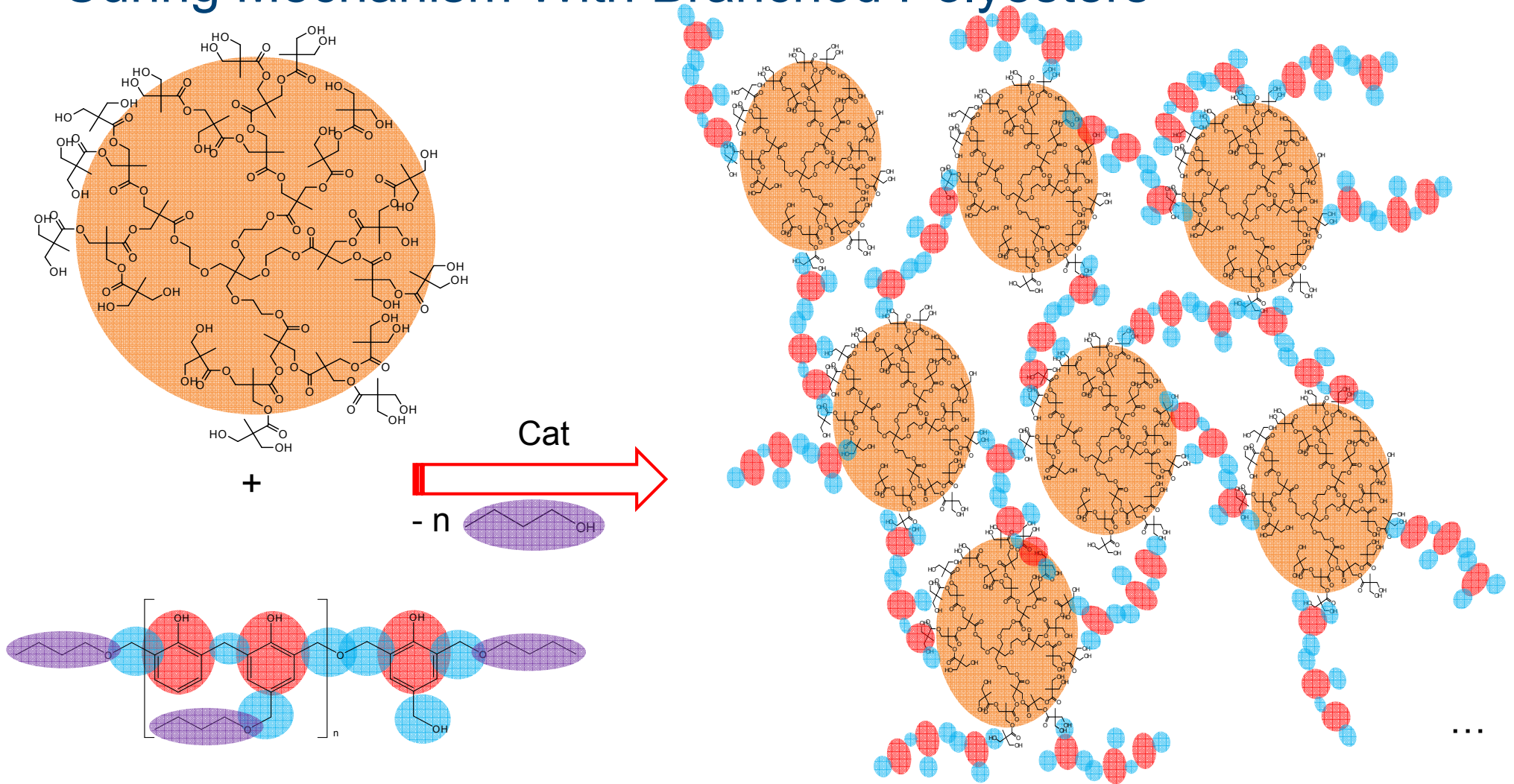


# Resole - Butylation





# Curing Mechanism With Branched Polyesters





# Classification of Formaldehyde

CH<sub>2</sub>O



Until 2016: Suspicion of a carcinogenic effect; category 2

Since 2016: Probably carcinogenic to humans; category 1B

“...presumed human carcinogen, classification is largely based on animal evidence”

Special feature: Concentration trigger for free formaldehyde,  $\geq 0,1$  % carc. cat 1B; H350

**Task: Reduction of free formaldehyde of the resin or at least in the final formulation <0.1wt%!**

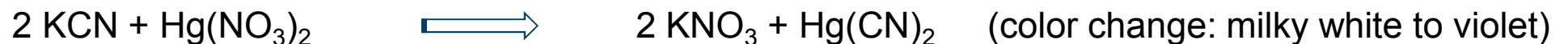
## Quantification of Formaldehyde

- Hydroxylammonium chloride-method



Titration of „released“ hydrochloric acid with 0.5 N NaOH-solution (color change: yellow to green)

- Potassium-cyanide-method

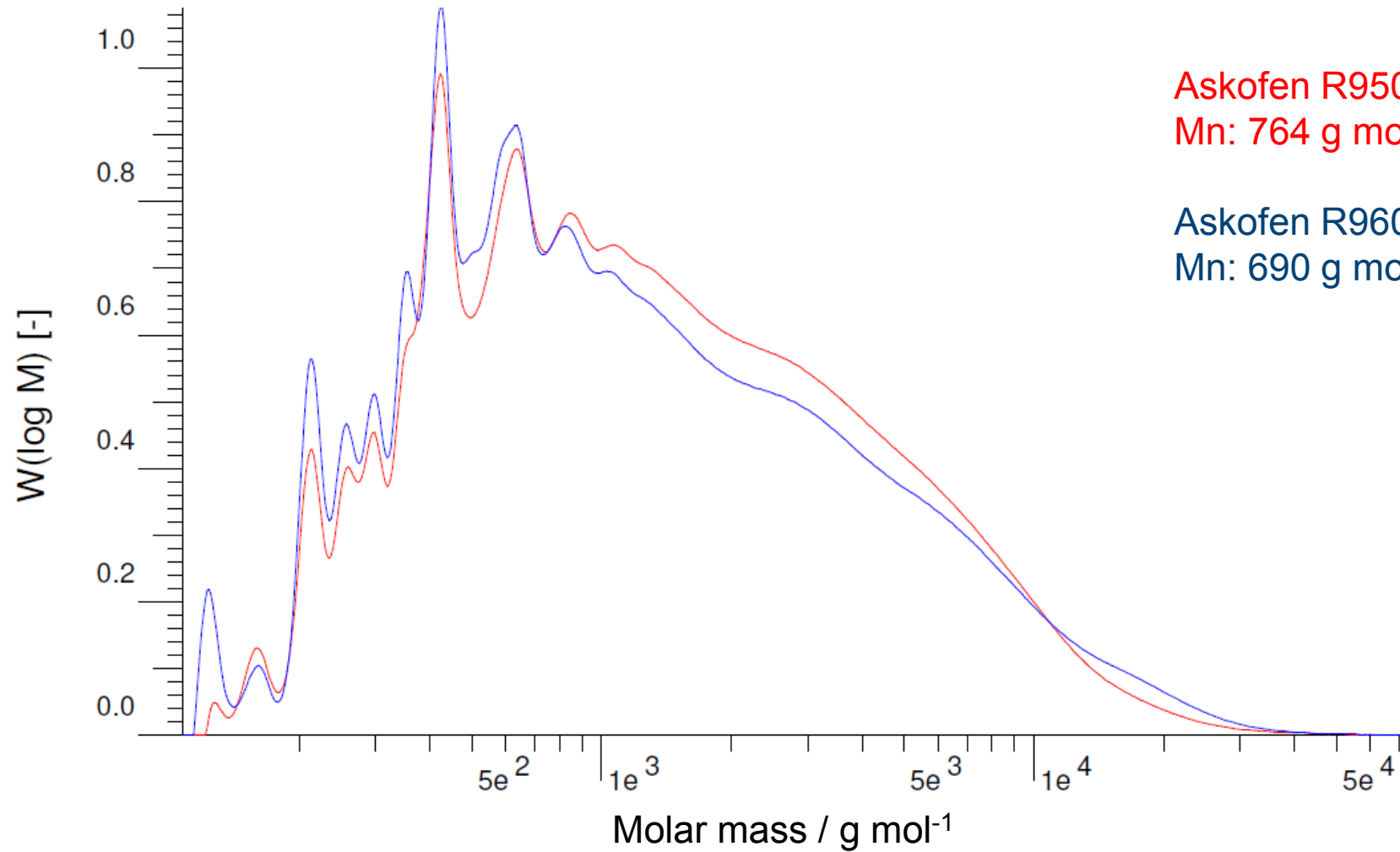




# GPC-Analysis

Askofen R9500  
Mn: 764 g mol<sup>-1</sup>

Askofen R9600  
Mn: 690 g mol<sup>-1</sup>



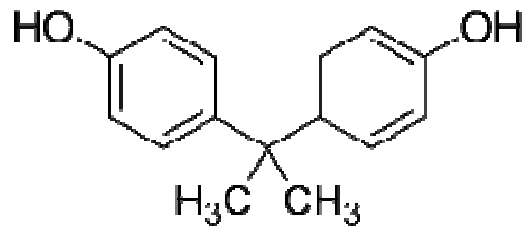


## Askofen R9500 vs. Askofen R9600 - Specifications

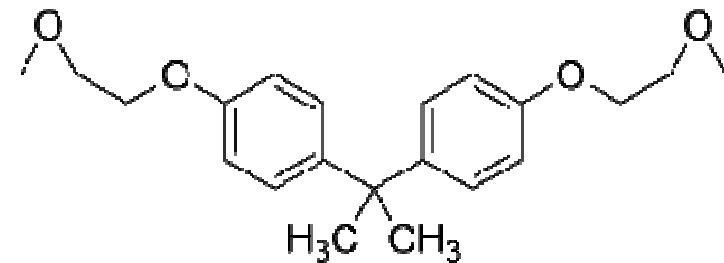
Specifications	Askofen R9500	Askofen R9600
Solid content	40 - 42 wt%	46 - 50 wt%
Viscosity ( <i>preliminary</i> )	55 - 85 m Pas	60 - 80 m Pas
Color (Gardner)	0 - 5	0 - 6
Free Formaldehyde	< 2.0wt%	< 0.5wt%



## Bisphenol A / BADGE-Issue



Potential Endocrine Disruptor: Acts as estrogen



IARC: Listed as group-3 carcinogen  
„...not classifiable as to its carcinogenicity to humans...”

**Since 2015:** Prohibition in France for use in food contact materials  
**Further states of the European Union will follow!**

## Starting formulation

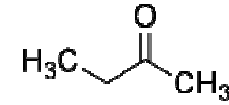
Component	wt.-%	wt.-%	wt.-%
Benester B	58.3	48.3	38.3
Butyl diglykolacetate	15.0	15.0	15.0
Askofen R9600	10.0	20.0	30.0
Askofen R9500	11.7	23.4	35.1
Cymel 1156	2.0	2.0	2.0
Solvent naphtha	14.5	14.5	14.5
Nacure 5076	0.2	0.2	0.2



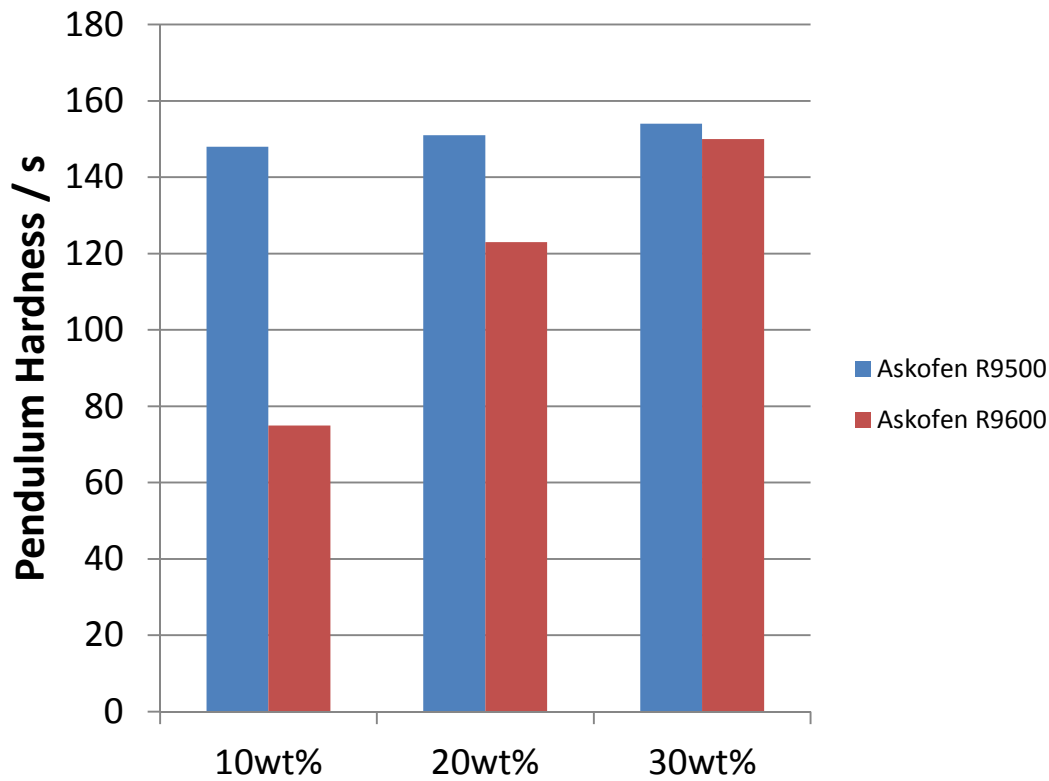
- ✓ Doctor blade application on tin-coated steel (200  $\mu\text{m}$ ); Wet-film thickness of 50 $\mu\text{m}$
- ✓ Curing @180°C for 20 min (12  $\mu\text{m}$  dry-film thickness)



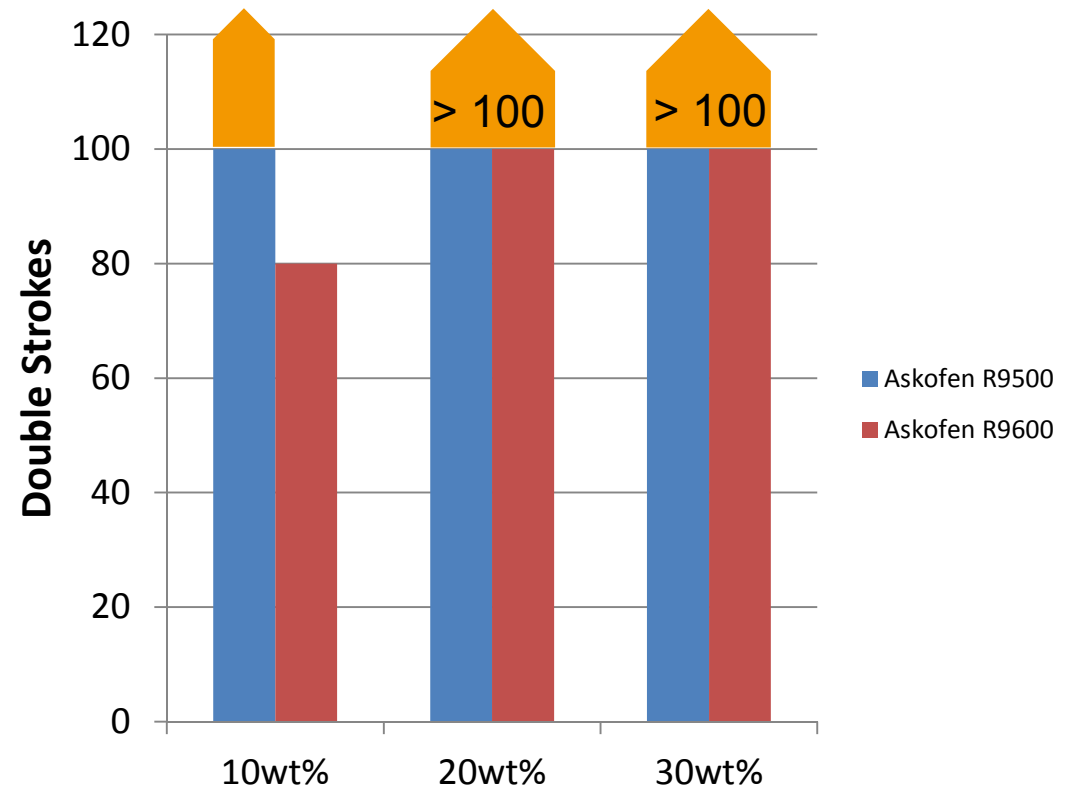
# Results



Pendulum Hardness (3°-6°)



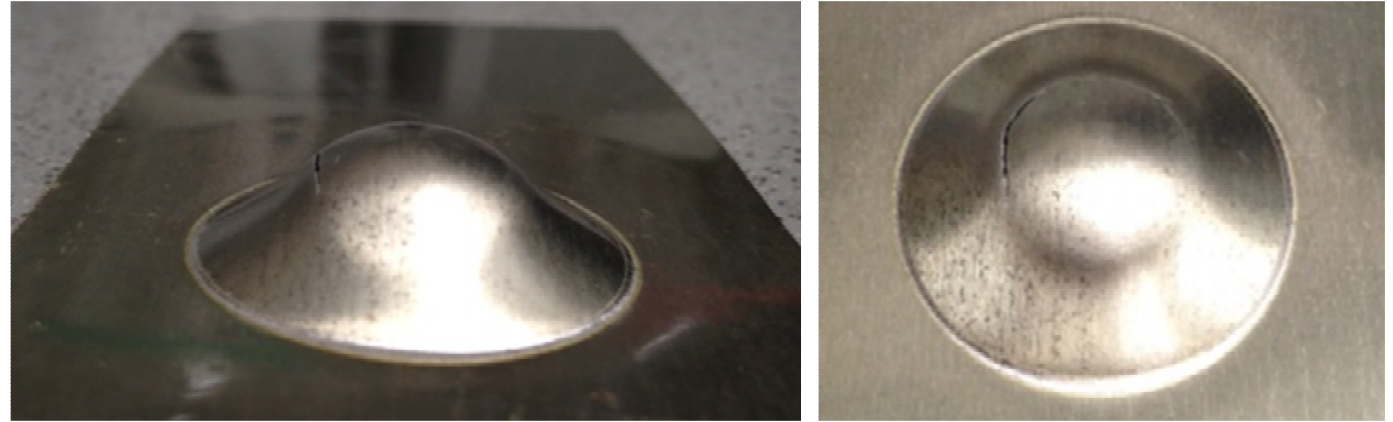
Methylethylketon (MEK)-Resistance



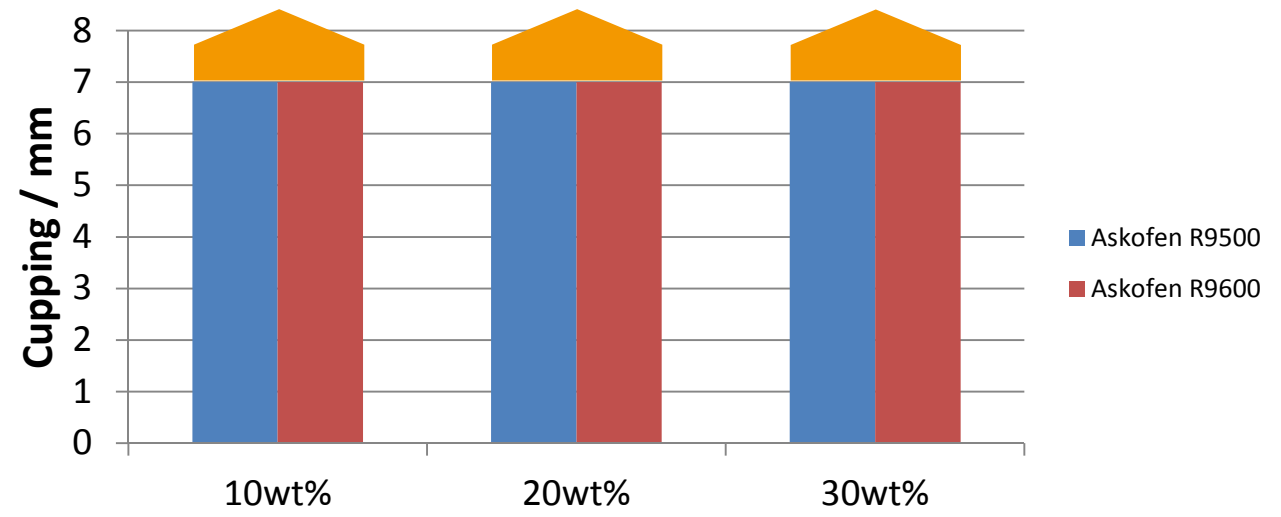
# Erichsen-Cupping



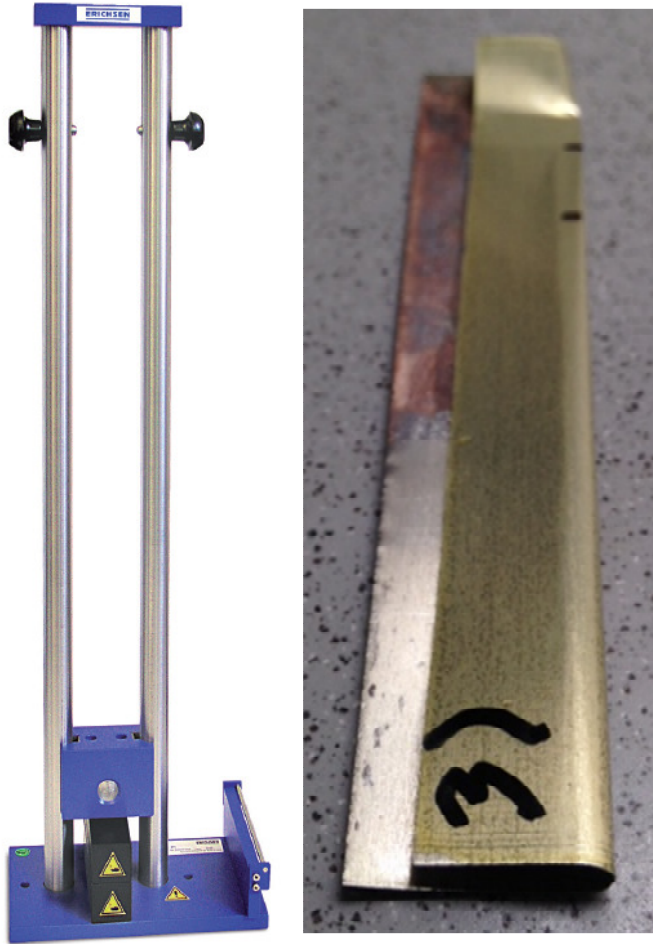
<https://www.erichsen.de/oberflaechenpruefung>



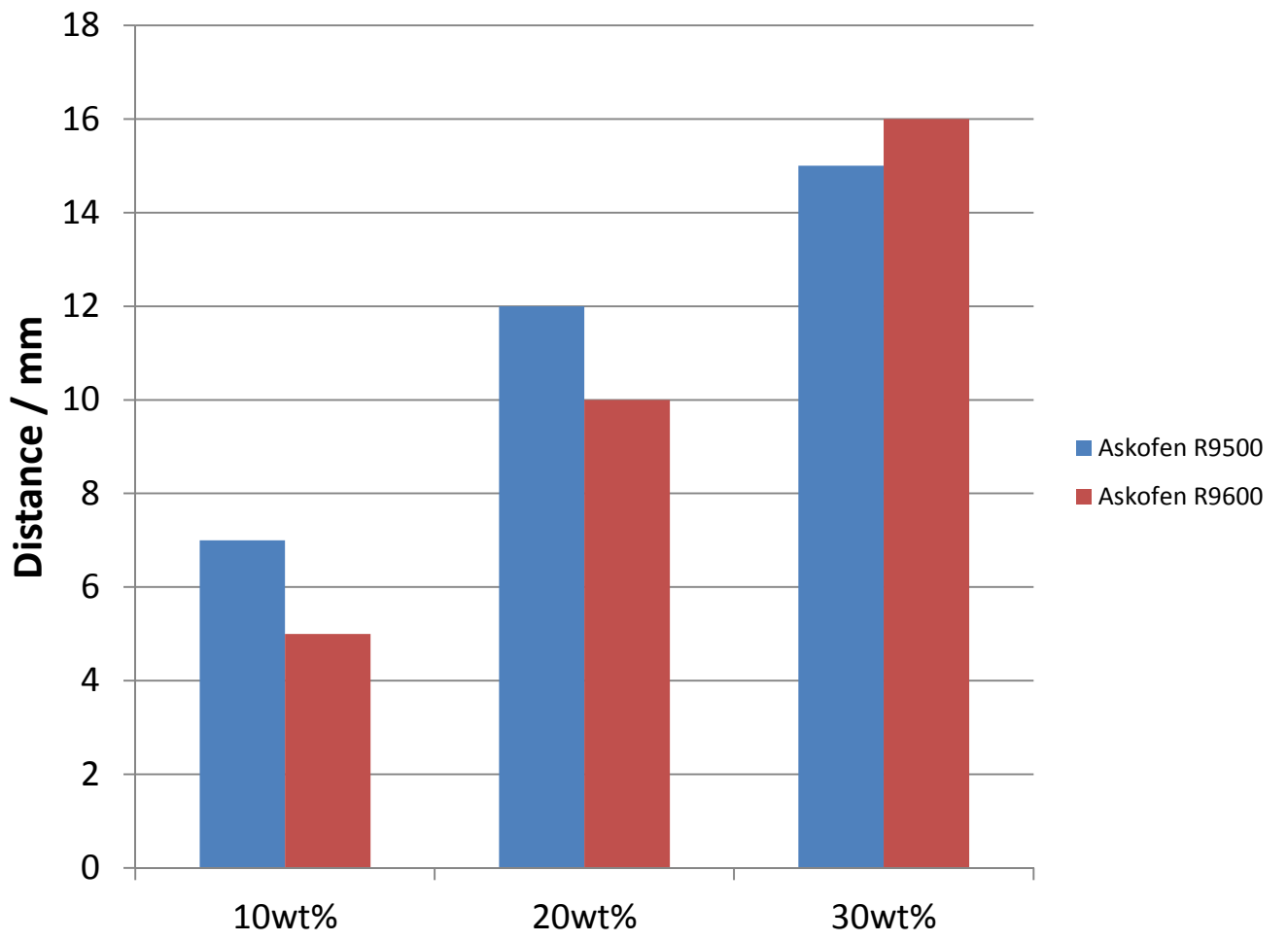
Tin-coated steel plate (200 μm): **Tinplate rips @ 7 mm**



# Impact -Test



[www.erichsen.de/oberflaechenpruefung](http://www.erichsen.de/oberflaechenpruefung)



The lower the distance, the better the flexibility!

## Sterilization resistance

✓ Sterilization resistance against different test solutions @128°C für 1 h

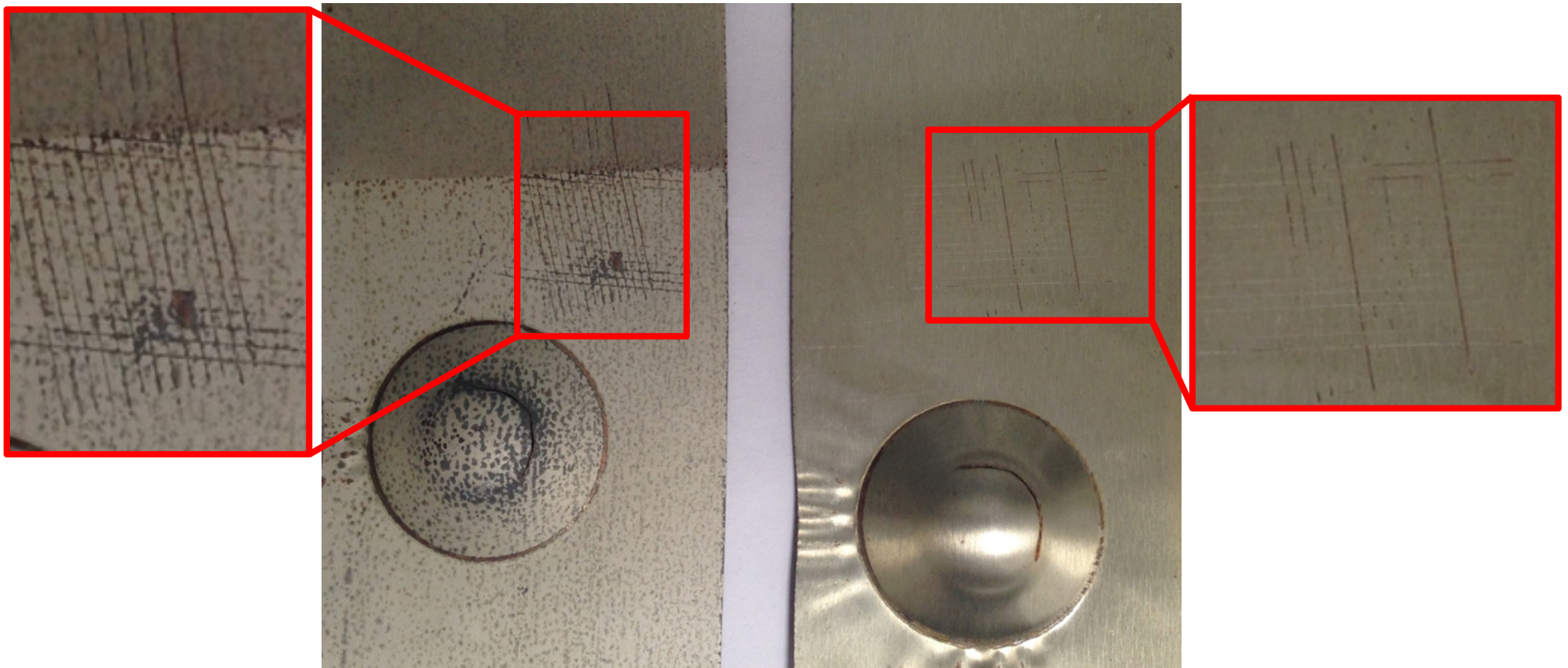
- 1) Deionized water
- 2) Acetic-acid solution (3.0 wt.-%)
- 2) Lactic-acid solution (1.0 wt.-%)
- 3) Acetic acid- (3.0 wt.-%) und sodium chloride (2.0 wt.-%)
- 5) Cysteine-hydrochloride solution (0.5 wt.-%)

Defects and porosities are visualized via copper-sulfate test

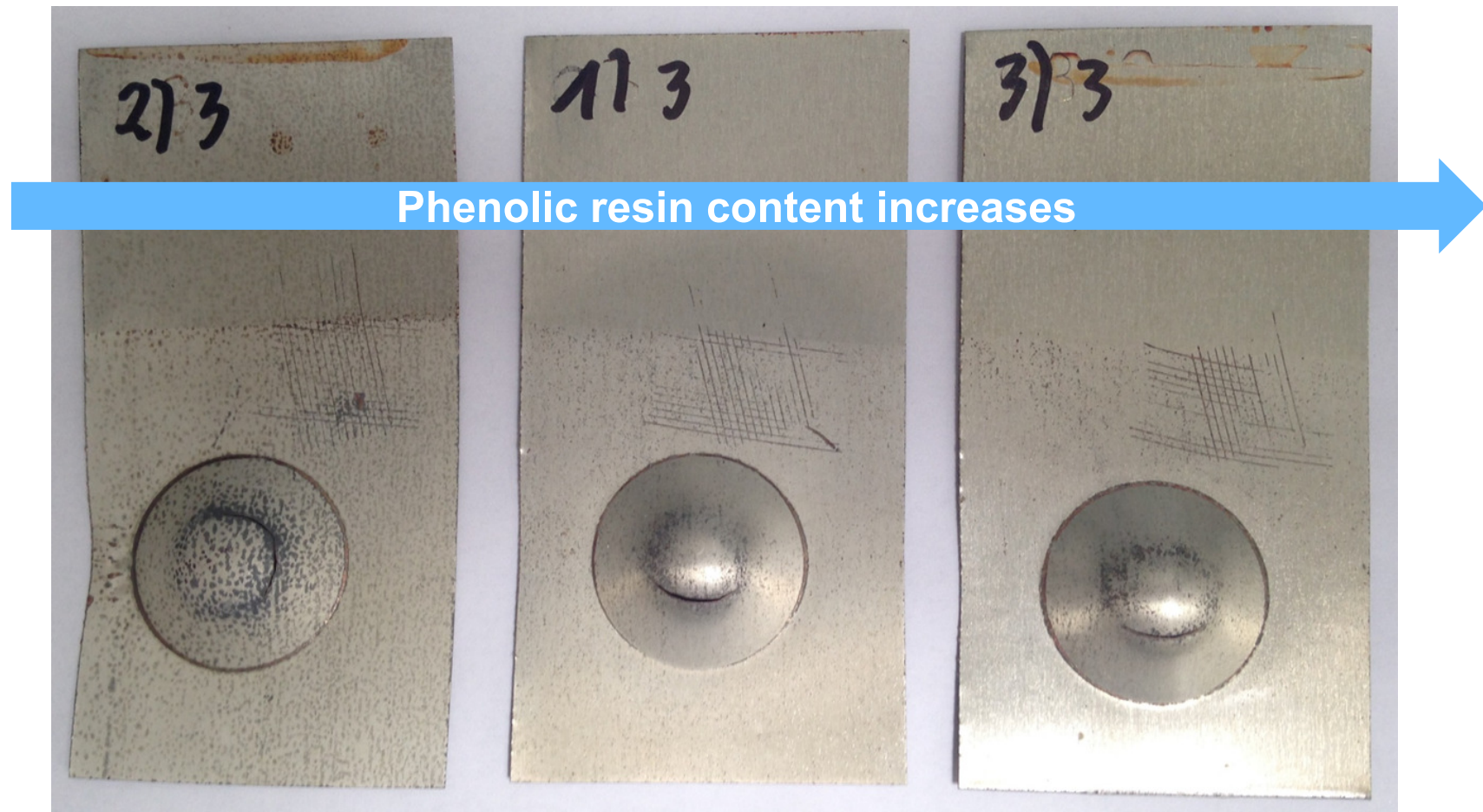


<http://sanoclav.de/la-20-liter.html>

## Sterilisation resistance - Adhesion

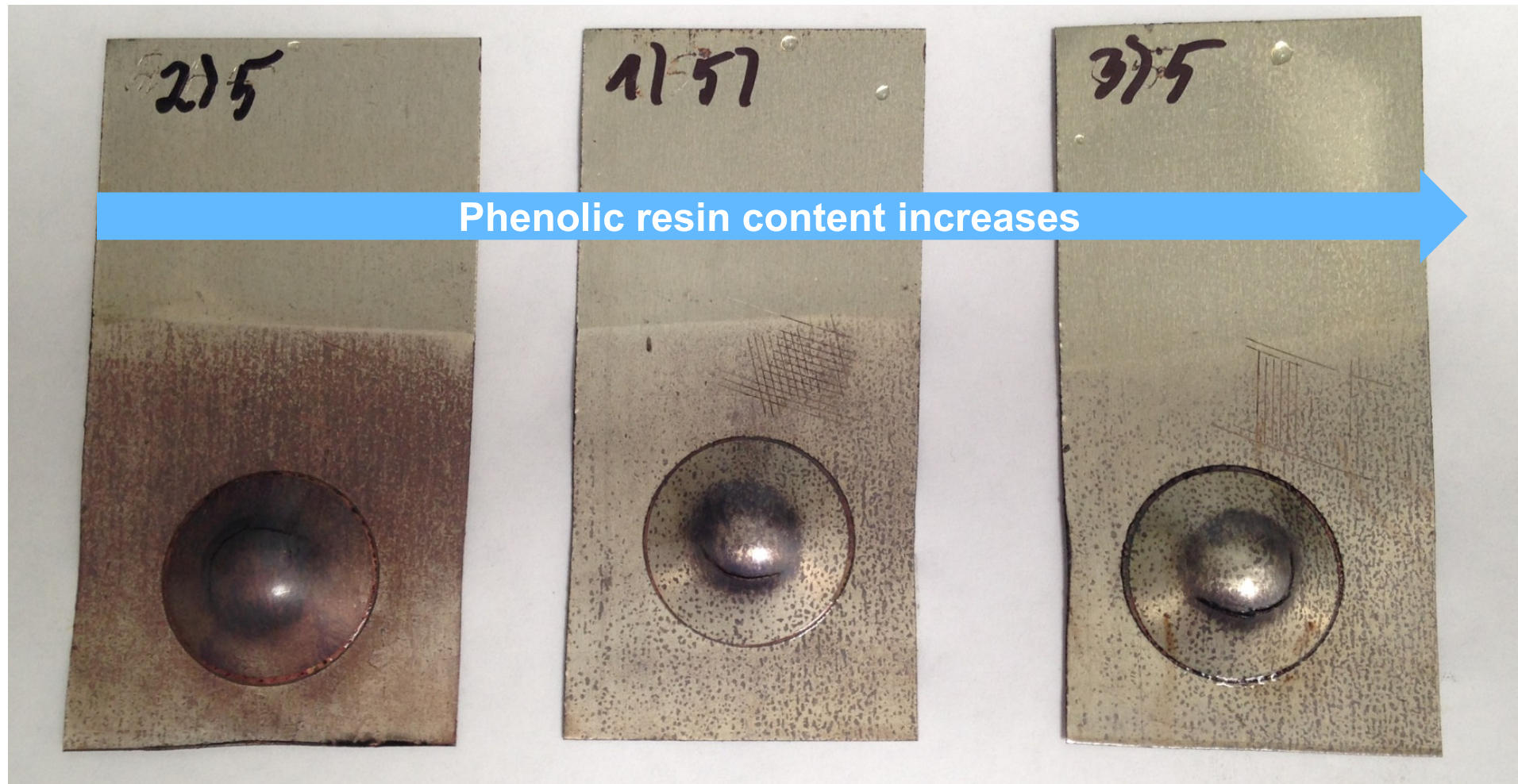


## Good resistance against Lactic-acid solution






## Poor resistance against Cystein-hydrochloride solution





## Summary and Outlook

- ✓ New phenolic-cross linker with reduced free formaldehyde (<0,5wt%)
  - ❖ New goal: Formaldehyde-reduction <0.1wt%
- ✓ BADGE- und Bisphenol A-free formulations
- ✓ Acceptable sterilization- and chemical-resistance against different test-solutions
  - ❖ Resistance against cystein-hydrochloride must be optimized; new formulations will follow
- ✓ Good flexibility
- ✓ Good adhesion
- ✓ Askofen R9600 shows better flexibility:chemical resistance ratio
- ✓ Lower reactivity of Askofen R9600 compared to Askofen R9500
- ✓ Mn Askofen R9600 < Mn Askofen R9500;  higher solid, reduced emission of solvents

Thanks!