



# P-free household dishwashing detergents - alternative substitutes for STPP

Ralf Moritz

BU Functional Chemicals

BL Phosphorus Chemicals

Malmö, 2013-05-06, SEPAWA Nordic Conference

**LANXESS**  
Energizing Chemistry

# Agenda

## **Regulation (EC) No 648/2004 and impact of annex VI a of Regulation (EU) 259/2012**

- EU harmonized restrictions on phosphorus in consumer laundry and dishwasher detergent

## Phosphonates as potential substitute for phosphate in builder/co-builder systems of dishwasher detergents

- P-content and limits of use

## Biodegradable chelating agents as potential substitute for phosphate in builder/co-builder systems of dishwasher detergents

- selected properties

## Summary and conclusion

# EU harmonized restrictions on P in consumer laundry and dishwasher detergents in Dec. 2011

## Annex VIa - REGULATION (EU) No 259/2012 \*

### LIMITATIONS ON THE CONTENT OF PHOSPHATES AND OF OTHER PHOSPHORUS COMPOUNDS


Detergent	Limitations	Date as of which the limitation applies
1. Consumer laundry detergents	<p>Shall not be placed on the market if the total content of phosphorus is equal to or greater than 0,5 grams in the recommended quantity of the detergent to be used in the main cycle of the washing process for a standard washing machine load as defined in section B of Annex VII for water of hard water hardness</p> <ul style="list-style-type: none"><li>— for “normally soiled” fabrics in the case of heavy-duty detergents,</li><li>— for “lightly soiled” fabrics in the case of detergents for delicate fabrics,</li></ul>	30 June 2013
2. Consumer automatic dishwasher detergents	Shall not be placed on the market if the total content of phosphorus is equal to or greater than 0,3 grams in the standard dosage as defined in section B of Annex VII	1 January 2017 <sup>1</sup>

\* Annex VI a of REGULATION (EU) No 259/2012 of 14 March 2012 amending Regulation (EC) No 648/2004

# Article 16 of Regulation EU No. 259/2012 will force STPP-substitution in dishwasher detergents

## Decided and approved

	2012				2013				2014				2015				2016				2017				2018 et seq.							
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4				
Household laundry detergents									30th June 2013 : total P max. 0,5g*																							

 STPP : max. 1,98 g (1,41 %)

\* for a standard washing machine load (4,5 kg fabrics) and based on 140 g of a heavy-duty laundry detergent

## Article 16 comprises two milestones

	2012				2013				2014				2015				2016				2017				2018 et seq.			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Household automatic dishwasher detergents	Member States may maintain or may restrict P-content on a voluntary basis																											
																	1st Jan. 2017 : total P max. 0,3g*											

Revision : assessment on P-free formulations on the market and progress in the development to replace P



if appropriate, new legislative proposal to force P-free formulations before 1st. Jan. 2017



STPP : max. 1,19 g (5,95 %)

\* for a standard machine load (12-place settings) and based on a 20 g dishwasher tablet

STPP calculated as fully neutralized sodium salt

# Sweden and Finland already implemented P-restrictions to protect the Baltic Sea

## P-limits

### Sweden

- |                        |      |              |
|------------------------|------|--------------|
| ▪ laundry detergent    | 2008 | 0,2 weight % |
| ▪ dishwasher detergent | 2011 | 0,5 weight % |

### Finland

- |                     |      |              |
|---------------------|------|--------------|
| ▪ laundry detergent | 2012 | 0,2 weight % |
|---------------------|------|--------------|

- 0,28 g STPP in laundry detergent per 140 g dosing level
- 0,71 g STPP in dishwasher detergent per 20 g tablet

STPP calculated as fully neutralized sodium salt

# The Chemical Industry offers various alternatives to replace STPP as builder ingredient

## Household laundry detergents

- builder:
  - carbonates, bicarbonates
  - silicates,
  - acids (e.g. citric acid)
  - polycarboxylates (non-biodegradable)
  - polycarboxylates (biodegradable\*)
- sequestrants:
  - chelating agents (non-biodegradable)
  - **chelating agents (biodegradable\*)**
  - **phosphonates**

## Household automatic dishwasher detergents

- builder:
  - acids (e.g. citric acid)
  - polycarboxylates (non-biodegradable)
  - polycarboxylates (biodegradable\*)
  - **chelating agents (almost biodegradable\*)**
- sequestrants:
  - **phosphonates**

\* under OECD 301 test series

# Agenda

## Regulation (EC) No 648/2004 and impact of annex VI a of Regulation (EU) 259/2012

- EU harmonized restrictions on phosphorus in consumer laundry and dishwasher detergent

## **Phosphonates as potential substitute for phosphate in builder/co-builder systems of dishwasher detergents**

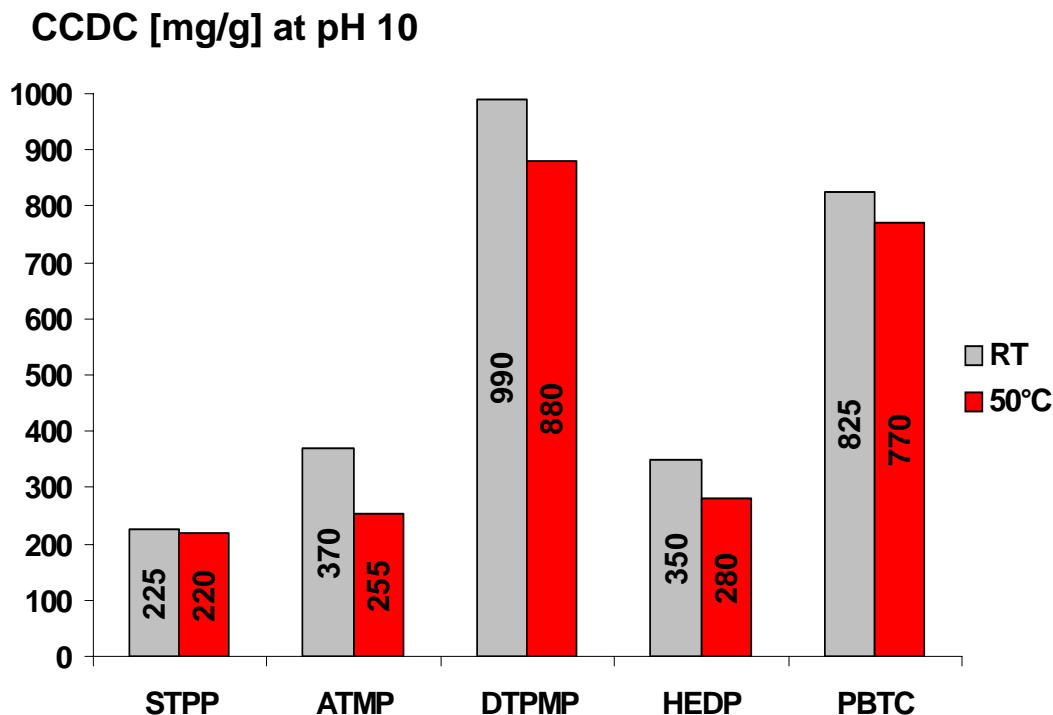
- P-content and limits of use

## Biodegradable chelating agents as potential substitute for phosphate in builder/co-builder systems of dishwasher detergents

- selected properties

## Summary and conclusion

# Calcium carbonate binding capacity of the most common phosphonates in comparison to STPP



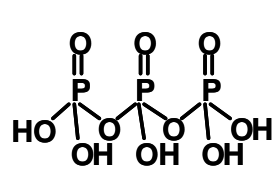
**DTPMP and PBTC are most favorable**

## Test conditions

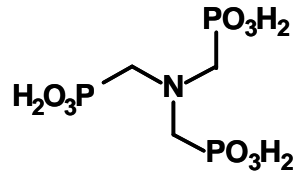
- 1500 mg scale inhibitor (as active ingredient) in 90 ml deionized water
- 10 g of a 10% sodium carbonate solution
- adjustment of pH to 10 with sodium hydroxide
- room temperature and 50°C
- titration against calcium acetate solution (17,6 g/l)
- end point at 90% transmission at 620 nm



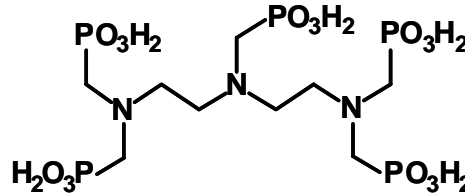
# P-restriction of EU No. 259/2012 impacts the use of phosphonates in dishwasher detergents



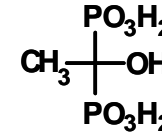
STPP



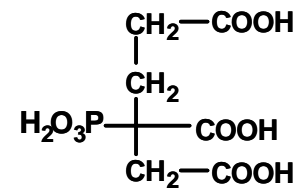
ATMP



DTPMP



HEDP



PBTC

P-content based on sodium salt [weight %]

25,3

22,7

21,3

21,1

8,1

Cmax in dishwasher detergent at 0.3 g P [g/standard load\*]

1,19

1,32

1,41

1,42

3,70

Cmax in dishwasher detergent\* [g/kg]

59,3

66,1

70,4

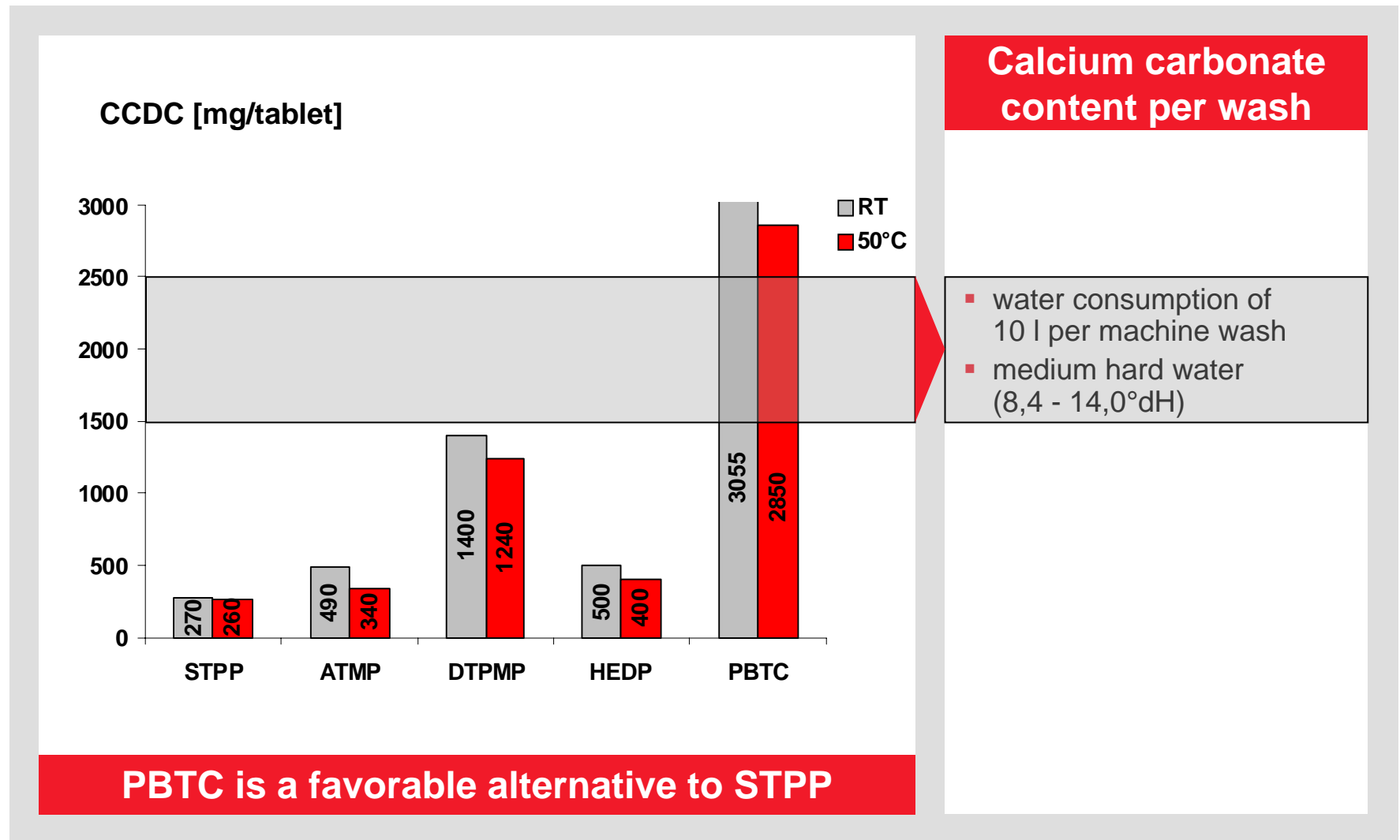
71,1

185,2

**PBTC has the lowest P-content of the most common phosphonates**

\* standard load = 20 g dishwasher tablet, 12 place settings.

# CCDC of selected phosphonates in a 20 g dishwasher tablet at max 0,3 g P per standard load



# Agenda

## Regulation (EC) No 648/2004 and impact of annex VI a of Regulation (EU) 259/2012

- EU harmonized restrictions on phosphorus in consumer laundry and dishwasher detergent

## Phosphonates as potential substitute for phosphate in builder/co-builder systems of dishwasher detergents

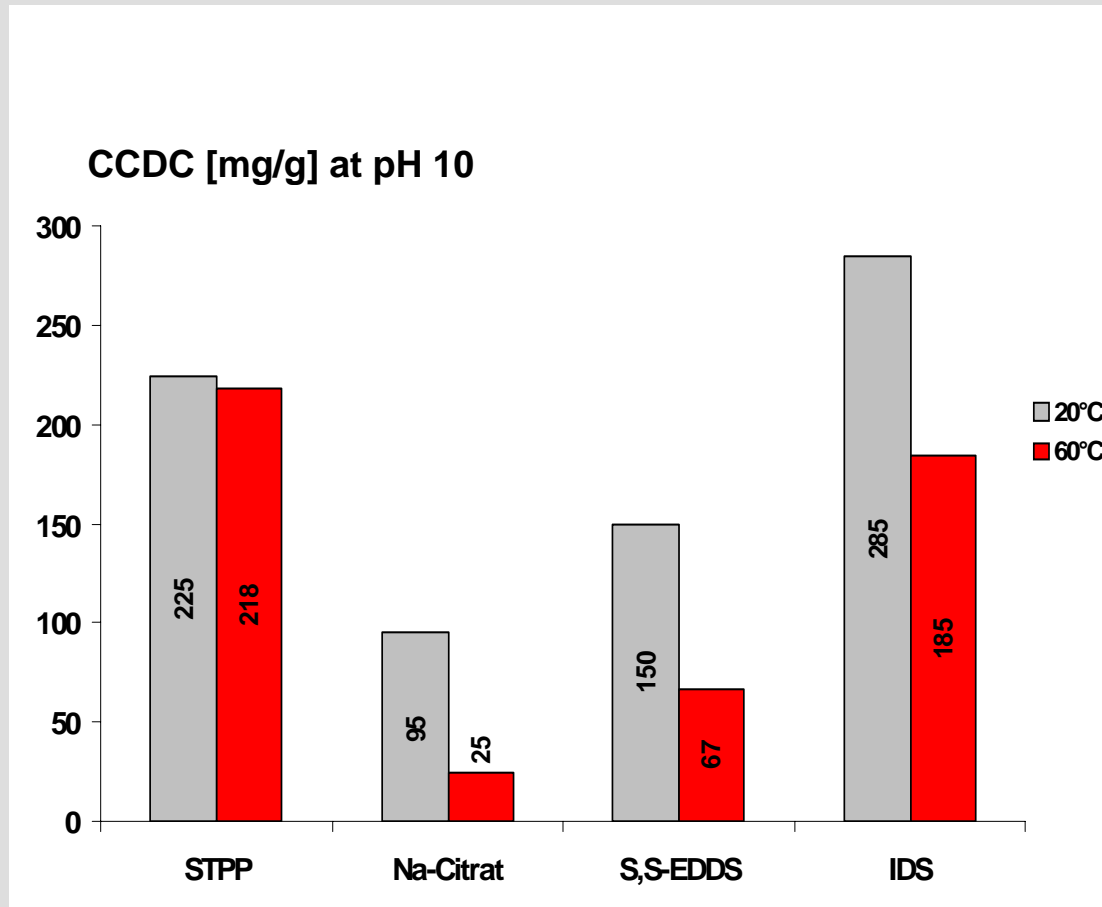
- P-content and limits of use

## **Biodegradable chelating agents as potential substitute for phosphate in builder/co-builder systems of dishwasher detergents**

- selected properties

## Summary and conclusion

# Calcium carbonate binding capacity of biodegradable chelating agents versus STPP



**IDS and STPP have similar CCDC**

## Test conditions

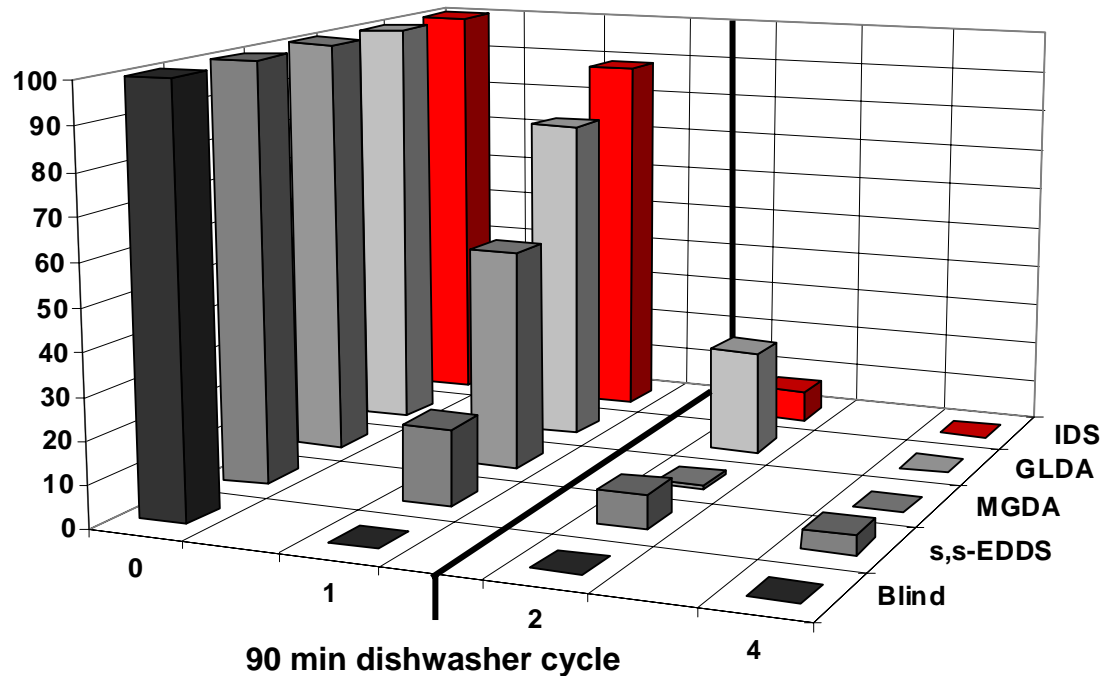
- 1500 mg chelating agent (as active ingredient) in 90 ml deionized water
- 10 g of a 10% sodium carbonate solution
- adjustment of pH to 10 with sodium hydroxide
- room temperature and 60°C
- titration against calcium acetate solution (17,6 g/l)
- end point at 90% transmission at 620 nm

# Hydrogen peroxide stabilization by biodegradable chelating agents

## Test conditions

- 5 mg  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  each
- 2% hydrogen peroxide (as active ingredient)
- 0,6% chelating agent (as active ingredient)
- 60°C
- pH adjusted to 10
- titration of remaining hydrogen peroxide against potassium iodide with sodium thiosulfate and starch

residual hydrogen peroxide [% abs.]

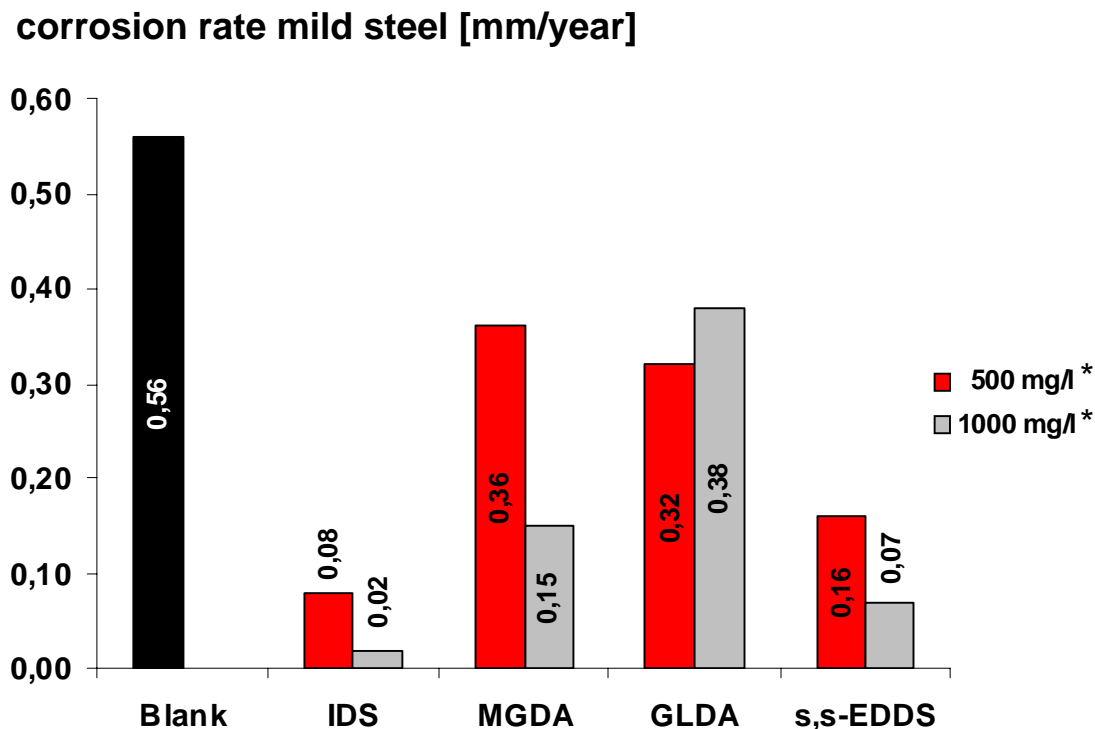


**IDS preferred hydrogen peroxide stabilizer**

# Corrosion rates of mild steel under influence of biodegradable chelating agents

## Test conditions

- weight difference method
- mild steel rings RSt. 37-2 material number: 1.0038
- synthetic tap water total hardness: 300 mg/l, alkalinity: 160 mg/l both calculated as calcium carbonate.
- 500 / 1000 mg/l chelating agent (as active ingredient)
- duration of 4 days
- pH adjusted to 10



**IDS with best corrosion protecting properties**

\* 500 / 1000 mg/l of active chelating agent are equivalent to 5 / 10 g per dishwasher tablet of 20 g

# Examples for builder systems of phosphate-free automatic dishwasher detergents

## Brand name products

Sun Tablets All in 1  
Green Power

**MGDA**

Polyacrylic acid  
Sodium acrylic acid/  
MA copolmer

**HEDP**

**Unilever, NL\***

Sun All in 1 Tabletter  
für Maskindisk

Sodium citrate

Polyacrylic acid

Sodium acrylic acid/  
MA copolymer

**Unilever, S\***

W5 All in one MGR-  
Tabs Phoshatfrei

**IDS**

**GLDA**

Sodium Citrate

Polyacrylic acid

Sodium acrylic acid/  
MA copolymer

**HEDP**

**Lidl Stiftung &  
Co. KG, D \*\***

AlmaWin Maschinen-  
spülmittel

**IDS**

Sodium citrate

Sodium polyaspartate

**Almawin  
GmbH, D \*\*\***

\* <http://www.unilever.com/pioti/EN/p1.asp>. ; \*\* <http://www.lidl-info.com/cps/rde/xchg/detergenzien/hs.xsl/24.htm>;

\*\*\* [http://www.violey.com/de/almawin-maschinenspuelmittel\\_p\\_14995.html](http://www.violey.com/de/almawin-maschinenspuelmittel_p_14995.html)

# Agenda

## Regulation (EC) No 648/2004 and impact of annex VI a of Regulation (EU) 259/2012

- EU harmonized restrictions on phosphorus in consumer laundry and dishwasher detergent

## Phosphonates as potential substitute for phosphate in builder/co-builder systems of dishwasher detergents

- P-content and limits of use

## Biodegradable chelating agents as potential substitute for phosphate in builder/co-builder systems of dishwasher detergents

- selected properties

## Summary and conclusion



# Summary and conclusion

- **PBTC appears to be an attractive alternative to phosphate due to a low P-content and an outstanding calcium binding capacity based on a 20 g dishwasher tablet**
- **MGDA and GLDA have good calcium binding properties but lower corrosion protecting properties**
- **IDS has good peroxide stabilizing properties combined with good corrosion protecting properties**
- **Wherever sodium citrate is the main builder component a substitution by IDS should increase the performance due to a higher calcium binding capacity**

# Thank you for your attention

## Disclaimer

This information and our technical advice - whether verbal, in writing or by way of trials - are given in good faith but without warranty, and this also applies where proprietary rights of third parties are involved. Our advice does not release you from the obligation to verify the information currently provided - especially that contained in our safety data and technical information sheets - and to test our products as to their suitability for the intended processes and uses. The application, use and processing of our products and the products manufactured by you on the basis of our technical advice are beyond our control and, therefore, entirely your own responsibility. Our products are sold in accordance with the current version of our General Conditions of Sale and Delivery.

**LANXESS**



Energizing Chemistry