



Biodegradable, Low Foam Surfactants for Automatic Dishwashing Applications

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The Dow Chemical Company
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Consumer & Industrial Solutions

■ Biodegradable, Low Foam Surfactants for Automatic Dishwashing Applications

- **Dish Care Global Trends**
- **Regulatory Drivers**
- **Challenges Formulating with Non-Phosphate Builders
- Prototypical Formulations**
- **Surfactant Design/Characteristics**
- **Performance in ADWs/Rinse Aids**
- **Summary/Conclusions**



Dish Care Global Trends



A large part of the world is still using hand dishwashing formats (mostly liquids)

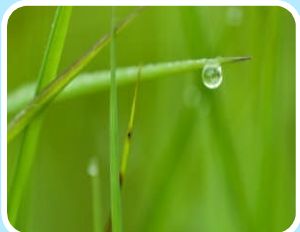


ADW sales are mostly in Europe and North America (~90%) :

- Eastern Europe is one of the major growth areas for ADW in volume and value
- Powders are still dominant but tablets gain quick market share in WE and North America.



Main value growth driver is machine penetration, available income and as a result increased penetration of – premium priced - tablet format (Europe)



The move toward more sustainable products is a global trend

(Regulatory-driven reformulations move out of phosphates))

Regulatory-Driven Innovation: Phosphate-Free Formulations

North America

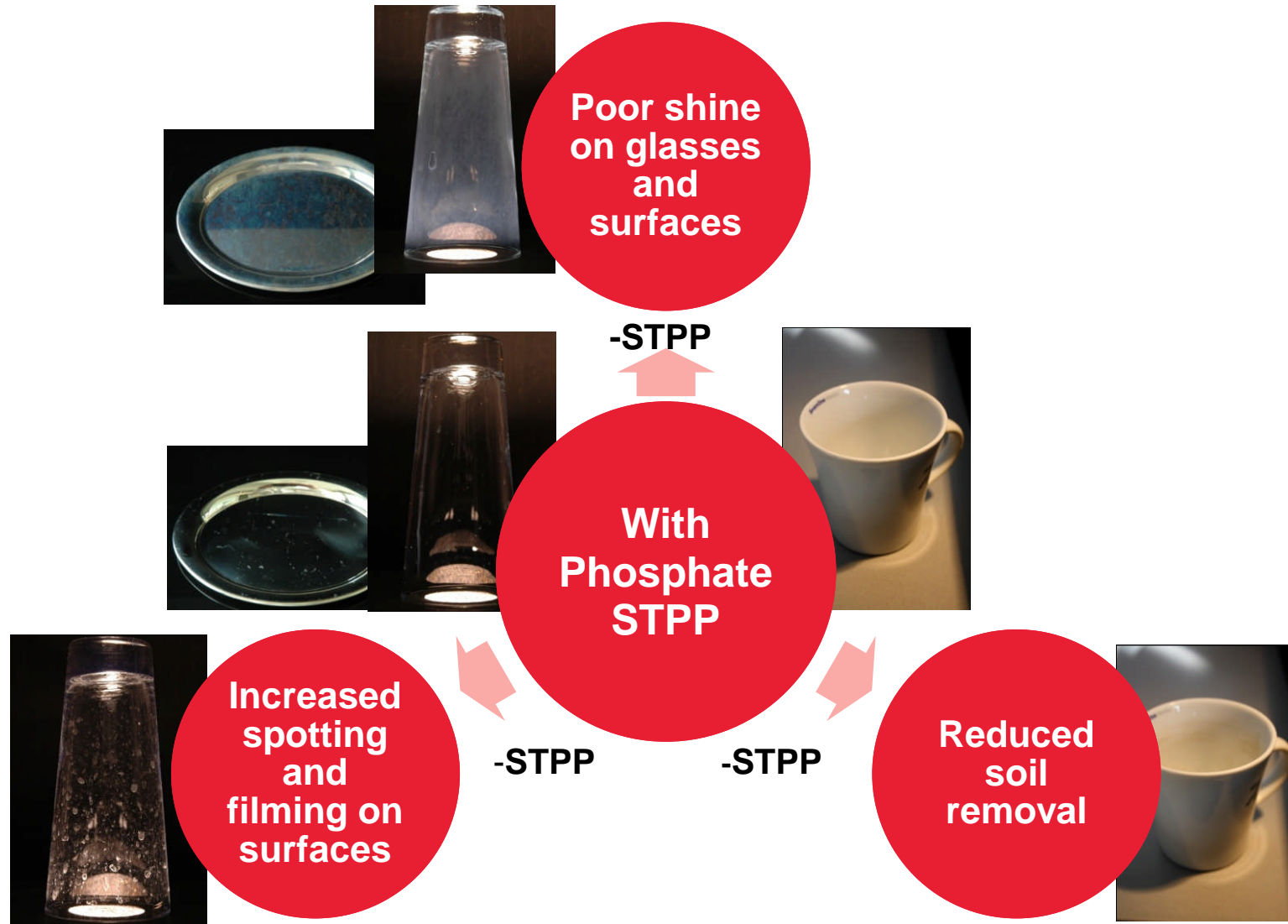
- Regulatory driven re-formulations were initiated July 1, 2010.
- Law enforced limitation of total phosphorus content to 0.5% in ADW detergents in 16 U.S. states.
- Based on this regulation, many manufacturers voluntarily removed phosphates for other states.

Europe

- European Parliament has approved phosphate ban:
 - Standard Phosphate dosage for automatic dishwasher detergents will be limited to 0.3g on January 1, 2017
- Sweden moves to phosphate-free ADW formulations as of July 2011
- Pressure on Baltic Sea countries to follow Sweden
- In France, a tax is paid on phosphates:
 - complete move to phosphate-free in 2012



When Phosphates (STPP/TKPP) are Removed...



Factors Influencing Inorganic/Organic Scale Formation and Deposition

- **Washing Parameters**
 - **Water Hardness/Temperature**
 - **Type of Surface (Glass, Ceramic, Plastic)**
 - **Concentration of Food Soil**
- **Selection of the Builder/Polymer System**
 - **Detergent Concentration in the Wash Bath**
- **Selection of the Low Foam “Emulsifying” Surfactant**
 - **Structure/Functionality/Concentration**

Detergent Builders

(Precipitating/Non-Precipitating)

- **Phosphates (STPP, TKPP)**
- Carbonates (Soda Ash, Bicarbonate)
- Citrates
- **Aminocarboxylates (MGDA, GLDA)**
- Organics (NTA), Inorganics (HEDP)
- Silicates
- Polycarboxylates/Builder Assists (Acrylics, Acrylic/Maleics, Acrylic/Sulfonated Co/terpolymers)

Phosphate vs. Phosphate-Free Automatic Dishwashing Products

<u>Components</u>	<u>Phosphate</u>	<u>Non-Phosphate</u>
	% (Actives)	
<u>Builders</u>		
STPP/TKPP	5-35	0
Soda Ash	5-20	15-35+
Sodium Bicarbonate	0-15	0-15
Sodium Citrate·2H ₂ O	0-10	5-40
Aminocarboxylates	0	5-30
Sodium Disilicate (Corrosion Inhibitor)	2-10	2-10
Percarbonate (Peroxygen Bleach)	0-15	0-15
TAED (Bleach Activator)	0-4	0-3
Surfactants (Emulsification/Degreasing)	0.5-2	1-5
Enzymes (Protease/Amylase/Lipase)	0-2	0-2
Polymers (Scale Inhibition)	0-2	2-10
PEG (Tablet Binder), PVOH (Film)	As Needed	As Needed
Filler (Sodium Sulfate/NaCl)	Balance	Balance



■ Low Foam Surfactants for ADW Applications (Ideal Properties)

- **Designed to facilitate the removal of baked on, burnt on food soils**
- **Emulsification of food soils**
- **Prevent redeposition of oily/greasy soils back on ceramics and flatware.**
- **Rapid wetting, mitigate spotting/streaking on glassware**
– Shine enhancement
- **Readily biodegradable (OECD 301)**
- **Control excessive foam formation (keep dishwasher jets clear to insure appropriate mechanical action)**

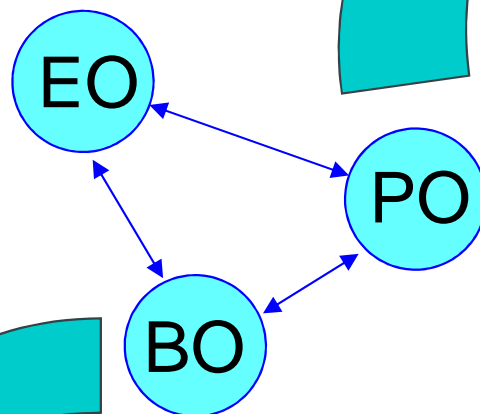


Alkyl/Block EO/PO/BO Surfactants

- Water solubility, oil insolubility
- High molecular weights
- Primary OH
- Solid products (at high EO content)



- Water insolubility, dispersibility
- Oil solubility, low foam
- Limited molecular weights
- Liquid products
- Secondary OH



- Oil solubility, water insolubility
- Limited molecular weights
- Liquid products
- Secondary OH



Low Foam Surfactant Structures

	Designation	Chemistry	HLB	Cloud Point
#1	Tergitol L-61	EO/PO/EO	3	24
#2	Tergitol L-64	EO/PO/EO	15	62
#3	Ecosurf LF-20	Sec-alcohol alkoxyate:EO-BO	10-11	20
#4	Ecosurf LF-30	Sec-alcohol alkoxyate:EO-BO	11-12	33
#5	Dowfax 20B102	Linear-alcohol alkoxyate:EO-BO	11	32
#6	Benchmark	Alcohol alkoxyate	4-5	18
#7	Triton CF-32	Alkyl amine EO/PO	11	25

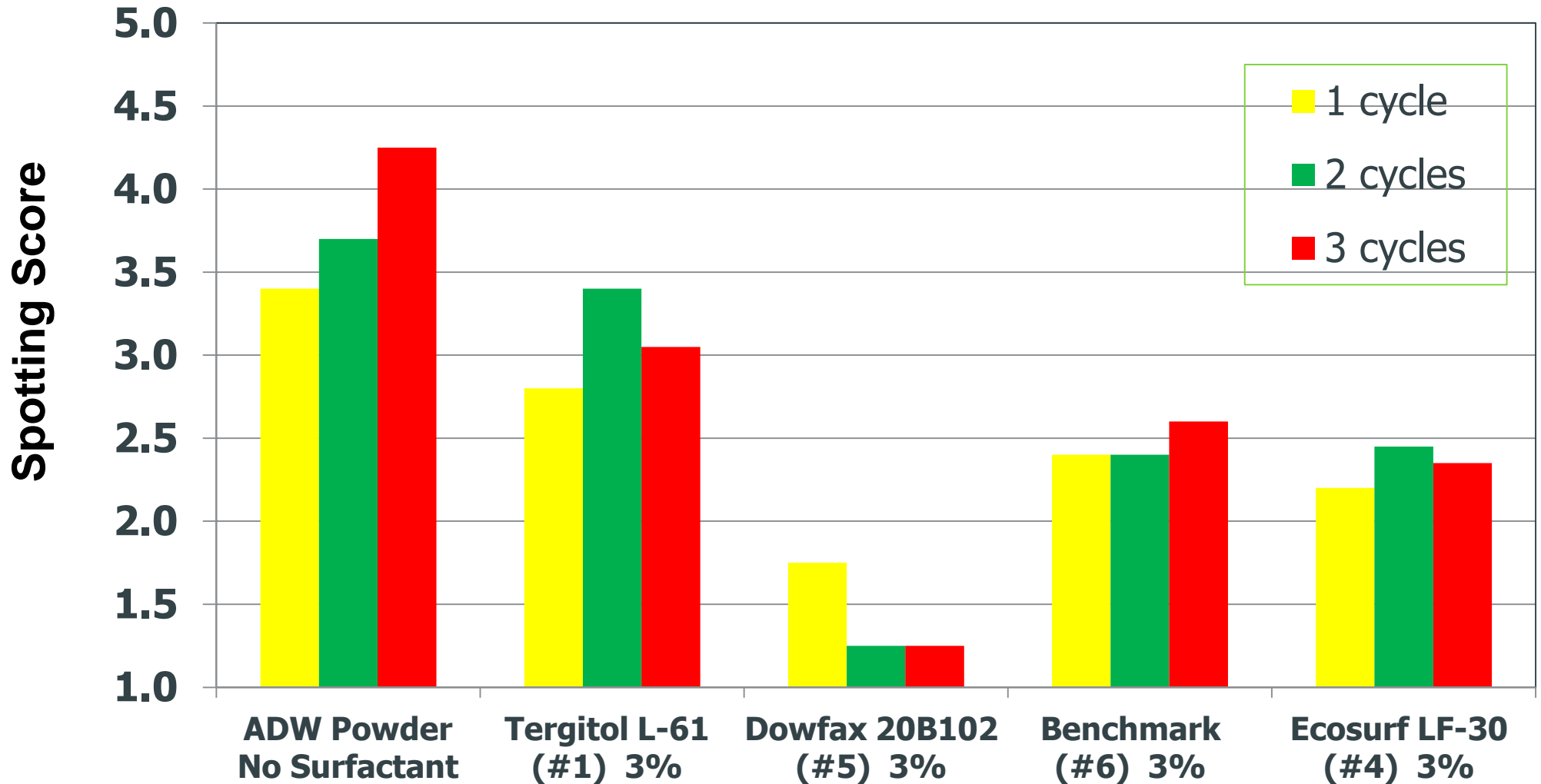
Automatic Dishwashing Conditions

Washing Parameters	
Dishwasher	Sears Kenmore
Cycle	Normal wash, 1-3 complete cycles
Temperature	55°C
Detergent Concentration	20 grams ADW Powder
Soil Load	40 grams ASTM (Milk/Margarine), added at time zero (start of the pre- wash cycle)
Water Hardness	17.1°GH (2/1 Ca/Mg)
Glassware	Libbey-Collins
Ballast Load	Ceramic plates, Fine China, Stainless Steel flatware, Plasticware
ASTM Rating	1 = clean, unwashed glass; 5 = heavily filmed or spotted



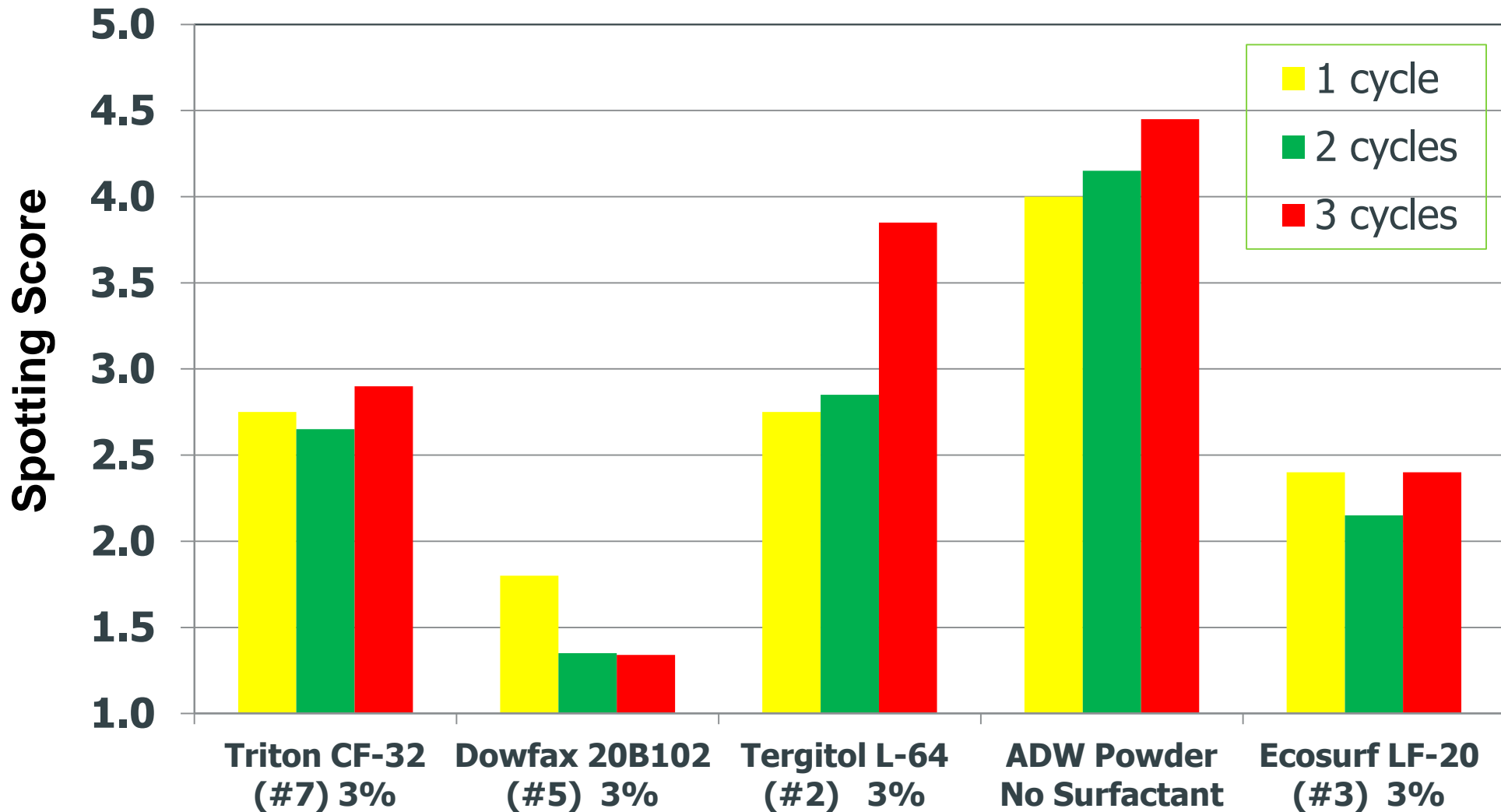
Non-Phosphate ADW Powder (Sachet)

Kenmore Dishwashers, 55°C, 300 ppm WH (2/1 Ca/Mg), 3 wash cycles, **ASTM Food Soil** (40 grams milk/margarine), 20 grams ADW Powder/Load, ASTM Rating System (1 = clean glass, 5 = heavily filmed)



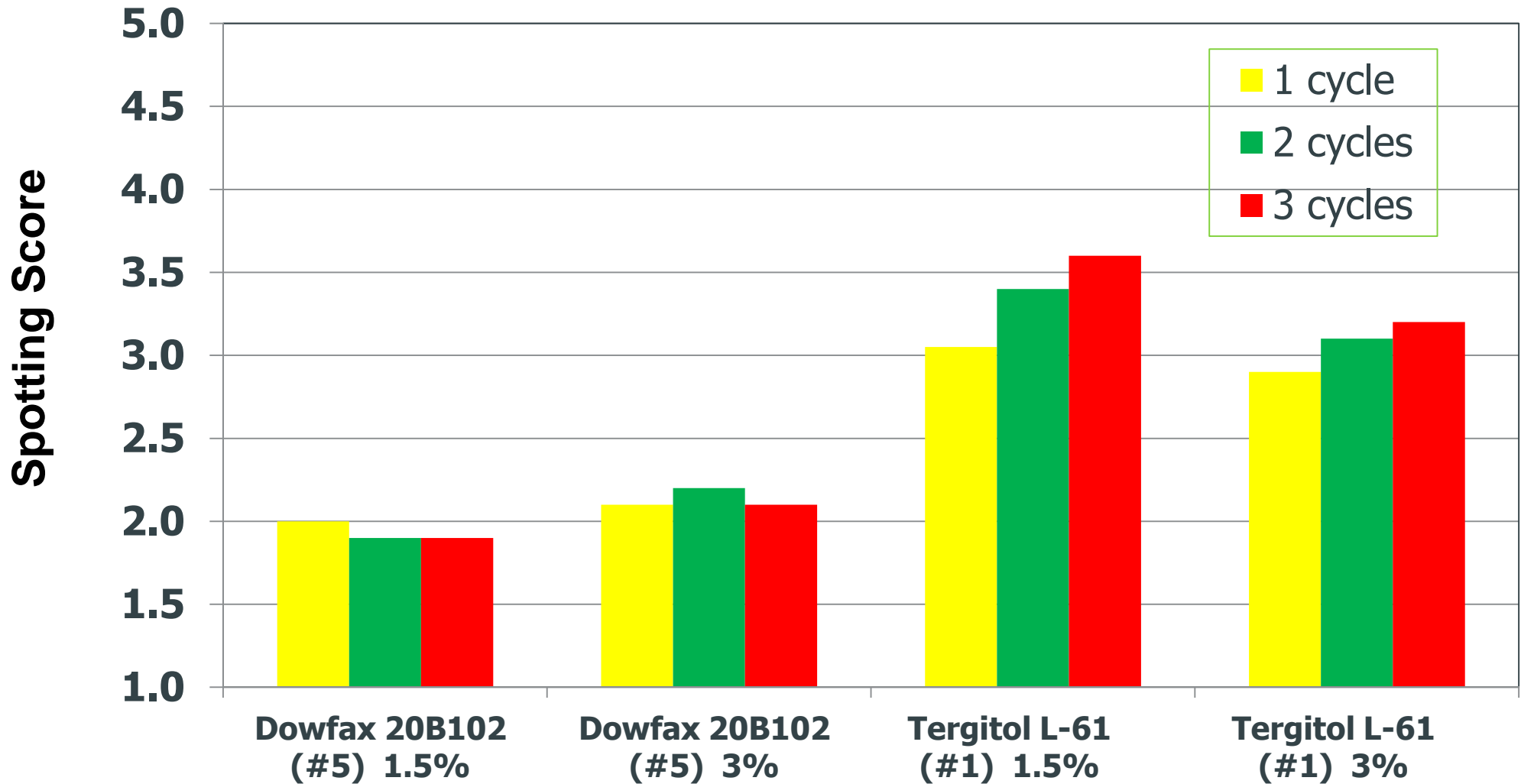
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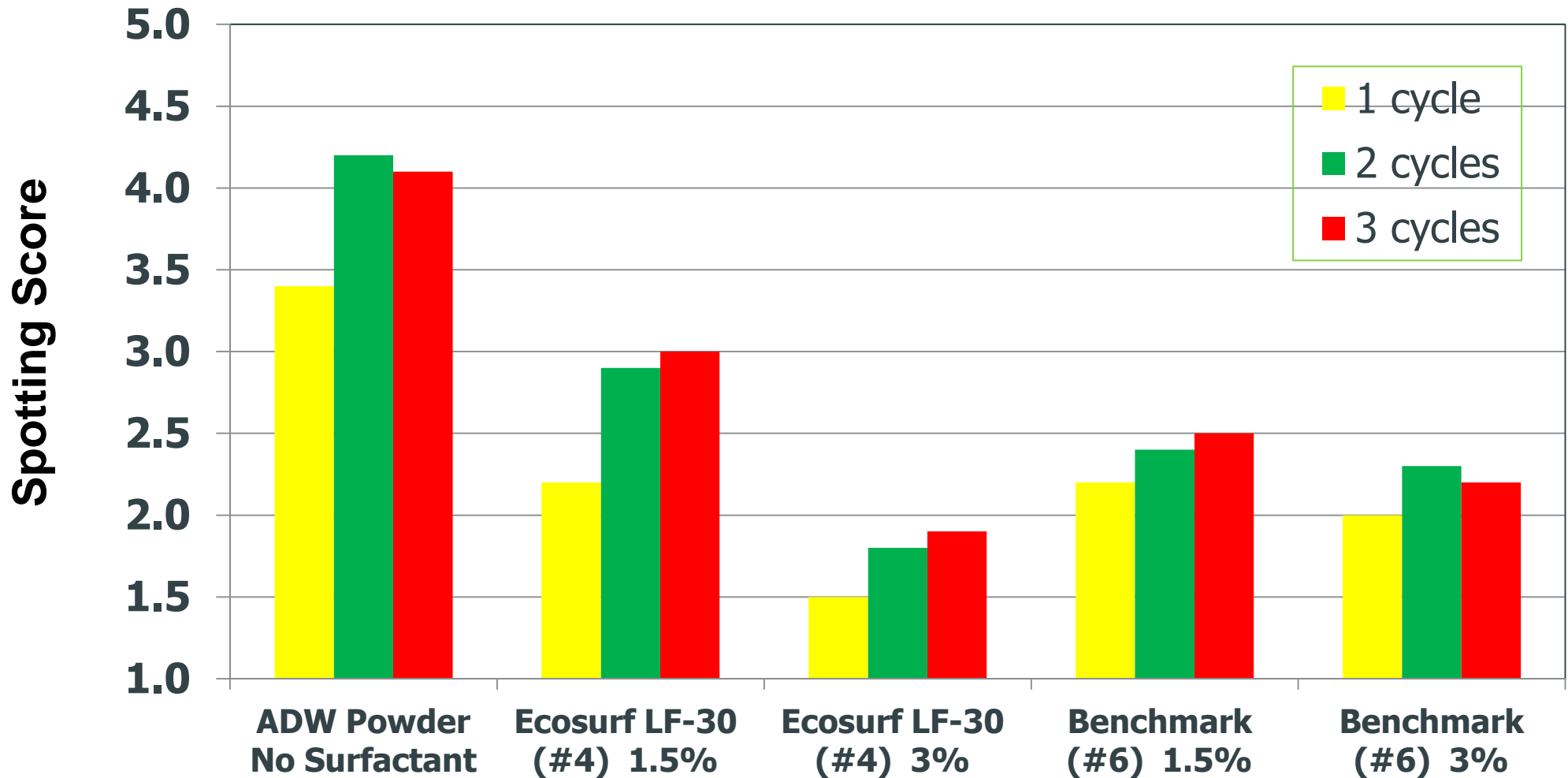
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Non-Phosphate ADW Powder (Sachet)

Kenmore Dishwashers, 55°F, 300 ppm WH (2/1 Ca/Mg), 3 wash cycles, **ASTM Food Soil** (40 grams milk/margarine), 20 grams ADW Powder/Load, ASTM Rating System (1 = clean glass, 5 = heavily filmed)



■ US Non-Phosphate ADWs - Conclusions

- **Dowfax 20B102 (#5) is clearly the best performing surfactant for spotting inhibition**
- **Performance at 1.5% surfactant solids is noticeably better than the current base containing a conventional nonionic alcohol alkoxylates (Benchmark, #6)**
- **Ecosurf LF-20 (#3) and Ecosurf LF-30 (#4) are also viable candidates under this testing protocol (utilizing the ASTM non-fat dry milk/margarine soil).**

Rinse Aid Evaluations

Surfactant Pool high chemical variety
Dow and competitive benchmark surfactants

1. Screening phase: Wetting characteristics small scale screen

2. Full Scale Test:

Surfactant added in rinse cycle

Starting point formulation

- 2.5% anh. citric acid
- 12% surfactant
- Qsp water



1. Shine on glass



2. Plastic drying

Surfactants in the Test

Designation	Chemistry	HLB
Tergitol 15-S-7	Secondary alcohol ethoxylate	12.4
Ecosurf EH-6	2- Ethyl hexanol alkoxyate	10.8
Ecosurf LF-20	Secondary alcohol alkoxyate	10-11
Ecosurf LF-30	Secondary alcohol alkoxyate	11-12
Ecosurf LF-45	Secondary alcohol alkoxyate	12-13
Dowfax 20A64	Linear alcohol alkoxyate	
Dowfax 20B102	Linear alcohol alkoxyate	11
Triton DF-12	Capped alcohol ethoxylate	10.6
Tergitol L-61	EO/ PO/EO Tri-block	3
Tergitol L-64	EO/ PO/EO Tri-block	15

✓ Different chemistries

✓ Different degree of ethoxylation in the same series.



Select best chemistry / properties in applications test

Benchmark 1	Alcohol ethoxylated propoxylated	Cloud point = 33°C
Benchmark 2	Alcohol ethoxylated propoxylated	

Rinse Aid Studies - Results

Dow surfactants: select best candidates from first screening round

Starting point formulation

- 2.5% anh. citric acid
- 12% surfactant
- Qsp water



Tergitol L-61 → Exceptional shine on glass
(excellent wetting)

Tergitol L-64 → Excellent drying on plastic



Calculation of drying properties (drying index calculation)

0 < drying index DI < 1

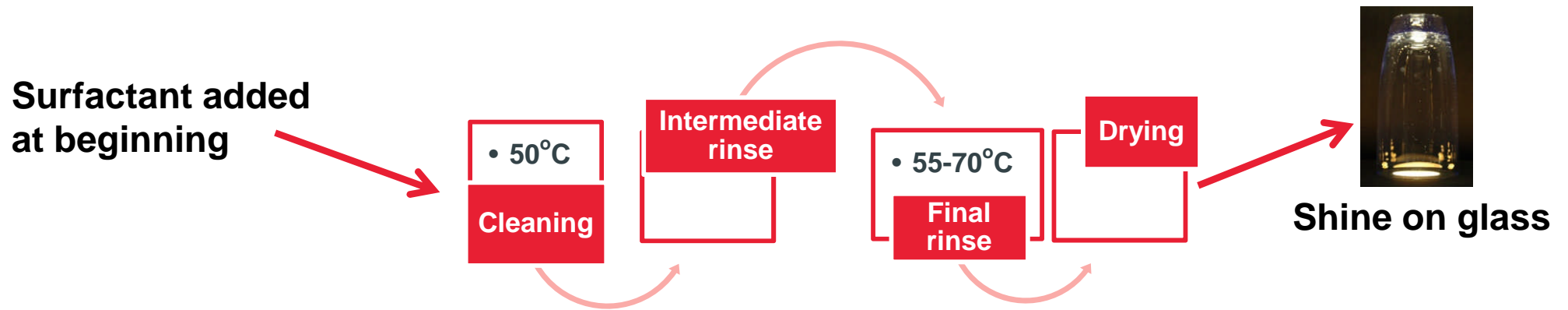
0 = wet dishes

1 = dry dishes

Surfactant	DI overall	DI porcelain	DI glass	DI cutlery	DI plastic
Tergitol L-64	0.82	0.82	0.98	0.98	0.49
Benchmark 1	0.82	0.84	0.85	0.99	0.50
Benchmark 2	0.69	0.60	0.65	0.95	0.32

Multi-Functional P-Free Detergent Study

- Evaluate rinse performance of non-ionic surfactants in multi-functional detergent vs. competitive samples



- Formulation
 - P-free powder formulation with organic builder MGDA

■ Multifunctional Phosphate-Free Formulation

Formula

<u>Ingredients</u>	<u>%</u>
Methylglycinediacetic acid (MGDA)	30
Sodium citrate	10
Sodium carbonate	20
Disilicate	10
Percarbonate	10
TAED	4
Surfactant	4
ACUSOL 588G	4
ACUSOL 420NG	2
ACUSOL 460ND	0.4
Protease	2.5
Amylase	1
HEDP	0.5
Sodium sulfate	Qsp 100

Spotting Results



Reference without surfactant

Wash conditions

Miele G1222 SC Labor

Water hardness = 37.5°FH, ratio Ca/Mg 3/1

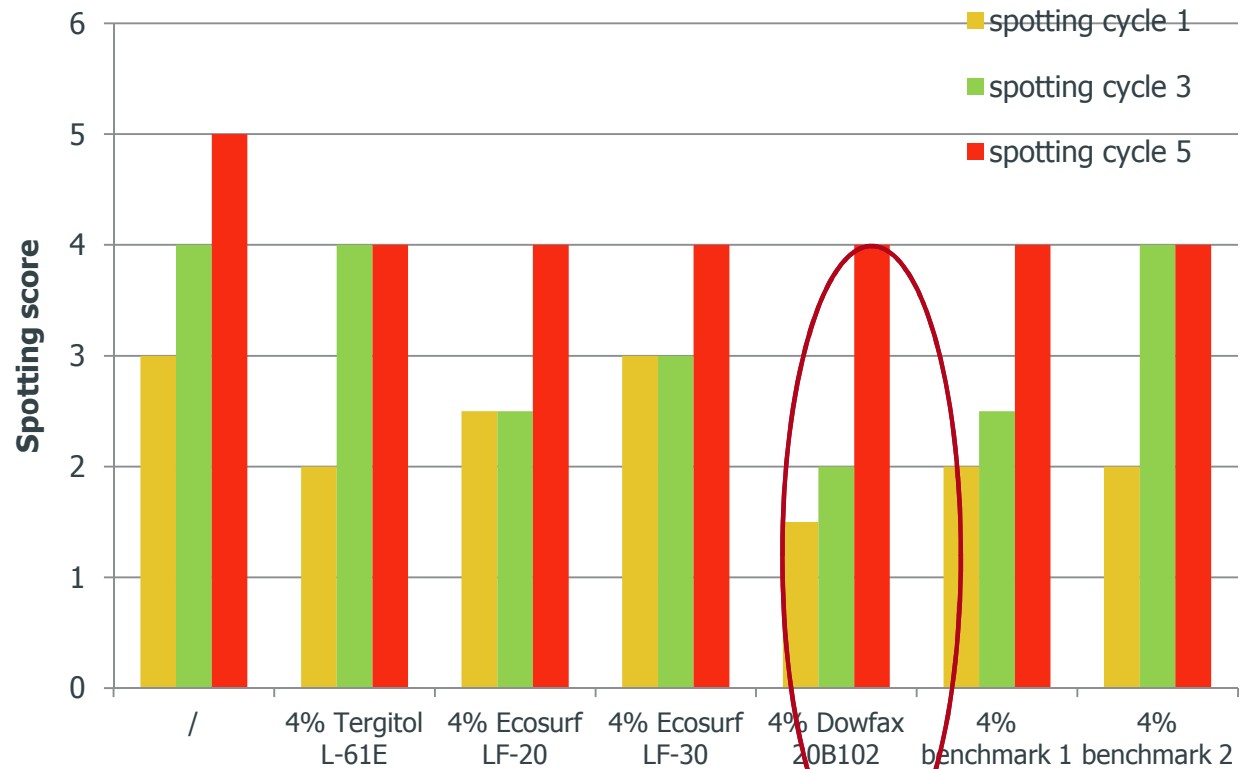
Wash temperature = 50°C (without prewash)

20g detergent per wash

With STIWA food soil (50g)

Rating: 1 = no spot; 5 = highly spotted

Spotting on Glassware



Dowfax 20B102



Benchmark 1

■ ER Non-Phosphate Formulation - Conclusions

We have found low foam surfactants with superior performance in automatic dishwashing applications:

1. In a rinse aid formulation...

- Tergitol L-61 and Tergitol L-64 provide for improved plastic drying and shiny glassware**

2. In a multifunctional, phosphate-free formulations...

- Ecosurf LF-20 (#3) and Dowfax 20B102 (#5) deliver reduced**

spotting and create shinier glasses

- With a performance on par or better than benchmark nonionic surfactants in the test**



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Thank You!

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STIWA Food Soil Composition

Ingredients for 1 kg (20 doses @ 50 grams/wash cycle)

- **25g ketchup**
- **25g mustard**
- **25g instant gravy**
- **5g starch**
- **1g benzoic acid**
- **3g egg yolk**
- **100g margarine**
- **50g milk (3.5% fat equivalent semi skimmed)**
- **700g tap water**