SPIGA nord
SOCIETA PRODUZIONE ITALIANA GLICERINE E AFFINI

Workshop on Glycerol Marketing Uses and Chemistry
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# *Polyglycerol chemistry and applications*

*Claudio Merlo*

# SPIGA NORD SPA, short presentation:

- Established in 1957 (Genoa), actually in Carasco (Ge)

- Manufactured products:

- Glycerol (min. 99,5% / min. 86,5%) for pharma / cosmetic / food applications

- Polyglycerols (Vegetable origin, Kosher)

  Diglycerine (also mentioned as PG2)

  Polyglycerine-3 (PG3)

  Polyglycerine-4 (PG4)

  Polyglycerine-6 (PG6)

# POLYGLYCEROL CHEMISTRY

*Summary:*

- *Definition*
- *Starting materials*
- *A mixture of oligomers*
- *Reaction path, first step*
- *Cyclic and side products*
- *Homogenous and heterogeneous catalysis*
- *Some physical characteristics*

## PG definition:

- *PGs are inter-molecular glycerol ethers formed by the condensation of "n" (2 or more) glycerol molecules with elimination of "n-1" water molecules.*

- Viscous, slightly hygroscopic liquid. Soluble in water, alcohols and glycerol in all proportions.
- Ether group C-O-C
- Hydroxyl group -OH
- Polarity
- Long chains (ref.: Glycerol)

# PG production: starting materials

| Reagent A | + | Reagent B | |
|---|---|---|---|
| Glycerol | | Epichlorohydrin * | * toxic compound |
| Glycerol | | Glycidol * | * toxic compound |
| Glycerol | | Glycerol carbonate ** | ** expensive, availability |
| Glycerol | | Glycerol | |

# PG production: a mixture of oligomers

Glycerol + Glycerol → Diglycerol + $H_2O$ $K_1$

Diglycerol + Glycerol → Triglycerol + $H_2O$ $K_2$

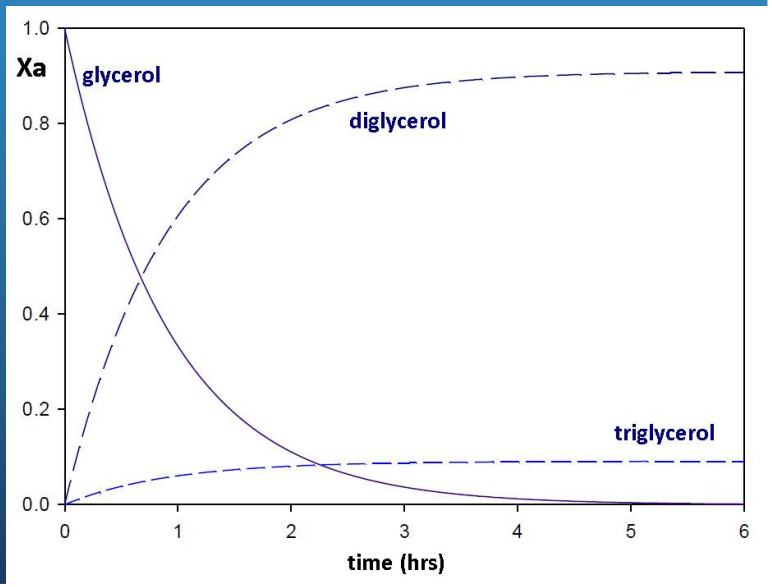
Triglycerol + Glycerol → Tetraglycerol + $H_2O$ $K_3$

Tetraglycerol + Glycerol → Pentaglycerol + $H_2O$ $K_4$

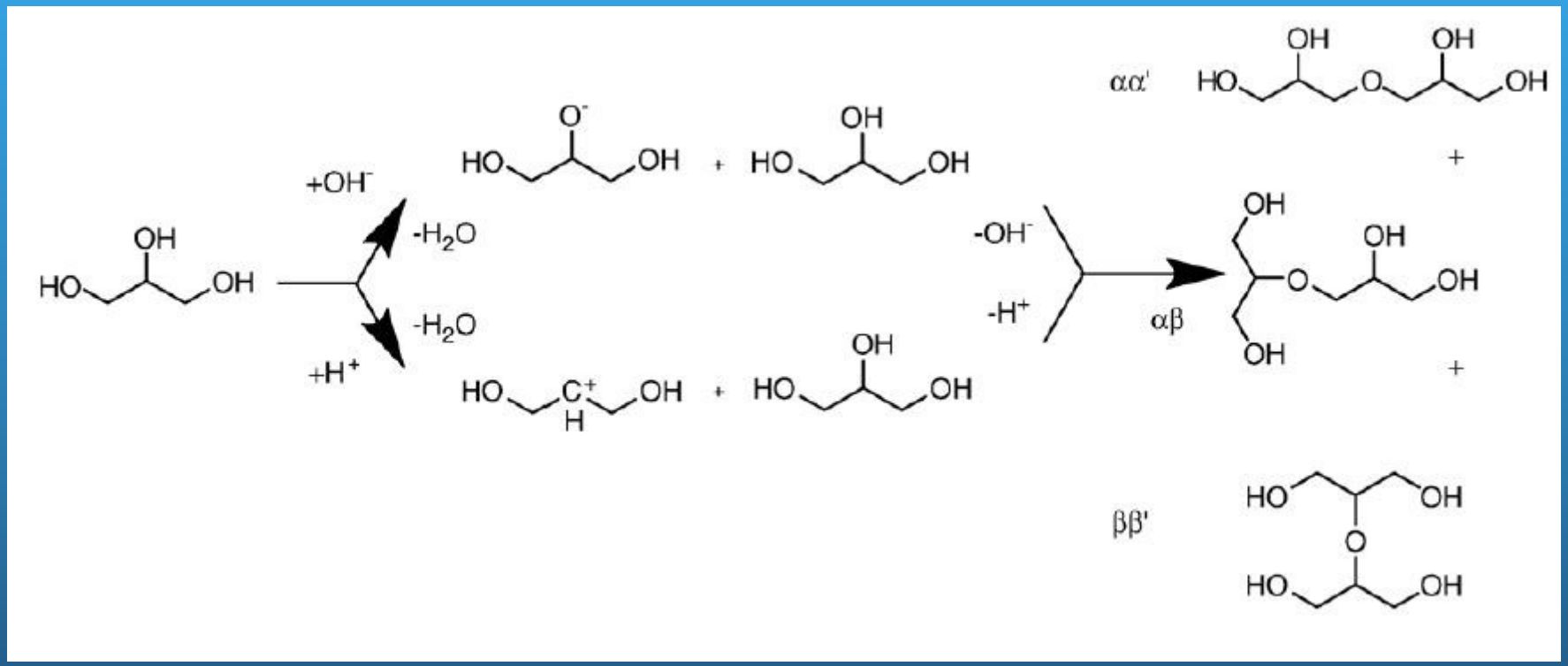
etc… etc…

Multi-step reactions:

consecutive + competing !

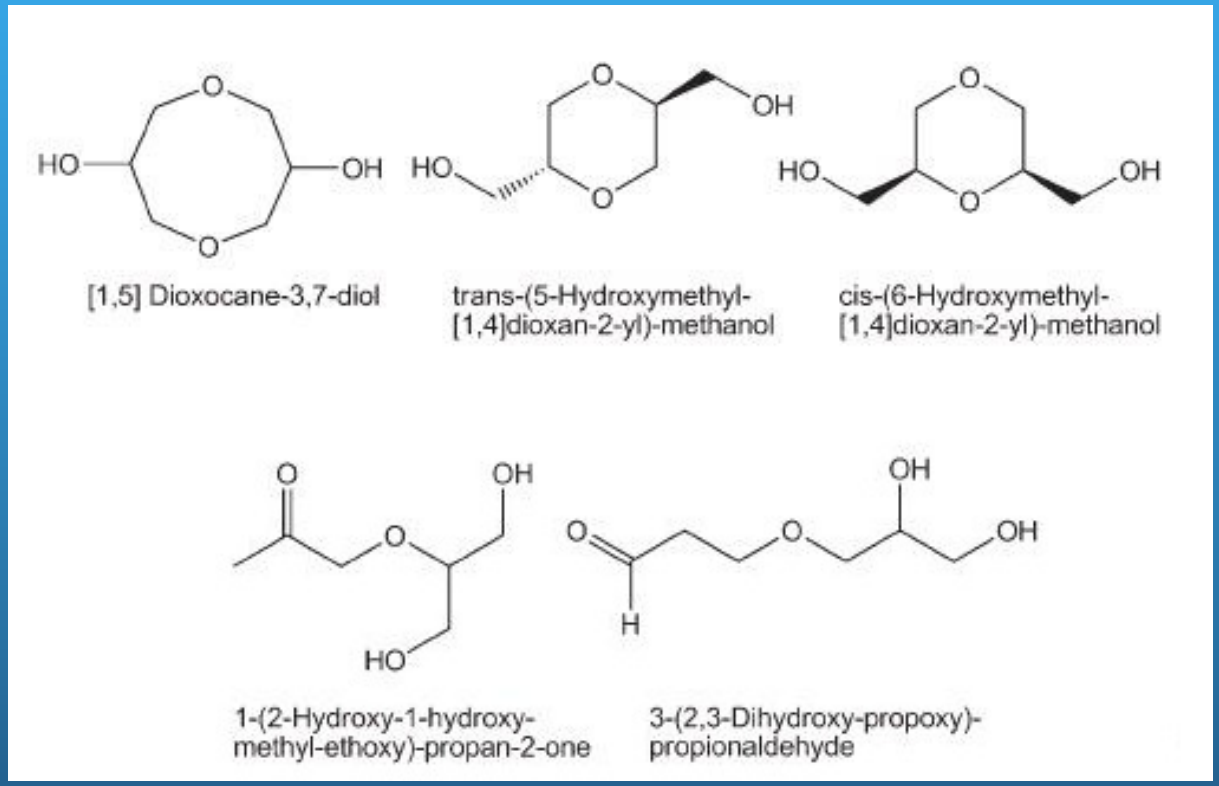


# PG production: reaction path, first step




Basic and acidic catalyzed reaction schematic paths of Glycerol conversion to Diglycerols

# PG production: cyclic and side products




Cyclic Diglycerol components and side-products (same chemical formula, $C_6H_{12}O_4$)

# PG production: homogenous catalysis

| Catalyst | $m_{Cat.}$ (wt%) | $T$ (°C) | $X_{Gly}$ (%) after t | $S_{Di}$ (%) | $S_{Tri}$ (%) | $S_{Tetra}$ (%) | $S_{Di,50}$ (%) |
|---|---|---|---|---|---|---|---|
| $Na_2CO_3$ | 2 | 240 | 76 (9 h) | 46 | 34 | 13 | 75 |
| NaOH | 2 | 240 | 63 (9 h) | 60 | 32 | 7 | n.a. |
| $Na_2CO_3$ | 2 | 260 | 96 (8 h) | 24 | 35 | 22 | 75 |
| $Na_2CO_3$ | 2 | 260 | 94 (8 h) | 27 | 31 | 21 | n.a. |
| $Na_2CO_3$ | 2 | 260 | 80 (8 h) | 31 | 28 | 17 | n. a. |
| $Na_2CO_3$ | n.a. | 220 | 80 (n.a.) | 45 | 36 | n. a. | 75 |
| $NaHCO_3$ | 0.2 | 260 | 75 (8 h) | 27 | 12 | 0 | 30 |
| $CsHCO_3$[a)] | 0.4 | 260 | 64 (8 h) | 23 | 9.5 | 2.5 | 75 |
| $Cs_2CO_3$[a)] | 0.7 | | 71 (8 h) | 39 | 19 | 6 | 75 |
| CsOH[a)] | 0.3 | 260 | 74 (8 h) | 32 | 21 | 5 | 75 |

Glycerol conversion with several alkaline homogeneous catalysts

# PG production: heterogeneous catalysis

| Catalyst | $m_{Cat}$ (wt%) | $T$ (°C) | $X_{Gly}$ (%) after $t$ | $S_{Di}$ (%) | $S_{Tri}$ (%) | $S_{Tetra}$ (%) | $S_{Di,50}$ |
|---|---|---|---|---|---|---|---|
| NaA[a)] | 2.4 | 240 | 84 (22 h) | 38.3 | 24.2 | n.a. | n.a. |
| NaX[b)] | 2.4 | 240 | 90.4 (22 h) | 34.2 | 24.3 | n.a. | n.a. |
| NaX[c)] | 4 | 260 | 68.8 (9 h) | 68 | 22 | n.a. | 80 |
| Na mordenite[d)] | 4 | 260 | 38.6 (9 h) | 73 | 22 | n.a. | n.a. |
| NaX[e)] | 2 | 260 | 100 (24 h) | 25 | 26 | 29 | 40 |
| NaY[f)] | 2 | 260 | 79 (24 h) | 47.5 | 18.5 | 8 | 38 |
| NaBeta[g)] | 2 | 260 | 52.5 (24 h) | 44.5 | 7.2 | 0 | 50 |
| $Na_{impr}$.MCM-41[h)] | 2 | 260 | 85 (16 h) | 63 | 30 | n.a. | 86 |

[a)] $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27\ H_2O$, Si/Al = 1,
[b)] $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264\ H_2O$, Si/Al = 1.2,
[c)] Si/Al = 1.2, surface area 780 $m^2/g$, 100% Na exchanged,
[d)] Si/Al = 5, surface area 330 $m^2/g$, 100% Na exchanged,
[e)] Si/Al = 1.1, surface area 868 $m^2/g$,
[f)] Si/Al = 2.3, surface area 918 $m^2/g$,
[g)] Si/Al = 12.9, surface area 655 $m^2/g$,
[h)] Si/Al = 20, Na = 2.5 mmol/g.
n.a.: data not available. $S_{Di,50}$ is the diglycerol selectivity at 50% glycerol conversion.

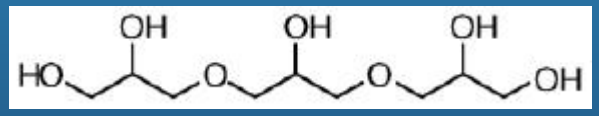
Glycerol conversion with several heterogeneous catalysts

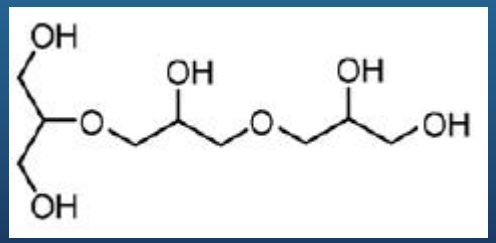
# PG physical characteristics

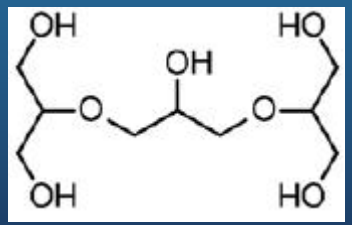
| Name | Molecular formula/ weight (g/mol) | Refractivity $n_D^{20}$ (-) | Density (g/cm$^3$) | Boiling point (°C)/(Pa) | Hydroxyl number[a] (mg KOH/g) |
|---|---|---|---|---|---|
| Glycerol | $C_3H_8O_3$ 92 | 1.4720 | 1.2560 | 290 | 1830 |
| Diglycerol | $C_6H_{14}O_5$ 166 | 1.4897 | 1.2790 | 205/133 | 1352 |
| Triglycerol | $C_9H_{20}O_7$ 240 | 1.4901 (40°C) | 1.2646 (40°C) | >250 /13.3 | 1169 |
| Tetraglycerol | $C_{12}H_{26}O_9$ 314 | 1.4940 (40°C) | 1.2687 (40°C) | 69–73 (melting point) | 1071 |
| Polyglycerol-3 | | 1.4910 | 1.2840 | – | – |

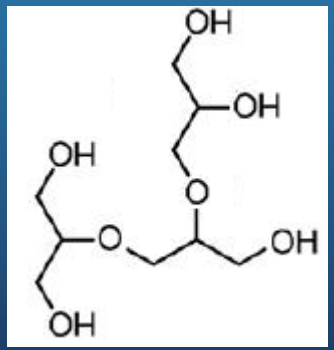
[a] The hydroxyl number is defined as the mg of KOH equivalent to the hydroxyl content of 1 g of sample.

Physical data of Diglycerol and other oligomers









Some Triglycerol linear + branched structures

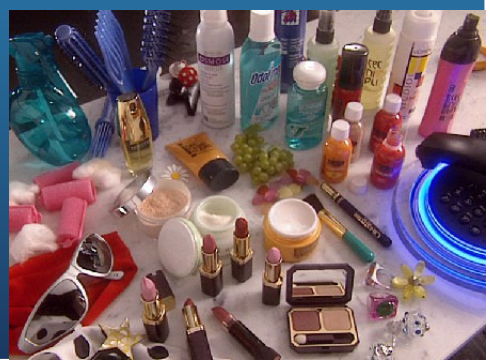
# POLYGLYCEROL APPLICATIONS

*Summary:*

- *PG in personal care products*
- *PG in foodstuffs*
- *PG for technical applications*
- *REACH status*

## PG IN PERSONAL CARE PRODUCTS: WHY?

- Development of “green” formulations (PEG free)
- Large variety of emulsifiers (PG chains+$C_8$/$C_{18}$ FA)
- Stability of emulsions
- Cold process manufacture
- W/O emulsions with high water content
- Low irritating and toxic potential

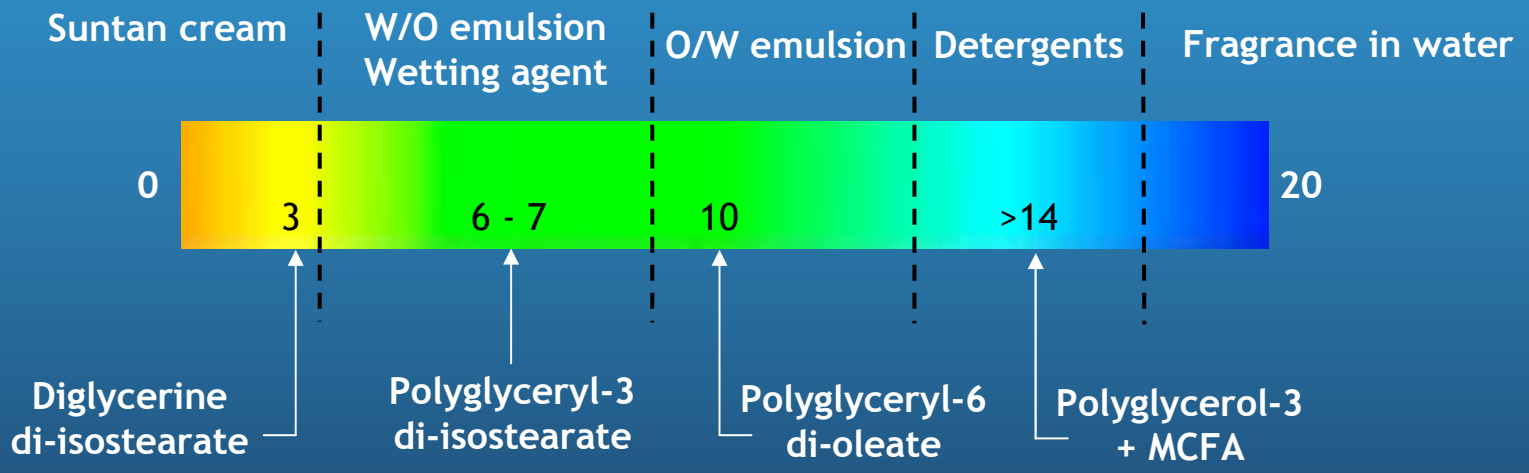


**HLB** (Hydrophilic-Lipophilic Balance) = $20x\left(\frac{M_h}{M}\right)$ (Griffin's definition)

Range: from 0 (fully lipophilic) to 20 (fully hydrophilic)

It is affected by:

- no. of polymerized glycerol chains and fatty acid length
- esterification degree (mono-esters, di-esters, etc.)
- types of esterified fatty acids (saturated, unsaturated or polyunsaturated)



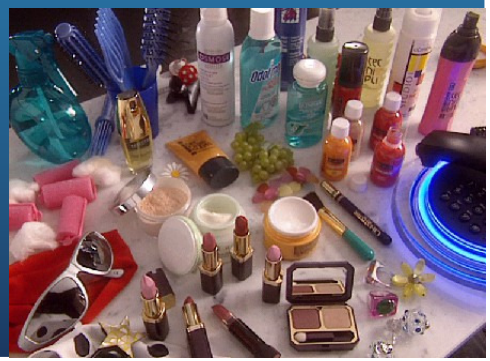
# PG IN PERSONAL CARE PRODUCTS: HOW?

PG (direct use):

- Solvent for fragrances (non volatile)
- Skin moisturizer (less irritant than Glycerol)

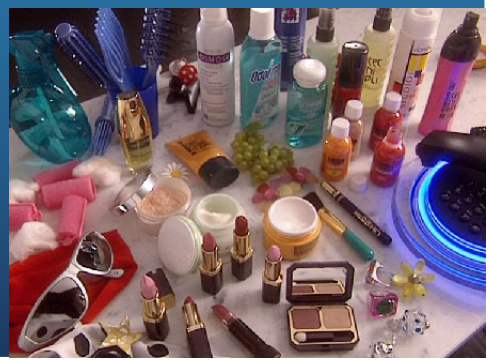
PG Esters:

- Non-ionic emulsifier, dispersant
- Emollient
- Wetting agent
- Thickener



# PG IN PERSONAL CARE PRODUCTS: HOW MUCH?

Total of pure PG + PGEsters = **0,5……5 % AND MORE!**



## PG IN FOODSTUFFS: WHY?

- Unesterified PG is not considered as direct food additive but…
- PG Esters are well-recognized food additives:

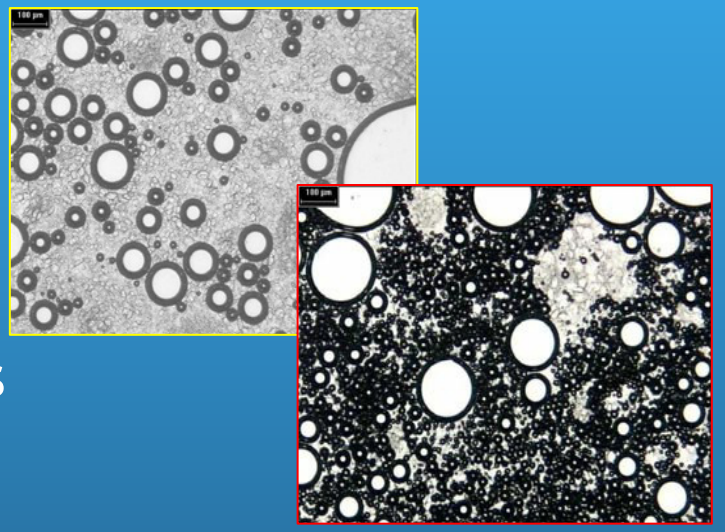
- EU: E475, E476

- US: CFR title 21, sect. 172.854

- PG Esters are versatile products: emulsifiers, fat-substitutes, effects on foodstuff's rheology, other

# PG IN FOODSTUFFS: WHERE?

- Margarines
- Cakes
- Baked products
- Chocolate, ice-creams
- Creams
- Fat-substitution



# PG IN FOODSTUFFS: WHO?

| | E475<br>(PG esters of fatty acids) | E476<br>(PG polyricinoleate) |
|---|---|---|
| | produced by esterification of PG with food fats/oils or with FA from fats/oils | prepared by esterification of PG with condensed castor oil FA |
| Polyol composition | mainly di-, tri-, tetra- | min. 75% |
| Hepta- and highers | max. 10% | max. 10% |
| Free glycerol and polyglycerol | max. 7% | - |
| F.F.A. | max. 6% | max. 6 (acid value) |
| Heavy metals | limit for arsenic, lead, mercury, cadmium | limit for arsenic, lead, mercury, cadmium |

## PG IN FOODSTUFFS: HOW MUCH?

PGEsters = **0,1.....2 %!**

## PG (PG DERIVATIVES) FOR TECHNICAL APPLICATIONS TOO?

- Additive for polymers:

  plasticizer, anti-fogging agent, anti-static, lubricant

- Additive for technical fluids:

  drilling fluids, hydraulic media, lubricant

- Additive for detergents (surfactant)

# PG / PG DERIVATIVES REACH STATUS

- *All polymers are exempt from REACH registration and evaluation*
- REACH definition of a *polymer*: "A substance consisting of molecules characterised by the sequence of one or more types of monomer units…distributed over a range of molecular weights…with a simple weight majority (>50%) of molecules containing at least three monomer units. No single molecules have the simple weight majority (>50%).
- Available composition of polyglycerol are placed into the market in the edge of polymer definition. Diglycerol and Polyglycerol-3 are considered *"standard substances"* and a registration dossier was been submitted. Longer chain polyglycerols (PG4, PG6) matches polymer definition.
- According to the a.m. polymer definition Diglycerol Esters are considered *"standard substances"* whereas PG3 Esters matches *polymer definition*

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# THANK YOU!

References


•Slide 7 - *A. Martin et al. / Catalysis Communications 25 (2012) 130-135*

•*Slides 8, 9, 10, 11 - Eur. J. Lipid Sci. Technol. 2011, 113, 100-117*

• Emulsifiers in food technology