A view on co-formulants – regulations and influence on formulation type
Regulations on co-formulants (in Europe and Germany)

Influence on formulation type

Co-formulants = formulants = inerts

Any substance (or mixture of substances)
other than the active ingredient
that is intentionally included in a formulation.

Examples:
Solvents, emulsifiers, carriers, antifoaming agents, dyes …
Statistics

- 273 active ingredients
- 1450 co-formulants (inerts)
- 224 adjuvants
- 44 formulation types (out of 63 defined)

(January 2015)
Challenges

• Co-formulants are difficult to handle for the regulation authorities (often no detailed information / only SDS)

• The applicants / formulators do not have all information in hand

• In general, the analytical determination of co-formulants is challenging
**US EPA**

Approved inerts (food or non-food use)

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**Europe**

Unacceptable co-formulants
Unacceptable co-formulants

A co-formulant should not be accepted where

- Its residues have a harmful effect on human or animal health or on groundwater or environment,
- Its use has a harmful effect on human or animal health or on groundwater or environment,

- Unacceptable co-formulants will be included into Annex III of Regulation (EC) no 1107/2009,

- The Commission may review co-formulants at any time.
Implementation

• National provisions may be applied until June 2016
• After that each Member State may prohibit or restrict the use of a co-formulant for a specified time

• In March 2012 Commission asked Member States to notify unacceptable co-formulants
• Proposals were prepared by two Member States
Following criteria were proposed:

- Restrictions according to the EU chemical legislation
- Cut-off criteria as given for active substances
- Classification as carcinogen, mutagen or toxic for reproduction category 2
- Classification for specific target organ toxicity after repeated exposure (STOT-RE) category 1, especially if a co-formulant shows other chronic effects or immunotoxicity or neurotoxicity
- Concerns within the assessment according to the Regulation (EC) No 1907/2006 (REACH) or No 1272/2008 (CLP),
- Co-formulants that contain impurities/additives/constituents of toxicological relevance above an established limit.
### Unacceptable co-formulants - Examples

Following substances are candidates for Annex III:

<table>
<thead>
<tr>
<th>Substance</th>
<th>CARC 1B</th>
<th>MUTA 1B</th>
<th>Destillates (mineral oil)</th>
<th>CARC 1B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solventnaphtha 64742-95-6</td>
<td>CARC 1B</td>
<td>MUTA 1B</td>
<td>64742-54-7</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>64742-52-5</td>
<td></td>
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<td></td>
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<td></td>
<td>64742-55-8</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>64742-65-0</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>64741-88-4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>64742-53-6</td>
<td></td>
</tr>
<tr>
<td>N-Methyl-2-pyrrolidone 872-50-4</td>
<td>REPR 1B</td>
<td></td>
<td>disodium tetraborate decahydrate, orthoboric acid, sodium salt</td>
<td>REPR 1B</td>
</tr>
<tr>
<td>2-Methoxypropanol-1 1589-47-5</td>
<td>REPR 1B</td>
<td></td>
<td>1303-96-4</td>
<td></td>
</tr>
</tbody>
</table>
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- Cut-off criteria as given for active substances
- Classification as carcinogen, mutagen or toxic for reproduction category 2
- Classification for specific target organ toxicity after repeated exposure (STOT-RE) category 1, especially if a co-formulant shows other chronic effects or immunotoxicity or neurotoxicity
- Restrictions according to the EU chemical legislation
- Concerns within the assessment according to the Regulation (EC) No 1907/2006 (REACH) or No 1272/2008 (CLP)
- Co-formulants that contain impurities/additives/constituents of toxicological relevance above an established limit.
Content of impurities / additives / substances of toxicological relevance:

- **oil-derived substances**
  (benzene 0.1 %, 1,3-butadiene 0.1 %, benz(a)pyrene 0.005 %, DMSO extract 3 %, naphthalene 1 %, toluene 3 %),

- **quartz sand, kieselgur, diatomaceous earth, Al-silicates**
  (crystalline silica 0.1 %),

- **Attapulgite, talc**
  (fibers > 5 μm).
Expectations

• Up to now Annex III is empty

• Low priority

What will happen?

• transition rules

• Rules apply for new applications

• For existing authorisations, authorisation holders will be informed, with request for formulation change
Unacceptable co-formulants - Germany

- Ethoxyethanol, 2- = Ethylenglykolmonoethylether = Ethylglykol
  - Codes: 110-80-5
- Methoxyethanol, 2- = Ethylenglykolmonomethylether = Methylglykol
  - Codes: 109-86-4
- Methoxyethylacetat, 2- = Ethylenglykolmonoethyletheracetat = Methylglykolacetat
  - Codes: 110-49-6
- Methoxypropanol-1, 2-
  - Codes: 1589-47-5
- Ethoxyethylacetat, 2- = Ethylglykolacetat
  - Codes: 111-15-9
- Dimethylformamid, N,N-
  - Codes: 68-12-2
- Epichlorhydrin = Chlor-2,3-epoxypropan, 1-
  - Codes: 106-89-8

Steinkohlenteeröle
- Benzol
  - Codes: 71-43-2
- Trichlorethan, 1,1,1- = Methylchloroform
  - Codes: 71-55-6
- Trichlorethan, 1,1,2-
  - Codes: 79-00-5
- Tetrachlorethan, 1,1,2,2-
  - Codes: 79-34-5
- Tetrachlorethan, 1,1,1,2-
  - Codes: 630-20-6
- Tetrachlormethan = Tetrachlorkohlenstoff
  - Codes: 56-23-5
- Pentachlorethan
  - Codes: 76-01-7
- Trichlorfluormethan (R 11)
  - Codes: 75-69-4
- Dichlordifluormethan (R 12)
  - Codes: 75-71-8
- Chlordifluormethan (R 22)
  - Codes: 75-45-6
- 1-[(2-Methoxyphenyl)azo]-2-naphthol
  - Codes: 1229-55-6
- Nonylphenoletoxylate
  - Codes: 009016-45-9 etc. 009036-19-5
Example: POE-Tallowamines

Wetting agent - mainly in formulations containing Glyphosate

First technical discussion in 2008

2014: last POE-Tallowamine containing glyphosate formulation

Other candidates:

Tetrahydrofurfuryl alcohol (THFA), CAS 97-99-4 (Repr. 2)

N-methyl-2-pyrrolidone (NMP), CAS 872-50-4 (Repr. 1B)
DC or SC?

SC  A stable suspension of active ingredient(s) with water as the fluid, intended for dilution with water before use.

DC  A liquid homogeneous formulation to be applied as a solid dispersion after dilution in water. (Note: there are some formulations which have characteristics intermediate between DC and EC).

A question of solvent…
How much water transforms an EC to an EW?

EW  A fluid, heterogeneous formulation consisting of a solution of pesticide in an organic liquid dispersed as fine globules in a **continuous water phase**.

Formulation containing 15 g/L water

Manufacturer stated it to be an EW.

Indeed it is a EC – for 1.5 % water may not form a continuous phase!

→ There is a FAO specification for EW requiring wet sieve test!
Formulation:

active ingredient: 25 g/L
vegetable oil: 200 g/L
water: 620 g/L
other co-formulants: 150 g/L

Use concentration: 0,4 – 0,6 % v/v
Concentration a.i. in spray tank: ca. 125 mg/L
Concentration a.i. in spray tank: ca. 125 mg/L

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>ca. 40 mg/L</td>
</tr>
<tr>
<td>Acetone</td>
<td>&gt;250 g/L</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td>250 g/L</td>
</tr>
<tr>
<td>Heptane</td>
<td>1 g/L</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>250 g/L</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>100 g/L</td>
</tr>
<tr>
<td>Xylene</td>
<td>50 g/L</td>
</tr>
<tr>
<td>Octanol</td>
<td>100 g/L</td>
</tr>
<tr>
<td>Toluol</td>
<td>50 g/L</td>
</tr>
<tr>
<td>Methanol</td>
<td>250 g/L</td>
</tr>
<tr>
<td>SC</td>
<td>A stable suspension of active ingredient(s) with water as the fluid, intended for dilution with water before use.</td>
</tr>
<tr>
<td>SE</td>
<td>A fluid, heterogeneous formulation consisting of a stable dispersion of active ingredient(s) in the form of solid particles and of water-non miscible fine globules in a continuous water phase.</td>
</tr>
<tr>
<td>EW</td>
<td>A fluid, heterogeneous formulation consisting of a solution of pesticide in an organic liquid dispersed as fine globules in a continuous water phase.</td>
</tr>
<tr>
<td>SL</td>
<td>A clear to opalescent liquid to be applied as a solution of the active ingredient after dilution in water. The liquid may contain water-insoluble formulants.</td>
</tr>
</tbody>
</table>
Can a dispersing agent transform an SG to an WG?

*Using a dispersing agent to accelerate the dispersion of the granules in a first step was the reason to denote the formulation initially as a water dispersible (WG) granule.*

*However, based on the water solubility of the active substance and the formulants compared to a maximum in use concentration, it can be also regarded as a water soluble granule (SG).*

*Thus the assignment of the formulation type depends on the interpretation of the definition of both, WG and SG.*
Applicant must give information on co-formulants

Manufacturer of co-formulant:

Water:

GOD
Ευχαριστώ!

Comments / questions?

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