Preservation of paints and coatings
Current regulatory developments and challenges

2019-09-19

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What is a biocide?

- „Biocidal product“ means any substance or mixture with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action.

- Bacillus spec. (bacteria)
- Rhodotorula rubra (yeast)
- Aspergillus niger (mold)
- Desmodesmus subspicatus (algae)
Why do paints need biocides?

Water is life…

…as well for fungi & bacteria

…as in the can

Consist mainly of water

Remain in the can for months

Have to be protected from microbial contamination

Paints
Why are biocides regulated?

The Biocidal Products Regulation (BPR, Regulation (EU) 528/2012) concerns the placing on the market and use of biocidal products […].

This regulation aims to improve the functioning of the biocidal products market in the EU, while ensuring a high level of protection for humans and the environment.*

*Source: https://echa.europa.eu/regulations/biocidal-products-regulation/understanding-bpr
Hazard based intrinsic substance classifications have direct regulatory consequence in BPR

Classification and Labeling

- CMR 1 or ED
- PBT or vPvB
- two of PBT
- Resp. sens.
- e.g. dermal sensitizer cat 1

Biocidal Product Regulation

- Active substance can only be approved under derogations (exposure, socio-eco)
- No DIY use permitted
- Comparative assessment for biocidal products
- Shorter approval period (BP max. 5, AI max. 7)
- Sensitizers will not be approved for DIY uses above set concentration limit (SCL)

Exclusion criteria fulfilled

Candidate for substitution

SCL
But:
What about risk assessment?
Hazard exclusion not balanced by a risk assessment reduces choice of available biocides

Evaluation of risks

- GHS-CLP is a hazard based evaluation whereas BPR is a risk based evaluation
- The risks of biocides are being evaluated within the approval process in BPR
- BPR should focus on individual risk assessments than limiting biocides based on GHS-CLP

Really dangerous?
Excursus Methylisothiazolinone (MIT): Restrictions for DIY use are the main concern

- New SCL of 15 ppm for MIT
- Effective May 1, 2020: MIT > 15ppm = H317
- Restrictions for DIY use could be possible → Legally binding after MIT BPR approval (2022)

* ATP – Adaptation to technical progress
** Within the whole implementation period it is allowed to produce, store, ship and sell any material according to old law
The few remaining biocides should be kept alive for the paint industry.
From 50 registered active ingredients in PT 6 only a few are appropriate for industrial preservation

- **Isothiazolinones**
  - BIT
  - CMIT/MIT
  - MIT
  - OIT
  - MBIT

- **Pyridine Derivates**
  - Zinc pyrithione
  - Sodium pyrithione

- **Formaldehyde Releaser**
  - O-formal
  - N-formal

- **Activated Halogen Comp.**
  - Bronopol
  - DBDCB
  - DBNPA
Only few active ingredients remain for in-can preservation

- **Isothiazolinones**
  - BIT
  - CMI/MIT
  - MIT
  - OH
  - MBIT

- **Pyridine Derivates**
  - Zinc pyrithione
  - Sodium pyrithione

- **Formaldehyde Releaser**
  - O-formal
  - N-formal

- **Activated Halogen Comp.**
  - Bronopol
  - DBDCB
  - DBNPA

Future uncertain

Repro. 1b

Without H317 ≤ 15 ppm no efficacy given

Rather for curative treatment
Combination products of the remaining actives necessary to achieve sufficient efficacy

### Isothiazolinones
- BIT
- CMIT/MIT
- MIT
- OIT
- MBIT

### Pyridine Derivates
- Zinc pyrithione
- Sodium pyrithione

### Activated Halogen Comp.
- Bronopol
- DBDCB
- DBNPA

- BIT is a stable combination partner
- CMIT/MIT will experience revival
- Bronopol and DBDCB – no IT → good alternative
- ZPT and NaPT – future uncertain

Without H317 ≤ 15 ppm no efficacy given

Future uncertain Repro. 1b

Rather for curative treatment
Options for H317 labeling free preservation still existing – for how long?

<table>
<thead>
<tr>
<th>BIT + CMIT/MIT</th>
<th>DBDCB + BIT + CMIT/MIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Preventol® BIT IT</td>
<td>- Preventol® DBC</td>
</tr>
<tr>
<td>- Fast acting</td>
<td>- Fast acting biocide with long-term efficacy</td>
</tr>
<tr>
<td>- Broad efficacy</td>
<td>- Very broad efficacy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DBDCB + Bronopol</th>
<th>BIT + IBPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Biochek® 722</td>
<td>- Preventol® BI</td>
</tr>
<tr>
<td>- Completely free from Isothiazolinones</td>
<td>- Broad spectrum with long-term efficacy</td>
</tr>
<tr>
<td>- Long-term efficacy</td>
<td>- No CMIT/MIT</td>
</tr>
<tr>
<td>Active</td>
<td>Description</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>DGH (Cas No. 13590-97-1)</strong></td>
<td>Dodecyl Guanidin Hydrochlorid</td>
</tr>
<tr>
<td>- Broad spectrum</td>
<td></td>
</tr>
<tr>
<td>- Main application – water treatment</td>
<td></td>
</tr>
<tr>
<td>- Kationic molecule</td>
<td></td>
</tr>
<tr>
<td>- In compatibel with anionic additives</td>
<td></td>
</tr>
<tr>
<td>- Registered for PT6 and PT11</td>
<td></td>
</tr>
<tr>
<td><strong>OPP Biphenyl-2-ol (Cas. No. 90-43-7)</strong></td>
<td>Mainly fungicide</td>
</tr>
<tr>
<td>- High pH and temp. Stability</td>
<td></td>
</tr>
<tr>
<td>- Effective in dirty environment</td>
<td></td>
</tr>
<tr>
<td>- Discoloration and pH shift possible</td>
<td></td>
</tr>
<tr>
<td>- Registered for PT1-7, 9, 10, 13</td>
<td></td>
</tr>
<tr>
<td><strong>PCMC / CMK Chlorocresol (Cas No. 59-50-7)</strong></td>
<td>Broad spectrum efficacy</td>
</tr>
<tr>
<td>- High pH and temp. Stability</td>
<td></td>
</tr>
<tr>
<td>- Effective in dirty environment</td>
<td></td>
</tr>
<tr>
<td>- pH shift + phenolic smell possible</td>
<td></td>
</tr>
<tr>
<td>- Registered for PT 1-3, 6, 9, 13</td>
<td></td>
</tr>
</tbody>
</table>
Eight actives relevant for dry film protection

**Fungicides**

- Isothiazolinones
  - OIT
  - DC OIT

- Others
  - IPBC
  - Zinc pyrithione
  - Carbendazim
  - Thiabendazol

**Algicides**

- Diuron
- Terbutryn
- Isoproturon
Eight actives relevant for dry film protection

**Fungicides**
- Isothiazolinones
  - OIT
  - DC OIT
    - \(^{SCL = 15 \text{ ppm}}\)
- Others
  - IPBC
  - Zinc pyrithione
  - Carbendazim
  - Thiabendazol

**Algicides**
- Diuron
- Terbutryn
- Isoproturon

- Paints with OIT and DC OIT has to be labelled in future
- Repro. 1B substances very likely banned for consumer products
- Fate of algicides still unclear
Biocide under several labels
Several labels make the use of biocides more complicated

<table>
<thead>
<tr>
<th>EU Ecolabel 2014</th>
<th>Nordic Swan 2015 - 2021</th>
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<tbody>
<tr>
<td>▪ Restricted hazard classifications</td>
<td>▪ Only interior</td>
</tr>
<tr>
<td>▪ Total biocide level limited to 600ppm indoor, 3600 ppm outdoor</td>
<td>▪ No bioaccumulatives</td>
</tr>
<tr>
<td>▪ Sum IT = 500ppm, BIT 500ppm, MIT 200 ppm, OIT 500 ppm, CMIT/MIT 15 ppm</td>
<td>▪ Total biocide level max. 700 ppm</td>
</tr>
<tr>
<td>▪ RAL UZ 102 (Interior wall paints)</td>
<td>▪ Sum IT 500ppm, MIT 100 ppm, CMIT/MIT 15 ppm</td>
</tr>
<tr>
<td>▪ No addition of biocides allowed</td>
<td>▪ Stronger restrictions than under BPR</td>
</tr>
<tr>
<td>▪ biocide free (sum &lt; 2ppm, &lt; 0.5ppm CMIT, 1.5ppm MIT)</td>
<td>▪ Assessment of each component of the total paint formulation &gt; 0.01%</td>
</tr>
<tr>
<td>▪ traces of biocides (BIT ≤ 10ppm, MIT &lt; 1.5ppm, CMIT &lt; 0.5 ppm, IT &lt; 2ppm, FA free &lt; 10 ppm)</td>
<td>▪ For biocides Gold or higher not easy to achieve due to mainly ecotoxicity, sensitization, toxicity or organohalogens</td>
</tr>
<tr>
<td>▪ RAL UZ 12 a (Varnishes) still refers to Annex I</td>
<td></td>
</tr>
</tbody>
</table>

Blue Angel 2019

- Only interior
- No bioaccumulatives
- Total biocide level max. 700 ppm
- Sum IT 500ppm, MIT 100 ppm, CMIT/MIT 15 ppm

Cradle to Cradle

- Assessment of each component of the total paint formulation > 0.01%
- For biocides Gold or higher not easy to achieve due to mainly ecotoxicity, sensitization, toxicity or organohalogens
Biocide free?
Think about biocide-free paints

No biocide at all – or not listed under BPR?

Stability of my paint?

Applicability of my paint?

What about binder, slurry, etc?

What can be biocide-free?

- “Antimicrobial” additives that have not been registered as biocides
  - Illegal use
- High pH paints without antimicrobial active ingredients
  - Irritant to skin and eyes
  - Corrosive to surfaces
  - Restricted to some paint types
Biocides are essential for sustainable paints