From pesticide quality control to textile chemistry-
Experiences with the draft CIPAC wash method for LN

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What are LN formulations (Long-lasting insecticidal net)?

“What are LN formulations
(Long-lasting insecticidal net)?

“Manual on development and use of FAO and WHO specifications for pesticides
(March 2006 revision of the First edition)”

“A slow- or controlled-release formulation in the form of netting, providing physical and chemical barriers to insects. LN refers to both bulk netting and ready-to-use products, for example mosquito nets.”
From pesticide quality control to textile chemistry | Experiences with the draft CIPAC wash method for LN

(source: press release Syngenta)
Why insectical coated nets?

Combination of physical barrier with an insecticide
1. net
2. pyrethroid, rapid knock down
Two types of nets (polymer fibre - influences the LN technology)

- HDPE \(\rightarrow\) incorporated insecticide
- Polyester \(\rightarrow\) insecticide coated with a „binder“

Coating or Integration- Pros and Cons

- **Coating**: more insecticide bioavailable, but good wash resistance and homogeneity more difficult to achieve.

- **Integration**: inherently more homogeneous, but surface replenishment difficult to show by chemical analysis.
Effects of washing

Coating Type

Incorporation Type

From a presentation of Sumitomo
Test design to answer the question:

- Quality of immobilisation of insecticide
- Long term behaviour during repeated washing steps
Don’t forget...

No laboratory test design can replicate in detail all kinds of possible

Consumer Reality
History

- WHO recommended nets for public health
- WHO wash method in combination with a bioassays (2005)
The WHO wash method

- Net samples (25 x 25 cm) are put in a 1-l beaker containing 0.5 l deionised water with 2g/l „Savon de Marseille“ (pH 10-11)
- 10 min shaking at 30°C and 155 beats per minute (bpm)
- Rinsed twice with deionised water, same conditions
- Dried at room temperature, stored at 30°C in the dark between the wash steps
- The regeneration time between the washes at 30°C was determined before with another standard test (comparing 1 and 3 days)
- The washed net samples are then tested with a bioassay after 0, 1, 5, 10, 15 and 20 wash cycles
WHOPES criteria for a recommended net

- Efficacy after 20 washes: KD (>95% 1 h) and mortality (>80% 24 h)
- Minimum 3 years usable under field conditions

<table>
<thead>
<tr>
<th>Wash No.</th>
<th>Surface active ingredient (mg/kg*)</th>
<th>KD (%)</th>
<th>Mortality (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PermaNet</td>
<td>0</td>
<td>73.2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>70.9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>66.6</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>62.5</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>53.4</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>45.7</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>39.0</td>
<td>87</td>
</tr>
<tr>
<td>Hiking</td>
<td>0</td>
<td>41.6</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>40.5</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>38.5</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>36.7</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>32.3</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>28.5</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>25.1</td>
<td>1</td>
</tr>
</tbody>
</table>

Source: Report of the eleventh WHOPES working group meeting 2007
WHOPES procedure

• Time consuming
• Specialised lab (bioassay)
• “Savon de Marseille” not readily available and not standardised
• Not easily transferable to a quality control lab

Definition „Savon de Marseille“

Marseille soap or Savon de Marseille is a traditional soap made from vegetable oils that has been made around Marseille, France, for about 600 years, the first recorded soapmaker in the area in about 1370. By 1688, Louis XIV introduced regulations (Edict of Colbert) limiting the use of the name savon de Marseille to soaps made in and around the Marseille area,[1] and only from olive oil. Today this law still stands (although the regulations now allow other vegetable oils to be used).
(Source Wikipedia)
Why a new standard wash method?

• Further standardization ... is necessary“ (recommendation 11th WHOPES meeting)
• “Savon de Marseille” → standard soap
• amplitude of movement
• drying and storage conditions

Goals

• Useable for retention/release index determination
• For comparison with WHOPES Phase I efficacy results
• Standardized sampling and sub sampling
• Method for quality and market control
• Usable in standard analytical pesticide control labs
• One wash method for all nets
The draft CIPAC wash method

• Net samples (25 x 25 cm) put in a 1-l beaker containing 0.5 l deionised water with 2.5 g/l IEC A* standard detergent
• 10 min shaking at 30°C and 155 bpm and defined amplitude (15 mm)
• Rinsed twice with deionised water by the same conditions
• Nets are dried at room temperature (protected from sunlight) for 30 min and then stored at 40°C in the dark for 22 hours
• The content of the insecticide is analysed in the unwashed and 4 times washed net

CIPAC draft method

\[
\text{Retention index: } \sqrt[4]{\frac{\text{content } t_4}{\text{content } t_0}}
\]

WHO interim specification

\[
\text{Retention index: } \frac{\text{content } t_3}{\text{content } t_2}
\]
Our experiment in a pesticide quality control lab

- 4 nets containing deltamethrin from 2 different manufacturers
- 5 wash steps, 5g/l IEC A* instead of 2.5 g/l,
- Amplitude 50 mm instead of 15 mm
- After each wash step determination of the total remaining deltamethrin content
CIPAC HPLC – method for LN formulation

- **Column:** Nucleosil 100 CN, 5 µm, 250 x 4 mm, 35°C
- **Eluent:** iso-octane : dioxane with 0.15% water; 94:6 (v/v)
- **Flow:** 1.5 ml/min
- **Detection:** UV 230 nm
- **Injection vol.:** 20 µl
- **Runtime:** 7 minutes
Sample preparation

• Cut small pieces
• Weigh sufficient sample to contain about 0.5 mg deltamethrin
• Add ISTD and 14 ml iso-octane : dioxane 80:20
• 15 min 80°C ultrasonic bath, then 30 min shaker (150 – 200 bpm room temp.)
• Filter and analyse
First results

Deltamethrin wash test

Deltamethrin content [g/kg net]

Wash cycles

Deltamethrin content [g/kg net]

Wash cycles

M1.1 IEC A*
M1.2 IEC A*
M2.1 IEC A*
M2.2 IEC A*

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First results

Deltamethrin wash test

- M1.1 IEC A*
- M1.2 IEC A*
- M2.1 IEC A*
- M2.2 IEC A*

Expon. (M1.1 IEC A*)
Expon. (M1.2 IEC A*)
Expon. (M2.1 IEC A*)
Expon. (M2.2 IEC A*)
Interpretation of the results

<table>
<thead>
<tr>
<th></th>
<th>Retention-index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CIPAC</td>
</tr>
<tr>
<td>M1</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
</tr>
<tr>
<td>M2</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>0.53</td>
</tr>
</tbody>
</table>

- Retention-index lower than in standard WHOPES wash test
- Differences between the two manufacturers products

Next step
- Wash with “Savon de Marseille” (2 g/l)
- Regeneration 30°C 22 h similar to WHO method
Results incl. „Savon de Marseille“

Deltamethrin manufacturer 2

Deltamethrin content [g/kg net]

Wash cycles

Deltamethrin manufacturer 1
M1.1 IEC A*
M1.2 IEC A*
M1 Savon de Marseille

Deltamethrin manufacturer 2
M2.1 IEC A*
M2.2 IEC A*
M2 Savon de Marseille

From pesticide quality control to textile chemistry | Experiences with the draft CIPAC wash method for LN
Results incl. „Savon de Marseille“

<table>
<thead>
<tr>
<th>soap/detergent</th>
<th>CIPAC</th>
<th>WHO</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1.1 (IEC A*)</td>
<td>0.82</td>
<td>0.77</td>
<td>0.99</td>
<td>0.74</td>
</tr>
<tr>
<td>M1.2 (IEC A*)</td>
<td>0.79</td>
<td>1.02</td>
<td>0.80</td>
<td>0.94</td>
</tr>
<tr>
<td>M1 (Savon de Marseille)</td>
<td>0.88</td>
<td>0.81</td>
<td>0.98</td>
<td>0.90</td>
</tr>
<tr>
<td>M2.1 (IEC A*)</td>
<td>0.55</td>
<td>0.63</td>
<td>0.69</td>
<td>0.88</td>
</tr>
<tr>
<td>M2.2 (IEC A*)</td>
<td>0.53</td>
<td>0.78</td>
<td>0.62</td>
<td>0.86</td>
</tr>
<tr>
<td>M2 (Savon de Marseille)</td>
<td>0.63</td>
<td>0.81</td>
<td>0.75</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Conclusion
• IEC A* wash more harsh
• Zeolite has a presumed abrasive behaviour
• But…
Open questions

Next step
• Question: Is IEC B more similar to „Savon de Marseille” than IEC A*?
• Wash test with 5g/l IEC B

Higher amplitude? Other insecticide?

Source: Retention/release characteristics Study N 22018 Dr. ir. Olivier Pigeon, CRA-W Gembloux
## Composition IEC A* and IEC B

<table>
<thead>
<tr>
<th>Component</th>
<th>IEC-B</th>
<th>IEC-A*</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS (linear alkylbenzene sulfonate; detergent)</td>
<td>6.4</td>
<td>8.8</td>
</tr>
<tr>
<td>Nonionic</td>
<td>2.3</td>
<td>4.7</td>
</tr>
<tr>
<td>Soap</td>
<td>2.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Anti foam</td>
<td></td>
<td>3.9</td>
</tr>
<tr>
<td>Phosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite (alkali aluminium silicates)</td>
<td>28.3</td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td></td>
<td>11.6</td>
</tr>
<tr>
<td>Acrylic acid, Maleic acid</td>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>Na-Silicate</td>
<td>6.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Mg-Silicate</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>CMC (carboxy methyl cellulose)</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>EDTA (ethylenediaminetetraacetic acid)</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Optical brightner</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulphate</td>
<td>16.8</td>
<td>6.5</td>
</tr>
<tr>
<td>Protease</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Water/Misc.</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>Perborate (bleacher)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAED (bleacher activator: N,N,N',N'-tetraacetyldiamine)*</td>
<td></td>
<td>3.0</td>
</tr>
</tbody>
</table>

*Bleacher pack not included in tests*
Particle size analyses by Laser Diffraction

Particle size distribution of the three tested wash solutions by laser diffraction
Particle Size analyses by Laser Diffraction

Malvern Mastersizer 2000 (Syngenta EZA Münchwilen)
Savon de Marseille
Under the microscope

IEC A*
Under the microscope

IEC B

100 μm
Results incl. IEC B

![Graph showing Deltamethrin content in g/kg net for wash cycles 0 to 5 for different manufacturers and IEC categories.]

Deltamethrin manufacturer 2

Wash cycles

Deltamethrin content [g/kg net]

M2.1 IEC A*  M2.2 IEC A*  M2 Savon de Marseille  M2 IEC B

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## Preliminary conclusions

- IEC B wash more similar to IEC A* than “Savon de ...”
- But IEC B seems to better mimic “Savon de Marseille”
### Remarks to the calculation methods

<table>
<thead>
<tr>
<th>Soap</th>
<th>Retention-index</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>CIPAC</td>
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<td>4</td>
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<td>T5/T1</td>
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<tr>
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<td>0.76</td>
<td>0.81</td>
<td>0.71</td>
<td>0.74</td>
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<td>0.94</td>
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</tr>
</tbody>
</table>

- CIPAC calculation method well suited
- For calculation of the retention-index, only two measurements necessary (t0 t4) as for WHO calculation
Overall conclusion

• CIPAC wash method easy to implement in a pesticide quality control lab
• IEC A* household detergent leads to less retention than „Savon de Marseille“
• IEC B seems to better mimic “Savon de Marseille” than IEC A*. Further work is needed to confirm this finding
• IEC A* and IEC B are not directly comparable with “Savon de Marseille”
• The wash method allowed to differentiate between nets of different qualities
• Calculation of the retention index: The CIPAC draft calculation method seems to have certain advantages
Involved team
Thank you for your attention!