Green Demulsifier Development
Crude Oil Demulsification

This presentation is a short introduction into crude oil emulsions, reasons for its stability, demulsification process, chemicals used and procedures, and contains 6 chapters:

I Emulsion in general, and crude oil emulsions in particular

II Crude oil demulsification process in general

III Chemicals used in crude oil demulsification and special requirements for North Sea

IV Demulsifier performance

V Demulsifier selection – the ‘Bottle Test’

VI Demulsifier performance verification – the ‘Field Trial’
I Emulsions

Definition:
Emulsions are disperse systems consisting of two (or more) mutually insoluble or sparingly soluble liquids.
Emulsions

Unstabilized emulsions will fall part easily
- Example is a vinaigrette prepared by stirring oil and vinegar vigorously, and let it stand for some time

Stabilized emulsions will not fall part easily
- Example is milk, an o/w emulsion, which upon standing is stable for weeks
# Crude Oil Emulsions

Crude oil is a complex mixture of organic and inorganic matters.

<table>
<thead>
<tr>
<th>Components</th>
<th>Surfactant</th>
<th>Film Active</th>
</tr>
</thead>
<tbody>
<tr>
<td>paraffines</td>
<td>no</td>
<td>yes (oil wet)</td>
</tr>
<tr>
<td>asphaltenes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>organic acids (e.g. naphthenates)</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>inorganic salt, minerals</td>
<td>no</td>
<td>yes (water wet)</td>
</tr>
<tr>
<td>corrosion products, sulphidic salts and ores</td>
<td>no</td>
<td>yes (oil wet)</td>
</tr>
<tr>
<td>(e.g. FeS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
II Demulsification Methods

1. Heat
2. Electricity
3. Time
4. Removal of solids
5. Chemicals

All methods have their advantages and disadvantages, like energy consumption and space/volume-time-yield
II Demulsification Process

No matter which method(s) are applied, demulsification follows some pattern

- Destabilization of the protective film (replacement of surfactants, water- or oil-wetting of solid particles)
- Flocculation (aggregation) of water droplets
- Coalescence of water droplets
- Sedimentation (creaming)
### Demulsifier Chemistry History

<table>
<thead>
<tr>
<th>Time period</th>
<th>Dosage [ppm]</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1920 - 1935</td>
<td>500 - 1.000</td>
<td>Naphthenic acids, aromatic and aliphatic sulphonates</td>
</tr>
<tr>
<td>1935 - 1950</td>
<td>100 - 500</td>
<td>Above + ethoxylated fatty alcohols, acids and phenols</td>
</tr>
<tr>
<td>1950 - 1970</td>
<td>50 - 200</td>
<td>Above + EO/PO block polymers and acid catalysed resins</td>
</tr>
<tr>
<td>1970 - 1980</td>
<td>10 - 100</td>
<td>Above + diepoxides and base catalysed resins</td>
</tr>
<tr>
<td>1980 - 1990</td>
<td>2 - 50</td>
<td>Above + polyesters and alkoxyalted polyamines</td>
</tr>
<tr>
<td>1990 -</td>
<td>2 - 30</td>
<td>Above + alkoxyalted silicones and polyacrylates</td>
</tr>
<tr>
<td>to be continued…</td>
<td>???</td>
<td>???</td>
</tr>
</tbody>
</table>
III Special Situation North Sea

North Sea oil production accounts for ca. 10% of the global offshore production

In general, older assets with high water cut

Strict regulations on chemicals used offshore (OSPAR)

- Ban of several types of chemistry working well (alkylphenol-formaldehyde resins)
- Toxicity (amines/quats) and low biodegradation (high molecular weight polymers) reduce kit further

⇒ As rule of thumb, max. 10% of a given demulsifier portfolio will fulfil OSPAR requirements

Why are more demulsifiers not available for North Sea

- Chemical manufacturers have often no tech service department and access to crude
- Service companies are often not back-integrated to synthesis of new molecules
- Challenging to introduce to the market, because developmental products don’t have a case history and are not readily available
### III Special Situation North Sea

#### Demulsifier Development
- **Building Blocks**
  - Availability
  - Polyfunctional starting materials
  - Alkoxyd
  - HLB
    - Alkoxy ratio
    - End group
- **Build-in lability**
  - pH
  - Ion concentration

#### Environmental Testing
- **Building blocks & breakdown products**
  - Toxicty
- **Sample screening**
  - Solubility
  - Biodegradation
  - Toxicity
- **GLP test**
  - BODIS
  - OECD 306

#### Application Tests
- **Different crudes**
  - API
  - Water cut
  - Asphaltenes and paraffins
  - Water clarity
- **Relative Performance**
  - Dropper
  - Treater
  - Polisher
- **Ranking**
Demulsifiers can either be grouped on their chemistry or according to their performance.

While chemical classification is straightforward, performance depends on type of crude, synergism on blending, field conditions etc.

Most common chemicals are *alkoxylated alkylphenol-formaldehyde resins (acid and base catalysed)*, pure EO/PO polymers, EO/PO polymers with multifunctional backbones (e.g. EDA, glycerol, sorbitol), *diepoxides*, *(crosslinked EO/PO polymers)* and *alkoxylated polymines*.
IV Demulsifier Performance

### Water Drop

- **Max Water**: fastest drop
- **Dropper**: slower drop
- **Treater**: intermediate drop
- **Polisher**: slowest drop
- **Blank**: no drop

### Top Cut BS&W

- **Water**: highest value
- **Emulsion**: intermediate value
- **BS&W**: lowest value

### Table: Chemistry and Performance

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Dropper</th>
<th>Treater</th>
<th>Polisher</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td>Light – Medium</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>EO/PO Polymers</td>
<td>Light – Medium</td>
<td>Light – Medium</td>
<td>---</td>
</tr>
<tr>
<td>Diepoxides</td>
<td>Medium – Heavy</td>
<td>Light – Heavy</td>
<td>Medium – Heavy</td>
</tr>
<tr>
<td>Polymines</td>
<td>---</td>
<td>Light</td>
<td>Light – Heavy</td>
</tr>
</tbody>
</table>
V Bottle Test

The ‘Bottle Test’ is an application test to check performance of demulsifiers on a small scale.

Bottle testing can determine several things, e.g.

- Performance of incumbent product
- Ratio of demulsifier
- Amount of emulsified water
- Demulsified oil quality
- Demulsified water quality
V  Bottle Test – BS&W

Determination of emulsified water

Besides ‘free’ water, some water and solids will be trapped in the oil, and not released. A centrifuge test is used to obtain the so called BS&W (emulsion & water)

\[ \text{crude oil + xylene 1:1} \]

centrifuged with sludge breaker  \[ \text{Oil} \]

centrifuged w/o sludge breaker  \[ \text{Oil} \]

\[ \text{W} \]

\[ \text{BS} \]

\[ \text{W} \]
Field examples

- Crude oil + xylene 1:1
  - Centrifuged without sludge breaker
  - Centrifuged with sludge breaker

- Centrifuged without sludge breaker
  - Centrifuged with sludge breaker
V  Bottle Test

Mimic plant conditions

- Due to differences in setup (surface area, temperature variation, agitation / mix / shear in plant, lack of possibility to simulate the electrical grid,…), field results should be simulated as good as possible
- Test for speed and completeness of water drop, top oil quality, water quality, interface quality
- Good droppers might leave water in the oil, good treaters will not drop all the water, but give clean top oil, so water drop is not the only criteria

In the end, selection criteria depends on customer requirement, typical are:

- Water drop (speed and amount similar / better to incumbent product)
- Top cut (residual water / emulsion at least similar to incumbent product)
- Water quality, salt content, interface
V  Bottle Test – North Sea demulsifiers

Performance is not everything for North Sea:

- Biodegradation; must be above 60% within 28 days (OECD 306 or BODIS)
- Toxicity; LC$_{50}$ or EC$_{50}$ > 100 mg/L
- Bioaccumulation; log$_{POW}$ < 3 or MW > 700

How to achieve:

- Introduction of labil bonds
- Raw material and breakdown products not toxic

![Chemical structures]

ORTHOOESTER  ESTER  AMIDE
Performance as most important criteria

- Application tests on a variety of crudes
  - >> 10 different crudes screened
  - API range from low 20’s to low 40’s
  - Emulsified water 5 – 65%, total BS&W up to 95%
  - Treatment temperature ambient to +60°C
  - Retention time 5 minutes up to several hours
- Regions: North America, West and North Africa, CIS, North Sea, Arabia
## Bottle Test – North Sea demulsifier development

<table>
<thead>
<tr>
<th>Sample</th>
<th>North Sea</th>
<th>CIS</th>
<th>Arabia</th>
<th>N. America</th>
<th>N. America</th>
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<tr>
<td>A</td>
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V  Bottle Test – North Sea demulsifier development

- 176 samples prepared
- Different screening methods (lab, on site,..)
- 6 samples identified
- Ecotox & Biodeg
- 3 samples passed

Total duration several years – to identify candidates

3-6 months
2-3 years
3-6 months
V Bottle Test – North Sea demulsifier development, 2nd set

- 105 samples prepared
- Different screening methods (lab, on site,..)
- 2-3 years
- X samples identified
- Ecotox & Biodeg
- Y samples passed
- 3-6 months
- A-B months
V Bottle Test – Drawbacks

A bottle test is just a ‘test’ which suffers from various differences between test and plant…

<table>
<thead>
<tr>
<th>Difference</th>
<th>Plant</th>
<th>Bottle Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size / Scale</td>
<td>Up to several 1,000 BFPD</td>
<td>100 mL test size</td>
</tr>
<tr>
<td>System Flow</td>
<td>Dynamic</td>
<td>Static</td>
</tr>
<tr>
<td>Interface Surface Area</td>
<td>Several square meters (depending on separator size)</td>
<td>Several square centimeters (diameter of bottle / tube)</td>
</tr>
<tr>
<td>Emulsion Quality</td>
<td>Pressurised and unchanged</td>
<td>Depressurised, aged due to contact with air and sunlight, most likely sheared / cut through valve</td>
</tr>
</tbody>
</table>
V Bottle Test – Drawbacks

…and is subjective to the bottle tester, and depends on the oil sample quality
Final confirmation

- Needed to overcome drawbacks in lab development
- Performance check and optimization on site
- Even a successful bottle test does not automatically mean a successful field trial (btw, what is ‘successful’?)

Still, field trial results can be questionable

- Water cut / gross fluid production might have changed between bottle test and field trial (new wells, water breakthrough)
- Alteration in plant setup (heaters on- or offline, different wells producing)
- Issues with pump / equipment (line blockage, different injection points)
- Operators used to a certain performance and will react according to gained knowledge
  - ...

...but we get there – eventually!
Thank You!