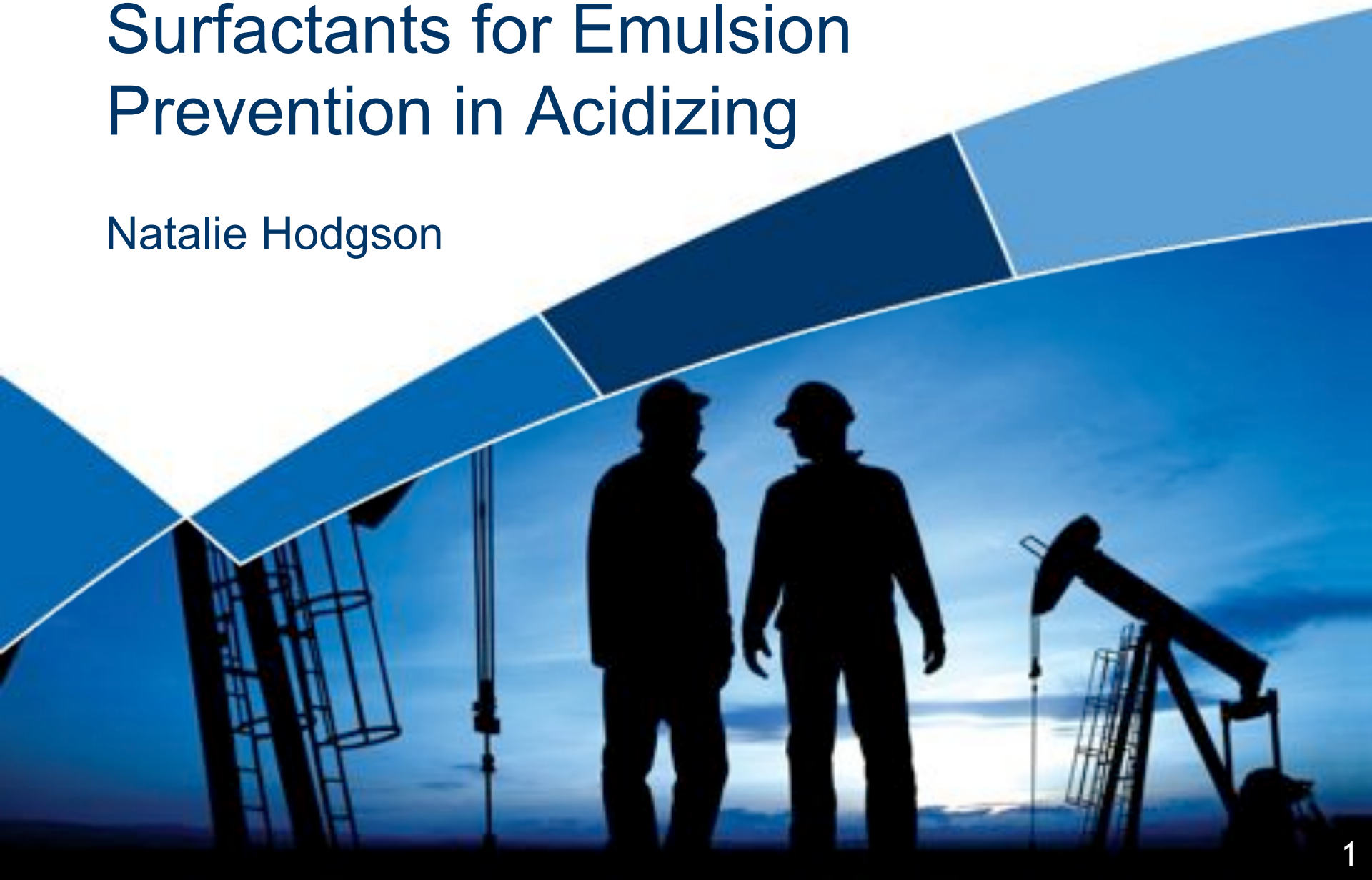


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# Surfactants for Emulsion Prevention in Acidizing

Natalie Hodgson



# Surfactants for emulsion prevention in acidizing

**Natalie Hodgson**, Helen Sarginson, Clare Temple-Heald – *Croda Europe Ltd.*  
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Introduction

Non-emulsifier screening:

- Testing method
- Results

Anti-sludge screening:

- Testing method
- Results

Further work

Conclusions & Acknowledgements

Questions

# Introduction: acidizing fluids



Improving the permeability of the formation by dissolving:

- Naturally occurring acid-soluble rock
- Products of formation damage



Two types:

- Fracture acidizing (higher pressure)
- Matrix acidizing



Acid is typically formulated with chemicals to prevent sludge and emulsion formation

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# Non-emulsifier screening



# Non-emulsifier: testing method

## Acid

- 15% unspent hydrochloric acid
- 1% anti-sludge agent (DDBSA)
- 200 ppm non-emulsifier candidate

## Crude oil

- Source: Colombia
- API Gravity: 10 °
- Water cut: 0%
- Preheat: 60 °C

## Experiment

- Crude to acid ratio: 3:1
- Mixing: 14,000 to 18,000 rpm for 30 seconds
- Turbiscan analysis

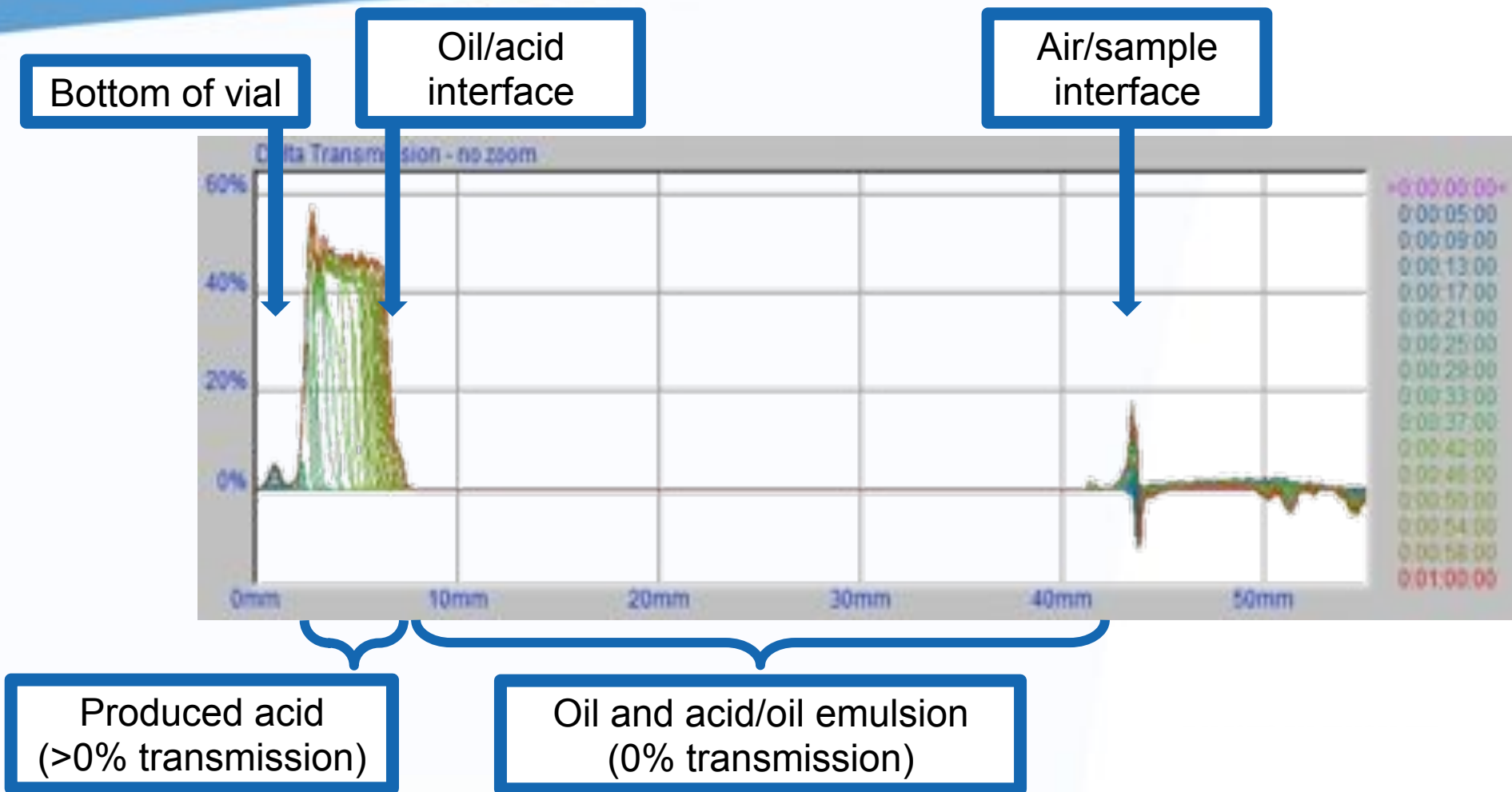
observing transmission each minute for one hour, near infrared light source

## API-RP42

Recommended Practices for Laboratory Testing of Surface Active Agents for Well Stimulation

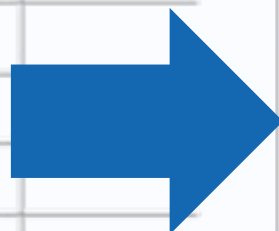
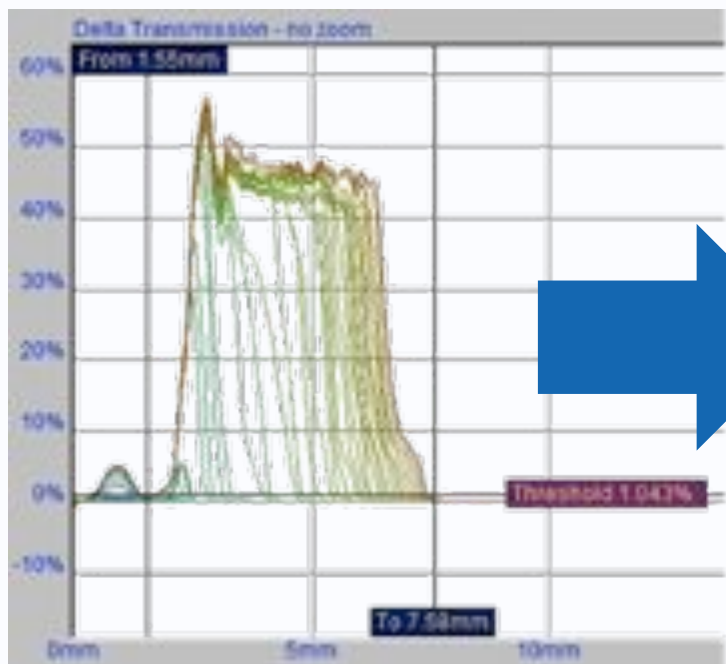


# Non-emulsifier: Turbiscan data

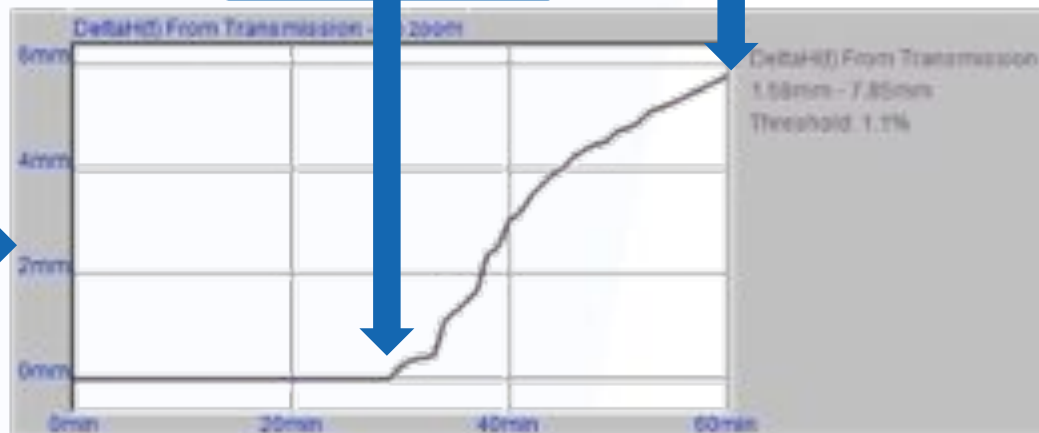


# Non-emulsifier: Turbiscan data

Peak thickness function



Start time



Extent of separation in one hour

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# Non-emulsifier: ranking performance

- Three chemistry classes: Polyimine alkoxyates, resin alkoxyates, modified polyols
- Candidates compared to a blank run (with no product) and a known industry benchmark

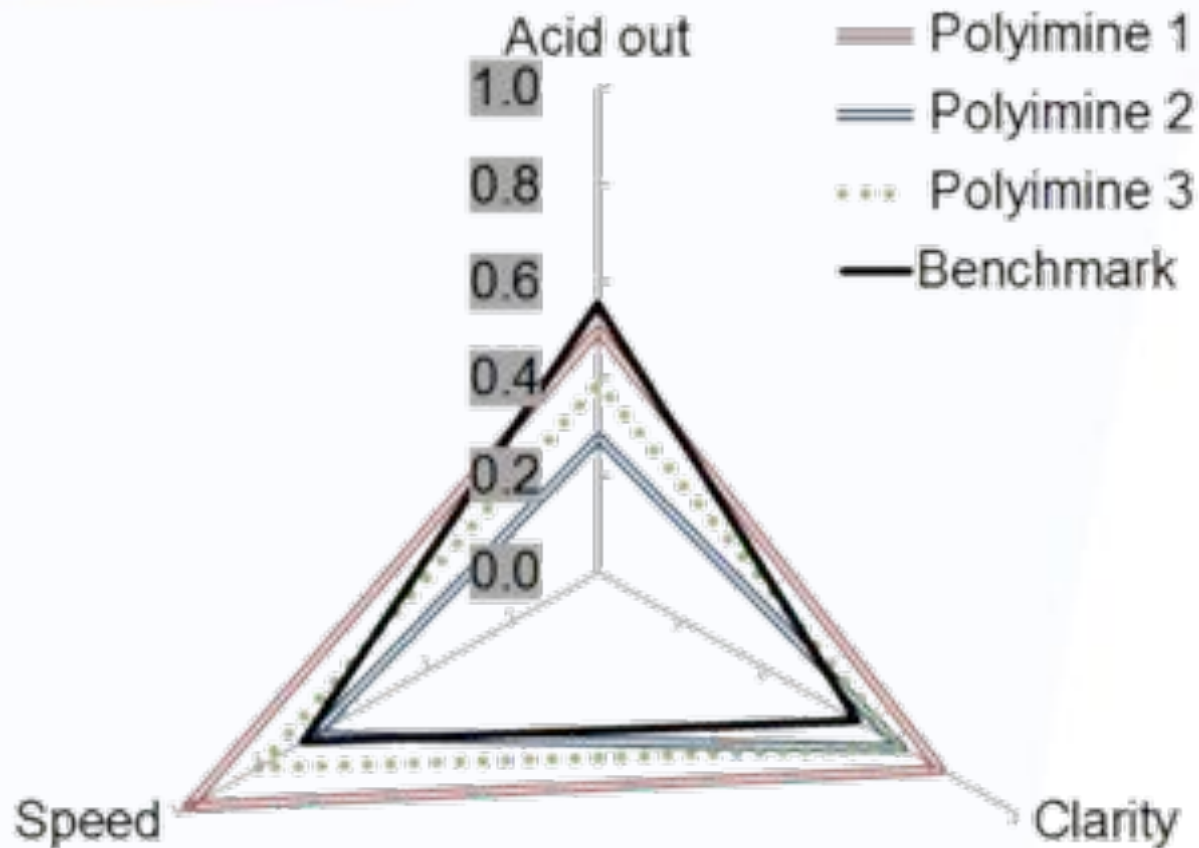
Clarity of  
produced acid

Speed of  
splitting  
initiation

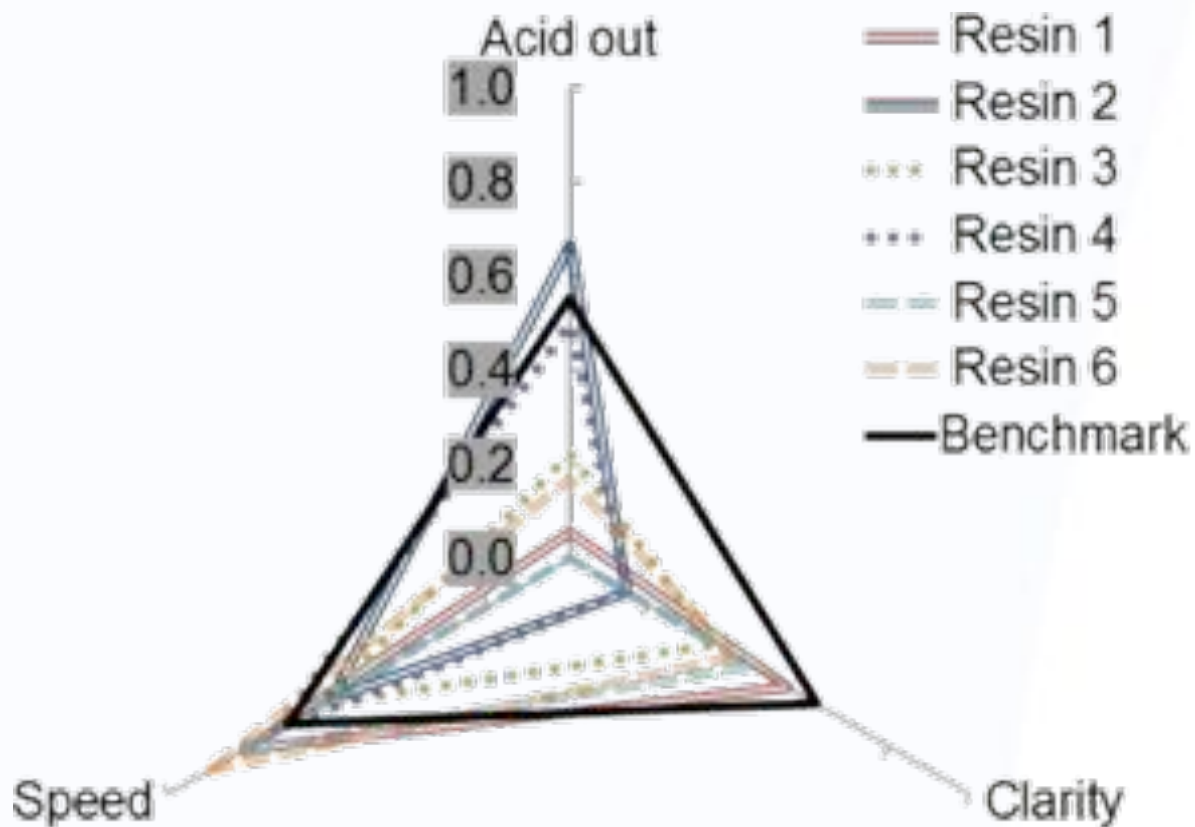
Extent of  
splitting in one  
hour



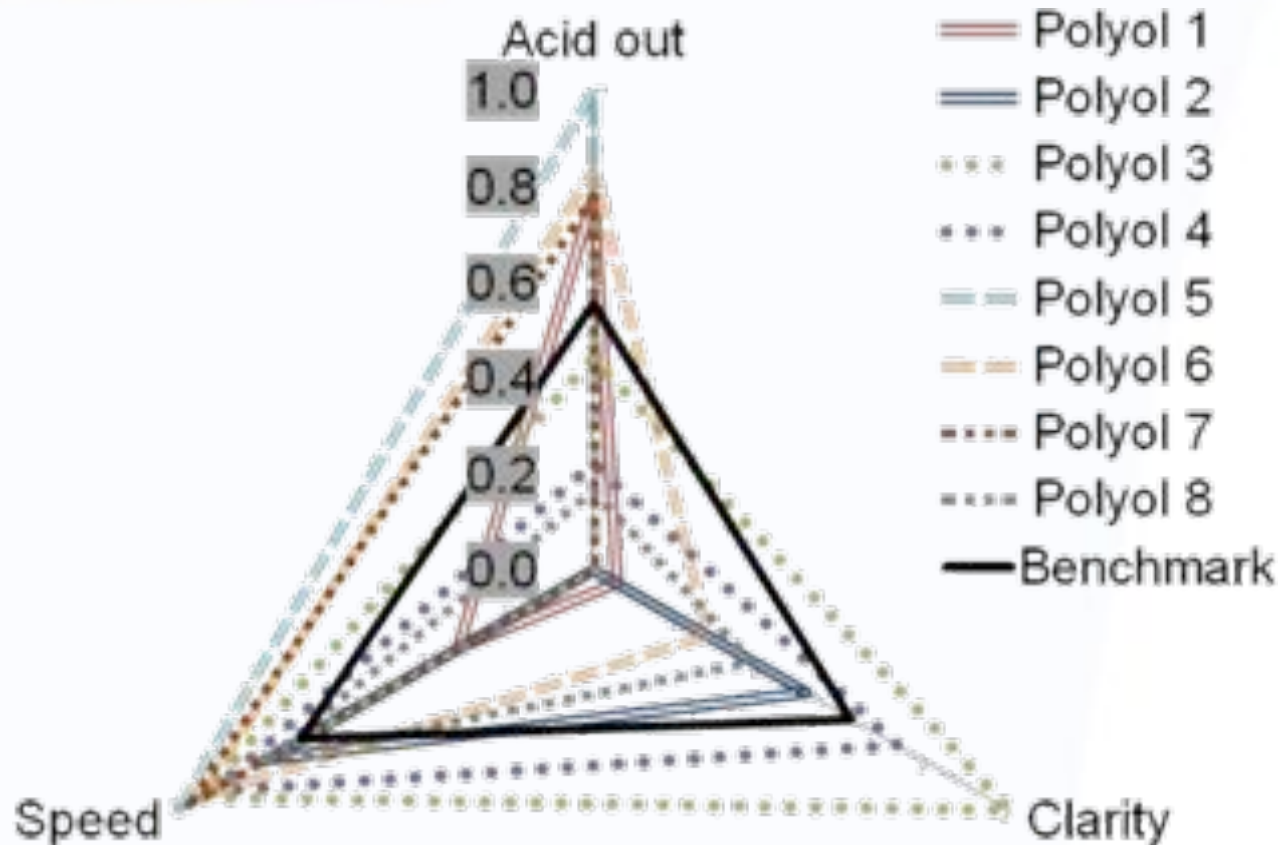
# Non-emulsifier: testing results



# Non-emulsifier: testing results



# Non-emulsifier: testing results



# Non-emulsifier: candidate summary

Name	RSN	Pour Point (°C)	Viscosity at 25 °C(cP)
Polyol 1	15	-6	1700
Polyol 2	17	-9	1300
Polyol 3	11	-9	800
Polyol 4	20	0	800
Polyol 5	20	9	1100
Polyol 6	10	-9	900
Polyol 7	17	3	1100
Polyol 8	21	12	700
Polyimine 1	9	-33	1400
Polyimine 2	7	-27	3900
Polyimine 3	7	-30	2800
Resin 1	18	-31	600
Resin 2	19	-12	>5000
Resin 3	23	-30	100
Resin 4	20	-15	700
Resin 5	17	-33	800
Resin 6	17	-39	400

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# Anti-sludge screening



# Anti-sludge: testing method

## Acid

- 15% unspent hydrochloric acid
- 1% anti-sludge agent candidate
- 200 ppm of a commercially available non-emulsifier
- 5000 ppm total  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (ratio 3:1)

## Crude Oil

- 1: Canada, 11 ° gravity, 19% water cut
- 2: Canada: 15 ° gravity, 29% water cut
- 3: USA: 45 ° gravity, 0.04% water cut
- 4: USA: 46 ° gravity, 0.1% water cut

## Experiment

- Crude to acid ratio: 1:1, mixed thoroughly
- Stored for at least one hour at 80 to 85 °C
- Phase separation was observed during the hour, complete separation expected within 3 minutes

# Anti-sludge: testing method

## Experiment

- The fluid was poured through a 100 Mesh screen
- Warm water (80-85 °C) was poured through to remove wax residue
- Hexane was poured through to remove remaining hydrocarbon residue
- Observed for sludge classification



None



Trace/Slight



Medium



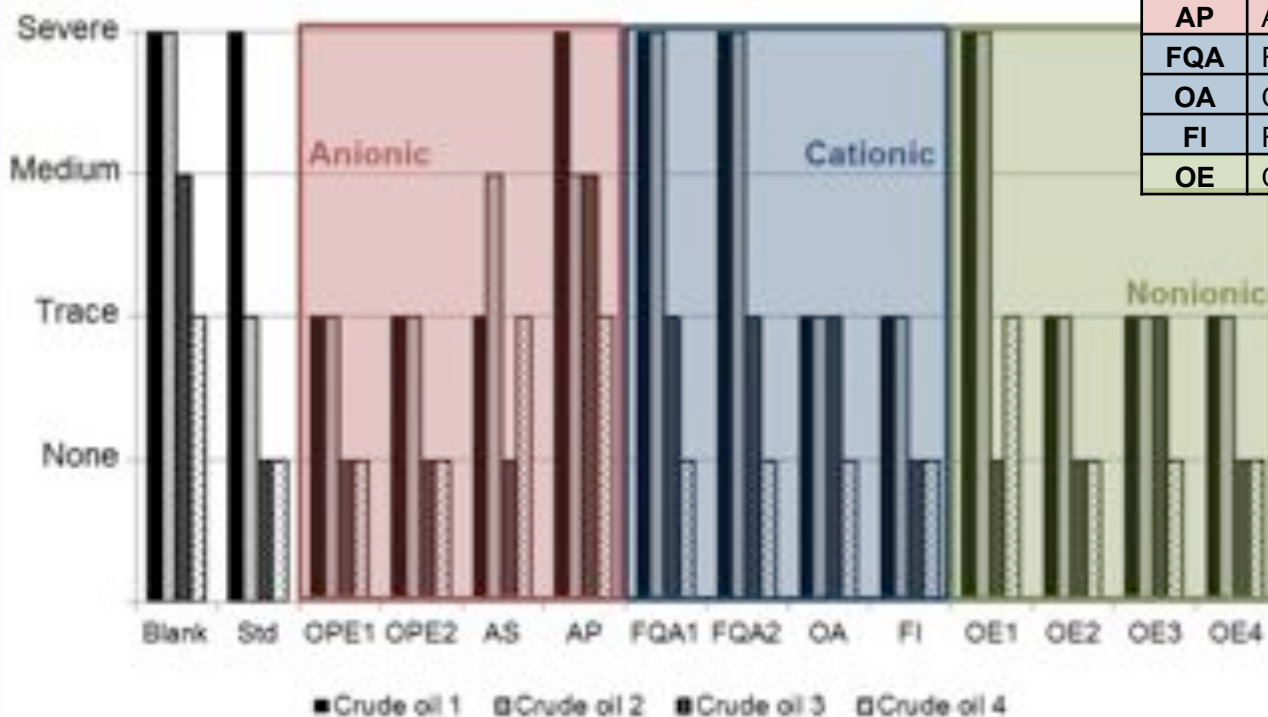
Severe

# Anti-sludge: results

## Crude Oils:

- 1: Canada, 11 ° gravity, 19% water cut
- 2: Canada: 15 ° gravity, 29% water cut
- 3: USA: 45 ° gravity, 0.04% water cut
- 4: USA: 46 ° gravity, 0.1% water cut

Label	Chemistry	Ionic character
Blank	Blank	Not applicable
Std	4-dodecylbenzenesulfonic acid (DDBSA) <i>Benchmark</i>	Anionic
OPE	Oxyalkylated phosphate esters	Anionic
AS	Alkylaryl sulfonate	
AP	Acrylic polymer	
FQA	Fatty quaternary amines	Cationic
OA	Oxyalkylated amine	
FI	Fatty imidazoline	
OE	Oxyalkylated esters	Non-ionic





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# Further work



# Further work: testing method

- Work carried out: September 2015
- Non-emulsifier screening on 4 new modified polyols

Name	RSN	Pour Point (°C)	Viscosity at 25 °C(cP)
Sample 1	14	-21	2000
Sample 2	14	0	6700
Sample 3	18	-18	3200
Sample 4	14	-30	1800

- New sample of crude oil
- Method adapted for the crude oil

# Further work: testing method

## Acid

- 15% unspent hydrochloric acid
- 200 ppm non-emulsifier candidate

## Crude oil

- Source: Texas
- Gravity: light
- Water cut: 0%
- Preheat: none

## Experiment

- Crude to acid ratio: 1:1
- Mixing: 14,000 to 18,000 rpm for 30 seconds
- Turbiscan analysis

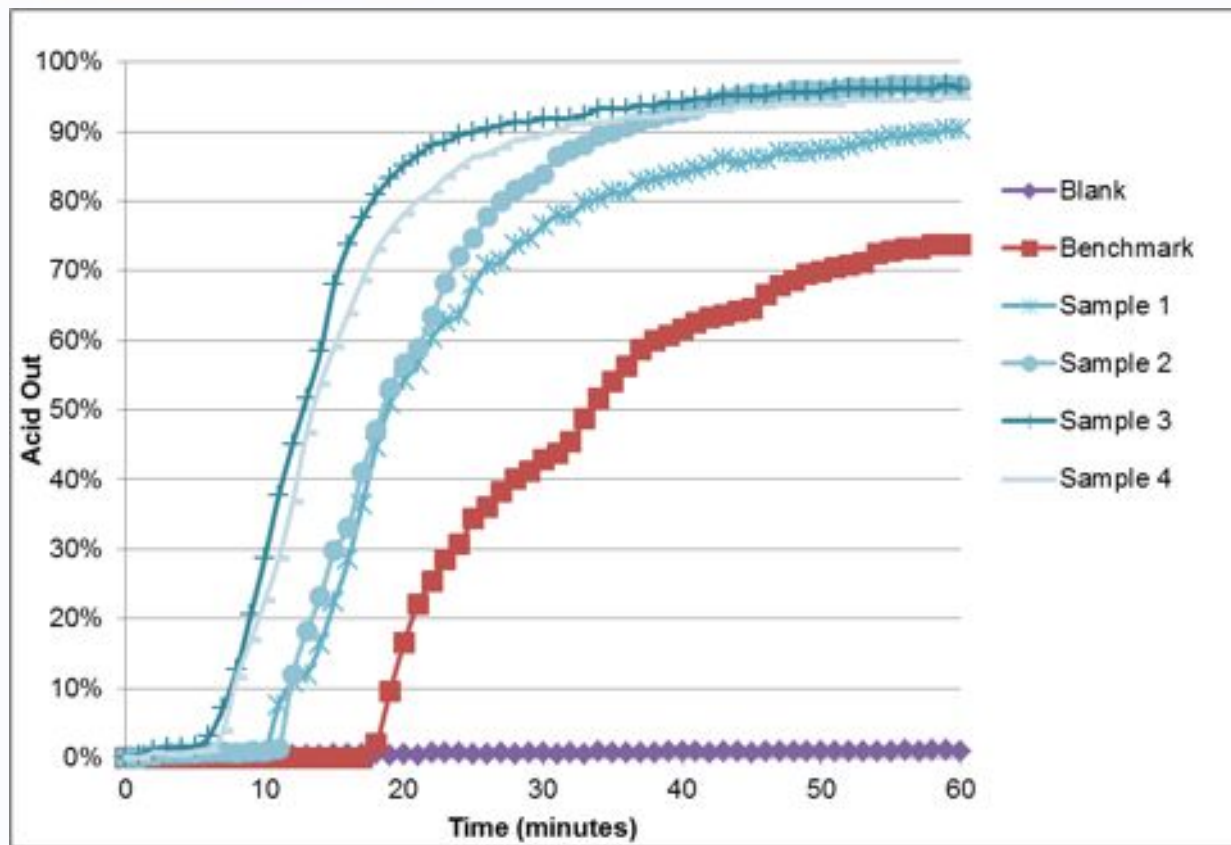
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observing transmission each minute for one hour, near infrared light source



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# Further work: results



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# Conclusions & acknowledgements



# Conclusions

- Candidate screening methods:
  - Able to be modified for different crude oils
- Proven technology:
  - Non-emulsifiers
    - Polyimine alkoxyates
    - Resin alkoxyates
    - Modified polyols
  - Anti-sludge agents
    - Cationic
    - Anionic
    - Non-ionic

# Acknowledgements

- The authors would like to thank the help and support of all Croda employees involved in the preparation of this paper and presentation
- The authors would also like to thank Chemioil, Weatherford, Dansbury and MI-Swaco for the supply of crude oil for this project
- Finally, the authors would also like to thank Fullbrook Systems for technical support using the TurbiScan

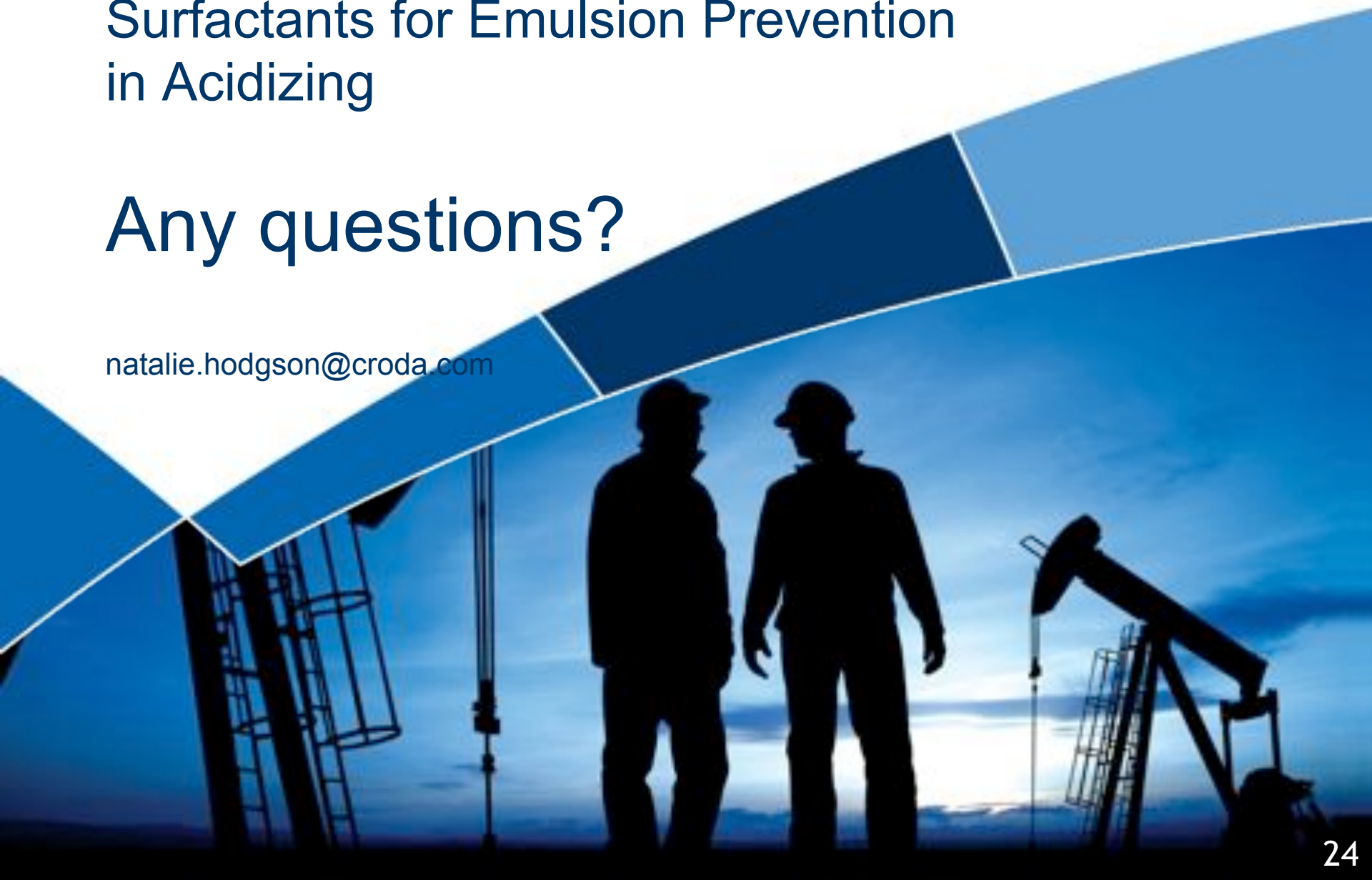
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## Any questions?

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