Synergy in Metalworking fluids

AKYPO® ROX (NIO) and AKYPO® (EC) based on PO-EO

STLE 2016 – Las Vegas

Wednesday 18.05.2016 10.30 – 11.00

Synergy in MWF

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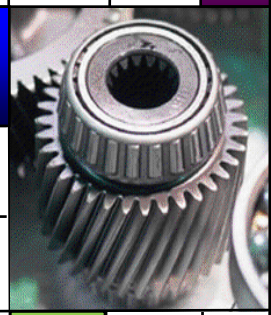

Synergy in Metalworking fluids

- Metalworking fluids formulations are based on a long list of different raw materials.
- A lot of combinations can be made and will lead to good results but…..
- ….. some product groups are working together and show even improved properties (Synergy).
- The so-called carboxylic acid triangle is a good example of an anionic synergy:
  - Alkyl ethercarboxylic acids (AKYPO® ,EC)
    - Long alkyl chain
    - Short alkyl chain
  - Fatty acids
  - In the right combination and ratio these 3 product groups can be the basic for long (sump) life emulsions.

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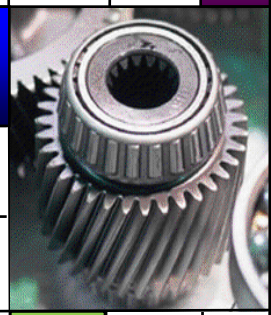

Anionic Synergy AKYPO® – Fatty acid

Trick for low foam and high stability

Short chain AKYPO®

low till medium foam

not sensitive for water hardness

Ca-soap solubilising

Long chain AKYPO®

medium till high foam

not sensitive for water hardness

Ca-soap dispersing

+

Solubilizer

(improves electrolyte stab.)

Co-emulsifier

(improves emulsion stab.)

Fatty Acid

low foam

sensitive for water hardness

EO degree →

Alkyl chain ->

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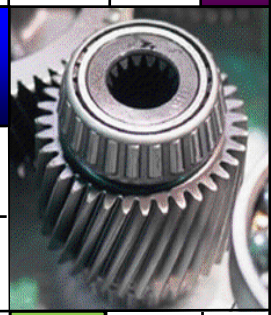
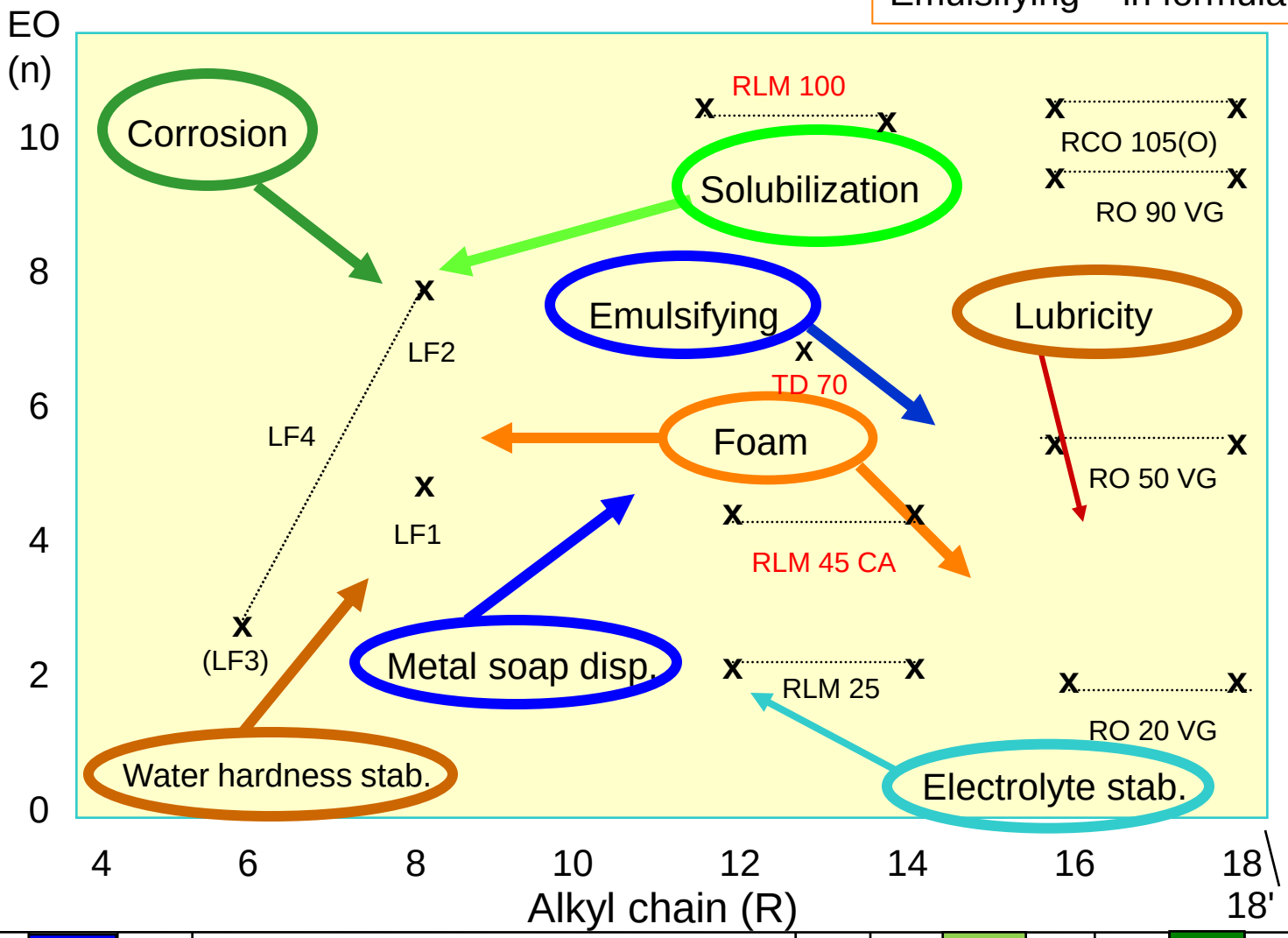


Anionic synergy : AKYPO®

(direction arrow means improvement for TA)

Foam = lower foam potential
Emulsifying = in formulation



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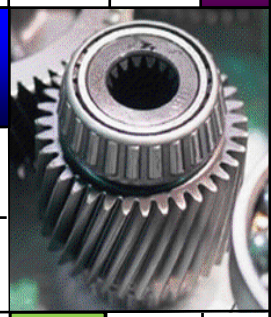
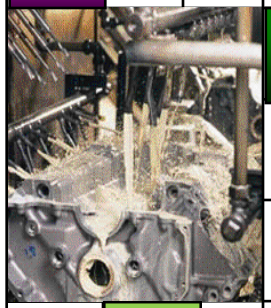


Synergy in Metalworking fluids

Nonionic – Anionic Surfactant

- Synergy is also found in combinations like:
  - Non-ionics (Alkoxylates),
  - Anionics (e.g. Alkyl Ethercarboxylic Acids (EC)).
- Well-known combinations are based on:
  - Ethoxylated Cetyl Oleyl alcohol types.
- Newly developed combinations are:
  - Ethoxylated Amide types,
  - Propoxylated and Ethoxylated types
- It is not completely clear how they support each other; the similar chemical structure (backbone) might have a strong influence.



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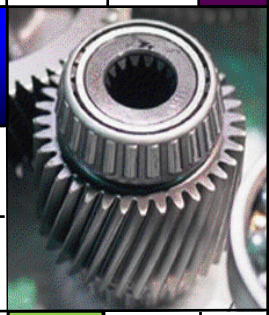

Propoxylated and ethoxylated Emulsifiers/Stabilizers

- PO-EO based nonionics and anionics are well-known.
- The synergy between both product groups was quite unknown.
- Chemistry:
  - The starting materials are saturated C16 and C18 alcohols,
    - Raw materials widely available (also Kao), Constant price level
    - Good starting material for low foam stability and strong emulsifying
  - Adding PO will make the material liquid at room temperature (next sheet),
    - Van der Waals forces, branching
  - Adding EO will make the product more hydrophilic,
  - Different EO length will give them specific emulsifier power ('HLB'),
  - In the case of an Anionic the products will become also good stabilizers.
- The high-lights can be found in:
  - Strong emulsifying and low foam stability.
- Target areas :
  - Global: High pressure applications
  - Mainly outside of Europe : Upgrade Sulphonate based formulations for a longer sump life.

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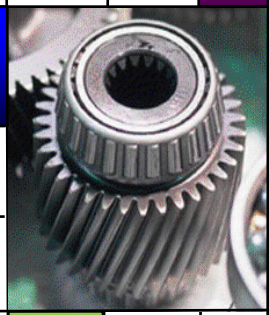

PO-EO based product

Nonionics – Anionics

Non-ionic types

- AKYPO® ROX RS 0602N
  - C18 6 PO – 2 EO NIO
- AKYPO® ROX RS 0606N
  - C18 6 PO – 6 EO NIO
- AKYPO® ROX RC 0960N
  - C16 6 PO – 9 EO NIO

Registration:

RS Types : global

RC type : China, Canada, Europe, Japan, Korea, USA, New Zealand

Anionic types

- AKYPO® RSPE 66
  - C18 6 PO - 6 EO Ethercarboxylic acid
- AKYPO® RC 0960
  - C16 6 PO - 9 EO Ethercarboxylic acid

Registration:

Europe and China

USA and Canada expected 06.16

- Non-ionic – Anionic Combination :
  - Strong emulsifiers
  - Low foam stability tendency

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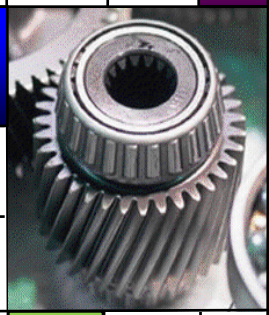

Experiments

- Part 1:
  - Replacement Cetyl oleyl based NIO and EC for the use in high pressure applications

- Part 2:
  - Upgrade Sulphonate based formulations for a longer sump life

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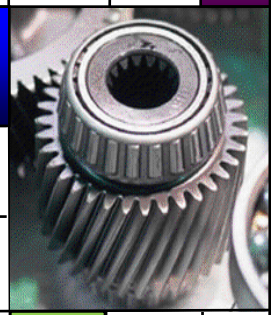
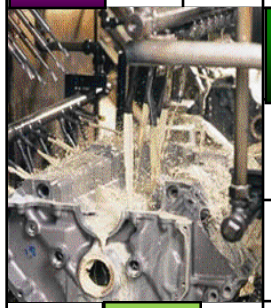


Part 1: Based on market formulation (Summary)

Cetyl-Oleyl versus PO-EO

(main) **function**	**component**	**% by weight**
lubrication	mineral oil	45 - 50
lubrication	ester	5 - 15
pH reserve / corrosion control	amines	5 - 10
emulsifier / corrosion control	sulfonate	5-10
boundary lubrication / foam control	fatty acid	5-10
corrosion control	fatty acid amides	3 - 5
EP lubricant	sulphur carrier	5
emulsifier	**alcohol** ethoxylate	**3**
co-emulsifier / stabilizer	**alkyl** ether carboxylic acid	**2**
biocide	isothiazolinones	max. 2
	water	ad 100%

	Nonionic 3 %	Anionic 2 %
Formulation 1	Cetyl-Oleyl 5 EO (oleyl)	AKYPO® RO 90 VG (oleyl)
Formulation 2	Cetyl-Oleyl 5 EO (oleyl)	AKYPO® RSPE 66 (PO/EO)
Formulation 3	AKYPO® ROX RS 0606N (PO/EO)	AKYPO® RO 90 VG (oleyl)
Formulation 4	AKYPO® ROX RS 0606N (PO/EO)	AKYPO® RSPE66 (PO/EO)



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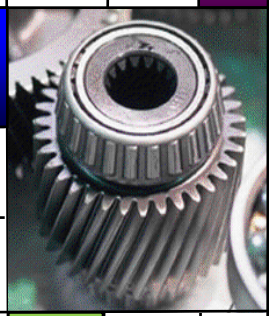
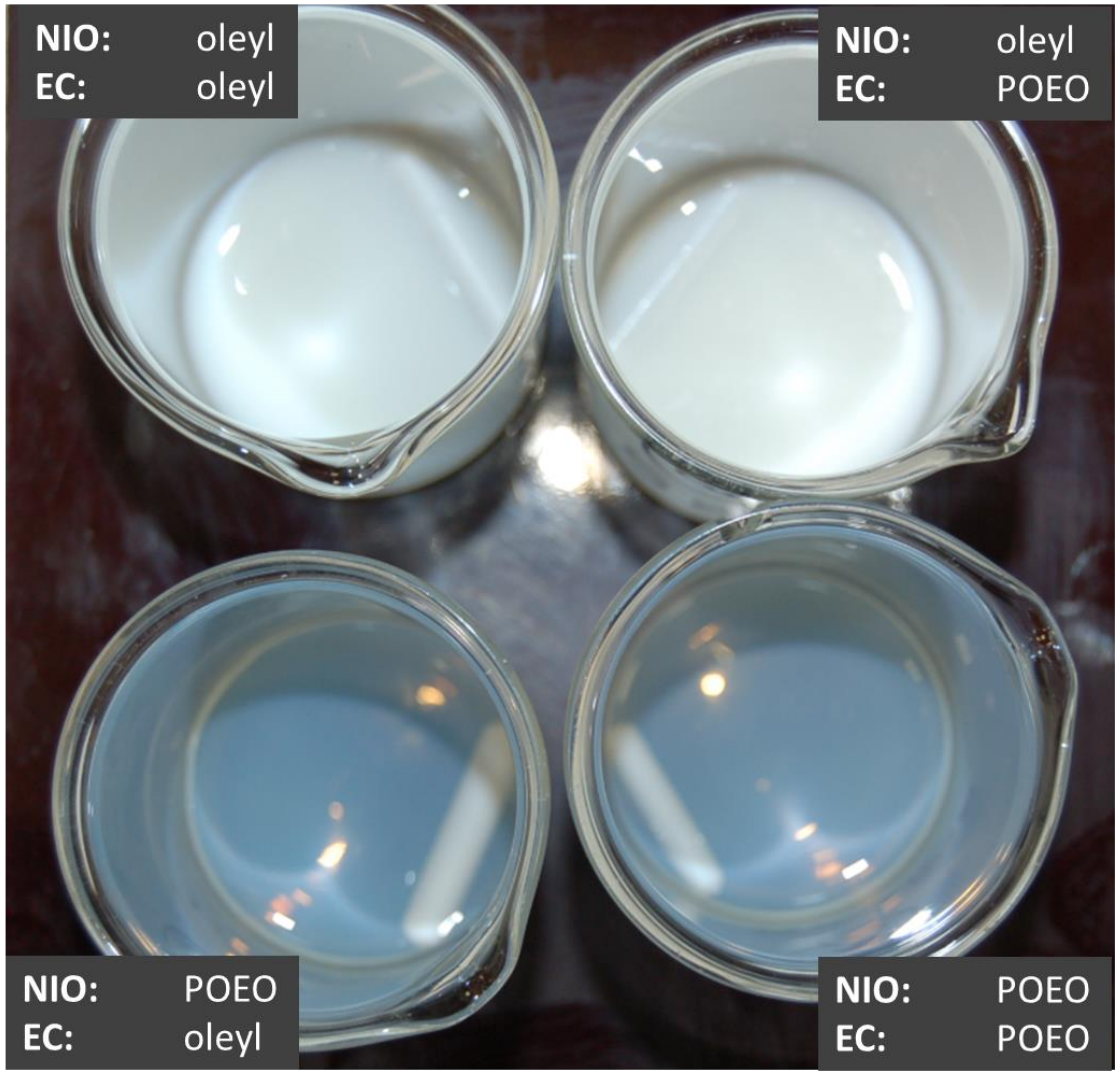


Appearance emulsions

(5% emulsion 10°gh, 180 ppm CaCO3)



1

2

3

4

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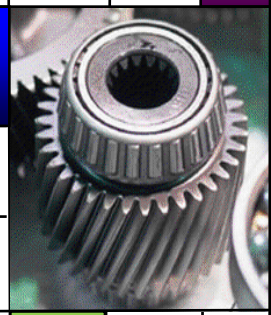
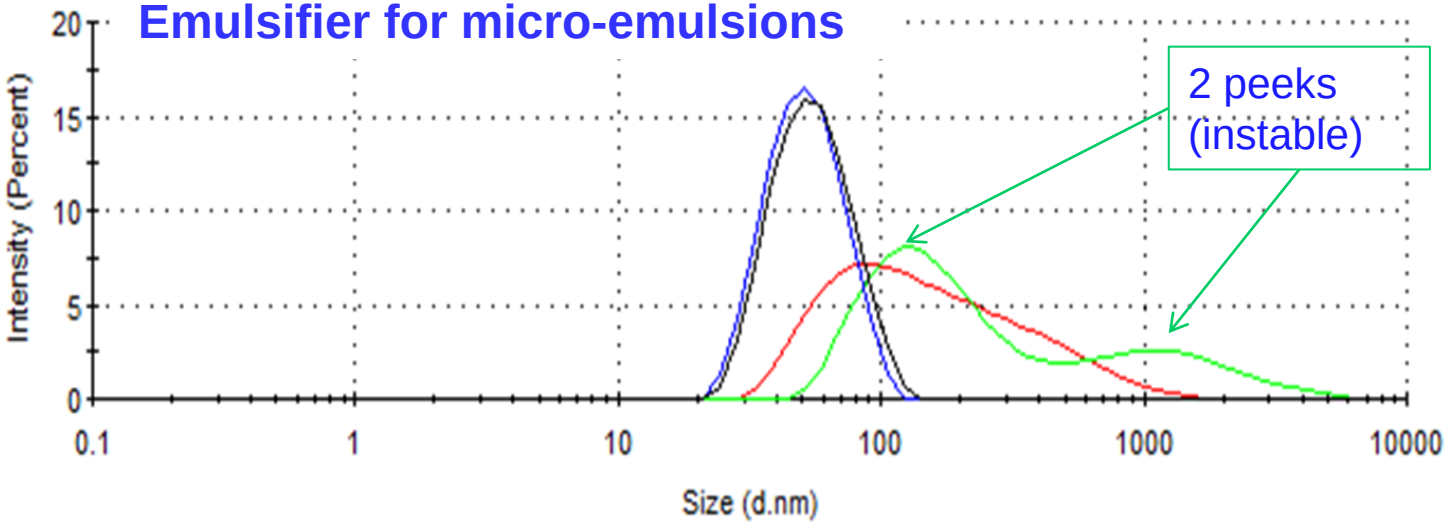


Partical size distribution emulsions

(5% emulsion - 10°gh, 180 ppm CaCO3)

	nonionic	anionic	*oil droplet size*
FORMULATION 1	oleyl	oleyl	~ 0,1 µm
FORMULATION 2	oleyl	POEO	> 0,1 µm
FORMULATION 3	POEO	oleyl	< 0,1 µm
FORMULATION 4	POEO	POEO	< 0,1 µm

Emulsifier for micro-emulsions



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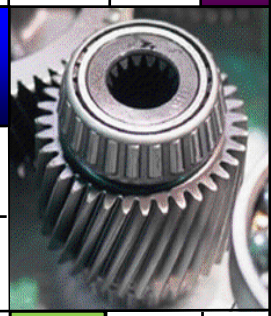
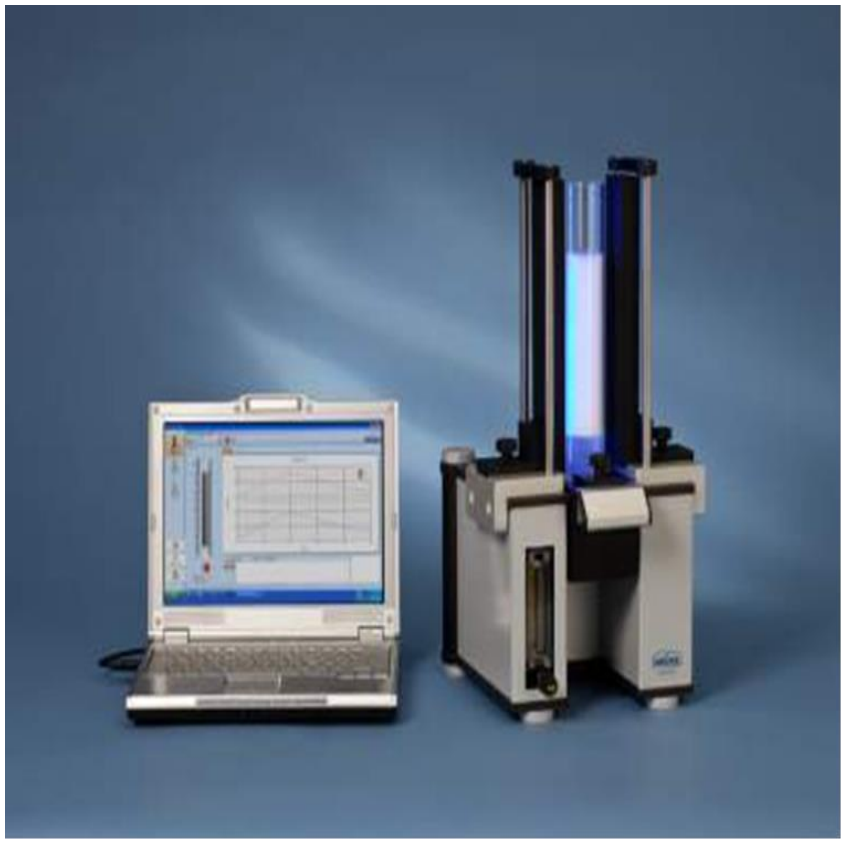
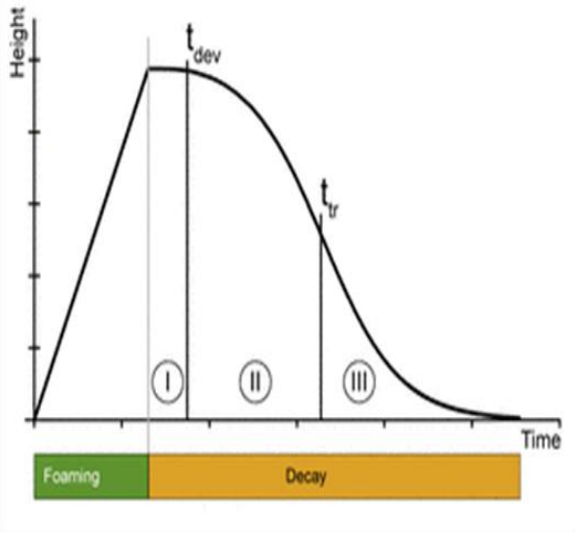


Foam control

Laboratory equipment to mimic high pressure appl.





I : Drainage without decay

II : Decay with simultaneous drainage

III: Decay after completed drainage

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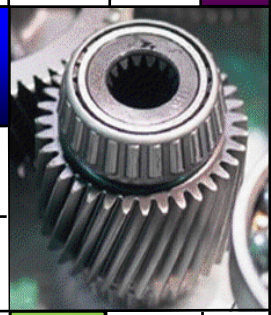
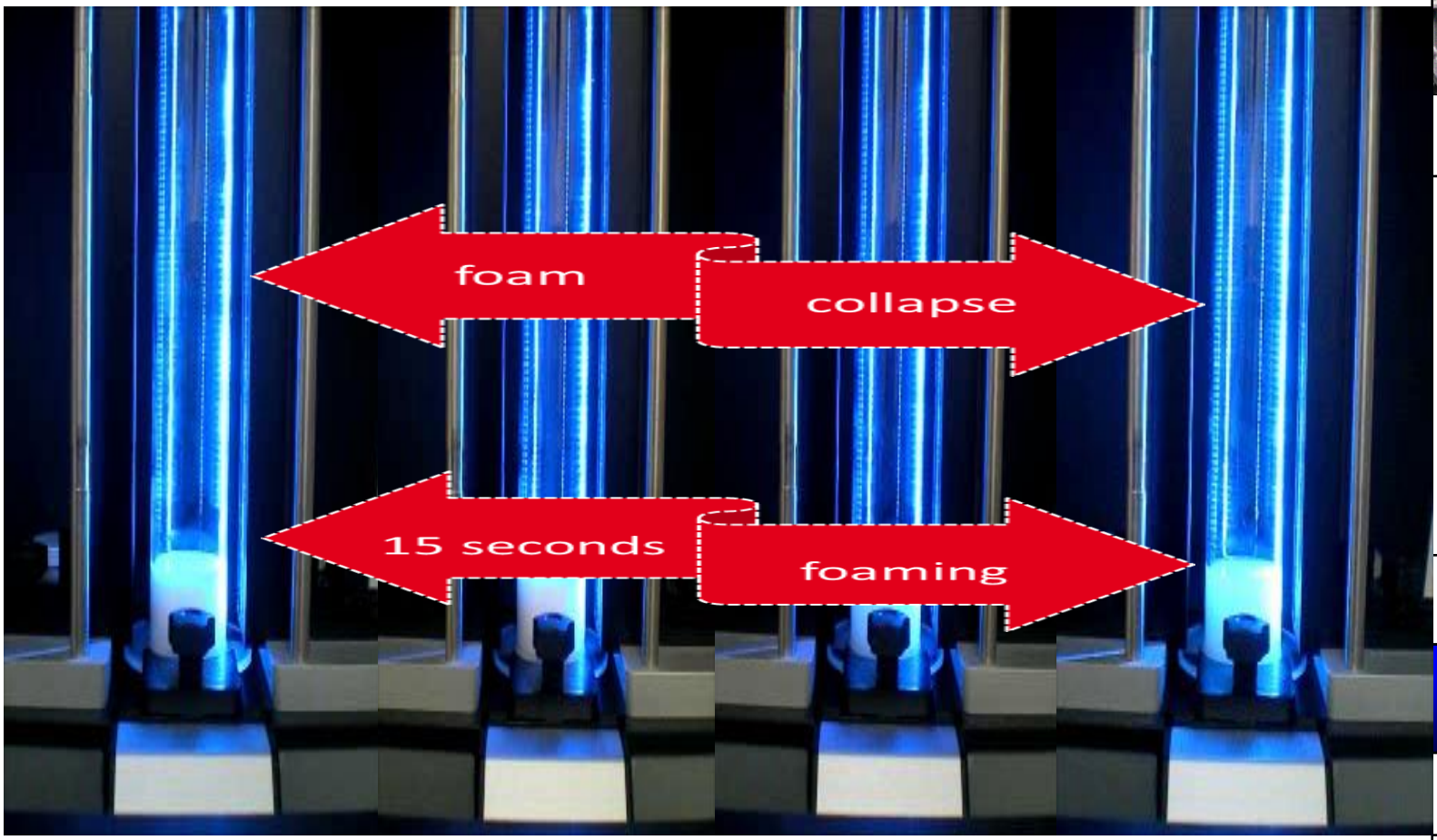


Foam tests results (5% emulsion - 10°gh,180 ppm)



Formulation 1 Formulation 2 Formulation 3 Formulation 4

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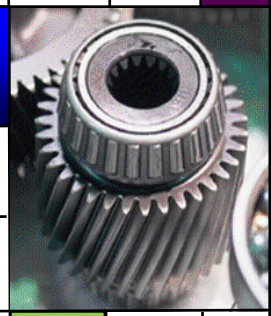
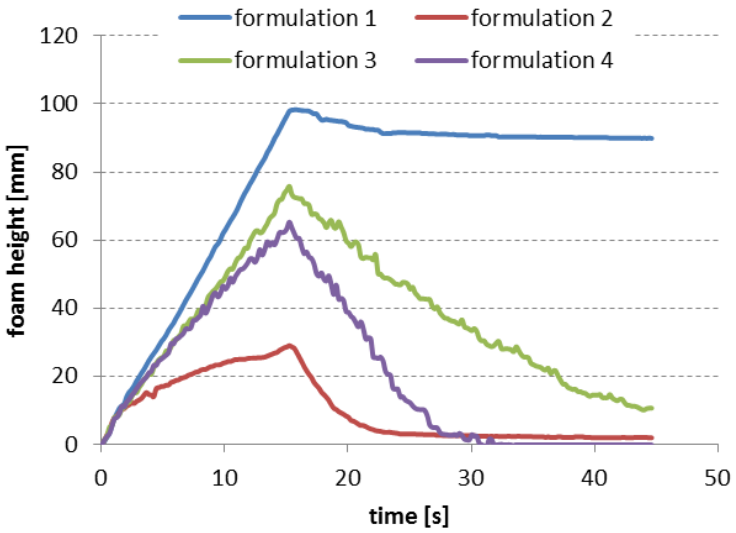
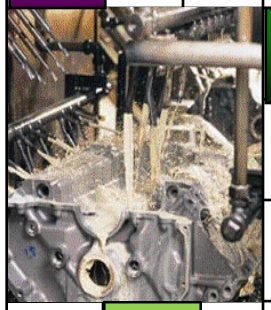


High pressure foam test (summary)



	Nonionic 3 %	Anionic 2 %
Form. 1	Cetyl-Oleyl 5 EO	AKYPO® RO 90 VG
Form. 2	Cetyl-Oleyl 5 EO	AKYPO® RSPE 66
Form. 3	AKYPO® ROX RS 0606N	AKYPO® RO 90 VG
Form. 4	AKYPO® ROX RS 0606N	AKYPO® RSPE 66

	foaming	*foam collapse*	
	max foam [mm]	**5 mm reduction**	**20 mm reduction**
formulation 1	98,3	4,8	> 30
formulation 2	29	1,2	4,4
formulation 3	75,8	1,2	5,8
formulation 4	65,3	1	3,6



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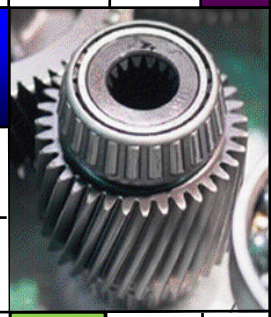
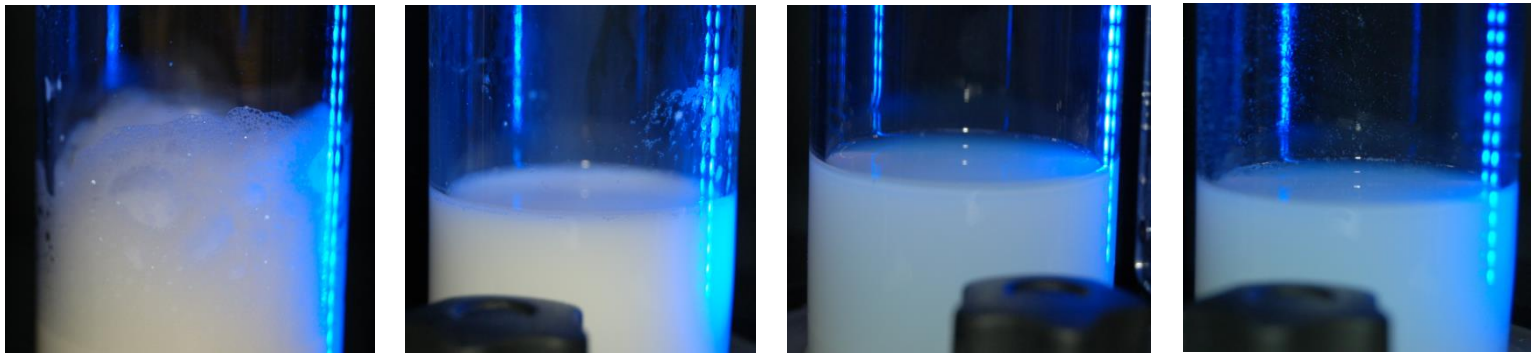


Residue control (5% emulsion - 10°gh, 180 ppm)

Formulation

1 2 3 4



	Nonionic 3 %	Anionic 2 %	Foam Control	Residue control
1	Cetyl-Oleyl 5 EO	AKYPO® RO 90 VG	moderate	excellent
2	Cetyl-Oleyl 5 EO	AKYPO® RSPE 66	excellent ←	moderate (instable)
3	AKYPO® ROX RS 0606N	AKYPO® RO 90 VG	good	good
4	AKYPO® ROX RS 0606N	AKYPO® RSPE 66	very good	good

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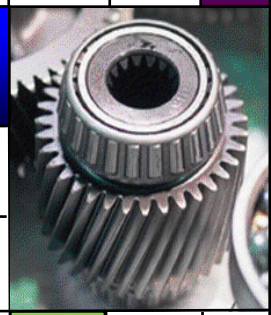
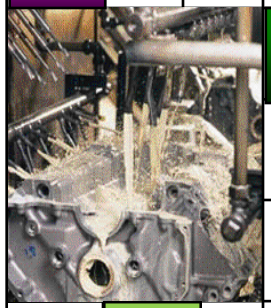


Part 2 : Upgrade Sulphonate based formulations for longer sump life (summary)

- Target:
  - Improve sump life sulphonate based formulation
    - Reduction of Sulphonate amount
- Tools:
  - Experimental design
  - Fine tuning mixture
    - Sulphonate
    - AKYPO (long alkyl chain PO/EO)
    - Fatty acid
    - Nonionic



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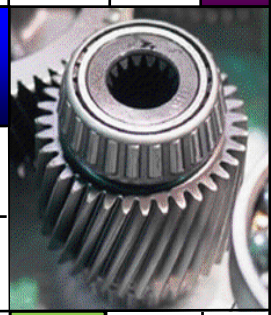

Typical semi-synthetic

	Material	Example 1
	Naphtenic Mineral Oil	10,0
	Aliphatic Dicarboxylic Acid	2,0
	Boric Acid	2,0
	MEA	10,0
	TEA	7,0
	Phosphate Ester	2,4
	Butyl Di Glycol	3,0
	Dest. Water	40,0
	Petroleum Sulphonate MW 450	14,0
	Tall oil fatty acid	6,0
	AKYPO® RO 90 VG (Oleyl Ethercarboxylic acid)	3,6
		100,0

Results:

- Very good electrolyte stability
- Too much foam

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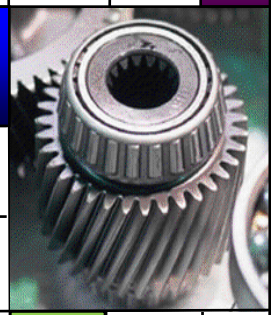
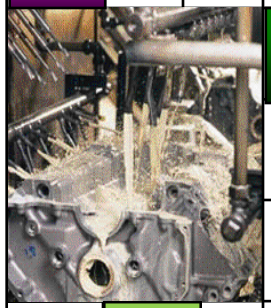


Variation of emulsifier package

	Material	Example 1	Example 2	Example 3
	Naphtenic Mineral Oil	10,0	10,0	10,0
	Aliphatic Dicarboxylic Acid	2,0	2,0	2,0
	Boric Acid	2,0	2,0	2,0
	MEA	10,0	8,5	8,5
	TEA	7,0	6,5	6,5
	Phosphate Ester	2,4	2,0	2,0
	Butyl Di Glycol	3,0	3,0	3,0
	Dest. Water	40,0	40,0	40,0
	Petroleum Sulphonate MW 450	14,0	14,0	14,0
	Cetyl oleyl 5 EO (NIO)		4,0	
	AKYPO® ROX RS 0606N (PO-EO alkoxylate)			4,0
	AKYPO® RO 90 VG (Oleyl Ethercarboxylic Acid)	3,6	2,0	
	AKYPO® RSPE 66 (PO-EO Ethercarboxylic Acid			2,0
	Tall oil fatty acid	6,0	6,0	6,0
		100,0	100,0	100,0

Results (2 and 3): - Good electrolyte stability
- Still too much foam



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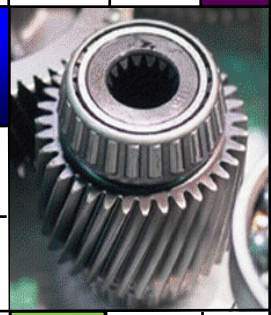
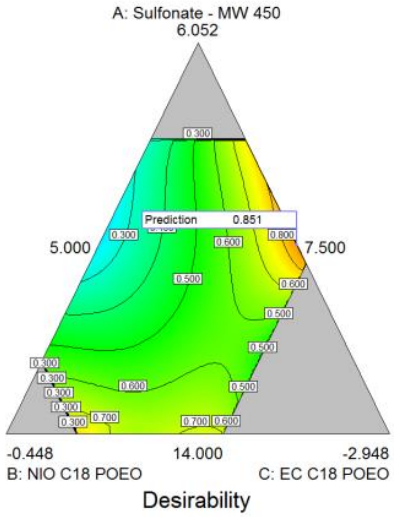


DoE – mixture design

	Material	Example 3
	Naphtenic Mineral Oil	10,0
	Aliphatic Dicarboxylic Acid	2,0
	Boric Acid	2,0
	MEA	8,5
	TEA	6,5
	Phosphate Ester	2,0
	Butyl Di Glycol	3,0
	Dest. Water	40,0
A	Petroleum Sulphonate MW 450 (Sulfonate-MW 450)	14,0
B	AKYPO® ROX RS 0606N (NIO C18 POEO)	4,0
C	AKYPO® RSPE 66 (EC C18 POEO)	2,0
D	Tall oil fatty acid (TOFA)	6,0
		100,0



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Design Summary

File Version	8.0.7.1				
Study Type	Mixture		**Runs**	22	
Design Type	*IV-optimal*	Point Exchang	**Blocks**	No Blocks	
Design Mode	Quadratic		**Build Time (ms)**	280.98	

Component	Name	Units	Type	Minimum	Maximum
A	Sulfonate - MW 4		Mixture	8.000	14.000
B	NIO C18 POEO		Mixture	1.000	7.500
C	EC C18 POEO		Mixture	0.500	5.000
D	TOFA		Mixture	3.000	9.000
				Total =	26.00

Emulsion stability

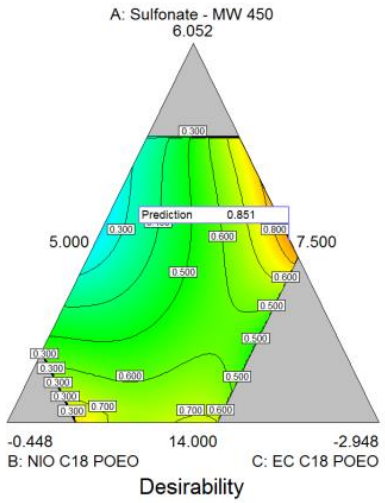
variations on example 3

	A	B	C	D
No.	Sulph.	A'ROX	AKYPO	TOFA
1	11,5	5,0	0,5	9,0
2	11,5	4,9	3,0	6,5
3	11,5	4,9	3,0	6,5
4	14,0	1,0	5,0	6,0
5	11,5	4,9	3,0	6,5
6	8,0	7,5	5,0	5,5
7	14,0	7,5	0,5	4,0
8	11,5	4,9	3,0	6,5
9	11,0	1,0	5,0	9,0
10	14,0	1,0	2,0	9,0
11	14,0	7,5	0,5	4,0
12	11,5	7,5	0,5	6,5
13	14,0	5,0	0,5	6,5
14	10,5	7,5	5,0	3,0
15	9,0	7,5	0,5	9,0
16	12,8	6,3	3,8	3,0
17	8,0	6,3	3,8	7,8
18	14,0	1,0	2,0	9,0
19	11,5	4,9	3,0	6,5
20	14,0	2,5	0,5	9,0
21	8,0	4,0	5,0	9,0
22	14,0	4,0	5,0	3,0

max: AKYPO / min: Sulphonate

max: Sulphonate / min: AKYPO

emulsion stability measured by:
electrolyte scan



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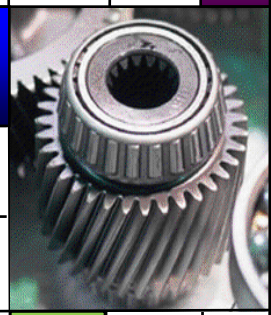
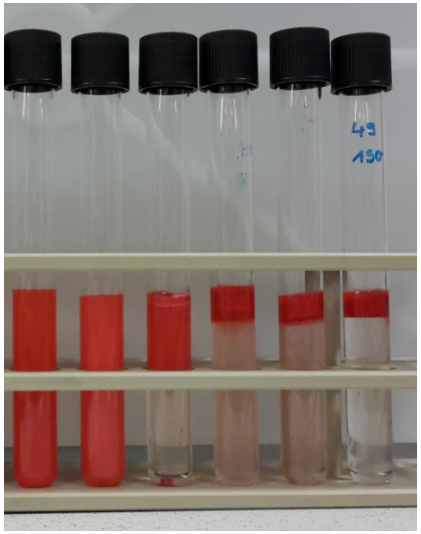
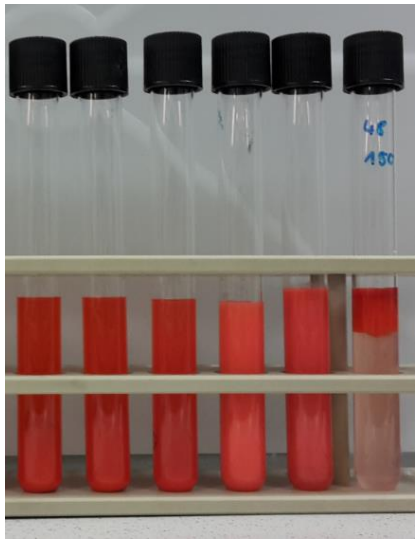


DoE - mixture design

No.	A Sulph.	B A'ROX	C AKYPO	D TOFA
1	11,5	5,0	0,5	9,0
2	11,5	4,9	3,0	6,5
3	11,5	4,9	3,0	6,5
4	14,0	1,0	5,0	6,0
5	11,5	4,9	3,0	6,5
6	8,0	7,5	5,0	5,5
7	14,0	7,5	0,5	4,0
8	11,5	4,9	3,0	6,5
9	11,0	1,0	5,0	9,0
10	14,0	1,0	2,0	9,0
11	14,0	7,5	0,5	4,0
12	11,5	7,5	0,5	6,5
13	14,0	5,0	0,5	6,5
14	10,5	7,5	5,0	3,0
15	9,0	7,5	0,5	9,0
16	12,8	6,3	3,8	3,0
17	8,0	6,3	3,8	7,8
18	14,0	1,0	2,0	9,0
19	11,5	4,9	3,0	6,5
20	14,0	2,5	0,5	9,0
21	8,0	4,0	5,0	9,0
22	14,0	4,0	5,0	3,0





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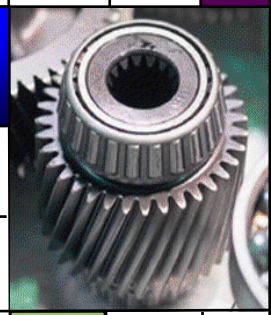
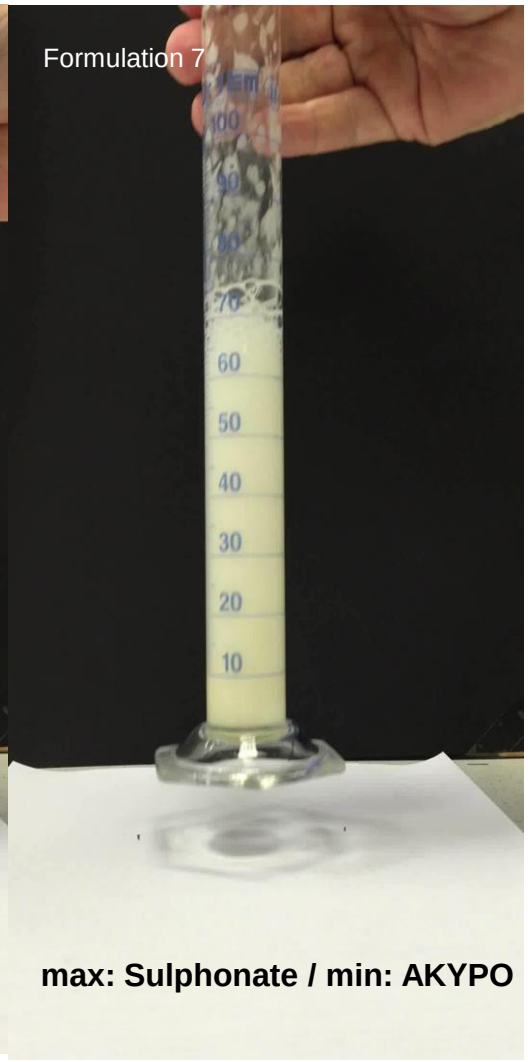
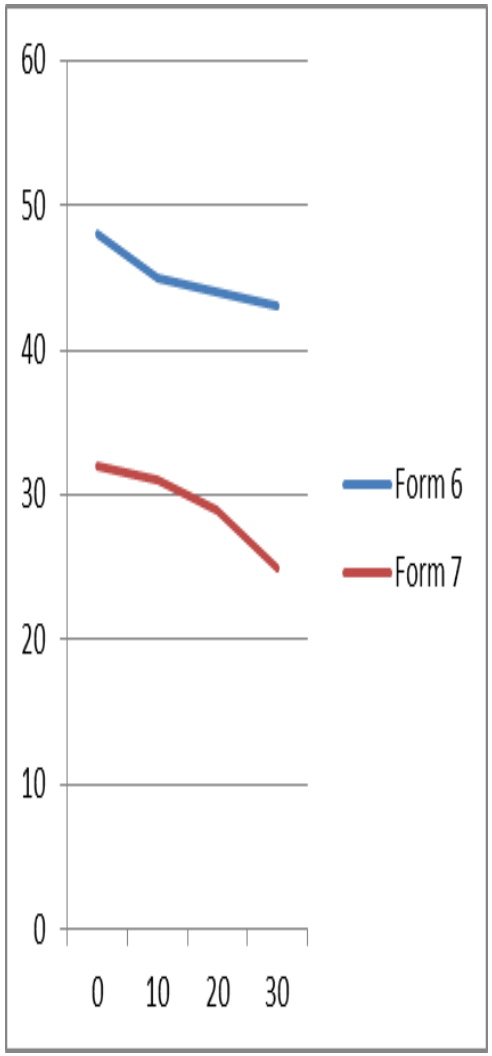


Shaking cylinder – 10% solution

After 12h storage – 250ppm Hardness – no defoamer





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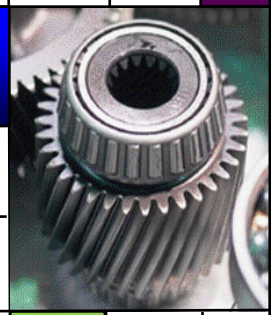
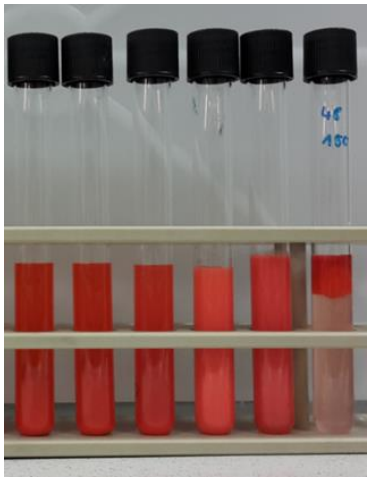


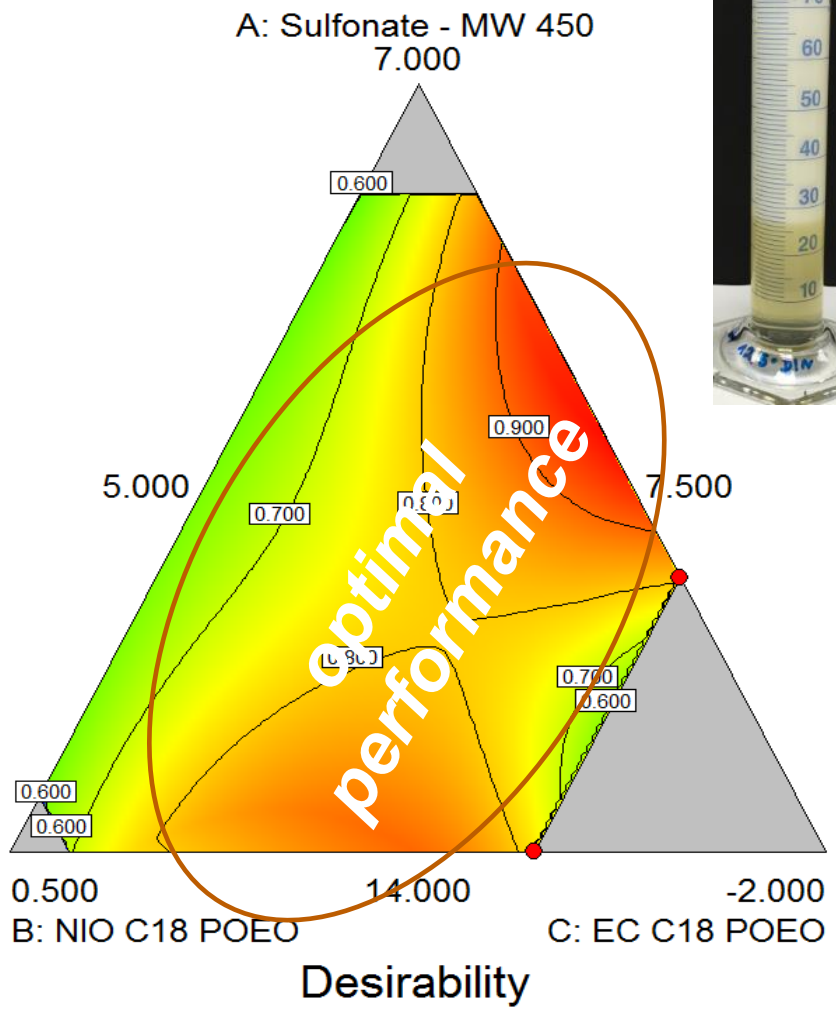
Optimization:
maximize stability & minimize foam stability

Design-Expert® Software
Component Coding: Actual
Highs/Lows inverted by U_Pseudo coding
Desirability
Design Points
1.000
0.000

X1 = A: Sulfonate - MW 450
X2 = B: NIO C18 POEO
X3 = C: EC C18 POEO

Actual Component
D: TOFA = 6.500





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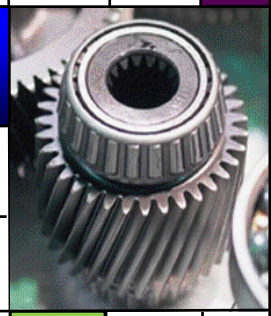
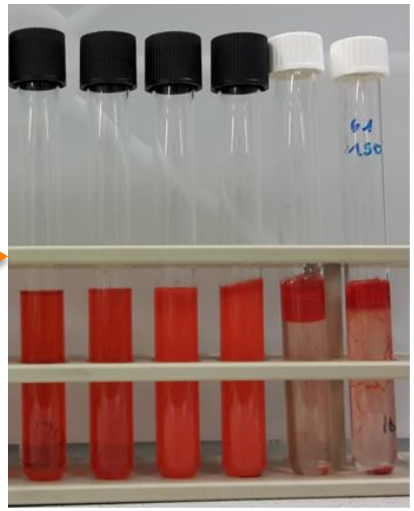


Result of clever design

- Good Electrolyte Stability
- Low Foam Stability



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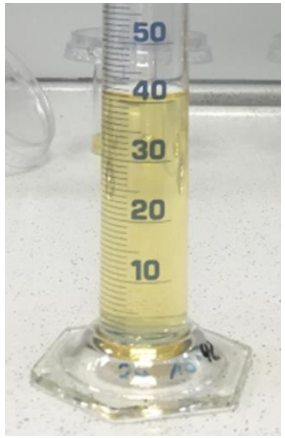
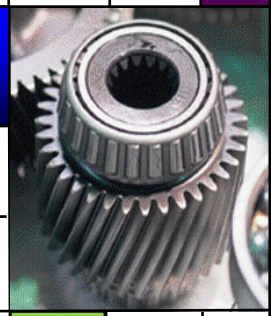
	A	B	C	D
No.	Sulph.	A'ROX	AKYPO	TOFA
1	11,5	5,0	0,5	9,0
2	11,5	4,9	3,0	6,5
3	11,5	4,9	3,0	6,5
4	14,0	1,0	5,0	6,0
5	11,5	4,9	3,0	6,5
6	8,0	7,5	5,0	5,5
7	14,0	7,5	0,5	4,0
8	11,5	4,9	3,0	6,5
9	11,0	1,0	5,0	9,0
10	14,0	1,0	2,0	9,0
11	14,0	7,5	0,5	4,0
12	11,5	7,5	0,5	6,5
13	14,0	5,0	0,5	6,5
14	10,5	7,5	5,0	3,0
15	9,0	7,5	0,5	9,0
16	12,8	6,3	3,8	3,0
17	8,0	6,3	3,8	7,8
18	14,0	1,0	2,0	9,0
19	11,5	4,9	3,0	6,5
20	14,0	2,5	0,5	9,0
21	8,0	4,0	5,0	9,0
22	14,0	4,0	5,0	3,0

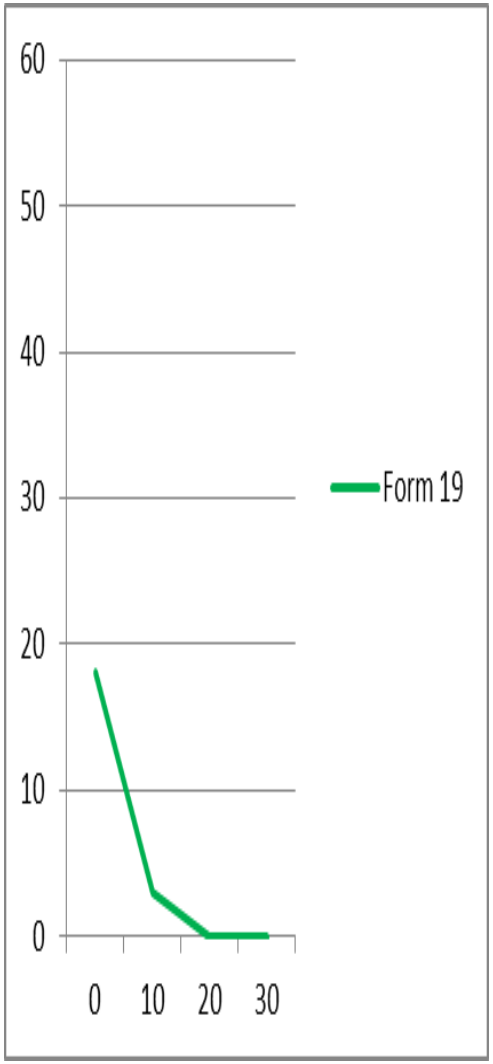


	Formulation based on sample 3	Form 19
	Naphtenic Mineral Oil	10,0
	Aliphatic Dicarboxylic Acid	2,0
	Boric Acid	2,0
	MEA	8,6
	TEA	6,5
	Phosphate Ester	2,0
	Butyl Di Glycol	3,0
	Dest. Water	40,0
A	Petroleum Sulphonate MW 450	11,5
B	AKYPO® ROX RS 0606N (PO-EO Alkoxylate)	4,9
C	AKYPO® RSPE 66 (PO-EO ethercarboxylic acid)	3,0
D	Tall oil fatty acid (TOFA)	6,5
		100,0



Shaking cylinder – 10% solution

After 12h storage – 250ppm Hardness – no defoamer



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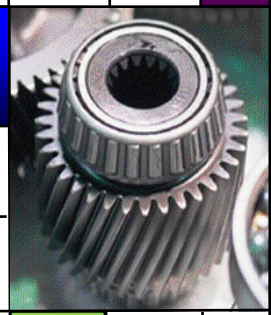
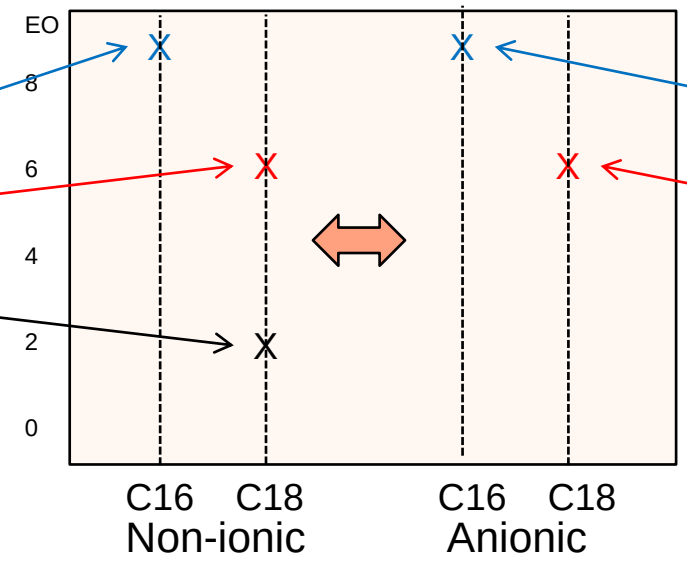


Other combinations are possible

Propoxylated-Ethoxylated based emulsifiers/stabilizers

Non-ionic types

- AKYPO® ROX RC 0960N
- AKYPO® ROX RS 0606N
- AKYPO® ROX RS 0602N



Anionic types

- AKYPO® RC 0960
- AKYPO® RSPE66

All products contain 6 Propylene oxide (PO) groups

- Non-ionic – Anionic Combination :
  - Strong emulsifiers
  - Low foam stability tendency
- Including AKYPO LF types will create the Anionic Synergy

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