

BASE OIL AND EMULSIFIER SELECTION PRINCIPLES PART II - A METALWORKING FLUID EMULSION STABILITY STUDY

Metalworking Fluids

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INTRODUCTION

The First part of this work was presented at the 2016 STLE Annual Meeting (Las Vegas). In the previous study, we did compare a Sorbitan type non-ionic emulsifier combination (Tween/Span) with a non-ionic emulsifier package from Solvay. In the present study, we expanded the HLB range of that system, to take a closer look at the emulsion stability variations, completing the soluble oil study (coarse milky emulsions) Part II.

In the second part of this paper, we introduce four new chemistries for Semi-synthetic translucent "micro" emulsion based on Naphthenic specialty base oils, Group I and Group II base oils

RESULTS AND DISCUSSION

Bases oils investigated

Four ISO VG 22 (~100 SUS) base oils

- Naphthenic T 22, Aniline Point (AP) = 76 °C
- SN 100, AP = 100 °C
- Nynas' Group I replacement "new range" 100, AP = 101 °C
- HP 4, a Group II base oil, 20 cSt (4 cSt @100 °C), AP = 108 °C

Water hardness

- De-ionised, °dH = 0 (similar to Reverse Osmosis)
- Synthetic hard water, °dH = 20 (357 ppm CaCO₃, e.g. Los Angeles)

We utilized two complementary analytical approaches

- 1. Droplet Size Distribution (DSD), determined by light scattering at high dilution
- 2. Light transmission and back scattering, determined "as-is" on the real liquid systems

Emulsion stability is correlated to the growth of droplet size by coalescence

- The emulsions in this project were based on four different base oils with a KV 40 of ca 22 cSt (shown previously)
- A commercial emulsifier package from Solvay was used in this project. The primary emulsifier was E1 (HLB value is 9.2) and the co-emulsifier E2 (HLB value is 5.6)



• Soft water was used (°dH 0)

NB! Three performance levels are clearly visible in this kinetic analysis A higher TSI score indicates more rapid change, in this case emulsion droplet growth rate

New results, Soluble oils (milky emulsion)

The emulsions in this project were based on four different base oils with a KV 40 of ca 22 cSt (shown previously). A commercial emulsifier package from Solvay was used in this project. The primary emulsifier was E1 (HLB value is 9.2) and the co-emulsifier E2 (HLB value is 5.6). Soft water was used (°dH 0). Half way results: The Naphthenic 22 cSt base oil gives the most stable emulsions under these test conditions:

- The DSD is the lowest for Naphthenic 22 cSt
- The median droplet size is the smallest for Naphthenic 22 cSt
- The optimum value was found to be HLB 8.5 for Naphthenic 22, SN 100 and Nynas' "New Range" 100
- For the Group II oil, the best stability was found at HLB 7.4

The Group II oil show high sensitivity to HLB matching, as seen by the rapid growth of emulsion droplet size at Day 7 for the mismatching HLB values



NB! Please note the rapid droplet size growth at Day 7

Semi synthetic emulsions Part I

The Naphthenic 22 cSt base oil gives the most stable emulsions under these test conditions. The DSD is the lowest for Naphthenic 22 cSt. The median droplet size is the smallest for Naphthenic 22 cSt. The optimum value was found to be HLB 8.5 for Naphthenic 22, SN 100 and Nynas' "New Range" 100. For the Group II oil, the best stability was found at HLB 7.4. The Group II oil show high sensitivity to HLB matching, as seen by the rapid growth of emulsion droplet size at Day 7 for the mismatching HLB values.

For (nearly) translucent semi-synthetic formulations, the droplet size was in general found be smaller (as expected) than for the milky emulsions. For two of the base oils (Naphthenic 22 cSt and SN 100), water hardness was found to be of more notable impact on DSD. Very small DSD changes were observed over the one week measurement period.

An order of merit was observed for the more complex emulsifier system of the semi-synthetic formulation:

Naphthenic > Group I > Group II

This follows the solvency properties by Aniline Point order for these base oils

Semi synthetic emulsion Part II

As a second phase of the study, we made semi-synthetic translucent "micro" emulsions of three different Naphthenic base oils. The aim of the project was to investigate the emulsion stability between different Naphthenic base oils, with three different emulsifier packages. The emulsifier chemistry was based on formulations from Sasol Performance Chemicals. We investigated three different oil viscosities: 9, 22 and 110 cSt (@ 40 °C). Thus, nine different semi synthetic emulsion concentrates were prepared. Hard or soft water in the final emulsion, giving 18 samples in all.





Summary result histogram, hard water

NB1 * = below detection range of 0.1 $\mu m,$ and low laser obscuration

Conclusions Soluble Oils

- In this study, we set out to investigate different parameters affection the primary emulsion stability of model metalworking fluids
- We could determine the optimal HLB value for the different base oils, and could also observe large differences in emulsion stability
- The Naphthenic 22 cSt base oil gives the most stable emulsions under these test conditions
- The optimum HLB value differs by more than one unit (8.5 vs. 7.4) between base oils traditionally employed in emulsions (Naphthenic and Group I) versus the Group II oil
- The Group II base oil showed rapid change over time compared to the other base oils
- This indicated that there are fundamental differences driving emulsion stability and ripening/coalescence phenomena
- The solvency, as indicated by the **Aniline Point**, mirrors this order, and thus apparently plays an important role for emulsion stability in the systems investigated

Conclusion Semi-Synthetic Emulsions:

- The second part of the study was on semi-synthetic translucent formulations, based on anionic and non-ionic surfactants
- For these samples, the DSD in general was much smaller, indicating even better emulsion stability

- These systems did display sensitivity towards water hardness, as expected from the anionic surfactant chemistry
- The extent and character of the effect was different for the different base oils
- The broad investigations of Naphthenic base oils (9, 22 and 110 cSt) clearly demonstrates the wealth of the semi-synthetic emulsion chemistry
- Even in a simple screening study like the present one, clear indications of suitable formulation chemistries may be learned
- However, the general stability trend follows what we found for the Soluble oils milky emulsions: Naphthenic > Group I > Group II

Final summary & Conclusions

- Emulsion stability is a key requirement of emulsion-type metalworking fluids
- Emulsion stability can be modelled in test systems
- The **droplet size distribution** (DSD) method offers a wealth of data, and can generate a well-resolved mapping of the stability properties
- The key base oil property difference identified was **solvency**, as expressed by the **Aniline Point**
- The **water hardness** made a difference in several ways in the semi-synthetic emulsion systems, containing also anionic surfactants
- We would like to propose that the results obtained in these studies would indeed be useful as a **component selection guide** to metalworking fluid formulator across geographical regions, with varying water hardness, and different access to base oils suitable for metalworking emulsion formulations

Key Words: Emulsion stability, surfactant, naphthenic, solvency, Aniline Point



Made with Nynas oil

Made with Nynas oil

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Base Oil and Emulsifier Selection Principles Part II - A Metalworking Fluid Emulsion Stability Study

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Nynas was founded in Sweden 1928

- Nynas is the largest specialty oil producer in Europe
- Offices in more than 30 countries around the globe
- Net Sales: 1.4 Billion USD (2016)
- Average number of employees: 1000
- Refineries in Nynäshamn (SE), Harburg (DE), Isla JV (Curacao), Eastham JV (UK), Gothenburg (SE)



Nynashamn



Harburg



What we can do for you





Metalworking Fluid: key performance and tasks

- Metalworking fluids (MWF) are used to aid the process of metal machining, mainly by Iubrication and cooling, and to provide corrosion protection
- MWF can be generally categorized as
 - emulsions ("coolants") which mainly cool and protect against corrosion
 - **neat oils** which can handle better high deformation, severe boundary lubrication and offer tool wear protection





Metalworking Fluids by formulation type



- * These concentrates are used at 5-10% and diluted with water by the end user
- ** Synthetic does not mean synthetic oil in this case, it actually contains no oil of any kind

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Water-miscible fluids



Typically emulsion of 5-10% mineral oil in water

- Used when cooling is most important
- Typical additional components:
 - Emulsifiers
 - Lubricity additives
 - Corrosion inhibitors
 - Biocides and Antifoams
 - Mist suppressants

Used as:

- Cutting fluids
- Protecting fluids
- Hot rolling fluids
- Suitable for high-speed cutting operations where much heat is generated



Naphthenic oils advantages in water-miscible MWF

High solvency (lower Aniline Point) which allows for:

- solution of high amounts of additives
- increased emulsion stability

Lower density difference between oil and water compared to paraffinic oils, therefore

- increased emulsion stability
- increased emulsion resistance to centrifugal forces during pumping



Previous work in the field of emulsion stability

- The First part of this work was presented last year in Las Vegas
- In the previous study, we did compare a Sorbitan type non-ionic emulsifier combination (Tween/Span) with a non-ionic emulsifier package from Solvay
- In the present study, we expanded the HLB range of that system, to take a closer look at the emulsion stability variations, completing the soluble oil study (coarse milky emulsions) Part II
- In the second part of this paper, we introduce four new chemistries for Semi-synthetic translucent "micro" emulsion based on Naphthenic specialty base oils, Group I and Group II base oils





Base oils utilized in all studies

- Four ISO VG 22 (~100 SUS) Base oils investigated
 - Naphthenic T 22, Aniline Point (AP) = 76 °C
 - SN 100, AP = 100 °C
 - Nynas' Group I replacement "new range" 100, AP = 101 °C
 - HP 4, a Group II base oil, 20 cSt (4 cSt @100 °C), AP = 108 °C
- Water hardness
 - De-ionised, °dH = 0 (similar to Reverse Osmosis)
 - Synthetic hard water, °dH = 20 (357 ppm CaCO₃, e.g. Los Angeles)





Emulsion stability determination by droplet size determinations over time

- We utilized two complementary approaches
- 1. Droplet Size Distribution (DSD)
 - Determined by light scattering at high dilution
 - We can monitor DSD changes over time
 - Coalescences and ripening can thus be detected
- 2. Light transmission and back scattering
 - Determined "as-is" on the real liquid systems
- Emulsion stability is correlated to the growth of droplet size by coalescence
- Emulsion stability can be directly assessed by light scattering and vertical scanning
 - Sedimentation, creaming, layering etc. can be observed directly and plotted time-resolved
 - Relation b/w different experiment through calculations



Malvern MasterSizer 3000E





DSD and TSI co-variation, Naphthenic 22 cSt in soft water



NB! A distinct optimum, in the form of minimum droplet size, at HLP 12 in soft water Histogram: DSD by MasterSizer Purple Line: TSI by Turbiscan transmittance



Reference case: Commercial Soluble oil package

The naphthenic base oil displays a clear maximum DSD at ca 0.5 μm

The paraffinic Group I and Group II base oils display a two-phase DSD behaviour, with a second stability maximum centered around 60 µm droplet size



We could not detect any significant droplet size distribution change over the test duration

 A commercial formulation could reasonably be expected to show emulsion stability over longer times



Commercial Soluble oil package, emulsion destabilisation kinetics by TSI



NB! Three performance levels are clearly visible in this kinetic analysis A higher TSI score indicates more rapid change, in this case emulsion droplet growth rate



Soluble oil Part II New experimental study



New results, Soluble oils (milky emulsion)

- The emulsions in this project were based on four different base oils with a KV 40 of ca 22 cSt (shown previously)
- Naphthenic T 22
- Conventional group I, SN 100
- Nynas' Group I replacement base oil "new range" 100
- Group II, 20 cSt (4 cSt @100 °C)
- A commercial emulsifier package from Solvay was used in this project. The primary emulsifier was E1 (HLB value is 9.2) and the co-emulsifier E2 (HLB value is 5.6)
- Soft water was used (°dH 0)



New results, Soluble oils (milky emulsion)

- A commercial emulsifier package from Solvay was used in this project. The primary emulsifier was E1 (HLB value is 9.2) and the co-emulsifier E2 (HLB value is 5.6)
- Soft water was used (°dH 0)

	1	2	3	4	5
Oil	75.0%	75.0%	75.0%	750.%	75.0%
E1, HLB 9.2	22.5%	20.0%	17.5%	15.0%	12.5%
E2, HLB 5.6	2.5%	5.0%	7.5%	10.0%	12.5%
Effective HLB	8.8	8.5	8.1	7.8	7.4



Droplet size distribution spectrum, HLB 8.5





Naphthenic 22 cSt histogram, five HLBs



NB! Please note the scale of the Y axis



Droplet size distribution spectrum, HLB 7.4





Paraffinic Group II histogram, five HLBs



NB! Please note the rapid droplet size growth at Day 7



Half-way summary of Soluble oils Part II

- The Naphthenic 22 cSt base oil gives the most stable emulsions under these test conditions
 - The DSD is the lowest for Naphthenic 22 cSt
 - The median droplet size is the smallest for Naphthenic 22 cSt
- The optimum value was found to be HLB 8.5 for
 - Naphthenic 22, SN 100 and Nynas' "New Range" 100
 - For the Group II oil, the best stability was found at HLB 7.4
- The Group II oil show high sensitivity to HLB matching, as seen by the rapid growth of emulsion droplet size at Day 7 for the mismatching HLB values



Semi-Synthetic formulations Part I – different base oils



Semi-synthetic emulsions

- As a second phase of the study, we made eight (8) new semi-synthetic translucent "micro" emulsions
 - These emulsions were based on Clariant chemistry and formulations
- The aim of the project was to investigate the emulsion stability between different base oil with the same emulsifier package
- The selection of emulsifiers and coupling agents originally optimized for Naphthenic 22 cSt by Clariant
- We applied this package also in the range of Gr I and Gr II oils shown previously, and again to hard or soft water



Preparation of semi-synthetic emulsions

- Each concentrate was diluted in water, hard or soft
- Treat rate of 5 % concentrate poured into 95 % water
- The emulsions were left equilibrating over the night
- The following day, a standardised mixing of the emulsion was done by using an Ultra-Turrax at the lowest setting for three minutes



Ultra Turrax high shear rotor-stator blender



A semi-synthetic formulation

Naphthenic base oil/Group I/Group II				
20- 22 cSt base oil	30%			
 Emulsifiers Tall Oil Fatty Acid (TOFA) Clariant emulsifiers Non-ionic, alkoxylated fatty alcohol Anionic emulsifier Emulsifier & Corr. Inhibitor 	3% 3% 1% 5%			
Biocide	3%			
Coupling agent	0.8%			
 Water soluble components MEA /TEA (4% + 8%) Corrosion Inhibitor (CI) BTZ Yellow Metal inhibitor 	12% 6% 0.2%			
Water , total of	36%			





Droplet size distribution (DSD) determination

- The DSD was determined using the same methodology as in previous studies
- The data can be presented either as histograms or in the form of droplet size spectra
- The interpretation of these observations give good insight into the stability of the emulsions formed



Malvern MasterSizer 3000E



Summary result histogram, soft water



NB! Small droplet size, small changes over the seven day period



Summary result histogram, hard water



NB! Group I droplet size decreases, all other increase somewhat A noticeable difference develops in this system between SN 100 and NR 100



Droplet Size Distribution, Day 7, hard or soft water





Results and conclusion of DSD test series

- For (nearly) translucent semi-synthetic formulations, the droplet size was in general found be smaller (as expected) than for the milky emulsions
- For two of the base oils (Naphthenic 22 cSt and SN 100), water hardness was found to be of more notable impact on DSD
- Very small DSD changes were observed over the one week measurement period
- An order of merit was observed for the more complex emulsifier system of the semi-synthetic formulation:
- Naphthenic > Group I > Group II
 - This follows the solvency properties by Aniline Point order for these base oils



Semi-Synthetic formulations Part II – Naphthenic oil viscosity range study



Semi-synthetic emulsions, 18 new samples

- As a second phase of the study, we made semi-synthetic translucent "micro" emulsions of three different Naphthenic base oils
- The aim of the project was to investigate the emulsion stability between different Naphthenic base oils, with three different emulsifier packages
- The emulsifier chemistry was based on formulations from Sasol Performance Chemicals
- We investigated three different oil viscosities: 9, 22 and 110 cSt (@ 40 °C)
- Thus, nine different semi synthetic emulsion concentrates were prepared
- Hard or soft water in the final emulsion, giving 18 samples in all

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Three semi-synthetic formulations

MWF formulations



MWL conc 1		
	%	
Fatty Acid	10	
Sodium Sulphonate	5	
Emulsifier low foam	15	
ECA	5	
Emulsifier low foam	2,5	
Coupling agent	1,5	
Corrosion Inhibitor	2,5	
Boric Acid	10	
MEA	20	
TEA	10	
BTA	0,5	
Biocide	5	
H2O	13	

MWL conc. 1 35% Nynas 9/22/110 30% Water (demin.) 35%

MWL conc 2			
	%		
Sodium Sulphonate	15,5		
Fatty acid	3		
Emulsifier low foam	12,1		
Emulsifier low foam	6,1		
ECA	6,1		
Coupling agent	5,3		
Corrosion Inhibitor	12,1		
MIPA	15,3		
TEA	17,5		
BTA (glyc sol*50%)	1		
Biocide	6,0		

MWL conc. 2 40% **Nynas 9/22/110** 30% 30%

MWL conc 3	
	%
Sodium Sulphonate	13,4
Fatty acid	2,65
Fatty acid	
ethoxylated	10,7
Emulsifier low foam	10,7
Emulsifier low foam	5,4
ECA	5,4
Coupling agent	6,2
Corrosion inhibitor	10,7
Lactic acid	2,65
MIPA	21,4
TEA	10.8

MWL conc. 3 40% **Nynas 9/22/110** 30% 30%



Concentrate MWL2 and Naphthenic base oils



Naphthenic110 cSt9 cSt22 cStMWL 2 and Demineralised water



Preparation of semi-synthetic emulsions

- Each concentrate was diluted in water, hard or soft
- Treat rate of 5 % concentrate poured into 95 % water (soft or hard)
- The emulsions were left equilibrating over the night
- The following day, a standardised mixing of the emulsion was done by using an Ultra-Turrax at the lowest setting for three minutes



Ultra Turrax high shear rotor-stator blender



Semi-synthetic emulsion of 22 cSt Naphthenic oil Hard (left bottle) and soft (right) water

Day 0



Day 30 (soft)



Translucent emulsions, stable over 30+ days



Summary result histogram, soft water



NB1 * = below detection range of 0.1 μm, and low laser obscuration.

... Possibly the "best" result anyway?



Summary result histogram, hard water



NB1 * = below detection range of 0.1 μm, and low laser obscuration



Select results Naphthenic 9 cSt base oil



NB! A huge difference between MWL 2 and MWL 1 or 3 for the 9 cSt base oil (substantial also for the 22 cSt base oil)



Select results Naphthenic 9 cSt base oil



NB! Almost no sensitivity to water hardness in this system The 9 cSt base oil showed best emulsion stability with the MWL 2 concentrate



Select results Naphthenic 22 cSt base oil in MWL 1



NB! No data obtainable for Soft water; below detection range of 0.1 µm, and low laser obscuration



Semi-synthetic emulsion of 22 cSt Naphthenic oil Hard (left bottle) and soft (right) water

Day 0



Day 30 (soft)



Translucent emulsions, stable over 30+ days



Select results Naphthenic 22 cSt base oil in MWL 3



NB1 Large peak shift (100x droplet size) due to water hardness difference



Naphthenic 22 cSt and MWL 3

Day 0



Day 7





Select results Naphthenic 110 cSt base oil



NB! Stable small emulsion in soft water Stable larger size emulsions in hard water



Select results Naphthenic 110 cSt base oil



NB! Large structural rearrangements after Day 0, especially In hard water (..not air bubbles!)



Select results Naphthenic 110 cSt base oil



NB! Soft water giving very small droplets and low lase obscurationpossibly the most stable emulsions? Again, some kind of rearrangement after Day 0...



Summary and Conclusions



Conclusion Soluble oils Part II

- In this study, we set out to investigate different parameters affection the primary emulsion stability of model metalworking fluids
- We could determine the optimal HLB value for the different base oils, and could also observe large differences in emulsion stability
- The Naphthenic 22 cSt base oil gives the most stable emulsions under these test conditions
- The optimum HLB value differs by more than one unit (8.5 vs. 7.4) between base oils traditionally employed in emulsions (Naphthenic and Group I) versus the Group II oil
- The Group II base oil showed rapid change over time compared to the other base oils
- This indicated that there are fundamental differences driving emulsion stability and ripening/coalescence phenomena
- The solvency, as indicated by the Aniline Point, mirrors this order, and thus apparently plays an important role for emulsion stability in the systems investigated



Conclusion Semi-Synthetic emulsions Part I & II

- The second part of the study was on semi-synthetic translucent formulations, based on anionic and non-ionic surfactants
- For these samples, the DSD in general was much smaller, indicating even better emulsion stability
- These systems did display sensitivity towards water hardness, as expected from the anionic surfactant chemistry
- The extent and character of the effect was different for the different base oils
- The broad investigations of Naphthenic base oils (9, 22 and 110 cSt) clearly demonstrates the wealth of the semi-synthetic emulsion chemistry
- Even in a simple screening study like the present one, clear indications of suitable formulation chemistries may be learned
- However, the general stability trend follows what we found for the Soluble oils milky emulsions: Naphthenic > Group I > Group II



Final Conclusions

- **Emulsion stability** is a key requirement of emulsion-type metalworking fluids
- Emulsion stability can be **modelled** in test systems
- The droplet size distribution (DSD) method offers a wealth of data, and can generate a well-resolved mapping of the stability properties
- The key base oil property difference identified was solvency, as expressed by the Aniline Point
- The water hardness made a difference in several ways in the semi-synthetic emulsion systems, containing also anionic surfactants
- We would like to propose that the results obtained in these studies would indeed be useful as a component selection guide to metalworking fluid formulator across geographical regions, with varying water hardness, and different access to base oils suitable for metalworking emulsion formulations

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