

NEAT OIL SOLUTION STABILITY AND MAXIMUM ADDITIVE LOADING - A METALWORKING FLUID STABILITY STUDY

Metalworking Fluids

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INTRODUCTION

Metalworking Neat Oils have to be able to dissolve high amounts of additives, creating concentrated solutions that must be stable over time, at varying transport, handling and storage temperatures. In this study, we have prepared concentrated solutions of seven (7) different additives, and studied their solution stability over time. We are subjected samples to different conditions: ambient, low temperature and elevated temperature, and made observations over half a year. Key observables are the formation of precipitates, insolubles, separation at low temperature etc. Results were obtained and analysed for seven (7) different Naphthenic, Group I and Group II base oils, that represent a spectrum of solvencies and have different base oil chemical composition, aromatic content and aniline points. The conclusions of this study will give additional insights into how base oil solvency and low temperature flow properties affect the formulation of neat oil metalworking fluids

RESULTS AND DISCUSSION

A study was initiated to chart the solubility of a range of additives commonly utilized in metalworking fluids (MWF:s), Figure 1. The additives were present in concentrations corresponding to high end treat rates (1-15 %). The samples were divided into four groups, and subjected to different temperatures:

- 1. +50°C
- 2. -25°C
- 3. Ambient temperature (+19°C)
- 4. Rotation between ambient, +50°C and -25°C

All samples were monitored for any apparent changes:

- Cloudiness
- Formation of a precipitate or separated phase
- Viscosity & flow properties

Figure 1. Additive types in this study



Base Oils utilised in this study

Four ISO VG 22 (~100 SUS) base oils were investigated

- Naphthenic base oil 22.7 cSt, Aniline Point (AP) = 75 °C
- Group I base oil SN 100, 17.6 cSt, AP = 98 °C
- Group II base oil, 19.9 cSt (4.0 cSt @100 °C), AP = 107 °C
- Group III base oil, 20.0 cSt (4.3 cSt @100 °C), AP = 115 °C

In addition, three of Nynas' Group I replacement base oil were investigated in Part II of the study:

- New range 100 SUS (20 cSt) Group I replacement fluid
- New range 150 SUS (30 cSt) Group I replacement fluid
- New range ISO VG 32 Group II replacement fluid
- •

Summary of our results:

Two half-year long term solution stability studies have been completed. Solution stability, of course, differs between additive classes. In general, additive solubility (or indeed base oil solvency) in the base oils follows the Aniline Point (AP) order. This is expected, as the additives have been developed over very long times for the AP 100 °C or lower type Group I and Naphthenic base oils.

Some of the long-term effect develop because of other chemical changes in the systems, notably oxidation. These model systems comprise base oil and EP/lubricity type additives, not any Antioxidant (AO). Some of the colour changes might have been different with AO present? The upper solubility limit in (maximum additive loading) appear to be quite high for these additive types. A significant difference was found for the vLCCP Chlorinated paraffin.

Key Words: Neat Oils, solution stability, solvency, Aniline Point



Neat Oil Solution Stability and Maximum Additive Loading - A Metalworking Fluid Stability Study Made with Nynas oil

Made with Nynas oil

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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



Neat oil basics

Typical mineral oil-based

- Used when lubrication is important
- Good cooling provided

Typical additives:

- Lubricity improvers
- Extreme pressure improvers
- Film-forming additives
- Antioxidants

Used as: Cutting Forming Protecting and treating fluids

Not suitable for high-speed cutting operations where much heat is developed



Introduction to this study



Objectives of this study

- Metalworking Neat Oils have to be able to dissolve high amounts of additives, creating concentrated solutions that must be stable
 - Over time
 - At varying transport, handling and storage temperatures
- In this study, we have prepared concentrated solutions of seven (7) different additives, and studied their solution stability over time.
- We are subjected samples to different conditions: ambient, low temperature and elevated temperature, and made observations over half a year
- Key observables are the formation of precipitates, insolubles, separation at low temperature etc.
- Results were obtained and analysed for seven (7) different Naphthenic, Group I and Group II base oils, that represent a spectrum of solvencies and have different base oil chemical composition, aromatic content and aniline points
- The conclusions of this study will give additional insights into how base oil solvency and low temperature flow properties affect the formulation of neat oil metalworking fluids



Previous work on neat Oil Solution Stability



Part I presented in Esslingen 2016





Solubility Stability Comparison Study

- A study was initiated to chart the solubility of a range of additives commonly utilized in metalworking fluids (MWF:s).
- The additives were present in concentrations corresponding to high end treat rates (1-15 %)
- The samples were divided into four groups, and subjected to different temperatures:
 - +50°C
 - -25°C
 - ambient temperature (+19°C)
 - Rotation between ambient, +50°C and -25°C
- All samples were monitored for any apparent changes
 - Cloudiness
 - Formation of a precipitate or separated phase
 - Viscosity & flow properties



Additive types selected



These seven different additive types were investigated at high treat rates





Base oils utilised in this study

- Four ISO VG 22 (~100 SUS) Base oils investigated
- Naphthenic base oil 22.7 cSt, Aniline Point (AP) = 75 °C
- Group I base oil SN 100, 17.6 cSt, AP = 98 °C
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Naphthenic Group I Group II Group III



Additional properties

Characteristics	Unit	Test method ASTM	P. G I	P. G II	P. G III	Naph.
Density, 15°C	kg/dm ³	D 4052	859.3	853.5	838.5	901.5
Viscosity, 40°C	mm²/s (cSt)	D 445	17.6	19.9	20.0	22.7
Viscosity, 100°C	mm²/s (cSt)	D 445	3.74	4.08	4.29	3.73
Viscosity index		D 2270	96	103	122	-7
Flash Point, PM	°C	D 93A	197	201	213	174
Pour point	°C	D 97	-21	-21	-15	-48
Sulphur	%	D 2622	0.159	0.002	0	0.039
Aniline point	°C	D 611	98	107	115	75



Blending and dissolving protocol



Base oil	Time (h)	Temperature (°C)				
Sulphurized	Sulphurized olefin					
Naph.	2.0	46				
P. GII	1.0	36				
P. GIII	5.0	41				
P. GI	1.5	38				
Overbased	sulphonate					
Naph.	3.5	44				
P. GII	3.5	50				
P. GIII	2.2	48				
P. GI	2.2	46				
Sulphurized	fat					
Naph.	3.7	39				
P. GII	3.7	34				
P. GIII	3.0	40				
P. GI	3.0	39				
Phosphate (ester					
Naph.	1.3	41				
P. GII	1.4	44				
P. GIII	2.0	47				
P. GI	2.0	43				
Synthetic P	olyol Ester (I	SO VG 46)				
Naph.	1.6	42				
P. GII	1.6	29				
P. GIII	1.2	43				
P. GI	1.2	33				
Chlorinated paraffin (C18-C30)						
Naph.	2.1	40				
P. GIII	6.6	50				
P. GII	16.8	68				
P. GI	4.9	49				
Tolyl Triazo	Tolyl Triazole					
Naph.	4.1	66				
P. GII	4.7	62				
P. GIII	10.0	70				
P. GI	3.0	54				



Additive dissolution in different base oils





Additive dissolution in different base oils

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Sulphurized olefin						
Naph.	2.0	46				
P. GII	1.0	36				
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Naph.	3.5	44				
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Sulphurized	fat					
Naph.	3.7	39				
P. GII	3.7	34				
P. GIII	3.0	40				
P. GI	3.0	39				
Phosphate e	ester					
Naph.	1.3	41				
P. GII	1.4	44				
P. GIII	2.0	47				
P. GI	2.0	43				
Synthetic Po	Synthetic Polyol Ester (ISO VG 46)					
Naph.	1.6	42				
P. GII	1.6	29				
P. GIII	1.2	43				
P. GI	1.2	33				
Chlorinated paraffin (C18-C30)						
Naph.	2.1	40				
P. GIII	6.6	50				
P. GII	16.8	68				
P. GI	4.9	49				
Tolyl Triazole						
Naph.	4.1	66				
P. GII	4.7	62				
P. GIII	10.0	70				
P. GI	3.0	54				





Lowest temp. 33°C in P. Group I

Longest time 16.8h in P. Group II

Highest temp 70°C in P. Group III



Solution stability during long term storage

Samples were store during six month at the following conditions:





Solution stability results

The solutions were observed and rated during a 25 week test period

- > At 50°C, for precipitation and changes
 - A rating of "4" for unchanged, clear solutions
 - A rating of "3" for cloudiness
 - A rating of "2" for precipitation
 - A rating of "1" for cloudiness & precipitation

At $- 25^{\circ}$ C, for flow properties

- A rating of "4" for readily flowing solutions
- A rating of "3" for thickened solutions
- A rating of "2" for very viscous solutions
- A rating of "1" for solid or frozen samples



Some select results from the study





Weekly observations and ratings



Week 1



Week 13



Week 25

-25°C



Close-up example: Sample D, Polyol Ester @ 19°C, 25 weeks



Group I & Naphthenic 22 cSt are overlapping at rating "4"



Results – Sulphurized olefin (12 wt.%)



Samples at +19°C:

- P. GI and Naph. clear
- P. GIII hazy (week1) with precipitation from week 2
- P. GII clear until week 17, then some precipitation

Samples at +50°C:

 All samples clear except P.GIII which was hazy, improved w 13

Samples at -25°C:

- Naph. clear
- All paraffinic samples frozen

Rotated samples:

- Naph. clear
- P. GIII precipitated after week 2
- P.GII frozen while at -25°C, after week 10 hazy and then precipitation
- P.GI frozen while at -25°C



Results – Synthetic polyol ester (ISO VG 46, 10wt.%)



Samples at +19°C:

- Naph. and P. GI clear
- P. GII and P. GIII clear until week 3, then some precipitation

Samples at +50°C:

- Naph. and P. GI clear
- P. GIII precipitation after 3 weeks
- P. GII precipitation after 4 weeks

Samples at -25°C:

- All paraffinic samples highly viscous or frozen
- Naph. viscous

Rotated samples:

- All paraffinic samples presented precipitation while at -25°C
- Naph. Clear to slightly viscous (at 25°C)



Results – Chlorinated paraffin (C_{18} - C_{30} , vLCCP, 10 wt.%)



- Samples at +19°C: Naph. clear during whole period
 - P. GII and P. GIII had precipitated from week 1
 - P.GI hazy and after week 4 precipitation

Samples at +50°C:

- Naph., P. GI and P.GIII clear during whole study
- P. GII precipitation after week 12

Samples at -25°C:

- P.GIII and P.GII frozen
- P.GI and Naph. viscous

Rotated samples:

- P. GIII frozen while at -25°C
- P.GII frozen while at -25°C (after • w12)
- P.GI and Naph. changed between clear to slightly viscous



Summary of observations, Part I

- The additives presenting a more homogeneous appearance both at +50°C, and ambient temperature in all samples were: the overbased Sulphonate, Phosphate ester and Tolyl triazole.
- The Paraffinic Group II and Group III samples had solubility problems with the synthetic polyol ester (ISO 46) and the chlorinated paraffins at ambient temperature
- P. Group I had a very viscous appearance in the presence of chlorinated paraffin
- Samples based on the naphthenic oil and on the paraffinic Group I oil retained a more homogeneous appearance
- Group II and III base oils samples presented a hazier appearance and some precipitation



Conclusions of Part I of the solubility study

- We could discriminate fairly well between the different base oils and additive combinations
- In general, the properties of the solutions displayed sensitivity of the conditions according to expectations
 - Some interesting details were uncovered, and are being studied further
- The thermal cycling generated some additional precipitation or change behaviour
- The Naphthenic 22 cSt showed very good additive solubility under all conditions, at what may be considered high treat rates





Part II – Group I and Group II replacement base oils



Base Oils in Part II of this study

The three base oils selected for this part of the study are from Nynas' novel range of Group I and Group II replacement base oils

The fluids were:

- New range 100 SUS (20 cSt) Group I replacement fluid
- New range 150 SUS (30 cSt) Group I replacement fluid
- New range ISO VG 32 Group II replacement fluid
- The purpose is to establish a benchmark correlation of solvency properties towards the Group I SN 100 and Group II 20 cSt oils used in Part I of this study



A few words on the Nynas new range base oils...



A new specialty base oil product range

- Can be widely applied in industrial lubricant formulations
- Naphthenic + Paraffinic blends
- Main advantages of the New Range (NR)
 - Most similar base oil compared to Group I oils
 - High degree of flexibility in blending
 - Will be available over time
 - Superior low temperature performance
- Main challenges vs Group I base oils
 - Lower Sulphur content
 - Slightly higher volatility
 - Lower flash point
 - Slightly lower VI





The New Range vs Group I SN and Group II reference base oils

	NR 100	SN 100	NR 150	SN 150	NR ISO VG 32	Group II
Density (kg/m3)	0.867	0.859	0.871	0.868	0.866	0.852
FP COC (°C)	196	206	222	224	212	212
PP (°C)	-24	-18	-24	-18	-18	-18
Viscosity @40 °C (cSt)	22	17	30	30	32	20
Viscosity @100°C (cSt)	4.2	3.7	5.0	5.2	5.3	4.1
VI	88	104	89	103	96	103
Aniline Pt. (°C)	100	98	101	102	105	107
Sulfur (m-%)	0.01	0.2	0.04	0.2	0.02	0.002
СА	2	3	3	3	1	<1
CN	36	32	35	33	31	28
СР	62	65	62	64	68	71
Refractive index	1.475	1.472	1.479	1.477	1.476	1.468



Solvency results Part II

Additive dissolution in different base oils, Part II



Additive dissolution in different base oils, Part II



Base oil	Time (h)	Temperature (°C)				
Sulphurized olefin						
NR 100	01:36	50				
NR 150	01:36	44.3				
NR ISO VG 32	02:59	41.3				
Overbased sulphonate						
NR 100	01:51	56.5				
NR 150	01:51	54.7				
NR ISO VG 32	03:14	47.9				
Sulphurized fat						
NR 100	01:21	40.1				
NR 150	01:21	36.1				
NR ISO VG 32	03:03	53.4				
Phosphate ester						
NR 100	01:00	46.6				
NR 150	01:00	44.6				
NR ISO VG 32	01:26	54.2				
Synthetic Poly	ol Ester (IS	O VG 46)				
NR 100	01:20	42.3				
NR 150	01:20	32.8				
NR ISO VG 32	01:26	50.4				
Chlorinated paraffin (C18-C30)						
NR 100	17:49	51.8				
NR 150	17:49	51.4				
NR ISO VG 32	22:30	71.8				
Tolyl Triazole						
NR 100	01:12	44.7				
NR 150	01:12	44.2				
NR ISO VG 32	03:03	46.5				







Lowest temp. 32.8°C in NR 150



Longest actual time, 22.5h in NR ISO VG 32 Highest temp 71.8°C in NR ISO VG 32



The same rating methodology was used again

Number	+50 °C and Ambient	-25 °C
4	Good	Good
3	Hazy	Viscous
2	Precipitation	Highly viscous
1	Hazy + Precipitation	Frozen





Select results and analyses



Sulphurized olefin, Ambient and -25 °C



-25: Better fluidity in NR 100 & NR 150 grades vs. Group I and Group II

Ambient: Better solvency in NR 100 & NR 150 grades vs. Group II after 16 weeks

Sulphurized olefin, Ambient temperature, Group II and NR ISO VG 32







Synthetic polyol Ester, Ambient and +50 °C



+50: Better solvency in NR ISO VG 32 vs Group II. (16 vs 4 weeks). NR 150 better than NR ISO VG 32. Paraffinic Group I better solvency than NR 100 after 9 weeks Ambient: Very stable solvency in NR grades; vs. Group II already after 3 weeks

Polyol ester, Ambient temperature, NR 100 vs Group II





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Chlorinated paraffin, Ambient and +50 °C



+50: Solvency stays high for NR 100, as for SN 100 and Naphthenic 22. Similar behaviour of NR ISO VG 32 vs Group II. (10 vs 13 w) to precipitation. Ambient: Solvency improves with time for NR ISO VG 32; Group II also show some precipitation

Chlorinated paraffin, Ambient temperature Group II and NR ISO VG 32







How does this add to what we knew?

- The repeat study (Part II) with the new range base oils yielded additional insights into the solvency behaviour
- A substantial spread in blending times and the required temperature
 - Some samples require quite long blending times
- In some cases (e.g. Sulphurized fat), the dissolution time was substantially shorter in the New Range Group I replacement fluids
 - This indicates that solvency may differ although the aniline Points are very similar – an additional naphthenic effect?



Part III – Maximum solubility limits



Base Oils in Part III of this study

- The seven (7) base oils selected for this part of the study are the combined base oils of the previous steps
 - Naphthenic base oil 22 cSt
 - Group I base oil SN 100 (22 cSt)
 - Group II base oil, 20 cSt
 - Group III base oil, 20 cSt
 - New range 100 SUS (22 cSt) Group I replacement fluid
 - New range 150 SUS (30 cSt)Group I replacement fluid
 - New range ISO VG 32 (32 cSt) Group II replacement fluid
- The purpose is to establish the maximum solubility of the seven additive classes in the seven base oils
- Select results only will be shared in this presentation (for brevity)



Limiting solubility select test results summary

Additive	Amount oil, (%)	Amount additive, (%)		
Sulphurized olefin				
Naph.	50	50		
P. GII	50	50		
P. GIII	50	50		
P. GI	50	50		
NR 100	49.5	50.5		
NR 150	49.7	50.3		
NR ISO VG 32	50	50		
Synthetic Poly	ہ ol Ester (ISO VG	46)		
Naph.	50	50		
P. GII	50	50		
P. GIII	50	50		
P. GI	50	50		
NR 100	50	50		
NR 150	50.1	49.9		
NR ISO VG 32	50	50		
Chlorinated paraffin (C18-C30)				
Naph.	48.9	51.1		
P. GII	89.0*	11.0*		
P. GIII	88.9*	11.1*		
P. GI	89.0*	11.0*		
NR 100	89.0*	11.0*		
NR 150	88.9*	11.1*		
NR ISO VG 32	88.9*	11.1*		

- High solubility in all base oils for six of the seven additive types
- Three representative additive types are shown here are
- The Chlorinated paraffin shows limited solubility, ca. 10% except in the Naphthenic 22 cSt base oil where the solubility is at least 50%

* This was not a clear solution so the max is probably already reached in the previous studies (10%) for this additive except with the Naph.



Conclusion of Part III

For all the additives except Chlorinated paraffin (C₁₈-C₃₀, vLCCP) the maximum amount in the different tested oils is above 50 % treat rate

- This is perhaps surprisingly high?
- For Chlorinated paraffin (C₁₈-C₃₀, vLCCP) dissolved in Naphthenic 22 cSt base oil, the maximum treat rate is also above 50 %
 - ... but for all other base oils the maximum treat rate remains around 10%
- This clearly shows why naphthenic base oils remain such a powerful tool for neat oil formulators!



Summary and conclusions



Total summary

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- Two half-year long term solution stability studies have been completed
- Solution stability of course differs between additive classes
- In general, additive solubility (or indeed base oil solvency) in the base oils follows the Aniline Point (AP) order
 - This is expected, as the additives have been developed over very long times for the AP 100 °C or lower type Group I and Naphthenic base oils
- Some of the long-term effect develop because of other chemical changes in the systems, notably oxidation
 - These model systems comprise base oil and EP/lubricity type additives, not any Antioxidant (AO)
- Some of the colour changes might have been different with AO present?
 - The upper solubility limit in (maximum additive loading) appear to be quite high
 A significant difference was found for the vLCCP Chlorinated paraffin

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