

Overcoming Obstacles in Water Resistant H1 Specialty Greases Using Polymer

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Introduction

Much of the longstanding experience in the grease industry is based on petroleum oils. Production-wise, 70% of reported grease production is lithium or lithium complex grease and 86% of grease uses conventional mineral oil with 7%, 5%, and 1% of reported greases using synthetic, semi-synthetic, or biobased.¹ Best practices and starting points for high performance grease formulating are well established based on the structure and properties of paraffinic or naphthenic oil and bright stocks and their interactions with additive chemistries which developed alongside the greases.

Trends continue to push for reducing the use of petroleum oils in lubricants and greases for varying reasons. Highly refined or synthetic stocks offer improved oxidative and thermal stability and offer the potential for longer life. Removal of aromatic carbon can greatly reduce the aquatic toxicity of grease used for both every day and in environmentally sensitive applications.

Whichever the reason, formulators who wish to develop greases in the specialty areas of NSF H1 incidental food contact (which tend to include synthetics like PAO) or environmentally acceptable lubricants often find unique challenges which were easily solved under standard practices in petroleum oil.

Properties like oxidation stability, dropping point, extreme pressure, or wear can typically be adjusted with the use of a simple additive or solved by proper selection of thickener chemistry. Something like an antioxidant can be expected to perform in a wide range of base oil types. However, water resistance is one of several types of performance which are highly complex.

The ASTM D4950 specification for automotive grease originally published in 1989 only contained water resistance testing with ASTM D1264 water washout as shown in **Table A**. The new High Performance Multipurpose (HPM) grease specification in ASTM D7594 adds ASTM D4049 water sprayoff with a limit of <40% as a new test for its Water Resistant (WR) subcategory.

Table A: ASTM D4049 water sprayoff requirements for NLGI grease specifications.

Grease Specification (Year)	NLGI Category	ASTM D4049 Limit	ASTM D1264 Limit
Automotive Service Greases - ASTM D4950 (1989)	GB	--	<15% @ 79C
	GC	--	<15% @ 79C
	GC-LB	--	<15% @ 79C
NLGI High Performance Multiuse Grease (2020)	HPM	--	<10% @ 79C
	HPM-WR	<40% @ 38C	<5% @ 79C

Hydrous calcium grease is an ancient technology and mixtures of lime and fat were the first soap-based grease as opposed to straight lard.² While old, this thickener chemistry is low cost, NSF HX-1, biobased, and biodegradable. Hydrous calcium has fair water resistance and a dropping point below 100°C making it uncommon for today's demanding applications.^{3,4} However, these qualities make hydrous calcium an excellent platform to demonstrate the versatility of polymers in improving water resistance, specifically water sprayoff (D4049) at 40°C which is the focus of this paper.

If a Bronze Age technology can be improved to or above the water resistance of modern calcium sulfonate or aluminum complex greases then perhaps there is something to learn from antiquity. Higher dropping point and stability of the grease can be achieved by replacing 20wt% of the calcium stearate with calcium acetate and adding a third temperature stage at 180-200°C to the process in the Methods section to allow the stearate and acetate to melt together as CaStAc.

Preliminary work with calcium stearate-acetate complex grease was prepared in order to allow future work with the higher temperature water washout test. Results were similar in performance to the calcium stearate data here.

2. Materials and Methods

2.1 Materials

Hydrous calcium and calcium complex greases were prepared from kosher calcium stearate and calcium acetate powders. The stearate/acetate ratio is kept proprietary. **Table B** summarizes all base oils and viscosity modifiers used to prepare base oil blends for grease at a constant ISO 150 viscosity grade. ISO 150 was chosen as a typical viscosity for calcium greases and to allow the use of the popular 750 SUS naphthenic oil in the preliminary work.

Table B: Summary of base oils and polymers with their abbreviated names used in the Results and Discussion

Base Oils Studied	Polymers Studied
600 SUS Solvent Neutral Group I ("600SN") **	HX-1 styrene copolymer flake ("HX-1 styrene grease polymer")
150 Bright Stock ("150BS") **	HX-1 polyolefin pellet ("HX-1 polyolefin grease polymer")
750 SUS Naphthenic Oil ("750Naph") **	1000 MW NSF HX-1 PIB ("PIB1000")
500 SUS White Oil ("500WO")	2500 MW NSF HX-1 PIB ("PIB2500")
8 cSt Group III, NSF H1 ("8 cSt Group III")	22 SSI Olefin copolymer in white oil ("22 SSI OCP VM")
6 cSt PAO ("PAO6")	75 SSI olefin copolymer in white oil ("75 SSI OCP VM")
10 cSt PAO ("PAO10")	30 SSI biobased viscosity modifier ("30 SSI bio VM") **
12 cSt Farnesene-based PAO ("BioPAO12")	50 SSI biobased viscosity modifier ("50 SSI bio VM") **
5 cSt Alkylated Naphthalene ("AN")	29 SSI biobased NSF H1 viscosity modifier ("HX-1 bio VM")
High oleic canola oil, 80% oleic ("Vegetable Oil")	

** = Not H1 or HX-1 but included to expand the range of the investigation.

H1 calcium stearate greases prepared 160°C were treated with 0.5wt% of a powder form NSF HX-1 high molecular weight phenolic antioxidant. Biobased calcium stearate-acetate complex greases prepared at 200°C were treated with 2.0wt% of a mixture of the NSF HX-1 phenolic antioxidant and a liquid aminic antioxidant in a proprietary ratio.

2.2 Equipment

Grease production occurred on 500 gram scale in a three-speed Hobart C-100 mixer with 10-quart bowl, "B"-style Hobart agitator paddle, and an electronic heating mantle (Glas-Col, 600W, 5000mL, silicone-impregnated fiber glass, #100AO414). A 120V Variac was used to regulate the heating mantle power and batch temperature. This setup was operated in a closed fume hood.

Greases were milled to good texture with a two-roll mill (Seattle Findings #28-281) adjusted to the finest gap setting that would allow material to pass through. The mill was modified with a motor (Dayton 6A198; 1/20 HP, 154 rpm, 20 ft-lbs torque) to power the 4:1 gear reduction. Grease was milled three times before use.

2.3 Hydrous Calcium Stearate and Calcium Stearate-Acetate Grease Production

Hydrous calcium stearate ("CaSt") and calcium stearate-acetate complex ("CaX") greases were prepared at NLGI #2 grade to evaluate the water resistance with added polymers. **Table C** summarizes the overall formulations for CaSt and CaX greases with thickener wt% based on base oil viscosity arranged in **Table D**. Water is used to induce and stabilize the unique structure of calcium stearate hydrate crystals.⁵⁻⁷ The low dropping point of hydrated calcium stearate grease was considered unsuitable for any further work with ASTM D1264 water washout at 79°C or preparation of biobased greases due to the water. Calcium stearate-acetate complex grease formulations were developed as an alternative.

Water-free calcium-acetate complex greases were used for all biobased base oil blends to avoid the effects of hydrolysis on the high oleic vegetable oil. The higher production temperature (200°C vs. 160°C) was offset by the use of 2wt% of a phenolic/aminic antioxidant blend. The stearate-acetate ratio can be adjusted to optimize for various properties like yield, dropping point, and low temperature fluidity.^{2,8-11} No excess calcium hydroxide or other base was added.

Table C: Hydrous calcium stearate and calcium stearate-acetate grease formulations

Component	wt% in CaSt	wt% in CaX
Base Oils	42.5 - 57.5%	34 – 74%
Liquid Viscosity Modifier	0 – 15%	0 – 40%
Calcium Stearate Powder	40%	--
Calcium Stearate / Acetate Powder Blend	--	24%
High MW Phenolic Antioxidant	0.5%	--
Phenolic/Aminic Antioxidant Blend	--	2.0%
Solid Grease Polymer	1.0%	0% (extra VM)
Water	1.0%	--

Table D: Typical thickener usage vs. NLGI grade for calcium greases depending on thickener and base oil

Grade	wt% CaSt	wt% CaX in ISO 150 PAO	wt% CaX (in vegetable oil)	wt% CaX (in ISO 1500+)
0	35%	23%	35%	19%
1	37%	26%	39%	21%
2	42%	28%	43%	24%
3	50%	30%	48%	30%

Order of operations:

1. Charge components to kettle at room temperature.
2. Set Variac for 80°C temperature and agitate on low until temperature reached.
 - a. Batch will be paste or dough-like.
3. Set Variac for 150-160°C temperature and agitate on medium until temperature reached.
 - a. Batch will take on a gelatinous, viscous quality.
4. If making calcium stearate-acetate grease: set Variac for 180-200°C temperature and agitate on medium until temperature.
 - a. Batch will take on a slight granular texture.
5. Mix for 30 minutes if using no grease polymer or the flake form HX-1 styrene grease polymer. Mix for 90 minutes instead if using the pellet form HX-1 polyolefin grease polymer.
6. Inspect every 15 minutes for residual grease polymer on walls of kettle to determine when grease is ready to cool.
7. Turn off heat, remove mantle, and mix of high until temperature of batch drops to 40°C.
 - a. Batch will have a grainy but paste-like consistency.
8. Mill 3x on grease mill until smooth texture is achieved.
9. Allow grease to rest overnight.
10. Check cone penetration. Adjust with more base oil and mill one more time.

Store hydrous calcium greases in airtight container and clean kettle immediately. Water added to the initial kettle charge was sufficient to produce working hydrous calcium greases despite temperatures of 150°C in mixing.

2.4 Physical Testing and ASTM Methods

Cone penetration and NLGI grade was assessed by ASTM D1403 quarter-scale cone penetration and converted to full scale for NLGI grading.

Water resistance was evaluated by ASTM D4049 water sprayoff under the default parameters: 40 psi stream of 38°C / 100°F water for 5 minutes.

Water washout data was not collected in this study. However, the specific grease polymers used in this study have historically performed very well in water washout wherever water sprayoff performance is good; in contrast, there are known grease polymers which perform well in water sprayoff but contribute little or no improvement to washout

Base oil composition as % paraffinic, % naphthenic, and % aromatic carbon types was collected based on: 1) reported ASTM D2140 carbon profile for most petroleum oils; 2) general values reported in literature (Group III and V oils); 3) known or approximate molecular structures for synthetic oils like 5 cSt alkylated naphthalene, PAO, PIB, viscosity modifiers, etc.

Results and Discussion

Why do some polymers work differently in varying greases?

This work was originally inspired by and intended to answer questions surrounding a specific grease polymer used to improve the water resistance of industrial petroleum-based greases. The styrene modified H1 grease polymer flake described in the Materials section has long been sold for use in petroleum greases. Over the years different formulators testing this material would report starkly different experiences with the performance and texture of the finished grease using the H1 styrene polymer. The polymer would either provide exceptionally low water sprayoff and washout results, provide no major effect, or result in excessive ‘texture’ and graininess to the finished grease. Why would one additive be the “best” and “worst” additive for petroleum greases at different customers?

Based on early findings from this study, it was determined that the type of petroleum oil was critical. Customers with great experiences adding the H1 styrene grease polymer to grease were predominantly using straight paraffinic oils like 600SN Group I, 600N Group II, or bright stock. Customers with poor results were using naphthenic oils like 750 SUS or roughly equal mixtures of heavy paraffinic and naphthenic oils.

Figure 1 demonstrates the variation in performance of the styrene grease polymer at 1wt% in NLGI #2 calcium stearate greases seen at customers was reproduced using ISO 150 base oil blends of varying composition. The higher solvency naphthenic (200Naph/3500Naph) and paraffinic (600SN/150BS) base oils showed significant reduction in water sprayoff. However, the naphthenic based grease gave an unacceptable rubbery texture. The more expensive and highly refined base oils (PAO and white oil / PIB) gave a slight improvement which would not justify the cost of adding the styrene grease polymer.

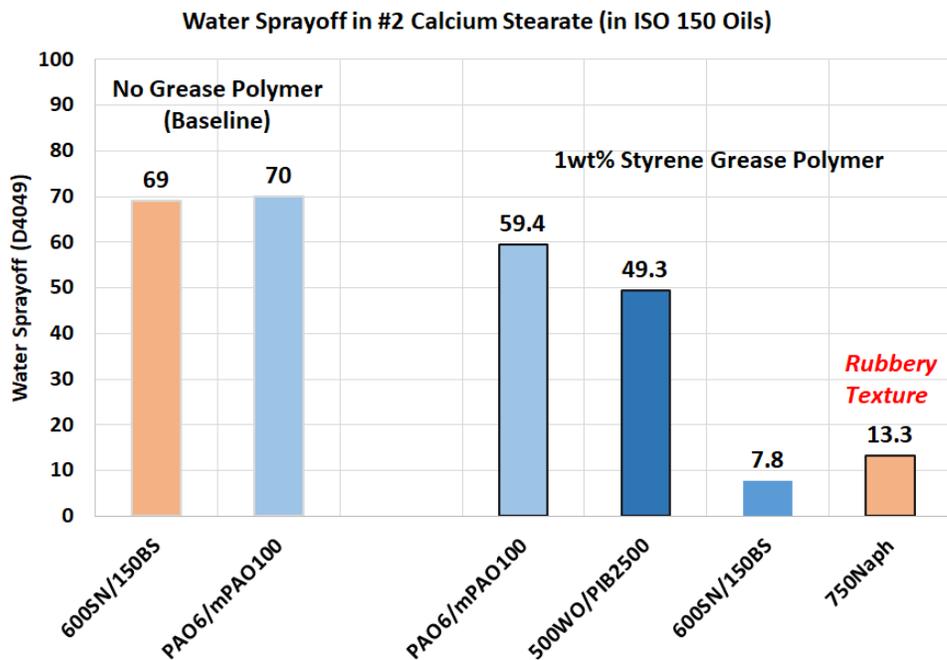


Figure 1: Water sprayoff for NLGI #2 calcium stearate greases using the styrene grease polymer at 1wt% in various base oil blends (600SN = 600 SUS Group I; 150BS = 150 Bright Stock; PAO6 = PAO 6; mPAO100 = mPAO 100; 500WO = 500 SUS white oil; PIB2500 = 2500 MW polyisobutene; 750Naph = 750 SUS naphthenic oil)

Figure 1 corroborates the range of different experiences formulators making different greases for different brands would see with this styrene grease polymer: excellent WSO improvement, no effect, or rubbery texture but good WSO. This explained when the H1 styrene grease polymer will perform but did not explain why. If the underlying reasons for the variations in performance based on base oil type could be explained then it was inferred that those parameters in the base oil blend could be tuned.

A difference in properties or performance of any material ultimately depends on composition and structure. **Table E** compares the composition of various base oils. Paraffinic oils are categorized under API Group I, II, and III depending on basic properties like viscosity index and percentage of saturates based on the level of refining. Several types of petroleum derived from naphthenic crude oil are categorized as Group V. PAOs and some Group III (GTL) are prepared from polymerizing short runs of ethylene or CO/H₂ into synthetic crudes which are then distilled as cuts.

Table E: Composition and statistics of various paraffinic and naphthenic petroleum oils. Group IV and V data collected from publicly available datasheets from major brands. Group I-III ranges from Espada, Jameel, and Ray.¹²⁻¹⁴

Structure/Properties	Group I	Group II	Group III	PAO	Naphthenic Oil	White Oil
Saturates – Alkanes, %	70	70	79.5	100	40	70
Saturates – Naphthenes, %	25	28	20	0	50	30
Aromatics – %	5	2	0.5	0	10	0
API Group	I	II	III	IV	V	V
Typical Viscosity Index	80 - 100	90 - 115	120 - 140	120 - 200	30 - 70	60 - 90
Flash Point, D92,C (ISO 32)	193	226	240	246	170	200
Aniline Point, C	95	100	110	126	80	105

Based on **Table E**, the composition of paraffinic and naphthenic oil varies mostly in the high levels of naphthenic (cycloalkane) and aromatic hydrocarbons in the naphthenic oil. This is regarded as “high solvency” due to the greater solvating abilities of aromatic and ring-like molecules, similar to the effectiveness of benzene, toluene, turpentine, or limonene as industrial solvents.

The key between the varying experiences with the styrene grease polymer is then the difference in solvent quality of the base oil affecting the cohesiveness or adhesiveness of the polymer in the final grease. **Figure 2** reimagines **Figure 1** and the range of customer experiences along a single ‘solvency of base oil’ axis.

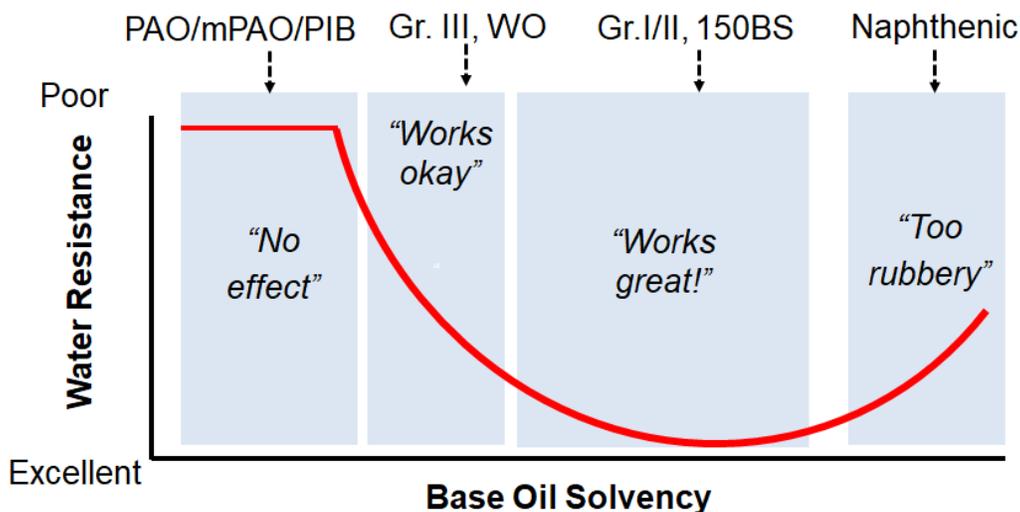


Figure 2: The range of customer experiences and grease performance with the styrene grease polymer is a function of base oil solvency – too much or too little solvency creates different results. The styrene polymer is base oil sensitive.

Figure 3 demonstrates the underlying mechanism for why performance with styrene polymers comes and goes with increasing base oil solvency. Styrene grease polymers have high styrene content making them insoluble in low solvency base oils at ambient temperatures – no long range interactions or network is formed. Medium base oil solvency allows the polyolefin midblock of the styrene copolymer to dissolve – the insoluble styrene ends anchor together to form a mesh-like network. Increasing the solvency further causes the styrene endblocks to dissolve into the oil

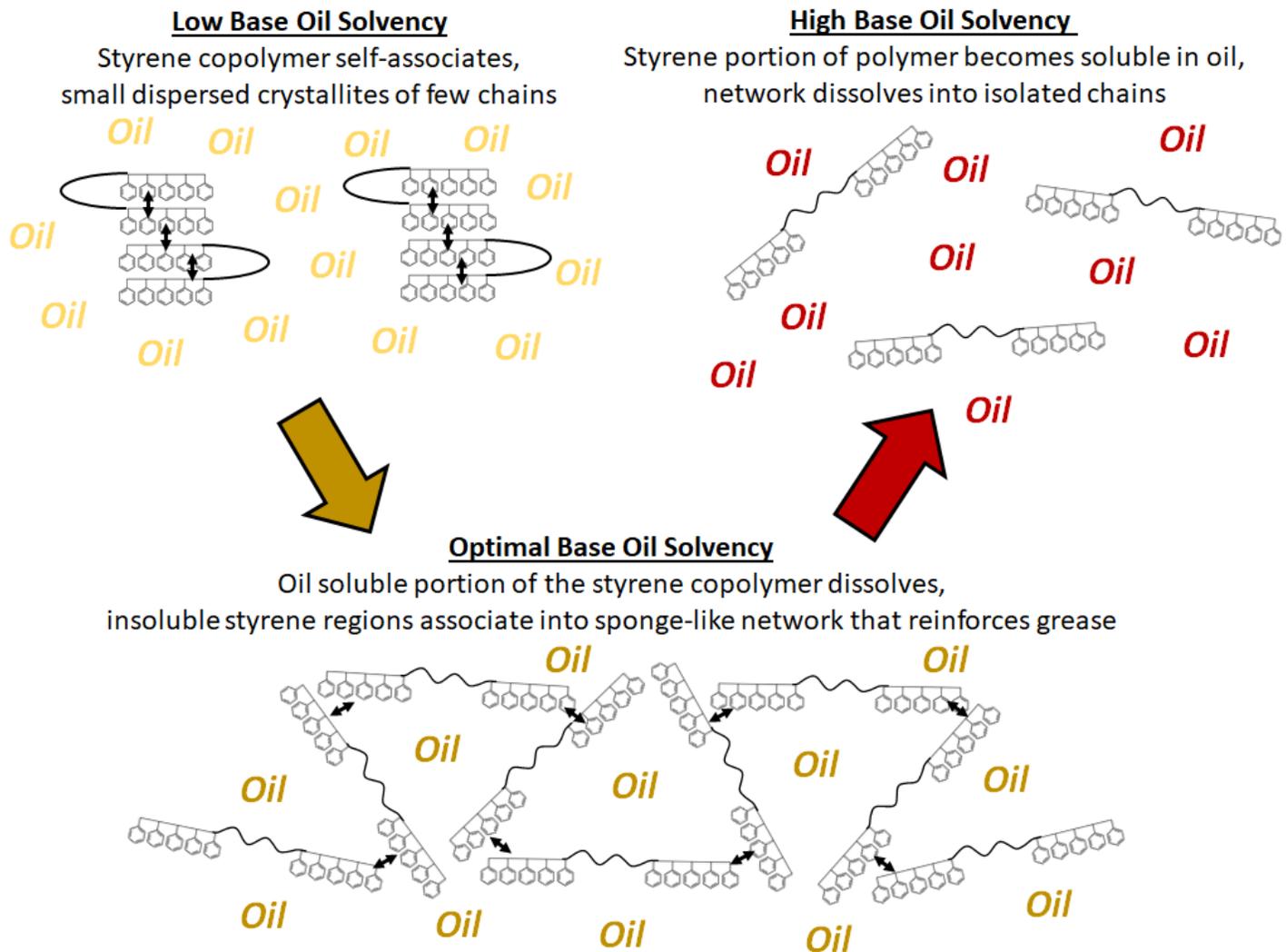


Figure 3: Mechanism for variations in observed styrene polymer performance with increasing base oil solvency.

Ironically, the styrene grease polymer was found to meet NSF H1 criteria and received HX-1 status although the results in **Figure 2** would suggest the polymer performs best in non-H1 oils. However it was thought that if the solvency of the petroleum or H1 base fluids could be quantified, measured, and controlled then it was possible to engineer one or more H1 oil blends with similar solvency to a Group I or II paraffinic oil. It was hypothesized that the HX-1 styrene grease polymer's performance could be tuned with a mixture of H1 base fluids same as the examples in Figures 1 and 2.

Setting up base oil solvency calculation

Polymer solubility is complex and has been approached from many different levels of theory from "like dissolves like" to Hildebrand's and later Hansen's use of quantitative "solubility parameters" which must be matched closely between base oil and polymer.¹⁵⁻¹⁸ Hildebrand solubility is a simple sliding scale like a ruler while Hansen solubility is a dart board with the height and width representing hydrogen bonding and polarity. It is possible to have 'too much' solvency in one direction such that the solvent or polymer prefer to associate with itself and avoid forming a solution between the two different materials. Thus in **Figure 2** the best performance fell within a narrow range of optimal solvency (Group

I/II/bright stock) and increasing the solvency further (naphthenic oil) caused a reversal in water sprayoff performance and poor grease texture.

A system of calculating solvency and estimating WSO based on the calculated solvency was developed here for the HX-1 styrene polymer in the NLGI #2 calcium stearate with ISO 150 base oils.

First, one looks at **Figure 2** and compares the WSO performance by base oil type versus the structure of the base oils shown below in **Figure 4**. It is apparent that naphthenic oils have the greatest solvency arising from the excess aromatic carbon content which most formulators have learned have higher solvency. It is also apparent that Group III based oil blends gave noticeably better performance than pure PAO/mPAO blends. The major difference between Group III and PAO, where neither contains aromatics, is the naphthenic content. The naphthenic content of naphthenic oil vs. Group I/II paraffinic should also be considered in the first example. Although aromatic structures receive much attention for their solvency it lesser known that even non-aromatic ring structures (naphthenes) have appreciable solvency – think of limonene, a powerful non-aromatic degreaser.

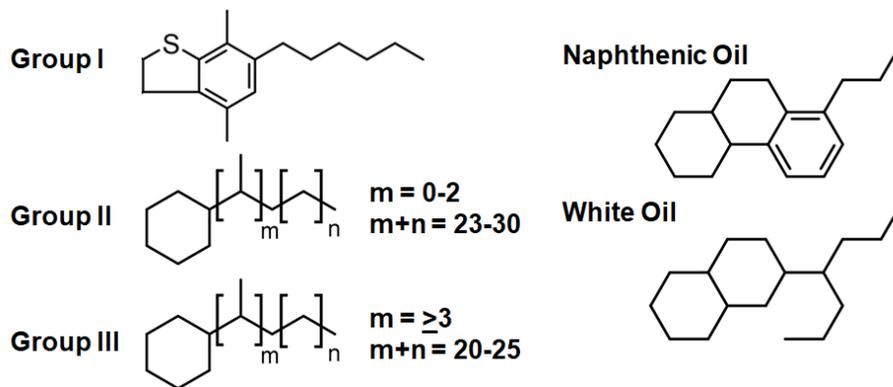


Figure 4: Idealized structures of different paraffinic^{12,14,19} and naphthenic²⁰ oils.

The first iteration of a mathematical model to relate the % of different hydrocarbons (alkanes, naphthenes, aromatics) began with plotting the % aromatic carbon of the base oil blends in **Figure 1** versus the WSO of the grease.

A quick second iteration added a term for % naphthenic carbon but applied a factor to count the naphthenic content as lower solvency than the aromatics. Roughly, WSO is a function of (% aromatic carbon in base oil blend) + (% naphthenic carbon) * N, where N < 1. Microsoft Excel was used to plot this x/y relationship using different polynomial fits and varying the coefficient N until the R² coefficient of fit was optimized to >0.95. N was found to be 0.24 where approximately 1wt% of aromatic carbon has the same solvency as 4wt% naphthenic carbon. Alkane carbon was assigned zero solvency. Molecular weight and the size of molecules is a factor that can affect solubility but was excluded so light or heavy oils were treated based only their carbon profile and not viscosity or molecular weight.¹⁸

Figure 5 shows the initial fit between solvency and WSO from the preliminary data points in **Figure 1**. This relationship can be used to engineer an H1 base oil blend that will work better with the HX-1 styrene grease polymer. The coefficients for % Aromatic C, % Naphthenic C, etc. shown in **Figure 5** and the following figures are based on fitting parameters determined from the final results of this study.

ISO 150 Base Oil Blend:	A	B	2	11	7	1
Grease Polymer (wt%)	0%	0%	1%	1%	1%	1%
600SN Group I	85		85			
150 Bright Stock	15		15			
750 SUS Naphthenic				100		
500 SUS White Oil					95	
PIB 2500 MW					5	
PAO 6		50				50
mPAO 100		50				50
% Paraffinic C	70.2	100	70.2	51.3	71.5	100
% Naphthenic C	25.7	0	25.7	30.2	28.5	0
% Aromatic C	4.2	0	4.2	18.4	0.0	0
Base Oil Solvency	10.3	0.0	10.3	25.7	6.8	0.0
WSO % (D4049, 38C)	69	70	7.8	13.3	49.3	59.4

$$\text{Base Oil Solvency} = 1.00 \times (\text{wt\% Aro. C}) + 0.24 \times (\text{wt\% Naph.})$$

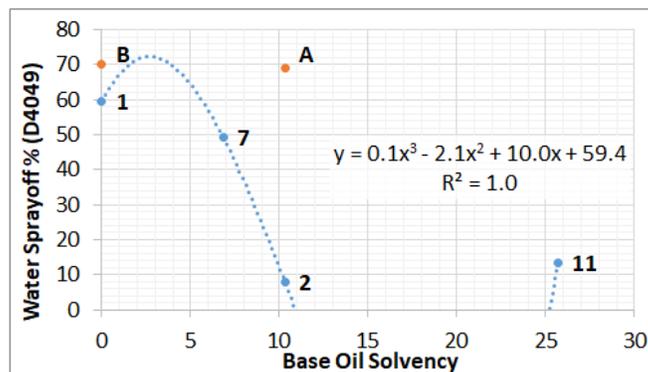


Figure 5: Preliminary fit of a WSO vs. base oil solvency relationship for the HX-1 styrene grease polymer. Key features are: sharp reduction in WSO with an increase in base oil solvency from oil blend #7 to #2; WSO slightly increases when base oil solvency is greatly increased from #2 (ISO 150 Group I) to #1 (ISO 150 naphthenic). More data points are needed to better correlation base oil selection to WSO.

Figure 5 is a crude fit but it captures the sharp decline in WSO with added base oil solvency and the plateau in WSO once a certain level of WSO performance is achieved. Actually the WSO for formulation #11 (naphthenic oil) is higher than #2 (Group I) and the #11 grease exhibited an unpleasant rubbery texture. Both findings support the idea of “too much solvent” established in **Figure 2**.

H1 base oil solvency vs. grease water resistance optimization

A rudimentary relationship between base oil solvency and water resistance (as WSO %) has been established. The hypothesis remains that this relationship will remain true for narrowing the range of base oils to only H1 base stocks. To investigate, this plot and dataset must be explained with more H1 base stocks. **Figure 6** compares the structures of various H1 base stocks from petroleum and synthetic sources.

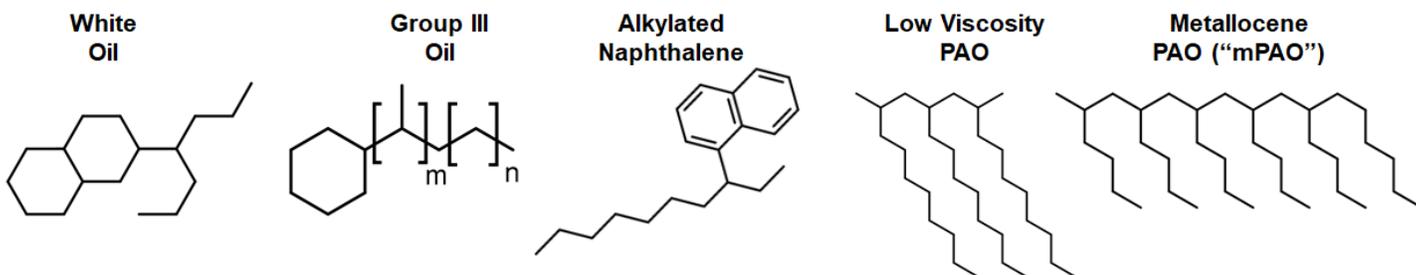


Figure 6: Common petroleum/synthetic H1 base stocks and their structures. Certain brands of Group III paraffinic oil meet 21 CFR 178.3620(b)(1) regulations and are listed NSF H1.

The two sources of solvency, naphthenes and aromatics, need to be found from H1 sources. This includes: white oils which are essentially dearomatized naphthenic oil (approximately 30% naphthenic carbon); H1 Group III oils containing lesser amounts of naphthenes; and alkylated naphthalenes which are PAOs attached to a naphthalene core and generally the only source of aromatics among the H1 base stocks with an estimated 45% aromatic carbon in the 5 cSt grade. Synthetic H1 base stocks include PAO, mPAO, EPO, PIB/PB, and biodegradable farnesene-based PAO are all isoalkanes with no naphthenic or aromatic content for solvency.

Since aromatics have the highest influence on solvency a 5 cSt grade of alkylated naphthalene (“AN”) was selected to add a controlled amount of aromatic carbon to the H1 base oil blend. The difference in aromatics was the largest difference in composition between the high performing Group I/bright stock blends (~4-5% aromatic carbon) versus the low performing ISO 150 PAO and white oil blends (0% aromatic carbon).

Figure 7 begins to include formulations using white oil + AN or PAO + AN as higher solvency H1 base fluid blends to properly dissolve the HX-1 styrene grease polymer according the hypothesized solvency-WSO response curve established in **Figure 2**. White oil and AN blends worked well to correct the deficiencies in H1 base stock solvency and improve WSO. However PAO and AN, specifically with high amounts of mPAO, did not perform as expected in the solvency-WSO model.

Base oil blends containing mPAO performed as if lower solvency. Another correction to the solvency-WSO model equation was added with a negative coefficient for the wt% mPAO. After retesting the fit, it was found that the remaining low viscosity PAO also appeared to reduce overall base oil solvency. The negative coefficient was extended to both the low viscosity PAO and mPAO. WSO is a function of (wt% aromatic carbon) + 0.24 * (wt% naphthenic carbon) – 0.07 * (wt% PAO or mPAO); if the calculated base oil solvency is less than zero then it becomes zero. In effect, adding 14% PAO or mPAO removes the equivalent of 1wt% aromatics in solvency. This is interesting as the choice to use PAO or mPAO are actively resulting in a net loss of solvency versus petroleum and white oils.

Figure 8 recalculates the Base Oil Solvency based on these observations and replots WSO vs. solvency with an added correction factor for the reduction in solvency when using mPAO or PIB (synthetic polyolefin oligomer base stocks).

ISO 150 Base Oil Blend:	Initial Data Points				White Oil + PB + AN Series				PAO + mPAO + AN Series			
	A	B	2	11	7	9	16	12	1	10	15	17
Grease Polymer (wt%)	0%	0%	1%	1%	1%	1%	1%	1%	1%	1%	1%	1%
600SN Group I	85		85									
150 Bright Stock	15		15									
750 SUS Naphthenic				100								
500 SUS White Oil					95	82.5	69	68				
PIB 2500 MW					5	7.5	16					
PAO 6		50							50	40	31	15
mPAO 100		50							50	50	44	50
5 cSt Alkylated Naph.						10	15	10		10	25	33
% Paraffinic C	70.2	100	70.2	51.3	71.5	70.8	81	75.1	100	95.5	88.8	85
% Naphthenic C	25.7	0	25.7	30.2	28.5	24.8	12	20.4	0	0.0	0.0	0
% Aromatic C	4.2	0	4.2	18.4	0.0	4.5	7	4.5	0	4.5	11.3	15
Base Oil Solvency	10.3	0.0	10.3	25.7	6.8	10.4	9.8	9.4	0.0	4.5	11.3	14.9
WSO % (D4049, 38C)	69	70	7.8	13.3	49.3	8.0	26	32.4	59.4	63.0	58.9	60.2

$$\text{Base Oil Solvency} = 1.00x(\text{wt\% Aro. C}) + 0.24x(\text{wt\% Naph. C})$$

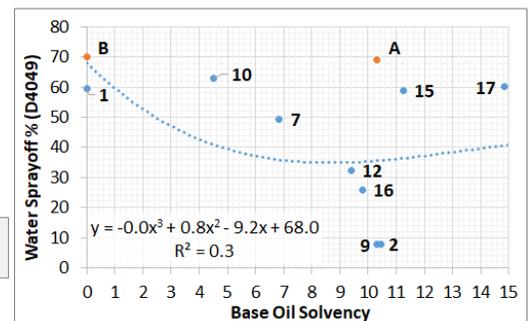


Figure 7: Expanded WSO-solvency relationship including alkylated naphthalene as a source of H1 aromatic carbon. Correlation with white oil based formulas was good but the inclusion of later PAO based formulas skewed the relationship. Some effect of the synthetic base oils has not been factored into the WSO-solvency equation. Data point #11 has been removed as an outlier due to the odd texture and it's being the only naphthenic formula.

ISO 150 Base Oil Blend:	Initial Data Points				White Oil + PIB + AN Series				PAO + mPAO + AN Series			
	A	B	2	11	7	9	16	12	1	10	15	17
Grease Polymer (wt%)	0%	0%	1%	1%	1%	1%	1%	1%	1%	1%	1%	1%
600SN Group I	85		85									
150 Bright Stock	15		15									
750 SUS Naphthenic				100								
500 SUS White Oil					95	82.5	69	68				
PIB 2500 MW					5	7.5	16					
PAO 6		50							50	40	31	15
mPAO 100		50							50	50	44	50
5 cSt Alkylated Naph.						10	15	10		10	25	33
% Paraffinic C	70.2	100	70.2	51.3	71.5	70.8	81	75.1	100	95.5	88.8	85
% Naphthenic C	25.7	0	25.7	30.2	28.5	24.8	12	20.4	0	0.0	0.0	0
% Aromatic C	4.2	0	4.2	18.4	0.0	4.5	7	4.5	0	4.5	11.3	15
Base Oil Solvency	10.3	0.0	10.3	25.7	6.5	9.9	8.7	7.9	0.0	0.0	6.0	10.3
WSO % (D4049, 38C)	69	70	7.8	13.3	49.3	8.0	26	32.4	59.4	63.0	58.9	60.2

$$\text{Base Oil Solvency} = 1.00x(\text{wt\% Aro. C}) + 0.24x(\text{wt\% Naph. C}) - 0.07x(\text{PAO/mPAO/PIB})$$

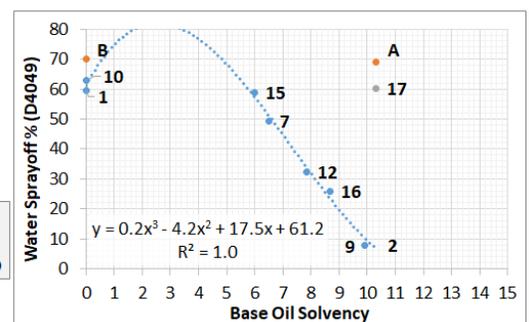


Figure 8: Corrected version of **Figure 7** by adding a $-0.07 * (\text{wt\% PAO} + \text{wt\% mPAO} + \text{wt\% PIB})$ correction factor. Data point #17 was a gross outlier likely due to the very high amount of alkylated naphthalene used to counteract the insolency of mPAO 100. The span between data points #1 / #10 and #15 should be treated as a plateau of 60% WSO until a base oil solvency of at least 6.5 is exceeded.

Viscosity modifiers

By limiting or eliminating the usage of mPAO (ISO 1000+) it became difficult to formulate the H1 base oil blends to ISO 150. 500 SUS white oil with 5 cSt alkylated naphthalene (ISO 32) requires a thickener to meet ISO 150. If using H1 Group III oil then the problem becomes worse as Group III is only available up to the ISO 46 “8 cSt” grade.

H1 polyisobutylenes (“PIB”) were sourced as an mPAO replacement. After fixing several new formulations with Group III + PIB + AN it was found that PIB causes faster loss of solvency than PAOs. WSO is a function of (wt% aromatic carbon) + 0.24 * (wt% naphthenic carbon) – 0.07 * (wt% PAO or mPAO) – 0.084 * (wt% PIB). However, PIBs are ISO 5000 to 100,000+ and can increase the base oil viscosity at lower wt% than the PAO. This results in PIBs producing a higher solvency ISO 150 than mPAO due to the lower wt% PIB than mPAO although the penalty to solvency per wt% is higher on PIB.

If using high amounts of polymer (mPAO and PIB) to increase viscosity reduces base oil solvency and WSO performance then a traditional viscosity modifier or viscosity index improver may be more effective. VI improvers are typically 5-10wt% of a high molecular weight polymer (10K-300K Mw) in light oil.^{21,22} Often less than a percent of active polymer is in the final product. This would greatly reduce the usage of polymer in the base oil as seen with replacing mPAO with PIB.

Two concentrated commercial H1 viscosity modifiers of greatly different shear stability (SSI by ASTM D6278) and MW were used to replace PIB in preparing H1 ISO 150 base oils in white oil or Group III plus the 5 cSt alkylated naphthalene:

- 22 SSI olefin copolymer in white oil (3000 cSt @ 100°C) – “Low MW OCP VM”
- 75 SSI olefin copolymer in white oil (3000 cSt @ 100°C) – “High MW OCP VM”

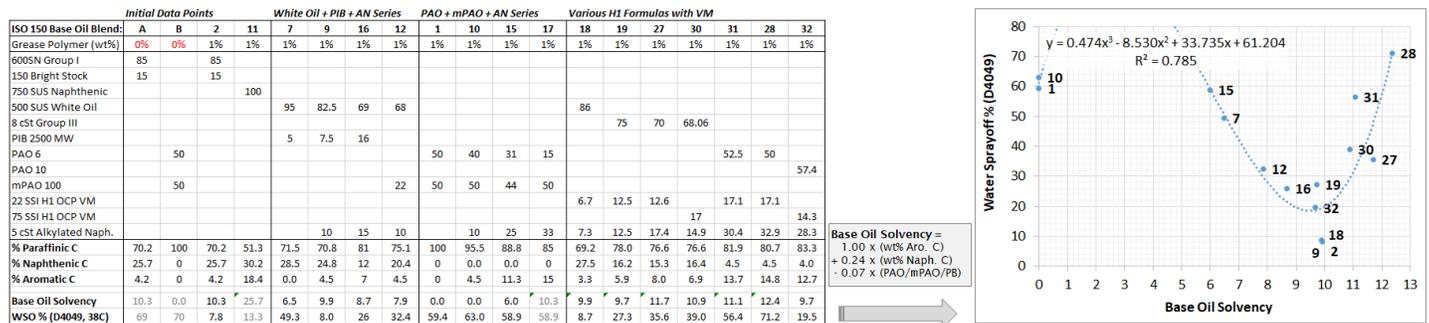


Figure 9: Initial fit of the VM modified base oil blends in an attempt to keep the use of PIB and mPAO low but still achieve ISO 150 oil blends.

A variety of formulations in 500 white oil, 8cSt Group III, and PAO 6 were prepared at ISO 150 using 22 SSI and 75 SSI liquid OCP VMs. Formulations were built using the establish base oil solvency calculation results established so far and to achieve an optimal 9-10 solvency rating for a target WSO of <20%. Formulations which should have been rated around 10 base oil solvency did not perform as expected. It was apparent than the OCP VMs required their own factor.

Initially, it was thought that the addition of viscosity modifier (VM) was further reducing solvency since calculated solvency was not correlating well with the addition of OCP VM in early models. More AN was added to compensate which further worsened WSO performance. Above 30% AN caused high WSO which was observed previously in the data point #17 outlier. This also supports the earlier hypothesis that the increase in WSO and unpleasant rubberiness in the full naphthenic oil formulation was due to too much solvency in the base oil. However, too much solvency in these later cases with high treat of OCP VM resulted only in higher WSO and not poor texture.

Rather than applying a solvency penalty, the data was best fit by adding a positive contribution to solvency with wt% OCP VM. WSO is a function of (wt% Aromatic C) + 0.24 x (wt% Naphthenic Carbon) – 0.070 x (wt% PAO + mPAO + PIB) ± 0.10 (wt% VM). **Figure 10** shows the new solvency-WSO equation and fit using this new factor.

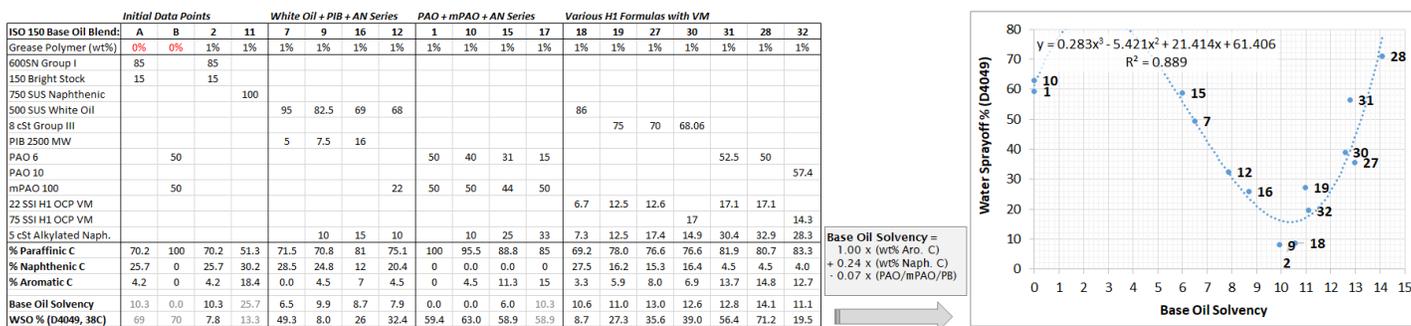


Figure 10: OCP viscosity modifiers were found to improve base oil solvency and actually cause a loss of WSO performance by adding too much solvency. The effects a fractional amount of very high MW polymer was offset by the larger addition of light (ISO 22) base oil in the VM additive.

This positive contribution of solvency and addition of too much solvency is most likely due to the light mineral oil (ISO ~22) in the viscosity modifier. Most commercial viscosity modifiers are a few percent of very high MW polymer (30K – 200K Mw) in a light ISO 20-25 oil. While all base oil blends were formulation to a constant ISO 150 the oil blends with added OCP VM at 5-20wt% will contribute very light base oil which has a greater capacity for solvency than higher MW heavy base stocks.

The fitting in **Figure 10** and prior plots was based on a 3rd order polynomial regression. Looking closely at **Figure 10** is apparent that the funnel shape from base oil solvency 6 to 14 is more of a sharp V or cone shape rather than a gentle curve. The response between WSO and base oil solvency is flat from 0 to 6 base oil solvency. This gives an overall shape like a square root sign (√) to the relationship between too little solvency, optimal solvency, and too much solvency vs. WSO performance of the HX-1 styrene grease polymer.

Table F: Summary of contributions to solvency in the base oil solvency-WSO relationship established for the HX-1 styrene grease polymer at 1wt% in ISO 150 NLGI #2 calcium stearate grease. Multiply each row by its coefficient and take the sum for the calculated base oil solvency. Some blends (100% PAO) will result in negative solvency.

Base Oil Composition	Multiply by...
wt% Aromatic Carbon (by ASTM D2140)	1.000
wt% Naphthenic Carbon (by ASTM D2140)	0.240
wt% PAO or mPAO or PIB	-0.07
wt% Viscosity Modifier (in light oil)	+0.10

This approach could be applied to other grease-oil-polymer systems. The amount of solvency per unit alkane or naphthene or aromatic carbon should remain constant between systems but the relationship between calculated solvency and WSO will vary.

H1 ester base oils like vegetable oils, oleates/stearates, and polyols could be amended to the solvency-WSO equation as positive sources of solvency. However, the scope of this work focused on hydrocarbons only and thus white oils and alkylated naphthalenes were heavily relied on. The same approach can be applied to esters and it is likely their individual contributions will be weighted by their Non-Polarity Indexes (i.e. the number of ester groups per molecular weight).²³

Other Polymers I – HX-1 polyolefin grease polymer for PAO

A second HX-1 polyolefin grease polymer with different chemistry exists to improve mechanical stability and reduce oil bleed in certain H1 greases. This polymer is known to be less polar than the HX-1 styrene grease polymer and its performance varies between base oils like the HX-1 styrene grease polymer but the specific responses are different. The HX-1 polyolefin grease polymer pellet was added in the same manner as the HX-1 styrene grease polymer but the final stage of heating was extended to 90 minutes to allow the larger pellets more time to dissolve fully into the grease.

Optimization of the H1 base oils was performed on this second polyolefin grease polymer using the solvency-WSO parameters established with the HX-1 styrene grease polymer: i.e. $WSO = 0.24 * (\text{wt\% aromatic carbon}) + 0.24 * (\text{wt\% naphthenic carbon}) - 0.07 * (\text{wt\% PAO or mPAO}) + \text{etc.}$

If the approaches developed earlier in this work could be applied to a second grease polymer system then it is most likely that it could apply to many more systems. Since the HX-1 polyolefin polymer lacks styrene one can anticipate the required solvency and solvency-WSO relationship equation to be different.

Figure 11 demonstrates the effectiveness of the styrene-free HX-1 polyolefin grease polymer in treating low solvency H1 base oils without the complexity of adding alkylated naphthalene. This polymer appears to be less base oil selective than the HX-1 styrene grease polymer which allows for the use of higher performance PAO and mPAO. However, 1wt% polymer was not sufficient to produce acceptable WSO. 2 or 3wt% polymer was ideal.

	Full PAO			PAO/PB		Bio PAO	
ISO 150 Base Oil Blend:	B	37	40	46	38	39	42
HX-1 Polyolefin (wt%)	0%	1%	2%	3%	1%	2%	2%
PAO 6	50	50	50	50	69	69	
mPAO 100	50	50	50	50			
PIB 1000 MW					31	31	20
12 cSt Farnesene PAO							80
% Paraffinic C	100	100.0	100.0	100.0	100.0	100	100
% Naphthenic C	0	0.0	0.0	0.0	0.0	0	0
% Aromatic C	0	0.0	0.0	0.0	0.0	0	0
Base Oil Solvency	0.0	0.0	0.0	0.0	0.0	0.0	0
WSO % (D4049, 38C)	70	64.2	34.3	17.0	66.0	48.1	35.4

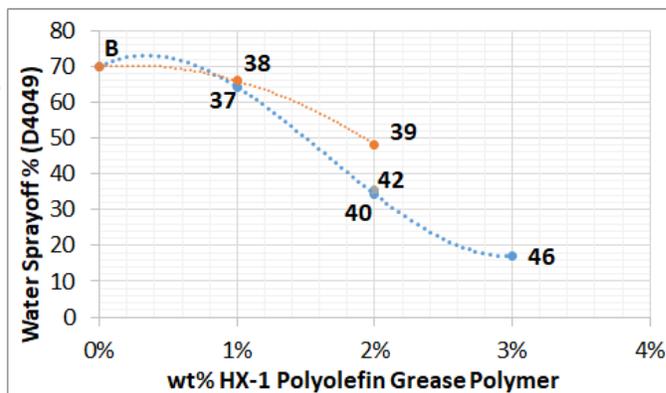


Figure 11: HX-1 polyolefin polymer works well at reduce WSO below the HPM-WR limit (<40%) at 2wt% in PAO/mPAO base fluids but performance lags behind in PAO/PIB. Using the highest viscosity non-metallocene PAO available (farnesene based 12 cSt PAO) to reduce the amount of PIB to replace mPAO to 20wt% gave similar performance to the PAO/mPAO. There may be a critical limit to the PIB and its effect on reducing solvency between 20-30wt%.

An interesting effect was noted by mixing the HX-1 styrene and HX-1 polyolefin grease polymers together at 2wt%. The polyolefin grants high amounts of cohesion and the styrene polymer gives high amounts of adhesion which work best when both effects are both present. **Figure 12** shows the effects of ratioing the two polymers together at a total usage rate of 2wt%. This gave similar performance to the HX-1 polyolefin polymer at 3wt% thus the mixed polymer approach would yield lower treat rate and cost to achieve very low WSO.

ISO 150 Base Oil Blend:	Sty. Polyol. Polyol. + Sty.					
	B	1	40	51	52	53
HX-1 Polyolefin (wt%)	0%	0%	2.0%	1.7%	1.4%	1.0%
HX-1 Styrene	0%	1%	0.0%	0.3%	60.0%	1.0%
PAO 6	50	50	50	50	50	50
mPAO 100	50	50	50	50	50	50
% Paraffinic C	100	100.0	100.0	100.0	100.0	100.0
% Naphthenic C	0	0.0	0.0	0.0	0.0	0.0
% Aromatic C	0	0.0	0.0	0.0	0.0	0.0
Base Oil Solvency	0.0	0.0	0.0	0.0	0.0	0.0
WSO % (D4049, 38C)	70.0	59.4	34.3	22.0	18.3	38.2

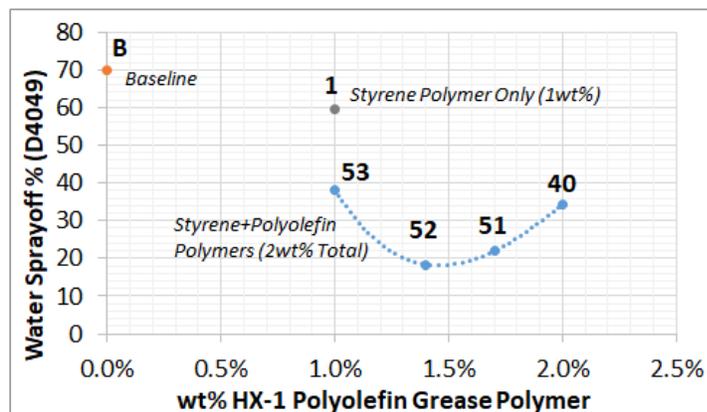


Figure 12: Investigating the synergy between two different types of semicrystalline HX-1 grease polymers

Thermoplastics like the HX-1 styrene polymer or polyolefin are known to have synergies when mixed in applications like engineered materials or thermoplastic sealants and adhesives. This approach appears to also be valid in a grease application. These are known as “polymer alloys” where two different polymers preferentially mesh to form a mixture of polymers with different properties.²⁴ Whether this effect is used to improve the grease or not, it has been shown here that two grease polymers used together can a unique interaction. The HX-1 styrene polymer by itself had no effect in the previous study when using in a full PAO/mPAO grease but when combined with the HX-1 polyolefin copolymer it halved the WSO value.

Other Polymers II – HX-1 polar grease polymer for H1 vegetable oil based grease

Based on existing work with biobased esters one should use polar or hydrogen bonding polymers for treating H1 biobased esters.²⁵ **Figure 13** compares a variety of possible polar and hydrogen bonding functional groups that may be used to treat ester fluids. Calcium stearate-acetate complex grease was prepared for biobased grease production to avoid the inclusion of water at high temperature which could risk hydrolysis of the vegetable oil base fluid.

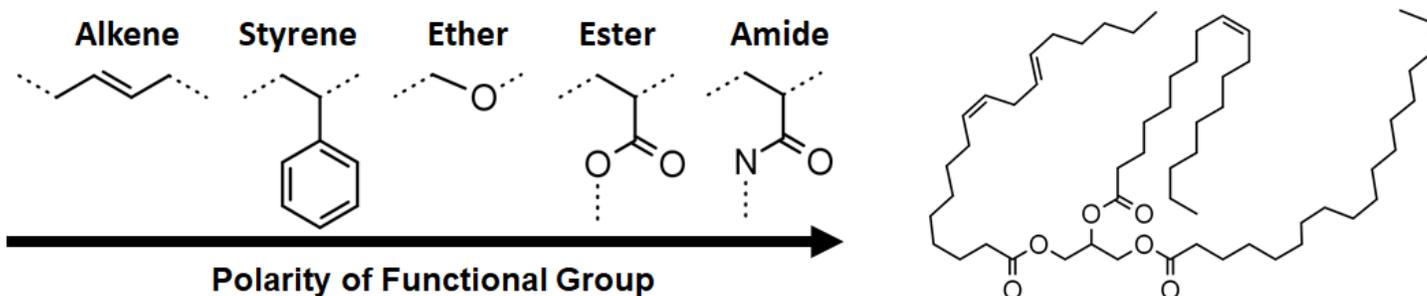


Figure 13: Structural features of ester-soluble polymers and viscosity modifiers (left) versus vegetable oil (right).²⁵ Electron density from C=C or C=O double bonds plus heteroatoms like N or O attached to C induce polarity.

The primary concern with vegetable oil based greases are the abnormally low base oil viscosity, ISO 32-36, compare to traditional petroleum grease made using ISO 100 – 460 or higher. The low base oil viscosity can be corrected by adding high MW polymer viscosity modifiers or low-medium MW polymeric base oils.

An NLGI #2 calcium stearate-acetate complex grease was produced in ISO 32 vegetable oil without the addition of polymers. WSO was approximately 96%. Since the very low base oil viscosity was the most significant different from prior grease formulations the base oil viscosity was increased using several commercial biobased viscosities modifiers.

An NLGI #3 base grease was made and ‘diluted’ to NLGI #2 with the addition of one of three biobased viscosity modifiers:

- 50 SSI biobased viscosity modifier – “50 SSI bio VM”
- 30 SSI biobased viscosity modifier – “30 SSI bio VM”
- 29 SSI NSF HX-1 biobased viscosity modifier – “HX-1 bio VM”

It was found that increasing the base oil viscosity with either of the three liquid viscosity modifiers greatly improved WSO to 7 to 35%. **Figure 14** plots the KV40-WSO relationship in the vegetable oil based greases. Two curves appear at lower viscosities (dash line) and higher viscosities (dotted line). The major factor appears to be the base oil viscosity increase and plotting the effective KV40 of the oil phase (oil + polymer) versus the WSO reflected this trend. WSO improvement slowed after ISO 3200 with 12% WSO at ISO 3200 and 8% WSO at ISO 12000.

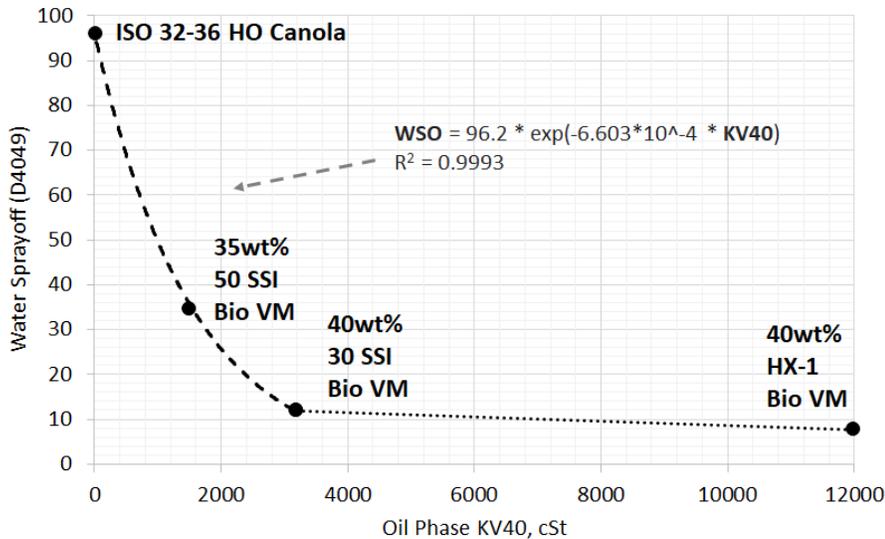


Figure 14: Water sprayoff in vegetable oil based NLGI #2 CaX grease using three different viscosity modifiers to increase the base oil viscosity from 32-36 cSt @ 40°C to very heavy ISO VG ranges. #2 greases were made by cutting a #3 grease with straight bio VM until #2 grade consistency was achieved. Then base oil VG was back calculated from wt% vegetable oil vs. wt% VM.

Based on **Figure 14**, the WSO improves with base oil viscosity in a logarithmic/asymptotic behavior with decreasing improvement as base oil viscosity increases. WSO is never eliminated to 0% but can readily exceed NLGI HPM-WR category requirements of <40% WSO. All three data points fit a smooth, asymptotic curve which does not suggest any one VM stands out in WSO performance versus the others.

The recommended ISO VG in the base oil blend for <40% WSO is ISO 1500. Water sprayoff is halved to 22% at ISO 2200 and halved yet again to 11% at ISO 3200. Exceeding this range of viscosities will continue to improve water sprayoff in a slow, linear fashion at a rate of -0.00048%/cSt. ISO 4600 should meet <10% WSO.

ISO VG 1500 with typical high MW viscosity modifiers prepared in vegetable oil is achievable at 30-50wt% concentrated viscosity modifier in the vegetable oil. After ‘dilution’ with the grease thickener the final usage in the finished grease can be 15-40wt%. Liquid viscosity modifiers are preferable to avoid long periods of dissolving solid polymer.

Overall, the approach to selecting HX-1 grease polymers for water resistance H1 greases follows an axis similar to the sliding scale, ruler-like Hildebrand solubility parameter theory. **Figure 15 summarizes the spectrum of base oil solvency and types in the H1 or biobased specialty markets and the optimal type of polymer to choose when trying to improve water resistance for specifications like the new HPM-WR and its D4049 water sprayoff test method.** These matches are presented along one axis in a Hildebrand-style sliding scale of polymer compatibility with different base fluids.

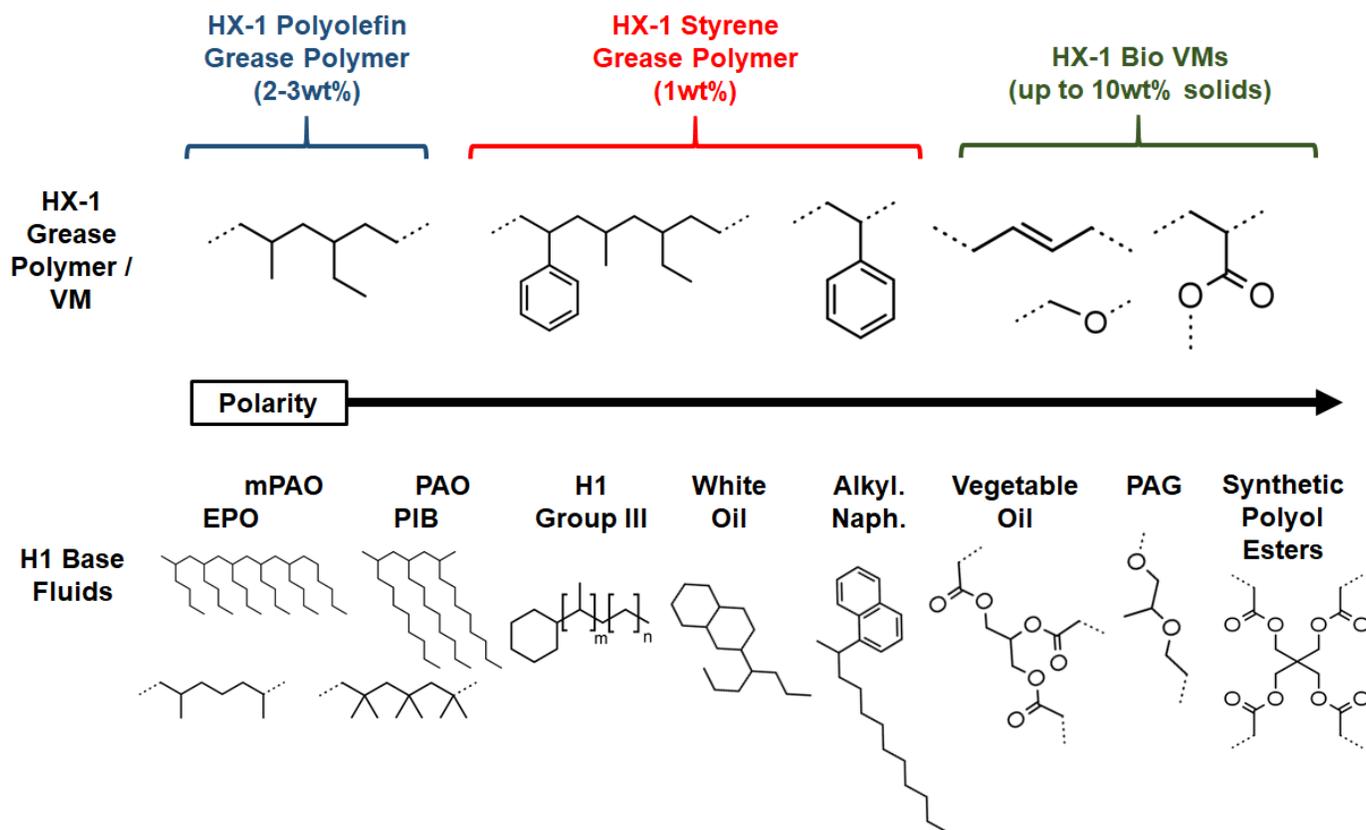


Figure 15: Structural similarities between H1 base fluids and HX-1 grease polymers to reduce water sprayoff based on the findings of this study for the HX-1 styrene grease polymer, HX-1 polyolefin grease polymer, and bio VMs. H1 or HX-1 status depends both on conforming to these structure identities plus meeting specific purity requirements set by the code of federal regulations (CFR).

Conclusions

Grease formulation is a complicated process and especially so whenever a project falls outside of the established knowledge which has predominantly been based on petroleum oils. Certain performance aspects can be changed easily with the addition of less than a percent of antioxidants or corrosion inhibitor. However, when water resistance is deficient in a grease it can involve a complete teardown of the existing formula which is extremely difficult late into a project when these problems tend to arise. This work is intended to extend the knowledge base of how to incorporate water resistant grease polymers for NSF H1 or biobased applications from the start.

It is a ‘tail wags the dog’ situation to dictate to formulators which base oils they should use in order to make 0.5 – 3wt% of an H1 grease polymers perform correctly in their incidental food contact greases. However, the number of overall polymer chemistries suitable for NSF H1 applications are small and the number of actual suppliers producing those grades of polymer to NSF/FDA tolerances is smaller yet.

The next steps of this work are to reverse the perspective – instead of designing a base oil blend to suit a polymer (which is quick and easy to iterate), how does one better design the polymer to suit the base oil using the relationships which have been developed in this paper? Almost a dozen structurally different NSF H1 polymers have now been made available to investigate and treat water resistance for a wide range of greases.

Another area to investigate is that alkylated naphthalenes are not the only source of solvency for NSF H1 formulations. Many natural and synthetic esters are strong polar solvents and routinely used to improve the solvency of PAO gear oils for the high treat of additives involved. The H1 grease study was limited to hydrocarbons to establish the groundwork without involving the complexity of different kinds of solvency with polarity and hydrogen bonding from esters.

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