Water-Soluble PAG's – The Environmentally Acceptable Lubricant (EAL) of the Future

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So You Want to Work Within U.S. Waters ?

US EPA 2013 Vessel General Permit

- Effective December 19,2013
- Applicable to discharges into “waters of the United States” (Defined in CFR and CWA)
- Covers vessels greater than 79 feet in length
- Requires the use of an EAL in all oil-to-sea interfaces, unless technically infeasible
- Covers all equipment that operates below the water line of a vessel

US EPA Definition of an EAL

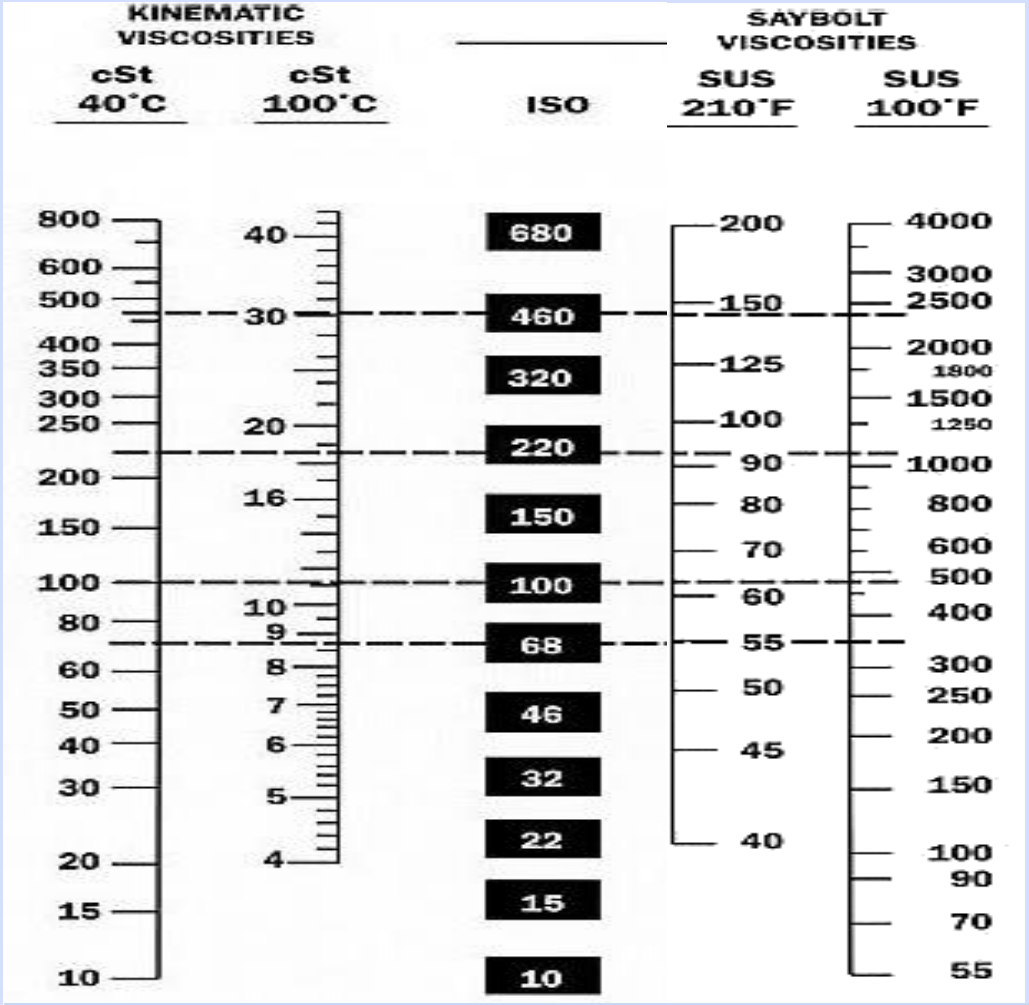
- Biodegradable - >60% in 28 days via OECD test method(s)
- Minimally Toxic - >100 mg/L LC50 for various aquatic species via OECD test method(s)
- Non-Bioaccumulative – by one of multiple routes
- Exempt if certified by a recognized Eco-labeling program

Recognized EAL Base Stocks – US EPA

- Polyglycols (HEPG)
- Vegetable Oil (HETG)
- Synthetic Esters (HEES)
- Bio-based PAO (HEPR)
- Water

Properties of PAG's

Viscosity: Increases with increasing molecular weight. Standard grades range from ISO 10 to 1000.



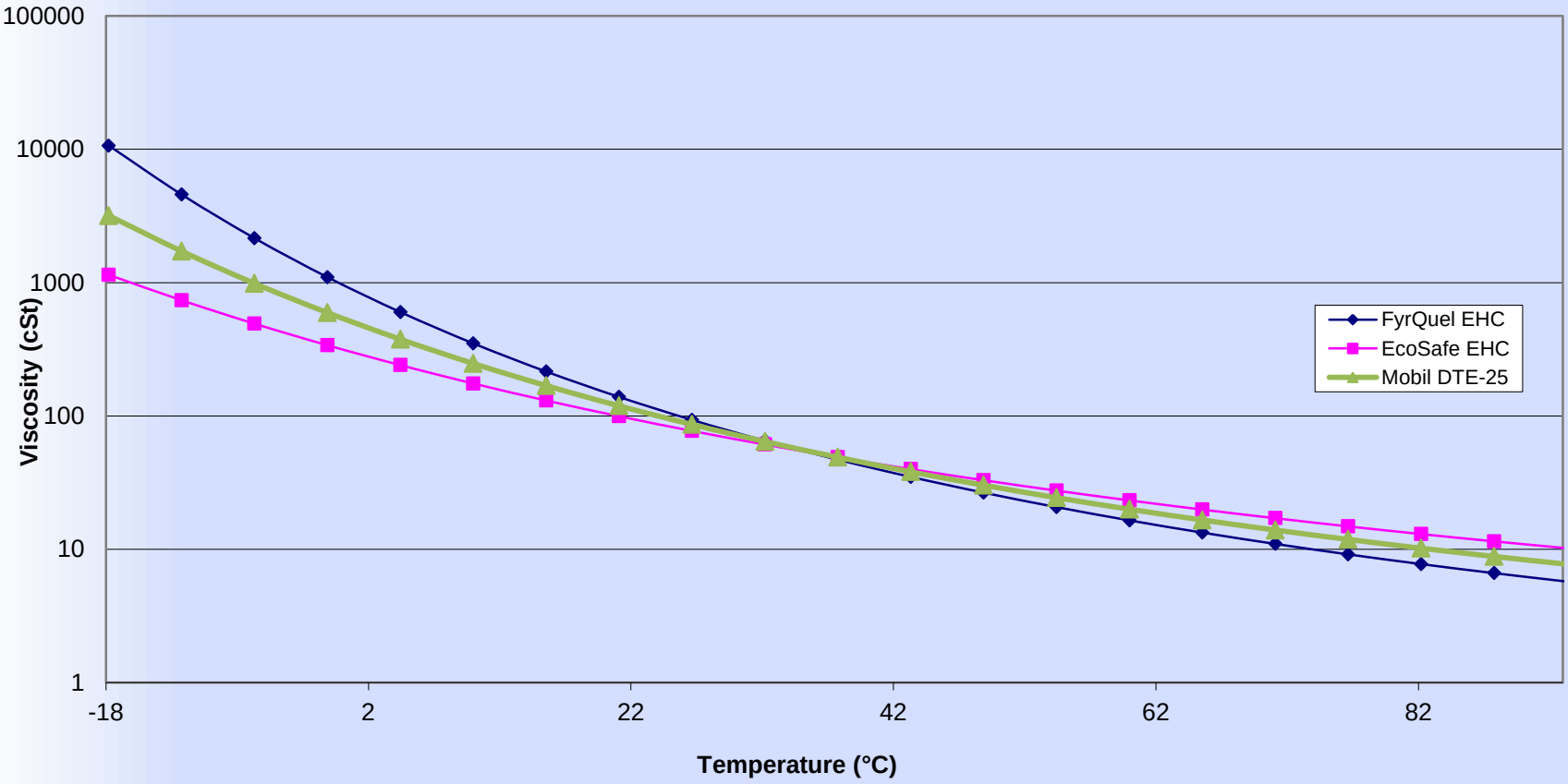
WS-PAG Environmental Properties

Property		**ISO VG 10 thru 1000**
% Biodegradation	OECD 301B	> 60
Aquatic Toxicity		
- Fresh Water Species		
LC50 Daphnia magna, 48H	OECD 202	330-1,000 mg/L
LC50 Pimephales promelas, 96H	OECD 203	700-1,200 mg/L
- Salt Water Species		
LC50 Mysidopsis bahia, 96H	OPPTA850.1035	600-1,000 mg/L
Algae Toxicity Test		
EC50 Green algae, 72H	OECD 201	> 1,000 mg/L
Bacteria Inhibition	OECD 224	NED
Bioaccumulation, log K_{ow}		< 3

NED - No ecological doubt

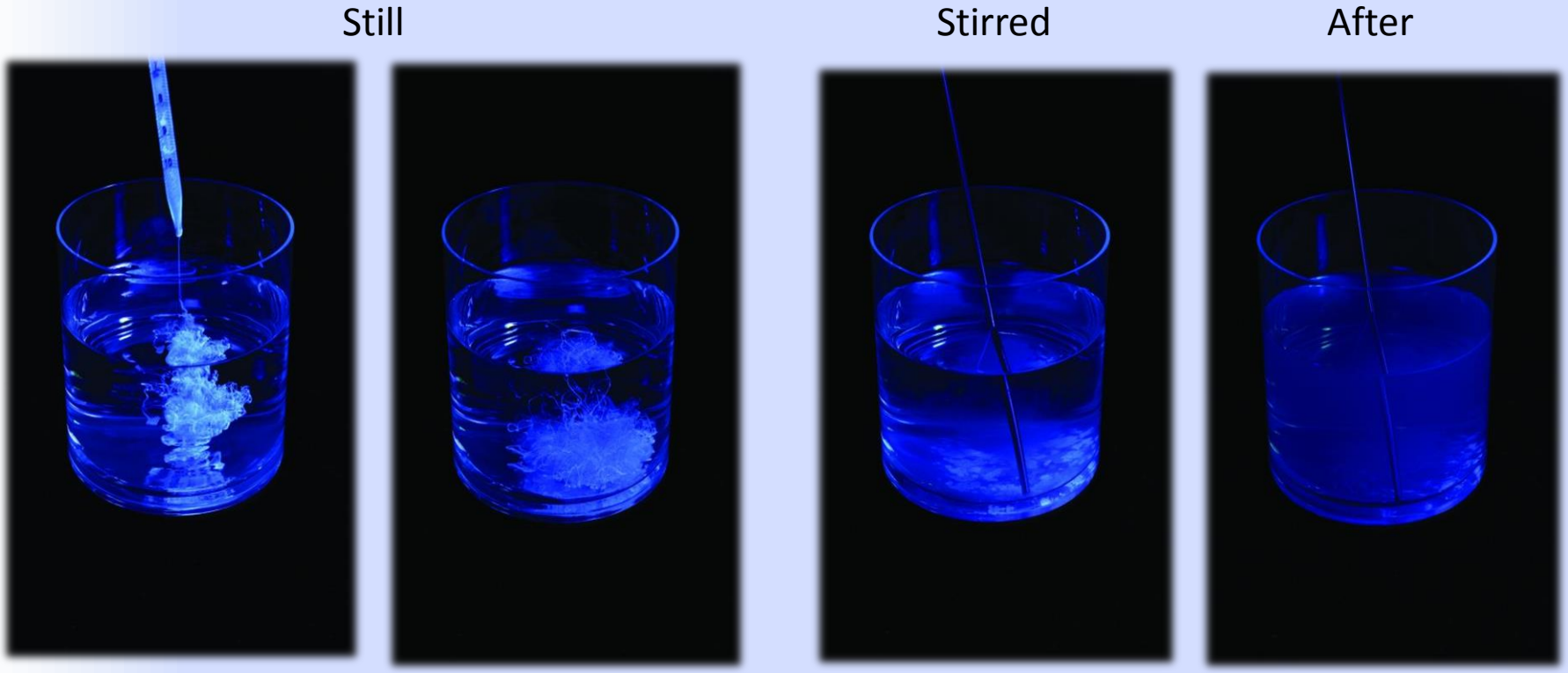
Properties of PAG's (cont.)

Viscosity Index: In general, very high VI compared to other base fluids. Values up to 400 can be reached.



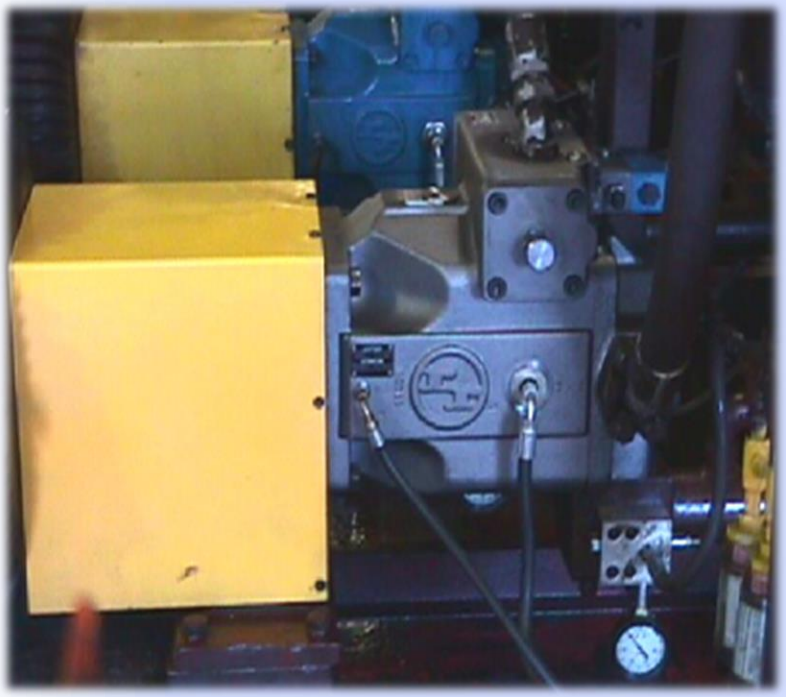
Properties of PAG's (cont.)

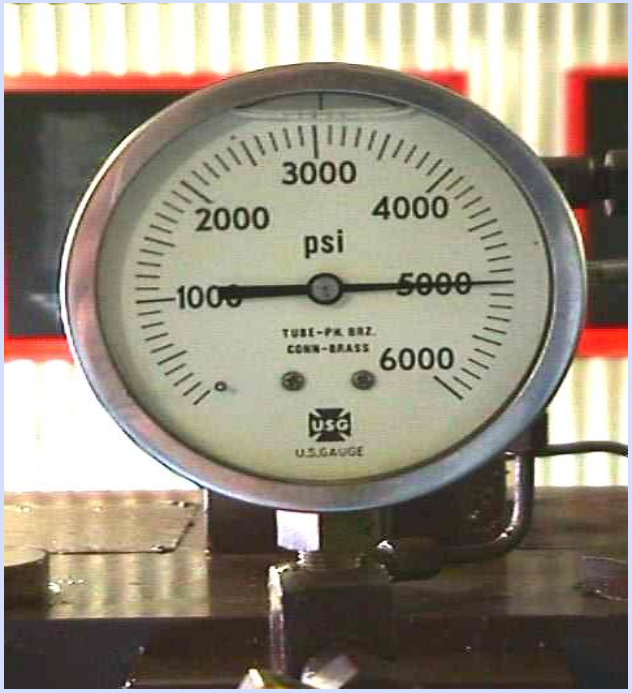
Solubility: It is possible to create PAG's with solubility ranging from complete water solubility to complete oil solubility.



Properties of PAG's (cont.)

Lubricity: Excellent lubrication properties, due to high affinity of the oxygen atoms with the metal surface.





Properties of PAG's (cont.)

Thermal Stability: Very good response to anti-oxidants (high-temperature applications up to 250°C can be achieved).

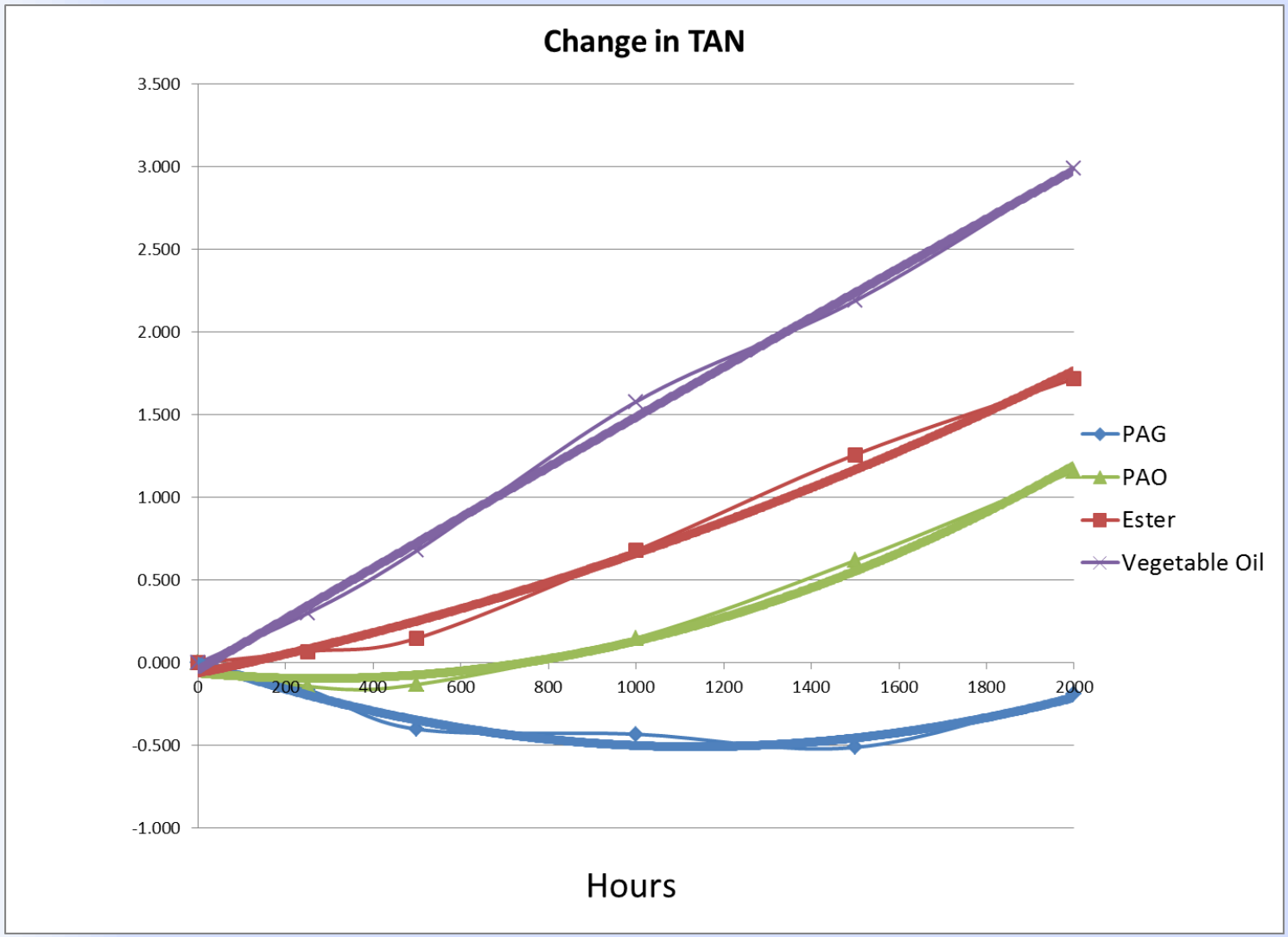
Hydrolytic Stability: PAG's **do not** hydrolyze. Hydrolysis leads to acid formation, corrosion potential and further fluid degradation. Major advantage over mineral oils, vegetable oils and synthetic esters.

Hydrolytic Stability - ASTM D2619

EAL PRODUCT	Change in Acid Number - mg KOH/g	Total Acidity of the Water Layer - mg KOH
Polyalkylene Glycol - PAG	**-0.01**	**Water Solubilized**
Polyalphaolefin - PAO	**-0.08**	**6.9**
Synthetic Ester	**0.83**	**19.37**
Vegetable Ester	**2.02**	**3.23**

Fluids which are unstable to water under conditions of the test form corrosive acidic and insoluble contaminants. **75g of fluid, 25g of water**, and a polished **copper strip** are sealed in a bottle then placed in a **200°F (93°C) oven** and rotated end-to-end at 5 rpm for 48 hrs. Reported values are Acid Number Change, Total Acidity of Water, Weight Change and Appearance of Copper Strip, and can also include Total Sediment Weight.

Modified TOST and EAL's



Modified TOST and EAL's

	TAN	Water Content (ppm)	Viscosity (cSt)
Water Soluble PAG			
Initial	1.31	805	46.48
2000 Hours	1.12	1689	52.43
Change	-0.19	+884	+5.95
Synthetic Ester			
Initial	0.65	389	46.28
2000 Hours	2.37	758	44.94
Change	+1.72	+369	-1.34
PAO			
Initial	0.50	217	49.55
2000 Hours	1.66	624	50.50
Change	+1.16	+407	+0.95
Vegetable Oil			
Initial	0.11	602	42.21
2000 Hours	3.10	893	59.06
Change	+2.99	+291	+16.85

Properties of PAG's (cont.)

Low Residue: Superior deposit control over all other base oil classes. Oxidation by-products are soluble in the base fluid.

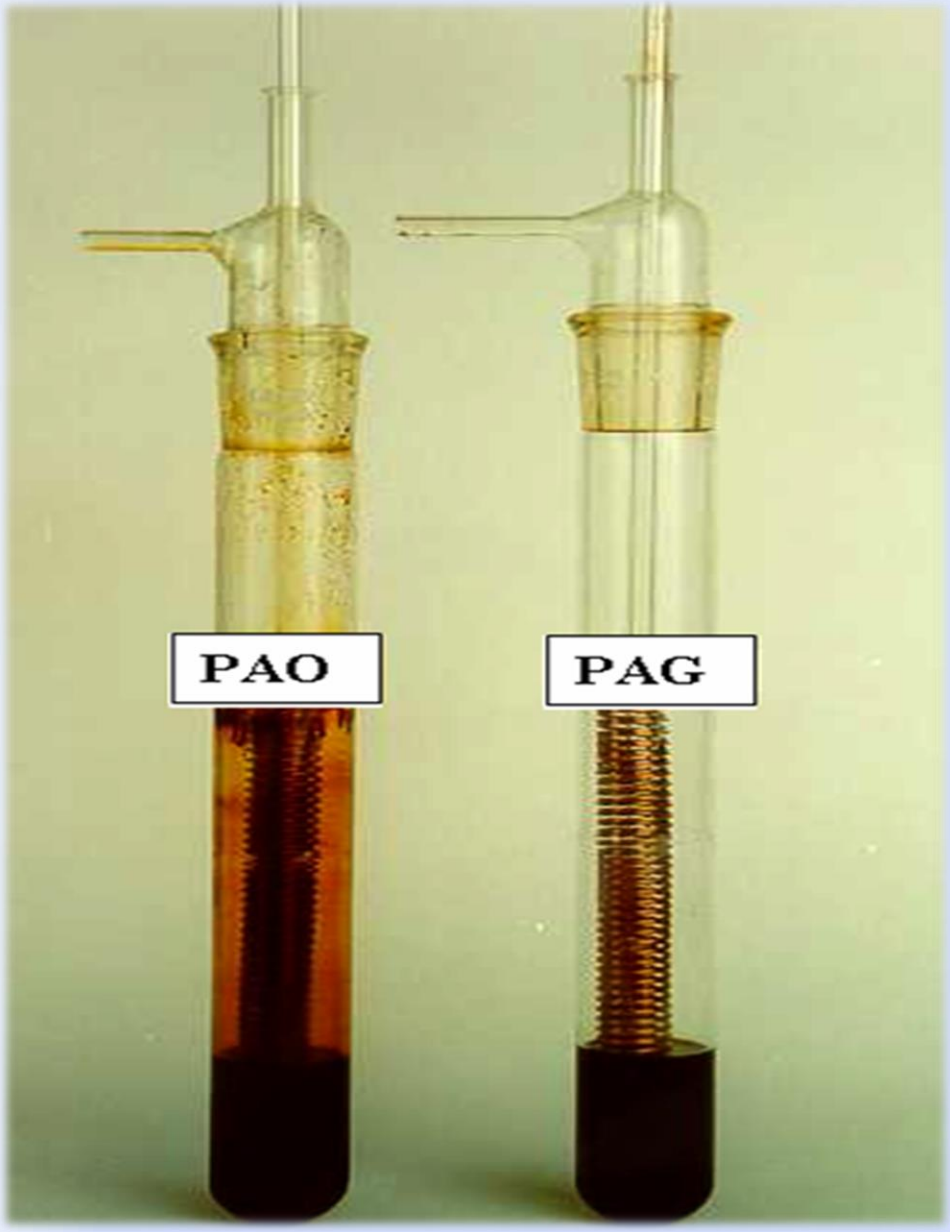
Varnish Formation Mechanisms

Mineral Oil: Agglomeration/Density

Esters: (natural & synthetic) Polymerization

Polyglycol: NONE - degradation results in low molecular weight by-products, soluble in the PAG base stock

Typical Varnish Residues



2,500 hours @ 120°C
ASTM D-943

Properties of PAG's (cont.)

Low Pour Points:	As low as -45°C can be obtained. Low pour point combined with high VI makes PAG's ideal for one fluid with all-season performance.
Thermal Conductivity:	In general, better than mineral oils. Better cooling characteristics.
Elastomer/Metal Compatibility:	Compatible with all commonly used elastomers and all metals.
Fire-Resistance:	Can be formulated to pass Factory Mutual Standard, Class 6930. Dependent on molecular weight of PAG.

Typical Hydraulic Fluid Properties (PAG-WS)

Property	Test Method	ISO VG 32	ISO VG 46	ISO VG 68
Viscosity @ 40°C, cSt	ASTM D445	32.93	46.96	67.97
Viscosity @ 100°C, cSt	ASTM D445	7.13	9.88	13.91
Viscosity Index	ASTM D2270	188	203	214
Specific Gravity @ 25°C, g/cm^3	ASTM D1298	1.02	1.03	1.03
Pour Point, °C	ASTM D97	-46	-40	-35
Acid Number, mgKOH/g	ASTM D664	1.0	1.0	1.0
Rust Prevention	ASTM D665A	Pass	Pass	Pass
Copper Strip Corrosion	ASTM D130	1B	1B	1B
Air Release @ 50°C, min.	ASTM D3427	5.0	7.5	7.0
Foam Tendency, Seq. I/II/III	ASTM D892	0/0	0/0	0/0
Four Ball Wear, Scar Dia.	ASTM D4172	0.39	0.38	0.20
Hydraulic Pump Test	ASTM D7043	2.2 mg		
Eaton Pump Test	35VQ25A	Pass		

EAL Base Stock Ratings

Rating of Fluid Base Stocks
Ratings: 1 (poor) to 5 (excellent)

Property	**MO**	**EAL PAO**	**VO**	**Syn Ester**	**WS PAG**
ISO Class	HLP	HEPR	HETG	HEES	HEPG
Readily biodegradable	2	4	5	5	4
Renewable content	1	4	5	4	1
Aquatic toxicity	5	5	5	5	4
EPA "Static Sheen"	1	1	1	1	5
Bioaccumulation	2	2	2	2	5
Worker friendly	5	5	5	5	5
Hydrolytic stability	3	3	2	3	5
Chemical Stability	4	3	2	4	5
Oxidative stability	3	4	2	4	5
Seal compatibility	5	5	5	4	4
Metals compatibility	5	5	4	3	5
High-pressure performance	5	5	5	5	5
All-season performance	3	4	2	5	5
Varnishes and residues	3	4	1	4	5
Fire-resistance	1	1	4	1	4
Paint and Sealant compatibility	5	5	4	4	3
Fluid maintenance	4	4	1	4	5
Ease of Conversion (from mineral oil)		5	2	4	3
Price	5	2	4	2	2
Total Score	62	71	61	69	80

WS-PAG Advantages for Dredging/Marine Industry

- ONLY non-sheening EAL pursuant to 40 CFR435 EPA Static Sheen Test
- Hydrolytic Stability
- Non-sludge or varnish forming
- Completely water-soluble
- Acts as polymeric sponge

Oil Sheen - Black Light Photos

Oils (still)

Mineral Oil

White Oil

Vegetable Oil

Synthetic Ester

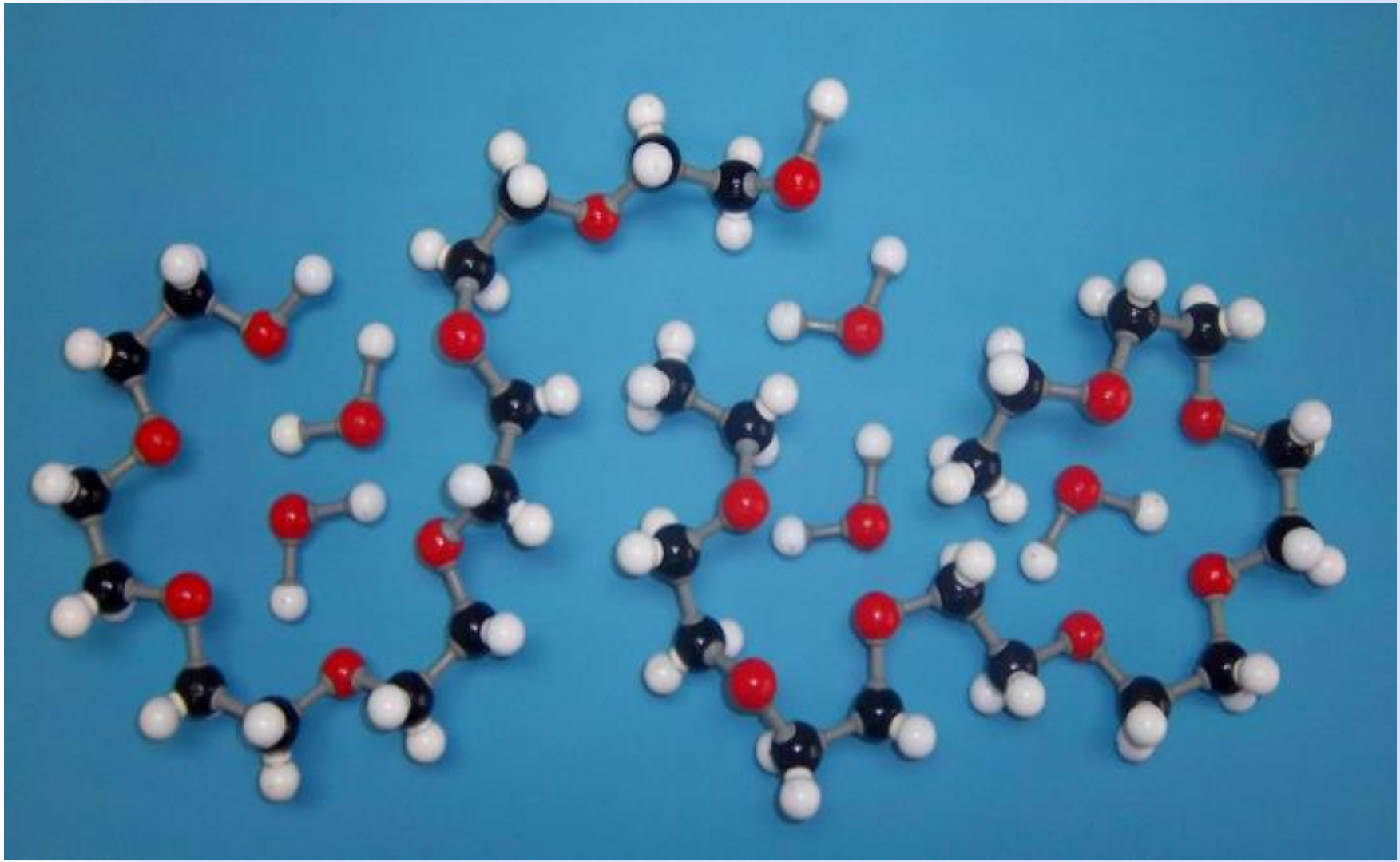
Oils (stirred)

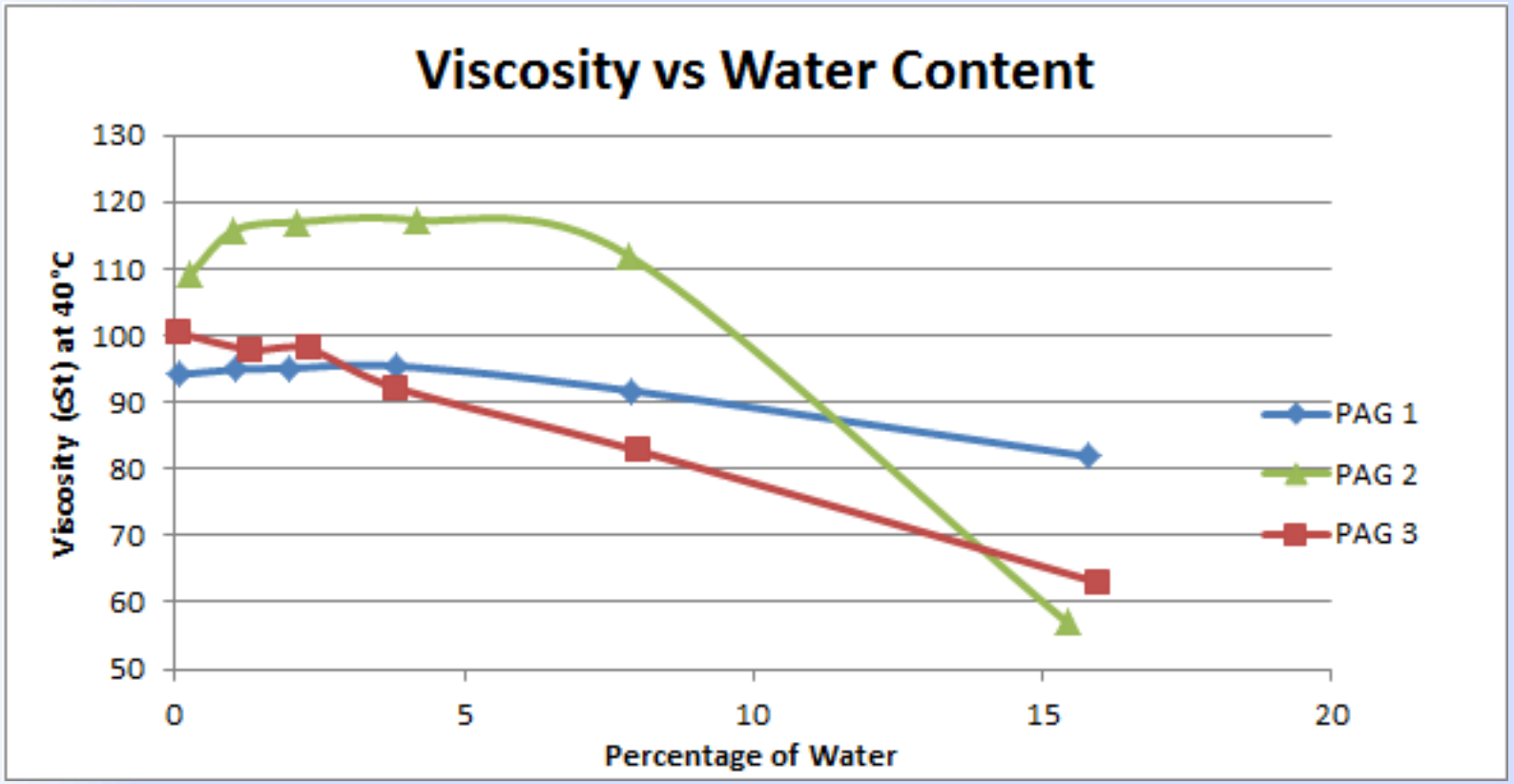
EPA 40 CFR435 Static Sheen Test

	WS PAG	Vegetable oil based hydraulic fluid	Synthetic ester based hydraulic fluid	White-oil based hydraulic fluid	Petroleum based hydraulic fluid
Silvery or metallic sheen	NO	NO	NO	NO	NO
Increased reflectivity	NO	NO	**YES**	**YES**	NO
Visual Color	NO	NO	NO	NO	NO
Iridescence	NO	NO	NO	NO	NO
Oil Slick exceeding 10% of surface area	NO	**YES**	**YES**	**YES**	**YES**
Appendix 1 to Subpart A of 40CFR435 result	**PASS**	**FAIL**	**FAIL**	**FAIL**	**FAIL**

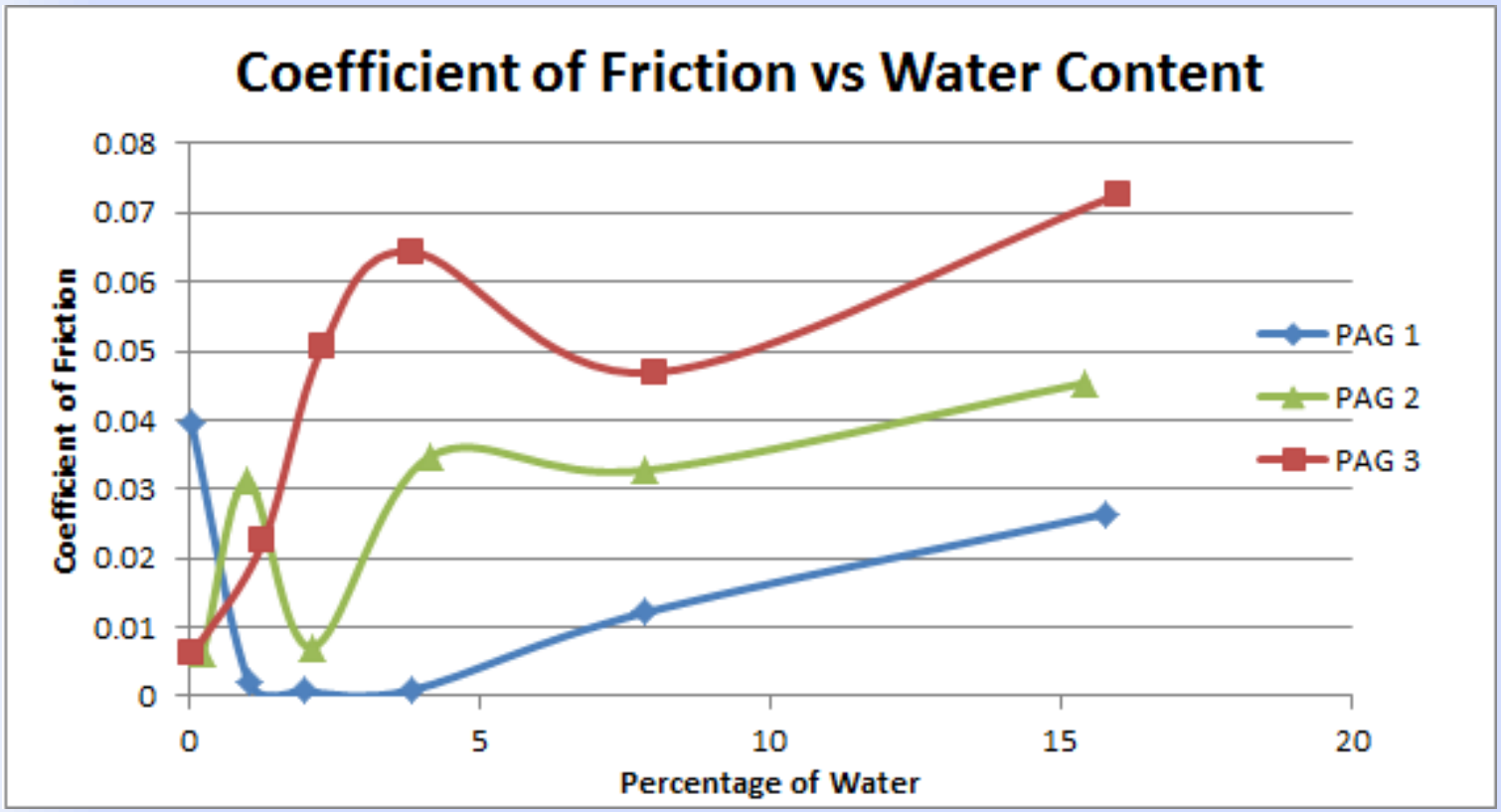
8.6 Detection of a "silvery" or "metallic" sheen or gloss, increased reflectivity, visual color, iridescence, or an oil slick on the water surface of the test container surface shall constitute a demonstration of "free oil." These visual observations include patches, streaks, or sheets of such altered surface characteristics. If the free oil content of the sample approaches or exceeds 10%, the water surface of the test container may lack color, a sheen, or iridescence, due to the increased thickness of the film; thus, the observation for an oil slick is required. The surface of the test container shall not be disturbed in any manner that reduces the size of any sheen or slick that may be present.

WS PAG and Water – Hydrolytic Stability



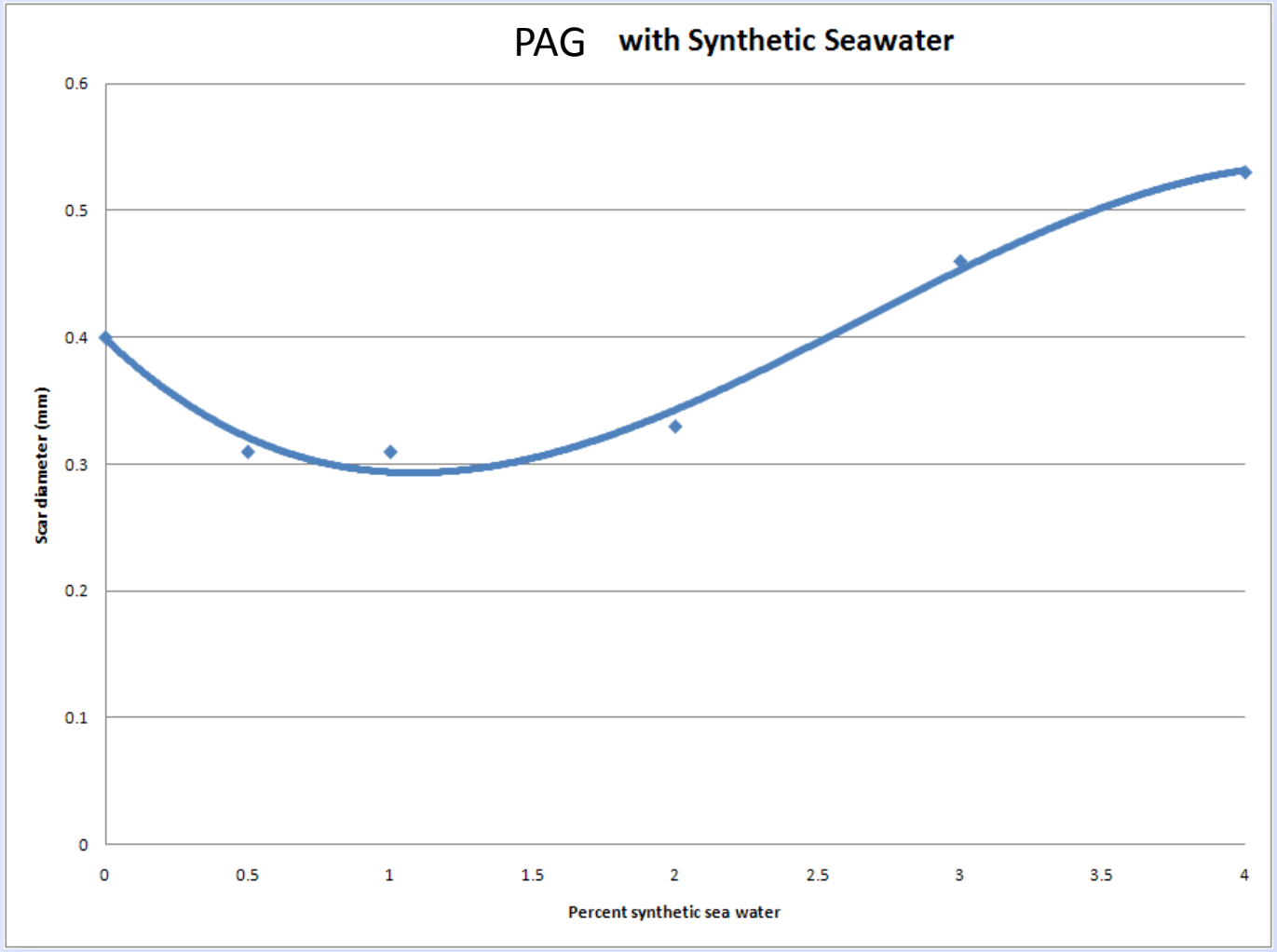


Kinematic viscosity (cSt) at 40°C



Average Coefficient of Friction at 40°C

Lube Testing with Salt Water



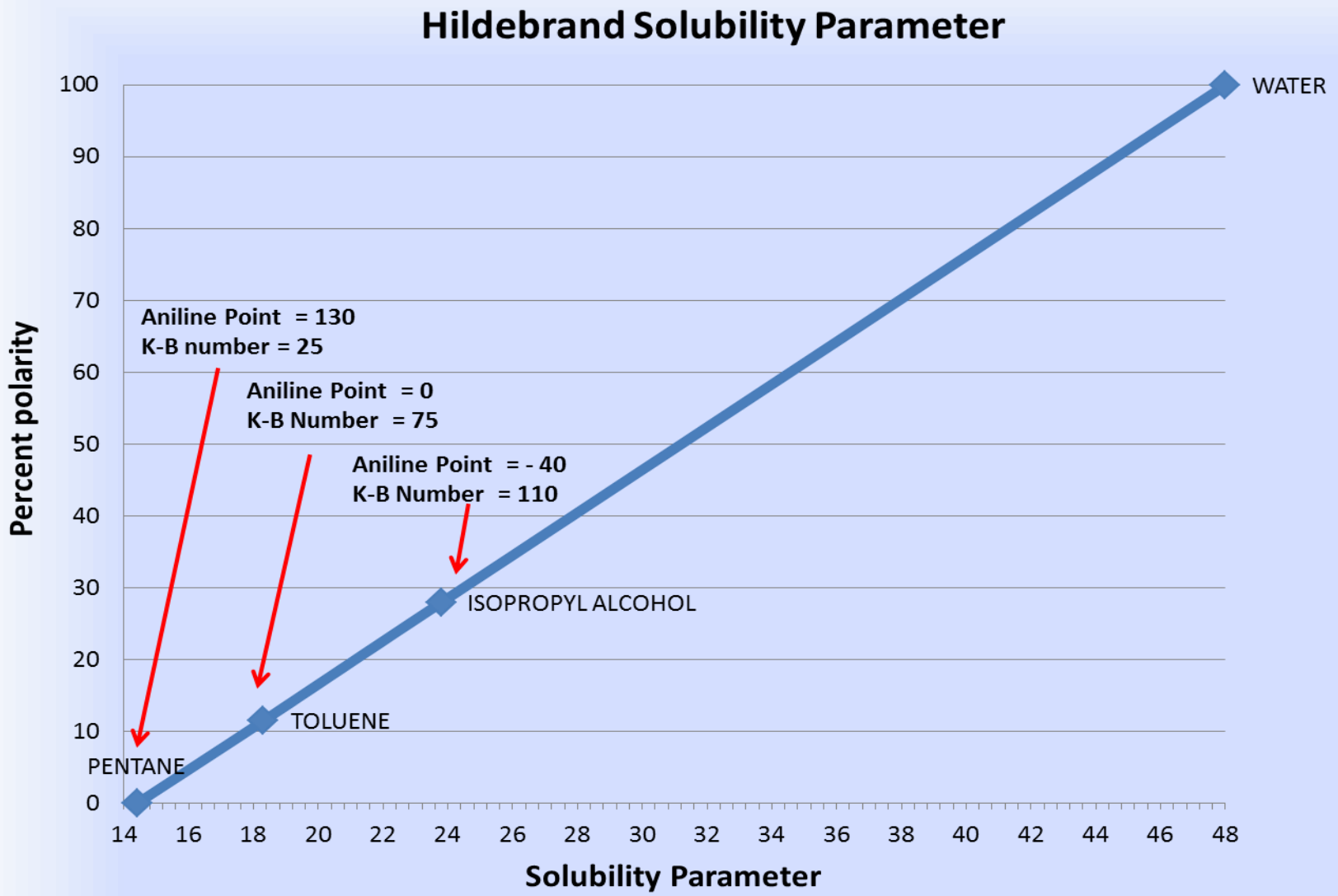
PAG WS ASTM D-4172 4 Ball wear with various amounts of synthetic sea water

Polyglycol Myths

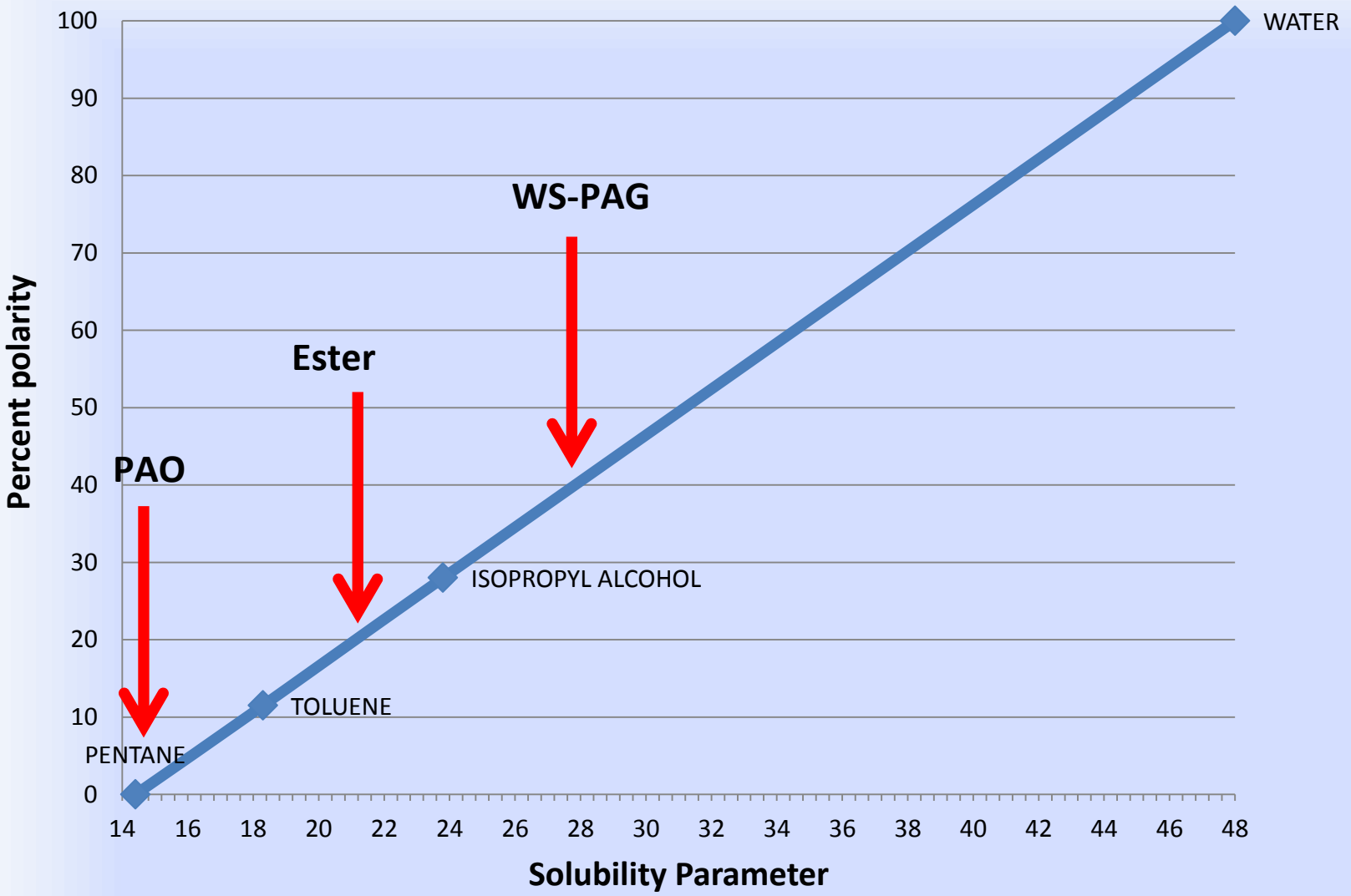
- Incompatible with mineral oil
- Aggressive to elastomers
- Attack paints/coatings
- Water toxicity

It is not a question of FEAR, rather an understanding of SOLUBILITY.

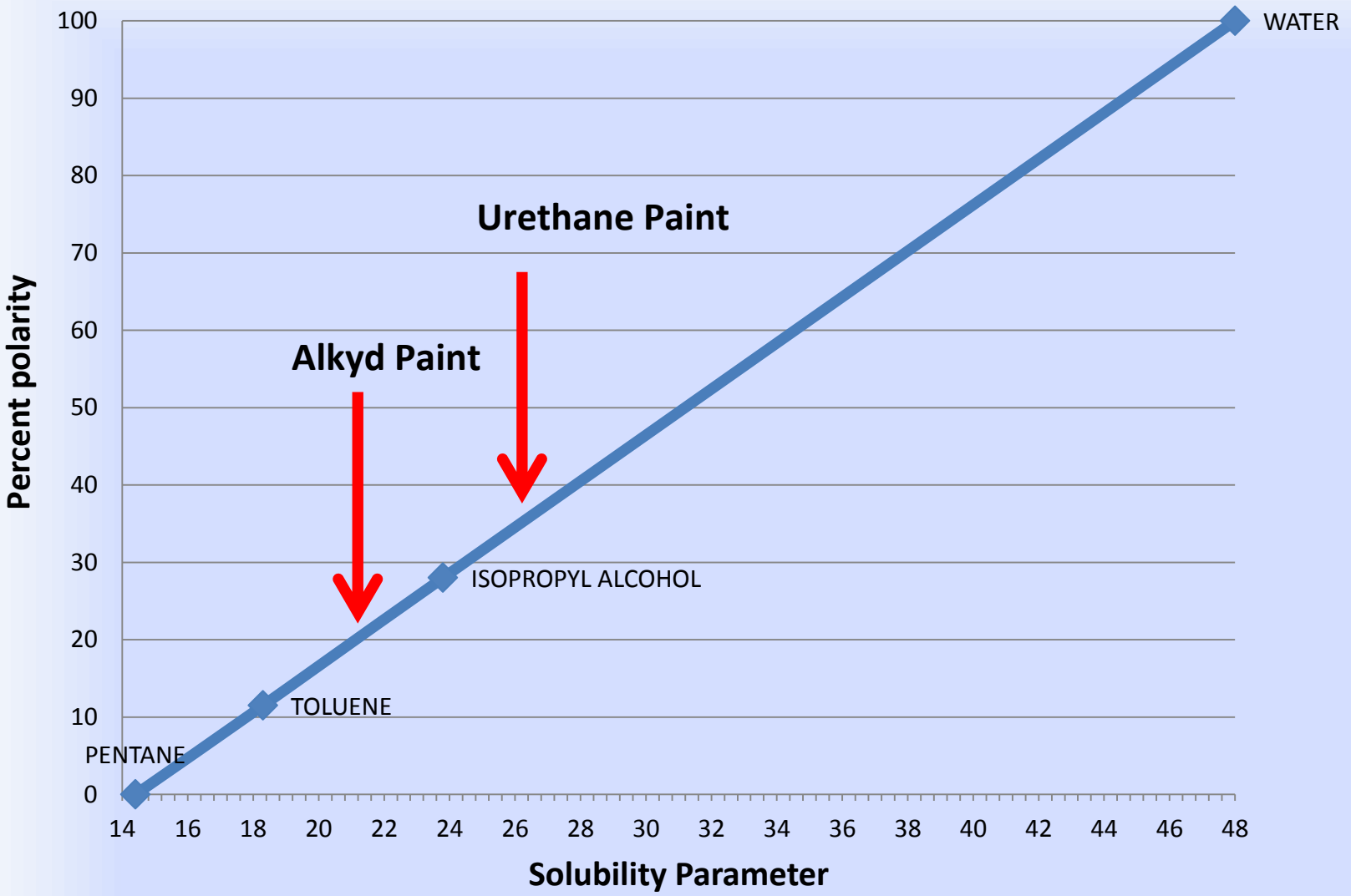
“Likes dissolve likes.”


Hildebrand Solubility Parameter
Percent polarity
Solubility Parameter
100
90
80
70
60
50
40
30
20
10
0
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
Aniline Point = 130
K-B number = 25
Aniline Point = 0
K-B Number = 75
Aniline Point = - 40
K-B Number = 110
PENTANE
TOLUENE
ISOPROPYL ALCOHOL
WATER

Hildebrand Solubility Parameter



Hildebrand Solubility Parameter



Solubility – Mineral Oil and WS PAG

Elastomer Compatibility - WS PAG

	NBR-1	HNBR	FKM	Neoprene	Urethane
Durometer, point change	-7	-2	0	-16	-8
Volume, % change	+16.4	+1.3	+5	+28.4	+5.3
Weight, % change	+14.4	+1.2	+1.9	+18.8	+4.3

1,000 hours @ 100C

Urethane elastomers are formulation specific.

EAL Toxicity

It's Okay…

It's Biodegradable

Industries Served by WS PAG Fluids

Benefits

Passes EPA 40 CFR 435 Static Sheen Test
Fully compliant with 2013 VGP standards
Fully compliant with USCG standards
Water soluble
Low aquatic toxicity
Readily biodegradable
Worker friendly
Thermal stability
Material compatibility
All-season performance
Excellent lubricant
Non-sludge or varnish forming
Hydrolytically stable
FM Approved fire-resistant hydraulic fluid

Applications

Dredging
Tunnel Boring
Power Plants
- Metso Equilibrium Crane
- Barge Unloader
- Tug Boat
- Lime Unloader
- Various Gear Boxes

Hydro Electric
- Trash Rake
- Wicket/Crest Gates
- Kaplan Turbine Pitch Controls
- Francis Turbine Upper Bearing

US Army Corps of Engineers
- Locks & Dams
- Tainter Gates
- Winches on Floating Crane

Tunnel Boring – 8 Year History

Loop Temp.: 165°F (74°C)

Pump Type: Axial piston, variable displacement

Pump Speed: 1,800 RPM

Pump Flow: 10-50 GPM (37.85-189.25 LPM)

Pump Pressure: 3,500 PSI – 4,500 PSI (241 – 310 bar)

Tunnel Boring Machine

PAG's in the Power Generation Industry

Equilibrium Cranes – 4 years

Hydraulic line over the water.

Dredging – 4 Years

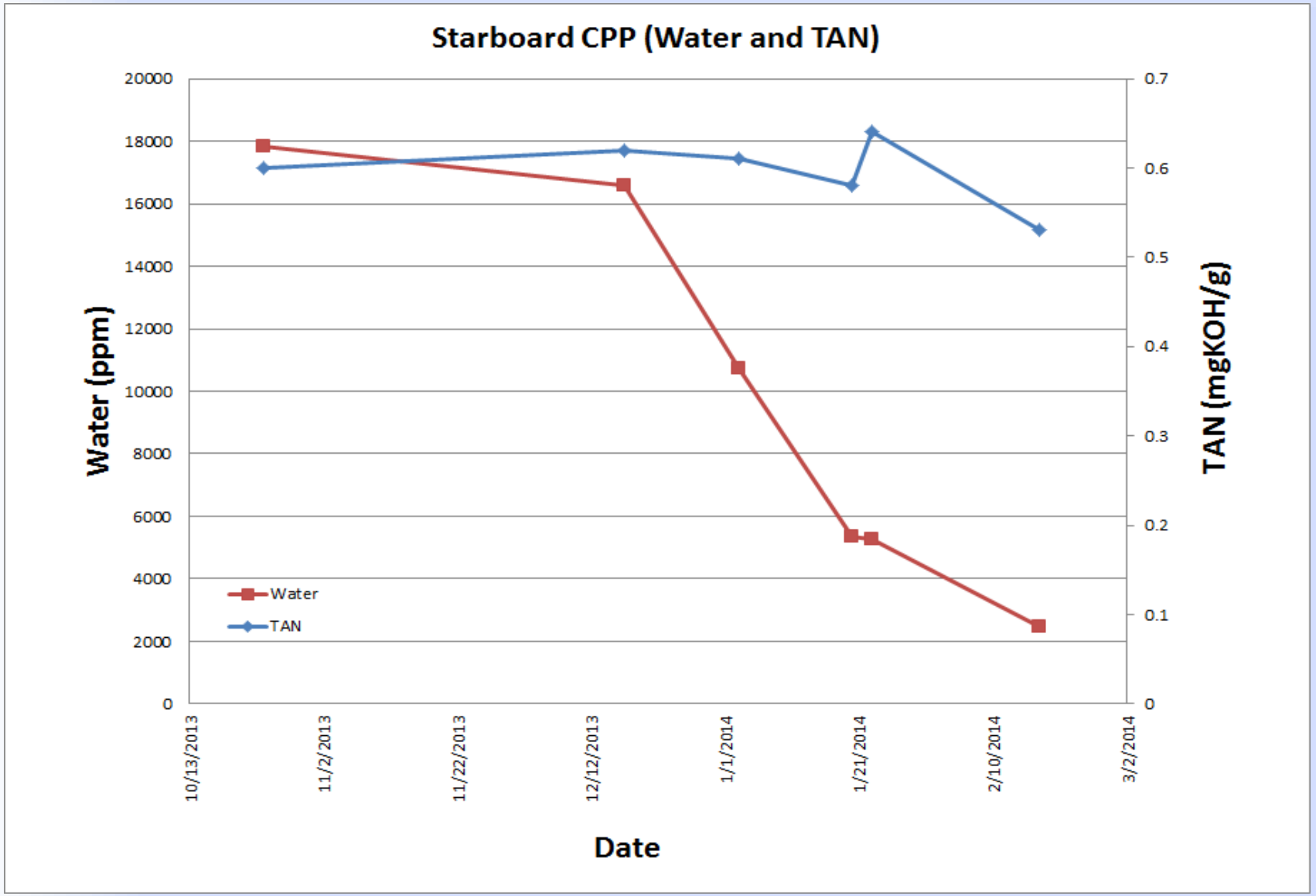
- Stern Tubes
- Hydraulics
- Cutter Heads
- Winches
- Gear Boxes
- Bow Thrusters

US Army Corp – Winches – 4 years

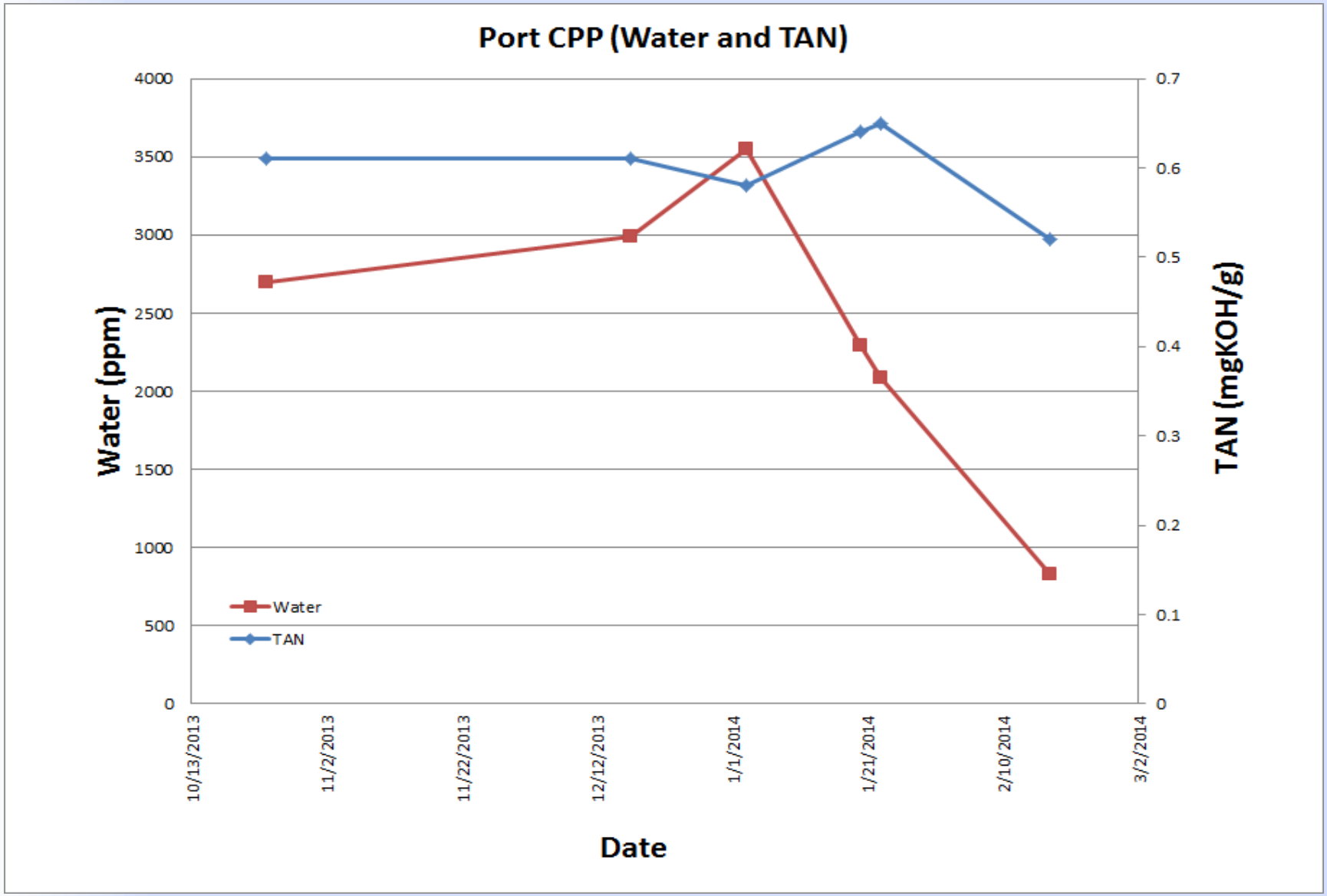
USCG – Mackinaw Ice Breaker – Bow Thruster (2 yrs)

USACE – Wheeler Dredge - CPP

Wheeler Dredge – Starboard CPP



Wheeler Dredge – Port CPP



Conclusion

Property	WS PAG	Syn Ester	Bio PAO	Veg Oil
Biodegradable	Pass	Pass	Pass	Pass
Minimally Toxic	Pass	Pass	Pass	Pass
Non-Bioaccumulative	Pass	Pass(a)	Pass(a)	Natural
USCG Classification	Chemical	Oil	Oil	Oil
EPA Static Sheen	Pass	Fail	Fail	Fail
Long-term Performance w/ Water	Excellent	Fair	Fair	Poor

(a) Synthetic materials made from natural fats and oils may exhibit bioaccumulation having a negative impact upon bio-organisms.