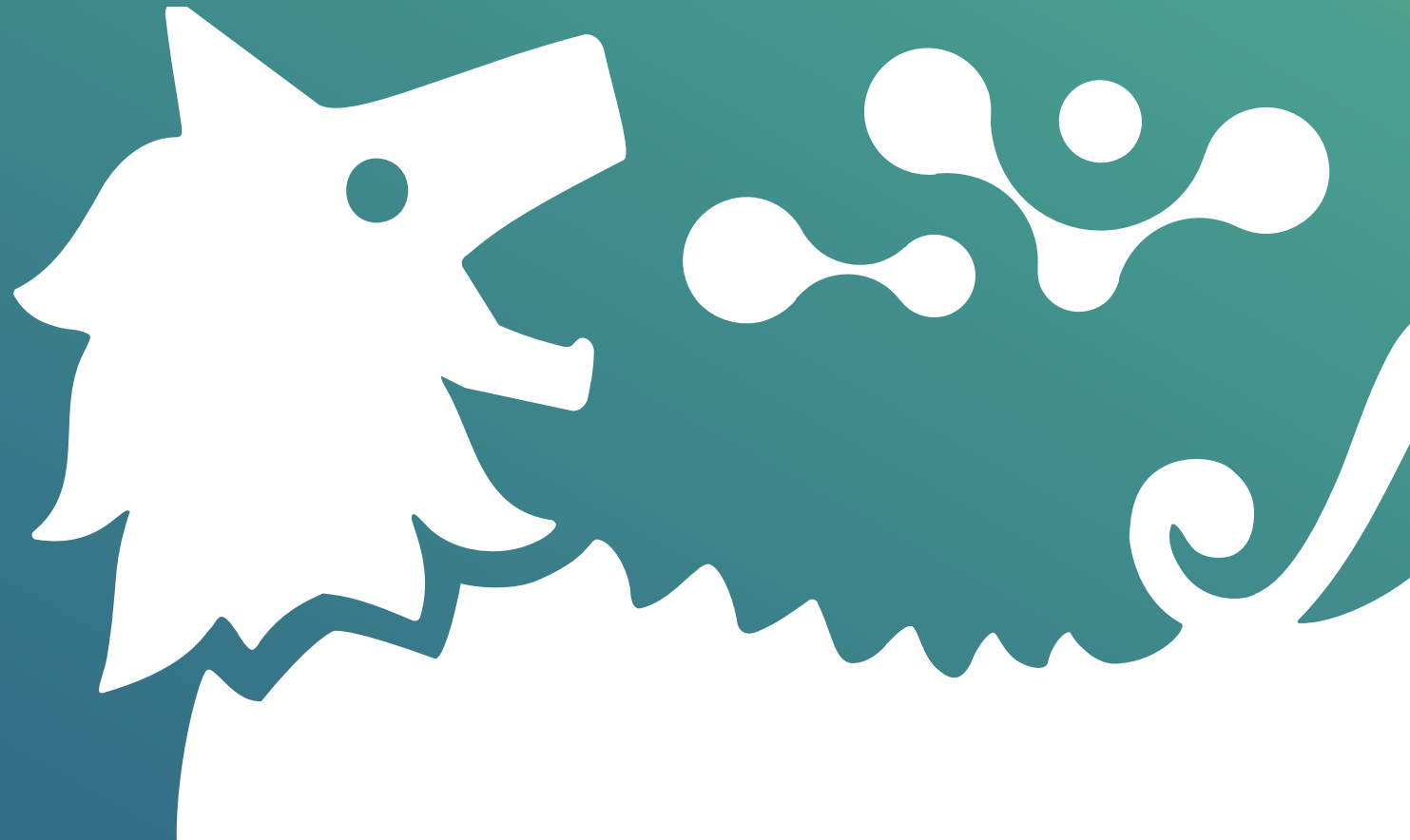


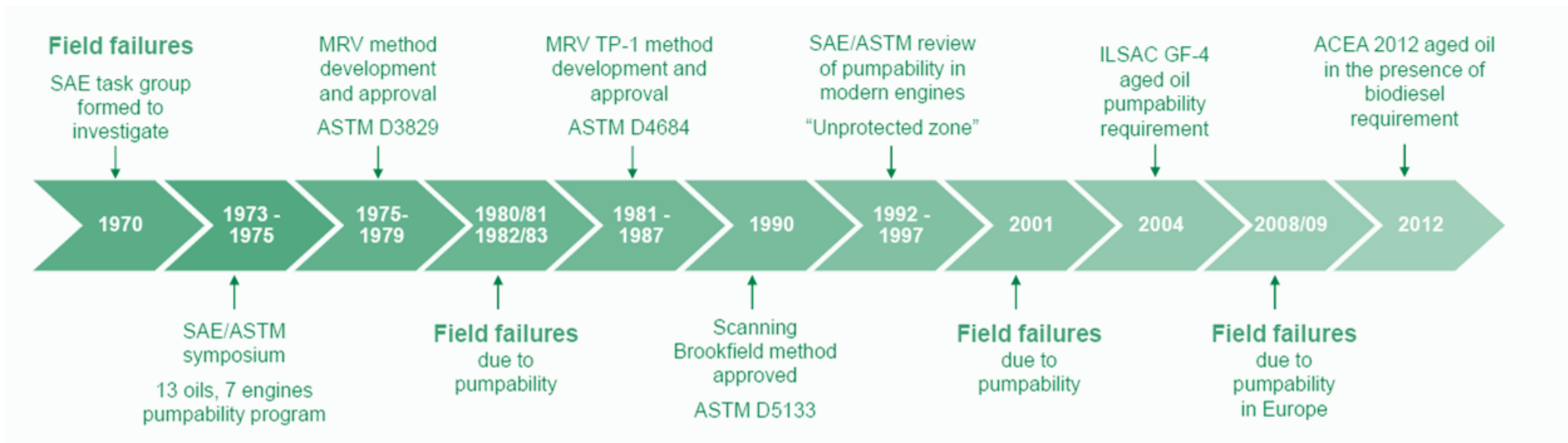
Understanding and Mitigating Gelation in Engine Oils: The role of OCPs

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Gelation: A Phenomenon Revealed Through Field Failures



Field failures have continuously driven specification evolution, highlighting that **cold-start reliability depends on oil structural stability, not viscosity alone.**

Events from the late 70's revealed that **viscosity alone is not sufficient to ensure low-temperature engine protection.**

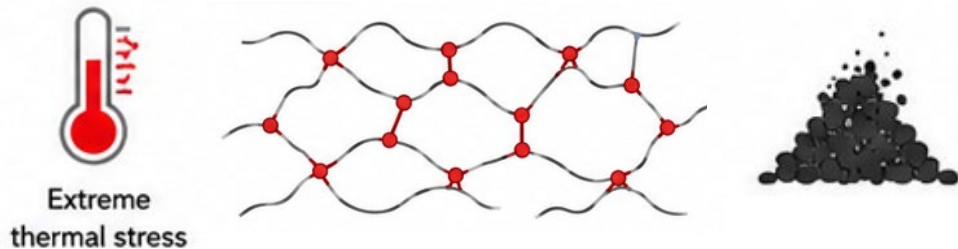
This understanding led to the development of advanced test methods and evaluation criteria, and to the emergence of dedicated research fields addressing oil gelation and low-temperature rheology.

Clarifying "Gelation" - One Term, Two Extremes

"Gelation" in lubricants actual refers to two completely different phenomena

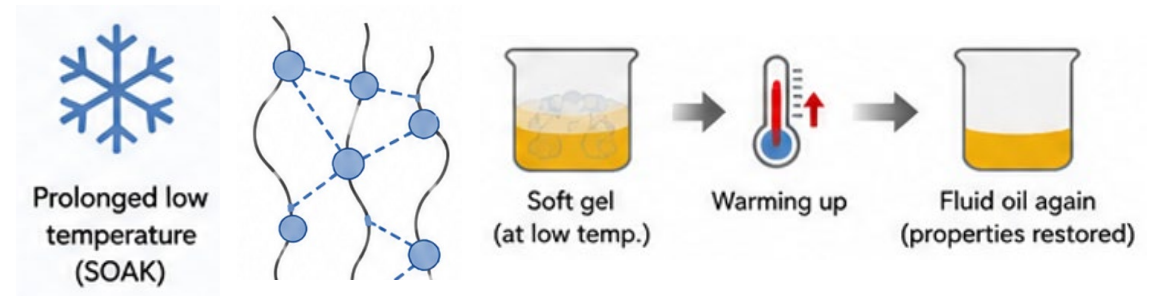
Irreversible Chemical Gelation

- It occurs through covalent cross-linking which create a permanent, rigid network that effectively "kills" the oil.
- It is triggered by extreme thermal stress, soot accumulation (17% to 25%), or radical reactions with biocomponents like FAME.



Thermally Reversible Physical Gelation (Our Focus)

- Caused by weak intermolecular interactions, such as van der Waals forces.
- It happens when a lubricant is kept at prolonged low temperatures (the "soak" period), allowing paraffins and waxes to form a 3D network.



Don't let the phrase "thermally reversible" fool you.

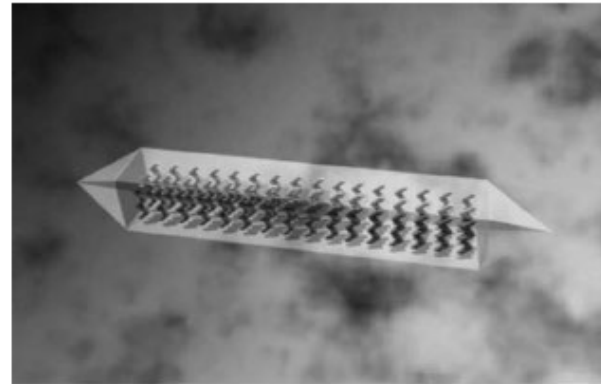
If the oil has gelled in the pan, the engine will fail long before the lubricant has a chance to melt

Clarifying "Gelation"

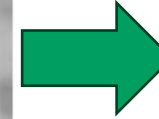
"Gelation is a rheological response of the oil in which a structural network encapsulated the more fluid portion of the engine oil."

Network Formation

- Mineral oils at cold temperatures often do not flow because they contain molecules that have a crystalline nature at low temperatures.
- At first, two-dimensional crystals (platelets) form and then ultimately three-dimensional needle-like structures form.
- The needle-like structures layer on one another, forming a **network of crystals that trap the non-crystalline oil molecules within the gel network**



Three-dimensional needle-like structure of crystal platelets.



Gel network of needle-like structures.

Certain oils gelled readily under normal cooling conditions, whereas others did so only under specific cooling combinations that can occur in real environments, sometimes even above 0 °C.

Gelation: Engine Effects

Research started in 70's identified two distinct pumpability failure modes:

- **Flow-limited pumpability failure** results from increased oil viscosity at low temperatures, leading to restricted flow and difficult engine starting. This type of failure is predictable and can generally be avoided through viscosity measurement and control.
- **Air-binding pumpability failure** is more severe and occurs when oil and additives form a gelled network. Under certain cooling conditions, only a small volume of oil near the pump inlet can flow, creating a void that allows air to be drawn into the pump. Air ingestion rapidly disrupts lubrication, potentially causing severe engine damage.

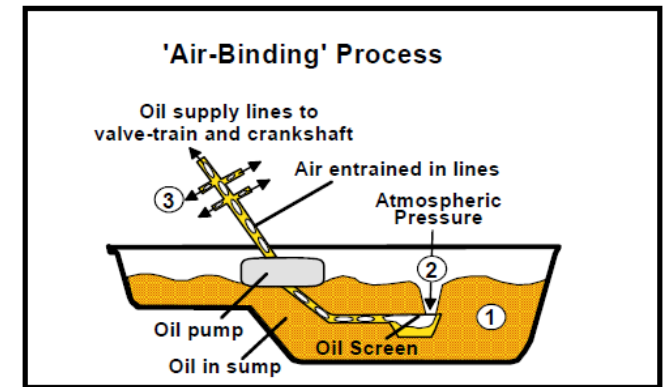
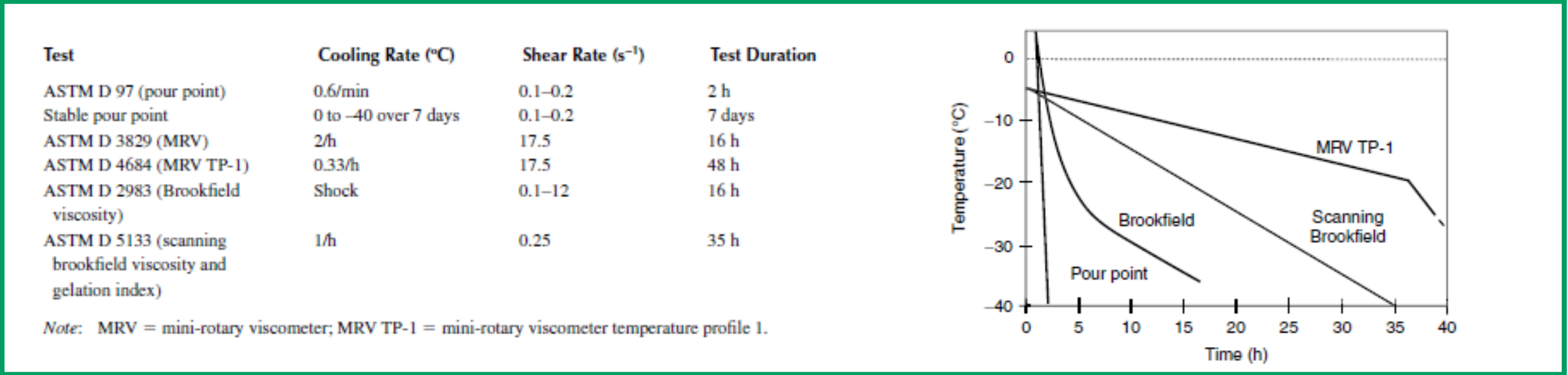


Fig. 1 – Diagram of 'air-binding' process – 1. Gelated engine oil, 2. atmospheric pressure forcing core of oil into screen followed by air, 3. air passing to lubrication sites.

Gelation: Engine Effects

Field failure understanding led to the development of bench test methods and evaluation criteria which now are the base of lubricants cold characterization

Common Bench-Test on Lubricants Cold Properties at Low Shear



These tests are not enough to replicate all cold “static” properties of lubricants and concentrates.

Taking in account the great dependency on specific thermal history for the comparison of gel structures, feasibility tests should include as good practice even low temperature exposure of specimens under testing at a reproduced cold climate in order to evidence it.

Source: Lubricant additives: chemistry and applications / Leslie R. Rudnick. -- 2nd ed.



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Gelation Contributing Factors: Base Oils

Low-temperature-crystallizing chemical species in base oils depends on:

- Crude oil source
- Refining route
- Dewaxing technology
- Final viscosity grade

Dewaxing mechanisms:

- Solvent dewaxing: removal of long-chain linear hydrocarbons (n-paraffins)
- Catalytic dewaxing: structural modification via cracking and isomerization, producing isoparaffins

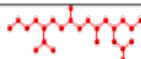
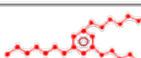
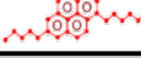
Group II & Group III base stocks:

- Increasingly prevalent due to high VI and excellent oxidation stability
- Predominantly paraffinic, but mainly composed of isoparaffins

Low-temperature implications:

- Crystallization phenomena are strongly mitigated, not fully eliminated
- Isoparaffins may form limited, weakly ordered, randomly distributed crystalline domains
- **These domains do not form extended wax networks or severely impair pumpability, however, they may act as heterogeneous nucleation sites for other crystalline species in the lubricant system**

Base stock composition impact

Molecule	Structure	VI	Low Temp	Oxidation	Solubility	Toxicity	Process
							Dewaxing
n-paraffin		Excellent	Poor	Excellent	Poor	Low	
Iso-paraffin		Good/Excellent	Good	Excellent	Good	Low	
Linear naphthenic		Good	Good	Good	Good	Low	
Naphthenic		Poor	Excellent	Good	Excellent	Low	
Substituted Monoaromatics		Poor	Good	Good	Good	Medium	
Poly Nuclear Aromatics		Poor	Poor	Very Poor	Good	Very high	
							Hydro-processing

Gelation Contributing Factors: The role of PPDs

Common chemistries include acrylates, methacrylates, ethylene/vinyl acetates, alpha-olefins, styrene-based copolymers, olefin/maleic anhydrides, and vinyl acetate/fumarates

All polymeric PPDs have comb-polymer structure composed by Long wax-like side chains interspaced with short, neutral side chains

Long waxy side chains:

- Interact with wax crystals proportionally to side-chain length
- **Require compatibility with the total wax content of the lubricant (Wax Interaction Factor)**
- Can be linear or branched
- Typically require $\geq$ C14 carbon atoms to be effective

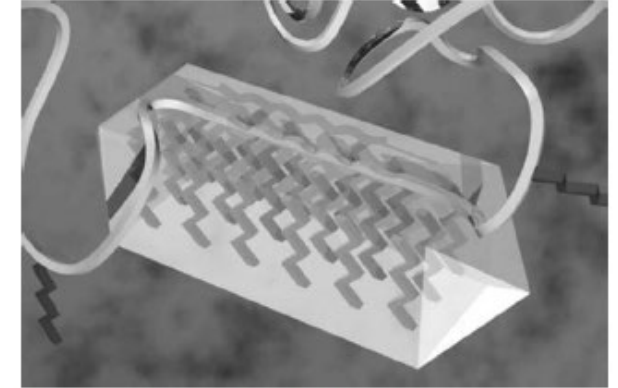
Short neutral side chains:

- Act as inert diluents
- **Control the extent and selectivity of wax interaction**

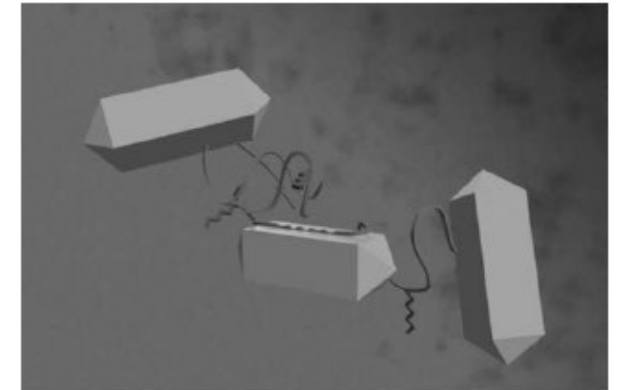
Operating Principle

Additional wax sources may be introduced by Detergent–inhibitor (DI) packages, Friction modifiers containing waxy hydrocarbon chains, VIIs: these low T crystalizing components can positively or negatively affect low-temperature performance.

A.E. In systems with low wax-interaction PPDs, waxy detergents may consume available PPD interaction sites and reduce its effective wax control, promoting gel formation at low temperature



Crystallization of a PPD with a needle-like structure.



PPD prevention of gel network formation.

Low temperature performance of VIIs

The most widely used VII polymers in engine oils are:

OCP (Olefin Copolymers)

- Supplied in different physical forms (pellets, bales), mainly linked to composition
- Depending on ethylene content, may contain semi-crystalline domains

SDH (Styrenic block copolymers)

- Produced via living anionic polymerization
- Enable a wide variety of architectures (linear, star...) and block distributions (di-block, tri-block)

TYPE		CCS -25° 1%w in SN 150 (cP)	Gelation Index
OCP Semi-crystalline	OCP 2530 PL	5800	10
OCP Amorphous	OCP 2550	6050	6
Star polymer	SOL THX 1050	6070	6
Linear block copolymer	Linear SDH tri-block LMW	6320	18
Linear block copolymer	Linear SDH2 HMW	6200	6

The results of high shear and low temperature (CCS) tests are quite aligned for the series of selected polymers, even with different TP, originating from very diverse synthetic chemistries.

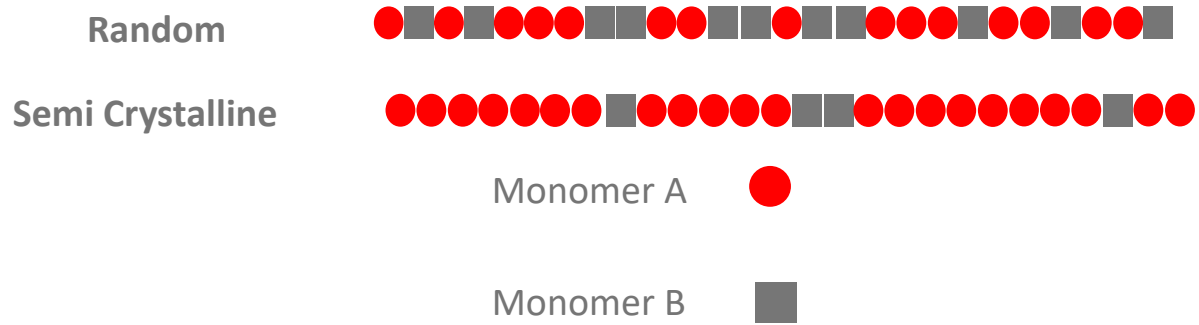
Particular attention must be paid to tests in which solutions are maintained at low temperatures and low shear (scanning Brookfield):

- For OCPs, **special attention must be given to polymers with higher ethylene content, which, depending on the formulation context, may have time to aggregate their crystalline component with waxes and paraffins present in the formulation that can be disaggregated under high shear or temperature.**
- An S-EB-S triblock at low temperature and low shear certainly constitutes a 3D network, which effect is not appreciable in CCS due to the breaking of weak bonds caused by the high shear imposed by the apparatus.

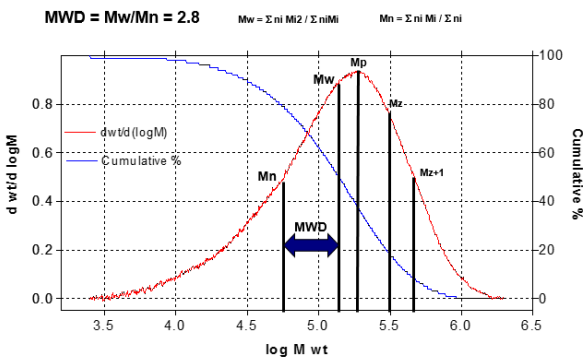


OCPs- Structural Features

Composition & Monomers Distribution



Molecular Weight & MW Distribution



OCPs are classified according to the ethylene content in the copolymer:

- Ethylene: 45-59 weight% amorphous solids, sold in bales
- Ethylene: 60-69 weight% semi-crystalline solids, sold in bales or pellets

On semi-crystalline grades what really matters is:

- Ethylene distribution along the chain
- Sequencing / blockiness
- Balance : backbone vs. random side chains

Dutral OCP Typical Range		
Mw	80 000	200 000
C3 Content	28	48
C2 Content	72	52



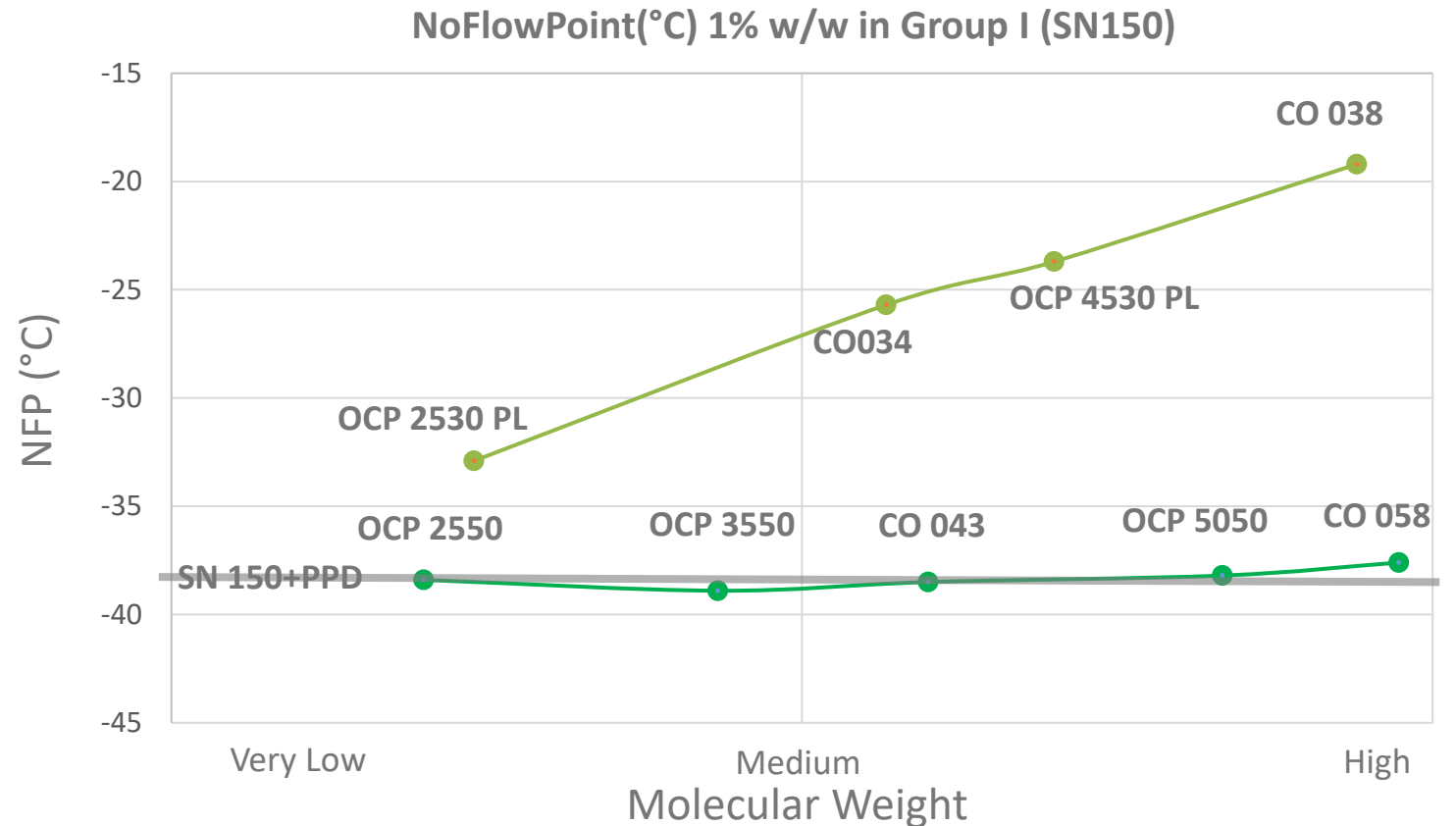
OCP-Cold Performances in diluted condition with PPDs

Amorphous grades do not suffer variations in terms of cold fluidity with increasing molecular weight

Semi-crystalline grades, on the other hand, show a progressive deterioration of cold properties as molecular weight increases

This behavior limits the possibility to simultaneously achieve:

- High thickening
- Easy dissolution performance (pellet form)
- Proper cold performance

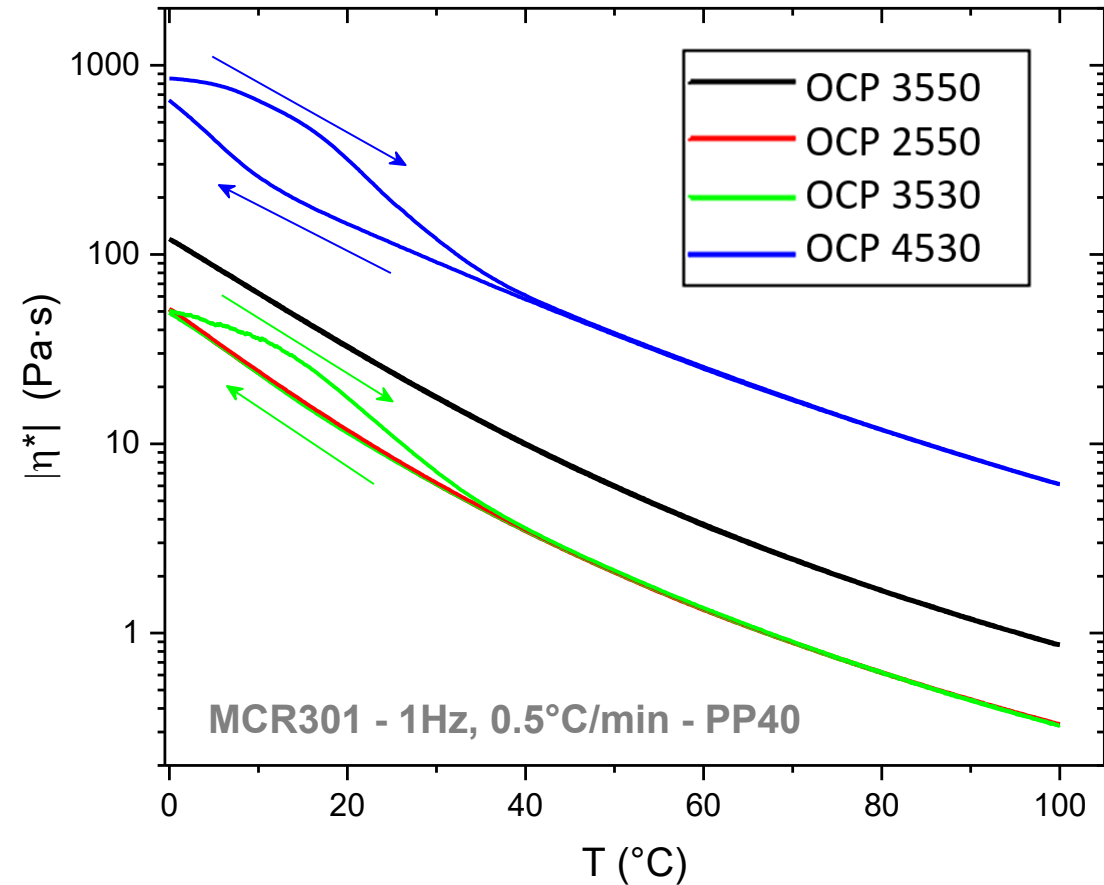


OCP-Cold Performances in concentrates

The graph to the side shows the trend of the complex viscosity as a function of temperature (oscillation test).

Specifically, we note the appearance of hysteresis cycles for OCP 4530PL and OCP 2530 PL samples: Amorphous OCPs are not affected by hysteresis

In particular, the hysteresis cycle of OCP 4530PL sample is larger than the OCP 2530PL sample.



Balancing performance: High TP grades in PL form with improved cold properties

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The market requires a pelletized viscosity index improver with reduced sensitivity to gelation phenomena while maintaining easier handling and dissolution process.

To address this need, development focused on copolymer composition as technical lever

From a theoretical standpoint, reducing ethylene content increases the amorphous character of the polymer, improving cold-flow properties and reducing exposure to gelation.
However, a fully amorphous material would not provide sufficient bulk stability to maintain a stable pellet form during production, transportation, and handling.

The development objective was therefore to identify the lowest ethylene content capable of sustaining a self-supporting pellet morphology, minimizing polymer crystallinity without compromising physical form.

Note well: the material remains partially semicrystalline, and the low-temperature performance of both the VII and finished lubricants must continue to be carefully assessed and validated through homologation trials.

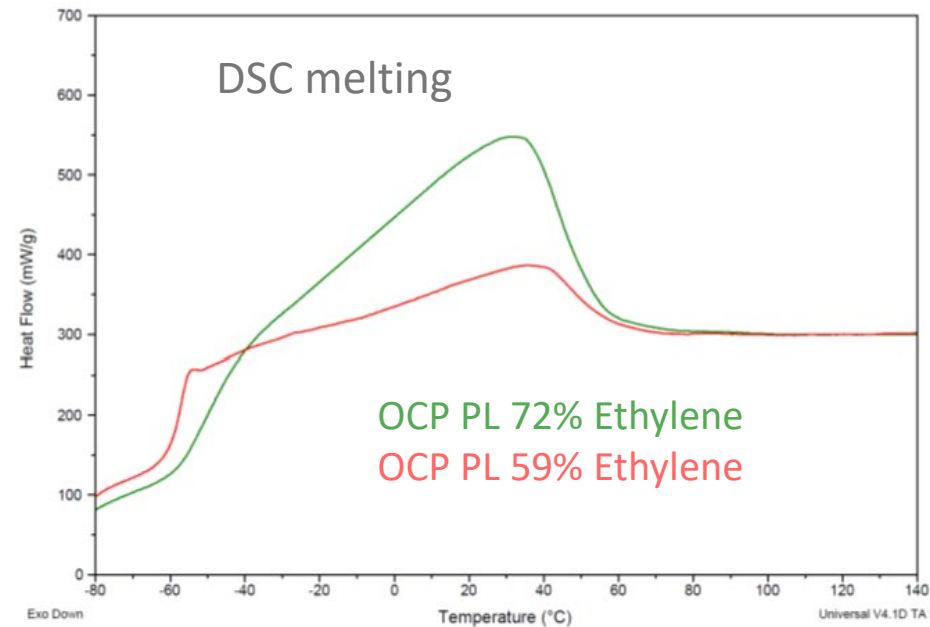
Balancing performance: High TP grades in PL form with improved cold properties

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To evaluate this balance, two OCP PL grades were developed and compared:

- 72 wt% ethylene OCP: representative of a more semicrystalline structure.
- 59 wt% ethylene OCP: minimum crystallinity at same molecular weight to preserve PL form.

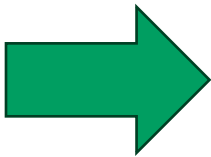
This approach enabled the identification of the optimum compromise between low-temperature performance and pellet physical stability.



High TP grades in PL form with improved cold properties: Concentrates

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OCP PL	72% C2	59% C2	72% C2	59% C2	72% C2	59% C2
Base Oil	GrI SN 150		GrIII (5,5 cSt)		RR 220	



72h later



Solution 6%w of OCP PL in base oil

-Conditioning Time and Temp: 14d at +7°C

-Pouring Temp: 20°C

-Acquisition time: 40 min

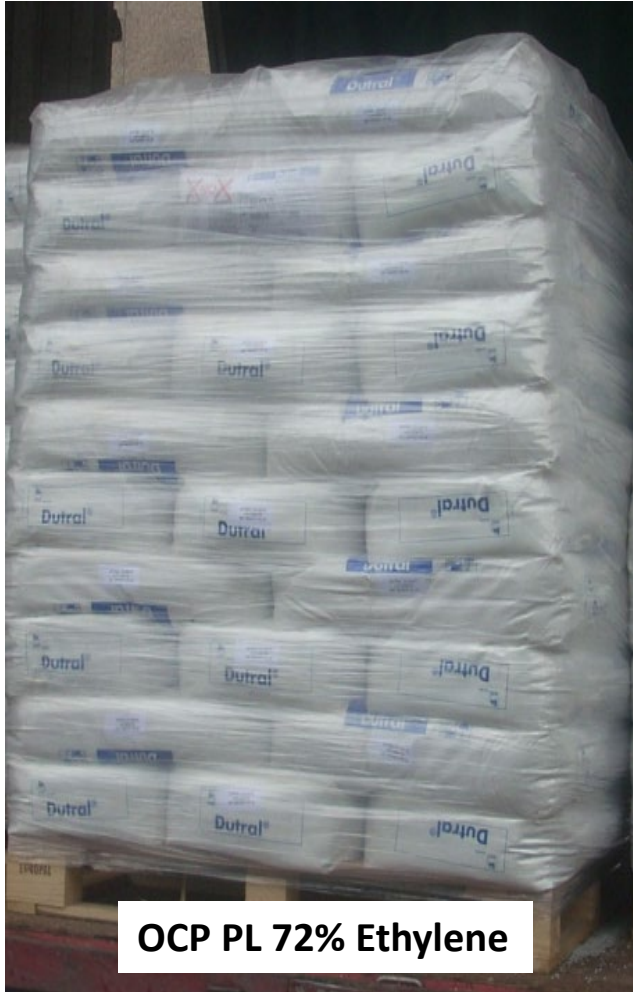
High TP grades in PL form with improved cold properties: 1% solution with PPD

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OCP PL 59% C2 dissolved 1% w in Group I base oil SN 150	
	12
KV at 100°C (cSt)	14,8
Thickening Power (100°C) (cSt)	9,4
SSI 30' %	49
V.I.	148
NFP (°C)	-39,2
CCS -25°C (cP)	7760
MRV -25°C (cP)	19000 (no yeld stress)

High TP grades in PL form with improved cold properties: keep PL form

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Key takeaways

- Gelation is a structural phenomenon, not a simple viscosity issue
- Time, shear and formulation context are crucial
- OCP composition and architecture play a decisive role
- Low-temperature performance must always be evaluated under realistic conditions



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