Aegis Tech Line

Aegis Chemical Solutions

Technical Newsletter

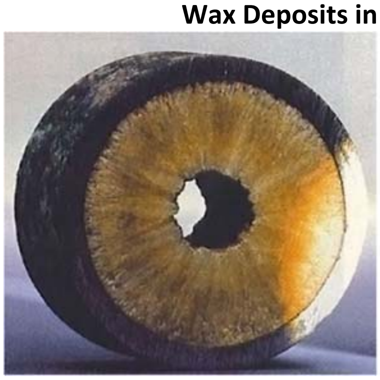
Volume 08, January 2019

WAX PROBLEMS IN OIL PRODUCTION

Many crudes contain dissolved waxes (**also called paraffin**) that can precipitate and deposit as a function of temperature decline (primarily) and pressure change as the oil flows through a system. Wax builds up in production equipment and pipelines, potentially restricting flow (reducing volume produced) and creating other problems. A pressure drop can also cause wax deposition, although it is usually less significant than temperature changes. If the concentration of wax in the crude is high enough, it may not precipitate as a separate phase as the temperature drops. The entire oil stream may become too viscous to flow or pump. The point where oil will not flow is called the **pour point**.

Waxes stabilize water-in-oil emulsions and emulsion pads in treating vessels. A wax dispersant, solvent or crystal modifier may solve some emulsion problems. It is not unusual to formulate a demulsifier with wax dispersants or wax solvents to solve emulsion and wax problems simultaneously. Tank bottoms (aged emulsions in stock tanks or pits) are often stabilized by wax and wax coated solids (sand, iron sulfide, scale).

Wax Deposits in Flowlines

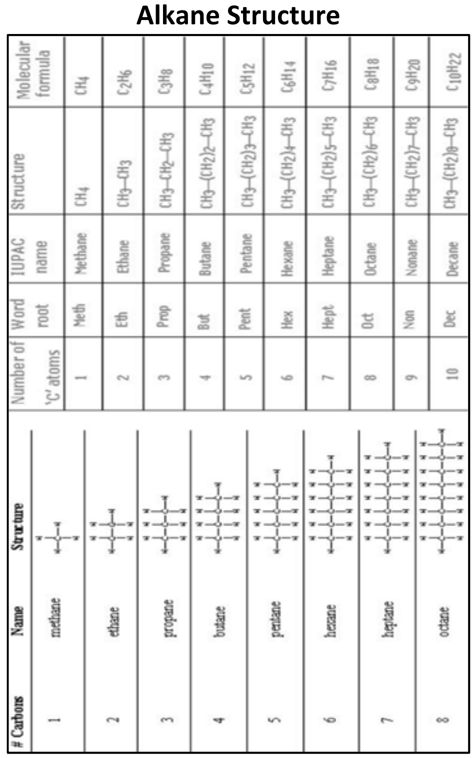


Other Wax Formation

SARA Classification of Petroleum Constituents

The components of the heavy fraction of a petroleum fluid can be separated into four groups: **saturates, aromatics, resins, and asphaltenes (SARA)**. **Saturates** include all hydrocarbon components with saturated (single-bonded) carbon atoms. These are the n-alkanes, i-alkanes, and cycloalkanes (naphthenes). This is typically called paraffin or wax.

Alkane Structure



Number of 'C' atoms	Word root	IUPAC name	Structure	Molecular formula
1	Meth	Methane	CH_4	CH_4
2	Eth	Ethane	$CH_3—CH_3$	C_2H_6
3	Prop	Propane	$CH_3—CH_2—CH_3$	C_3H_8
4	But	Butane	$CH_3—(CH_2)_2—CH_3$	C_4H_{10}
5	Pent	Pentane	$CH_3—(CH_2)_3—CH_3$	C_5H_{12}
6	Hex	Hexane	$CH_3—(CH_2)_4—CH_3$	C_6H_{14}
7	Hept	Heptane	$CH_3—(CH_2)_5—CH_3$	C_7H_{16}
8	Oct	Octane	$CH_3—(CH_2)_6—CH_3$	C_8H_{18}
9	Non	Nonane	$CH_3—(CH_2)_7—CH_3$	C_9H_{20}
10	Dec	Decane	$CH_3—(CH_2)_8—CH_3$	$C_{10}H_{22}$

# Carbons	Name	Structure
1	methane	
2	ethane	
3	propane	
4	butane	
5	pentane	
6	hexane	
7	heptane	
8	octane	

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Melting Point of Alkanes

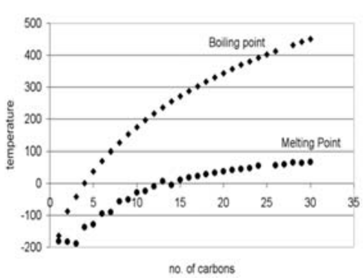
Table 2: Melting Point, Boiling Point and Density of n-Paraffins (Wikipedia: Alkanes...

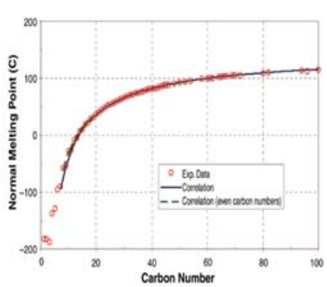
Alkane	Formula	Boiling point [°C]	Melting point [°C]	Density [g/cm3] (at 20°C)
Methane	CH4	-162	-183	gas
Ethane	C2H6	-89	-182	gas
Propane	C3H8	-42	-188	gas
Butane	C4H10	0	-138	gas
Pentane	C5H12	36	-130	0.626(liquid)
Hexane	C6H14	69	-95	0.659(liquid)
Heptane	C7H16	98	-91	0.684(liquid)
Octane	C8H18	126	-57	0.703(liquid)
Nonane	C9H20	151	-54	0.718(liquid)
Decane	C10H22	174	-30	0.730(liquid)
Undecane	C11H24	196	-26	0.740(liquid)
Dodecane	C12H26	216	-10	0.749(liquid)
Hexadecane	C16H34	287	18	0.769(liquid)
Icosane	C20H42	343	37	solid
Triacontane	C30H62	450	66	solid
Tetracontane	C40H82	525	82	solid
Pentacontane	C50H102	575	91	solid

Aromatics include benzene and all the derivatives composed of one or more benzene rings. **Resins** are components with a highly polar end group and long alkane tails. The polar end group is composed of aromatic and naphthenic rings and often contains heteroatoms such as oxygen, sulfur, and nitrogen. Pure resins are heavy liquids or sticky solids.

Asphaltenes are large highly polar components made up of condensed aromatic and naphthenic rings, which also contain heteroatoms. Pure asphaltenes are black, nonvolatile powders.

The experimental method used to determine the weight fractions of these groups is called SARA analysis.





Precipitation of Petroleum Waxes

Solid-wax formation consists of two distinct stages: nucleation and crystal growth. As the temperature of a liquid solution is lowered to the wax appearance temperature (WAT), the wax molecules form clusters. Wax molecules continue to attach and detach from these clusters until they reach a critical size and become stable. These clusters are called nuclei and the process of cluster formation is called nucleation. Once the nuclei are formed and the temperature remains below the WAT, the crystal-growth process occurs as further molecules are laid down in a lamellar or plate-like structure. Nucleation is described as either homogeneous or heterogeneous.

Homogeneous nucleation occurs in liquids that are not contaminated with other nucleating materials. In this case, the development of nucleation sites is time dependent.

Heterogeneous nucleation occurs when there is a distribution of nucleating material throughout the liquid. If there is sufficient nucleating material, heterogeneous nucleation can be nearly instantaneous.

Pure hydrocarbon mixtures in laboratories rarely undergo heterogeneous nucleation; whereas crude oil in the reservoir and production tubing will most likely nucleate this way because of the presence of:

- Asphaltenes
- Formation fines and clay
- Scales
- Corrosion products

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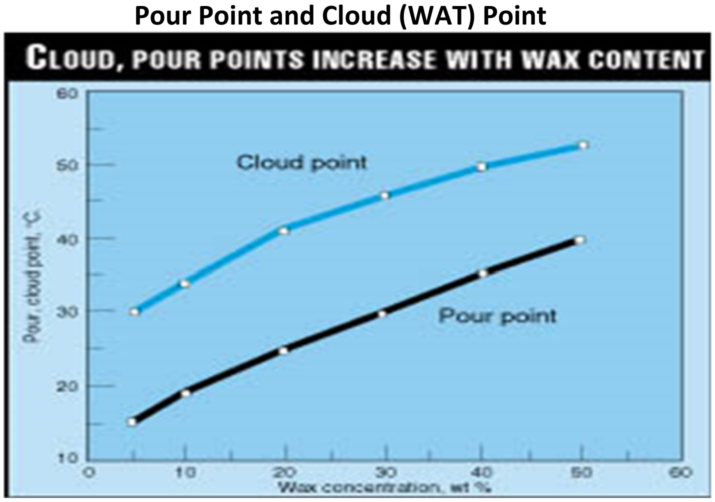
Crude Oil Testing

The primary chemical parameter to establish is the critical temperature at which these wax nuclei form—the **wax appearance temperature (WAT)**. The **WAT** (also called "cloud point") is highly specific to each crude. Differential scanning calorimetry (DSC) measures the heat released by wax crystallization to determine WAT. In some cases, the viscosity of the crude is measured at various temperatures, until the pour point is reached. At or near the wax appearance temperature (WAT) the viscosity can change significantly. Shifting of the viscosity/temperature curve is occasionally used to compare the performance of chemicals. Cold-finger testing can be used to approximate WAT and is also used to compare the performance of wax inhibitors (crystal modifiers). The reduction in pour point is also sometimes used to compare chemicals.

Pour Point and Cloud (WAT) Point



Example of DSC to Determine Wax Appearance Temperature

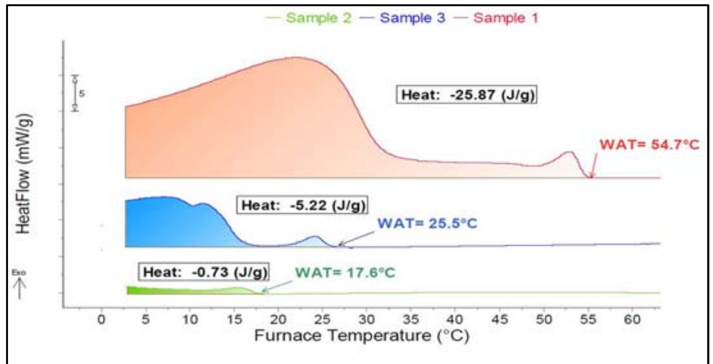
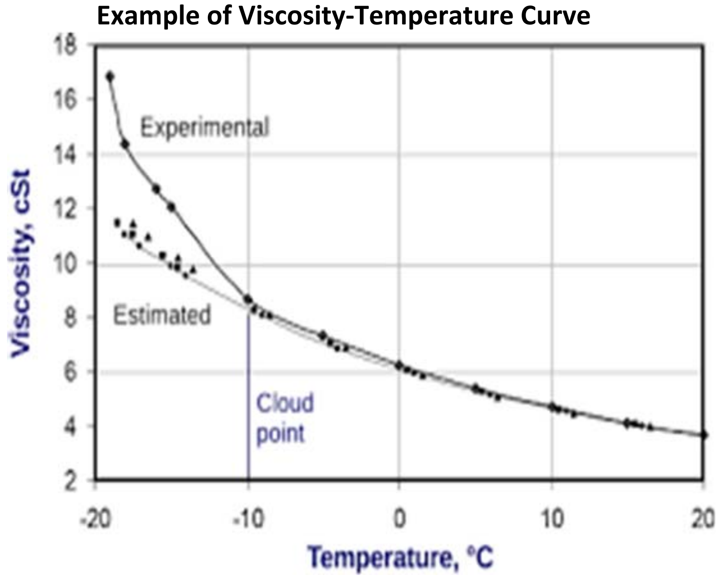


Figure 1 – Wax precipitation peaks of the three samples

Example of Viscosity-Temperature Curve



Oil is heated to above the wax appearance temperature. It is then cooled gradually and the viscosity is measure at various temperatures. When the viscosity deviates from a linear increase, the wax appearance temperature (WAT) has been reached.

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Paraffin Crystal Modifiers

Paraffin-crystal modifiers are chemicals that interact with the growing crude-oil waxes by co-crystallizing with the native paraffin waxes in the crude oil that is being treated. These interactions result in the deformation of the crystal morphology of the crude-oil wax. Once deformed, these crystals cannot undergo the normal series of aggregation steps. Types of paraffin-crystal modifiers include:

- Maleic acid esters
- Polymeric acrylate and methacrylate esters
- Ethylene vinyl acetate polymers and copolymers

For maximum effectiveness, paraffin inhibitors must be delivered into the crude oil at temperatures above the wax appearance temperature (WAT).

Testing for Wax Crystal Modifiers/Inhibitors

Cold Finger Testing: this testing consists of treating a sample of oil with wax inhibitor above the WAT and then contacting the oil with a metal cylinder (“finger”) that has a coolant circling inside it. The coolant and surface of the cylinder are below WAT. Wax will crystallize on the surface of the metal and can be measured by weighing the cylinder before and after contacting the oil. Oil with no added inhibitor is also tested to establish baseline paraffin deposition. The contact time of the cool metal cylinder with the warm oil can vary but is usually 1 to 2 hours.

Cold Finger Test Apparatus

Paraffin Dispersants

Dispersants act to keep the wax nuclei from agglomerating. Dispersants are generally surfactants and may also keep the pipe surface water wet, minimizing the tendency of the wax to adhere. Some water production is required. High levels of water alone may maintain the system in a water-wet state. A smooth surface tends to decrease wax adherence. Types of dispersants include:

- Salts of sulfonic acids, particularly DDBSA
- Non-ionic surfactants such as oxyalkylated alcohols, alkyl phenols, and amines
- Mutual solvents (butyl cellosolve, alcohols)
- Combinations of all the above, plus demulsifiers to aid in oil/water separation downstream of treatment

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Testing for Dispersants

Untreated – Field Wax in Water

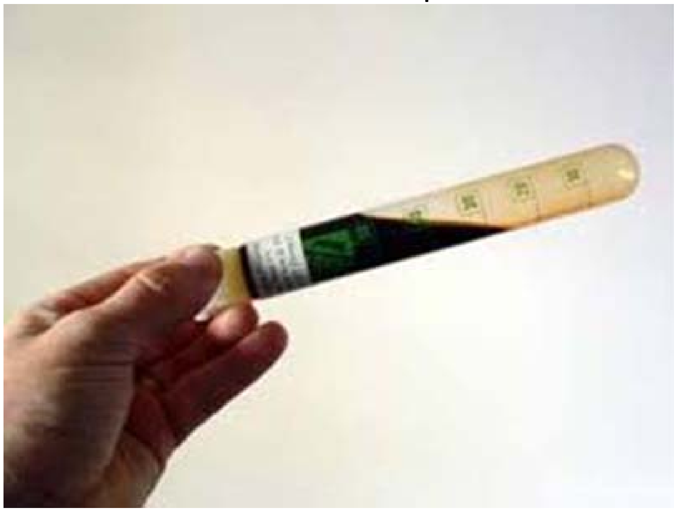
Treated with Dispersant – Heated to System Temperature

Pour Point Depressants (PPD)

PPDs must be injected while the oil is still hot and before wax crystals are first formed (above the WAT). The performance of PPDs depends very much on crude type. PPDs can significantly reduce normal pumping pressures after an extended shut down. Chemically, PPDs may be like wax crystal modifiers – long chain polymers and copolymers.

Testing Pour Point Depressants (PPDs)
ASTM D97 - 12 Method

Oil Above Pour Point Temperature



Oil Below Pour Point Temperature

Wax Removal

Physical - Cutting/Drilling: pigging is the primary mechanical method of removing wax buildup from the internal walls of pipelines. The pig cuts the wax from the pipe walls and a bypass can be set with a variable-flow pass, allowing the pig to prevent wax buildup in front. Pig sizing can vary, and multiple pig runs with pigs of increasing size can be used.

Coiled tubing with the appropriate cutters at the end also can be used for wax removal—the drawback for pipeline cleaning being the limited reach of the coiled tubing

Chemical dissolution: various aromatic solvents can be used to dissolve the wax. These are generally not heated, relying solely on the solvency properties of the fluid. Xylene has been one of the more effective solvents for waxes.

Melting—the use of hot oil, hot water, or steam: the use of hot oil has been the most popular of the melting process options. Normally the hot oil is pumped down the casing and up the tubular. It is intended that the high temperature of the liquid phase heat and melt the wax, which then dissolves in the oil phase.

Hot water, hot-water/surfactant combinations, and steam: these are alternatives to hot oiling. Plain hot-water treatments do not provide the solvency required to remove the wax, hence the use of surfactants to disperse the wax. The advantage of water is its greater heat capacity.

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Aegis Facilities / Locations

CONTACT NUMBER: *For all Aegis locations, call the toll-free number and select the from the options presented.*

Toll-free number - (855) 532-2033

Corporate Headquarters *Houston* 4560 Kendrick Plaza Dr., #190 Houston, TX 77032	**Permian Basin** *Midland* 2200 Market St. Midland, TX 79703	**Permian Basin** *Abilene* 4410 Vista Grande Abilene, TX 79606
Permian Basin *Breckenridge* 566 FM 2231 E Breckenridge, TX 76424	**Permian Basin** *Carlsbad* 2411A East Greene Street Carlsbad, NM 88220	**Permian Basin** *Forsan* 300 West 1st St. Forsan, TX 79720
Permian Basin *Lubbock* 13622 Hwy 87 S. Slaton, TX 79423	**Permian Basin** *Monahans* 1332 PR Thrasher Ln. Monahans, TX 79756	**East Texas** *Kilgore* 4524 State Hwy 42 N. Kilgore, TX 75662
East Texas *Teague* 931 W. Hwy 84 Teague, TX 75860	**East Texas (North Louisiana)** *Haughton* 140 Sligo Industrial Dr. Haughton, LA 71037	**South Texas** *Freer* 5743 Hwy 44 Freer, TX 78357
South Texas *Asherton* 664 Hwy 190 Asherton, TX 78827	**South Texas** *Cuero* 424 U.S. Hwy 87 S. Cuero, TX 77954	**South Texas** *Jourdanton* 8229 S. State Hwy 16 Jourdanton, TX 78026
South Texas *San Antonio* 311 N. Frank Luke Dr. Building 1440, Suite #103 San Antonio, TX 78226	**South Louisiana** *Elizabeth* 3552 Highway 10 Elizabeth, LA 70638	**South Louisiana (E. TX)** *Raywood* 203904 Hwy 90 East Raywood, TX 77582
Mid-Con *Ratliff City* P.O. Box 98, 1500 Old Hwy 7 Ratliff City, OK 73481	**Mid-Con** *El Reno* 801 N. Willie L. Minor, #B-1 El Reno, OK 73036	**Mid-Con** *Hennessey* 1117 S. Main Street Hennessey, OK 73742