

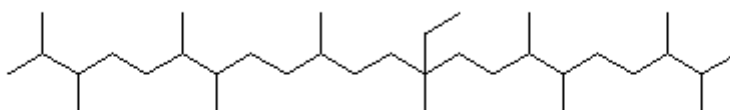
Waxes and Asphaltenes - Their Chemistry, Analysis and Relevance to Production Problems

Waxes

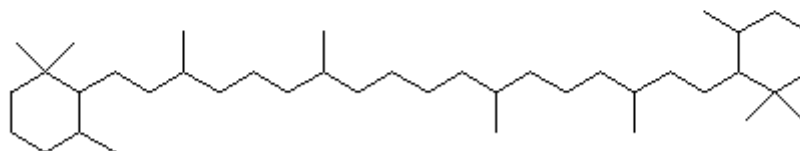
Waxes are complex mixtures of high molecular weight alkanes (paraffins in old terminology) of three structural types - straight chain, branched chain and cyclic (figure below). Waxes are solid or liquid at room temperature, a property exploited during the method for conventional wax determination in crude oils, which in the IP, ASTM or API methods involves cooling the oil to a specified temperature, precipitating the waxes, collecting and weighing them. This normally results in compounds containing 22 or more carbon atoms being precipitated.



a C₂₉ normal alkane or wax



botryococcane a C₃₄ branched alkane or wax



β carotene a C₄₀ cycloalkane or wax

The standard methods of wax determination have been reasonable indicators of potential production/ pipeline problems, although not perfect. This is somewhat surprising, as studies of the chemical composition of pipeline waxes indicate that the compounds which are deposited in pipelines are not those which are precipitated from oils during wax analysis. As can be seen in the illustrations overleaf, the deposits in the pipelines, up to C₇₅, comprise much higher molecular weight components than present in the oils which are up to C₄₅. Considering how different the two are, it is surprising that the conventional wax determination methods have achieved as much success as they have.

Comparative studies of recent with fossilized organic matter show waxes of the C₂₅ to C₄₅ carbon atoms to be sourced from land plants and bacteria which is why non-marine oils are richer in waxes than marine oils. An example of high non-marine wax oils would be the Junggar Basin of China, where ~80% of oils contain ~30% wax. The source of the high molecular weight waxes in oils has not yet been proven. The most likely explanation is that the high carbon number waxes are polymers of their

lower carbon number counterparts, formed during low temperature diagenetic reactions, thus a C₅₀ wax comprises two C₂₅'s, a C₇₀ two C₃₅'s and so on. This may also account for the success of the conventional wax method-if the lower molecular weight components which are normally determined are relatively abundant, then so will the high molecular weight components which cause pipeline wax problems.

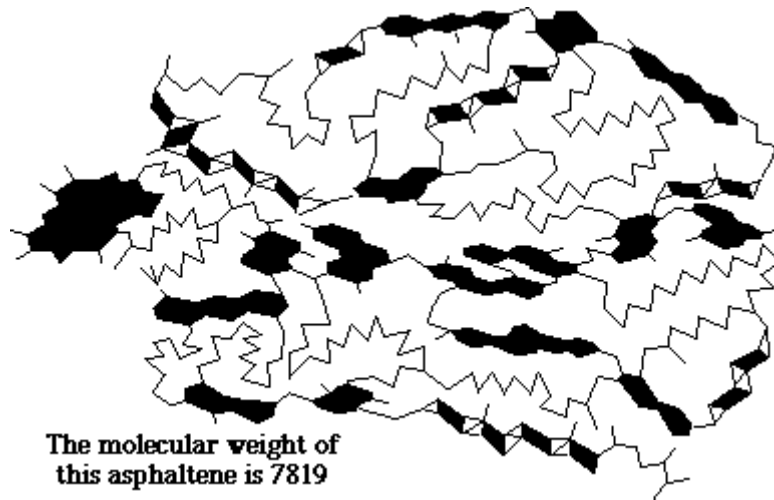
With increasing amounts of oil production from 'hostile' sub-sea deep water and climatic regimes, prediction of wax problems and their solutions become increasingly important. Deposition of the wax is caused by reduction in PVT between reservoir and pipeline, and physico-chemical conditions within the pipeline. New developments in computer simulation of multiphase flow in pipelines are leading to predictive models: however the models still have to be calibrated by analysis of pipeline deposits. Intelligent sampling of oil and wax is thus required in order to gauge the full extent of potential problems.

Recent advances in laboratory technology have enabled the analysis of an extended range of components present in pipeline deposits. High temperature gas chromatography (HTGC) and supercritical fluid chromatography (SFC) enable identification of waxes up to 100 carbon atoms, whereas previously C₄₀ was close to the limit of the method. During high temperature gas chromatography compounds of high boiling point are kept mobile as the column is heated to, and stable at, much higher temperatures 500°C compared with conventional analysis at 400°C.

Supercritical fluid chromatography involves "dissolving" the sample in a medium which is held at supercritical temperatures and pressures in a holding cell then the pressurised sample is transferred to the GC where it is depressurised and fed onto the analytical column. This avoids using the very high temperatures of HTGC which incurs less risk of sample decomposition. The technique is especially useful as a feed for biological marker analysis by GC-MS.

Asphaltenes

Asphaltenes are high molecular weight nitrogen-, sulphur-, and oxygen-containing compounds. The current popular belief is that they represent an intermediate product between kerogen and oil - a soluble low molecular weight kerogen. The division of the NSO components found in crude oils into 'resins' and 'asphaltenes' is man-made. They are a continuum of increasingly higher molecular weight NSO compounds. There is no implied genetic relationship between resins and asphaltenes- resins may polymerise to form asphaltenes and asphaltenes may break down into resins.



Asphaltenes may be dispersed in the crude oils by the action of resins. The polar resin molecules may form micelles with asphaltene molecules as the nucleus (a). In a resin-poor environment micelles may form from multiple asphaltene molecules (b). As a result of these physico-chemical shifts the chemistry of asphaltenes is extremely difficult to establish as it changes with the composition of the crude oil.

Petroleum may be considered to be an equilibrium mixture of different chemical compounds. Modification of the chemical composition of the petroleum either under natural conditions or in the laboratory leads to a shift back towards the equilibrium composition. Thus cracking of petroleum in the reservoir due to thermal stress causes a shift towards light saturated hydrocarbons and asphaltene precipitation occurs. The same effect in the laboratory is created by the addition of light hydrocarbon solvent. The asphaltene fraction of a crude oil is hence defined by the solvent chosen to 'displace' the asphaltenes from the oil normally pentane hexane or heptane. This equilibrium may be disturbed during production of oil leading to precipitation of asphaltenes in the pore spaces of a reservoir rock.

Asphaltenes may occur naturally to form impermeable barriers in reservoirs. They can be precipitated by thermal degradation - natural cracking of an oil by biodegradation or by gas injection.

Although waxes and asphaltenes are chemically unrelated wax deposition frequently accompanies asphaltene precipitation during laboratory analysis.

Analytical services

GHGeochemical Services offers conventional wax and asphaltene analysis as well as the newer HTGC and SFC analyses. We have compared conventional wax, and HTGC oil and pipeline wax analyses, and have found radically different results by the different methods. As can be seen from the attached HTGC traces, the pipeline waxes are not those precipitated during conventional wax analysis. We have also found that no two waxes are composed of the same alkanes, and that the compositional shifts are not reflected in melting points and pour points. We have a library of pipeline and other waxes, primarily from the UK, both onshore and offshore, and are building unequalled experience in these new wax analyses.

