

Chemicals Used in Crude Oil Production and Impact for Imported Crudes

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I. EINECS Definition of Crude Oil (232-298-5 & CAS : 8002-05-9)

Petroleum

“A complex combination of hydrocarbons. It consists predominantly of aliphatic, alicyclic and aromatic hydrocarbons. It may also contain small amounts of nitrogen, oxygen and sulfur compounds. This category encompasses light, medium, and heavy petroleums, as well as the oils extracted from tar sands. Hydrocarbonaceous materials requiring major chemical changes for their recovery or conversion to petroleum refinery feedstocks such as crude shale oils, upgraded shale oils and liquid coal fuels are not included in this definition.”

II. Crude Exemption

Crude oil is exempt from registration per Annex V of REACH and in accordance with Article 2(7)(b) of REACH.

III. Definition of Substance

REACH Article 3(1): Substance: means a chemical element and its compounds in the natural state or obtained by any manufacturing process, including any additive necessary to preserve its stability and any impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition.

IV. Chemicals Used in Crude Oil Production

Various types of chemicals (which themselves can be mixtures or formulations of various chemicals) are required to aid the production, handling and transportation of crude oil. The chemicals used fall into several types as outlined below. For most, only trace amounts may remain in the crude as impurities once it reaches the refinery. This document will review the various types of chemicals used in crude and their role in production.

Most Oilfield production chemicals (OFCs) are complex formulations of many different chemicals. Often the constituent chemicals themselves are not pure chemical species but a mixture of reaction products, reactants, and diluents. The formulation usually has one or two primary ingredients that give the additive its main functionality. In addition, the formulation is specifically designed for each oilfield, and within the oilfield, for each well, and for each well the recipe may vary depending upon the time and the operation conditions. The crude from a number of wells/fields is combined such that it is nearly impossible to ascertain the resulting combination of OFC's used for a crude oil at a loadport.

Chemicals are used in various stages of oilfield development namely drilling, cementing, well completion, and well stimulation/workover. These chemicals may end up as impurities in the crude oil.

During the production phase, the flow of oil out of the well needs to be assured by preventing the deposition of hydrates, wax, asphaltenes, or scale. Chemicals provide a means for

controlling such deposits. The presence of water, bacteria, and acids all result in a corrosive environment. Production of crude oil usually involves a significant bulk water phase, many (OFCs) are water-soluble by design. When used in continuous low dose injection they remain with the water phase at the upstream facilities. The production of oil usually involves its separation from water and gas. A small amount may be present in water droplets dispersed or partitioned in the oil phase as an impurity.

Additionally chemicals may be needed during the transportation and logistical handling of the crude oil, e.g. in a pipeline, tanker, or terminal. Drag reducing agents can be added in pipelines to improve flow. Pour point depressants, mercaptan scavengers, hydrogen sulfide scavengers are often added to cargoes in order to satisfy shipping or loadport requirements for stability. Chemicals can be added either by continuous dosage or in batch treatments. The concentration in the crude usually ranges from 10 – 200 ppm. These post-production chemicals help to control corrosion, scale, hydrogen sulfide, bacteria; help to prevent hydrate formation, wax deposition, asphaltene precipitation; and help to resolve emulsions. In other words, they are added to preserve the stability of the crude oil during transport so that the crude can reach the refinery for conversion to products.

Chemical families used in the production and transportation of crude oil include the following:

Function	Description	REACH Category
(a) Scale Inhibitors.	Used in the oil production process to prevent the deposition of mineral scale that may occur in the pores of rock formations, in downhole pipework and in surface treating facilities.	Impurity
(b) Corrosion Inhibitors:	Aqueous acids are used to stimulate production from reservoirs. Such acids expose oil production systems to the possibility of corrosion. Thus corrosion inhibitors are required to protect the downhole pipework and vessels of oil production facilities.	Impurity
(c) Oxygen Scavengers.	Often used to mitigate corrosion problems in water injection systems, in hydrotreating and drilling.	Impurity
(d) Biocides:	Bacterial growth in waters associated with crude oil production is controlled by the use of biocides. Biocides are water-soluble and removed with the water from crude.	Impurity
(e) Emulsion Breakers:	Production of Oil usually involves the co-production of large quantities of water. Natural surfactants present in the oil or water, other chemicals such as corrosion inhibitors combined with the shearing effect from turbulent flow and pumps may create emulsions. Demulsifiers are used to resolve water-in-oil emulsions.	Impurity
(f) Antifoam Agents:	Foaming problems occur in many oilfield processes. Problems occur when gas breaks out from crude oil in separators, or in gas processing plants	Impurity
(g) Drag reducing Agents	High molecular weight oil-soluble polymeric compounds are added to crude oil pipeline fluids in order to enhance flow and minimize pressure drop. A long pipeline can have more than one injection point	Impurity
(h) Hydrate Inhibitors	Gas hydrates are formed when water molecules crystallize around hydrocarbon molecules at certain pressure and temperature combinations. They can plug flowlines and	Stabilizer

	damage process equipment. In addition to specific chemicals, methanol or glycols (MEG, DEG, TEG) may be used to prevent crystallization of the water molecules.	
(i) Hydrogen Sulfide Scavengers	Hydrogen sulfide in produced oil and gas poses safety and corrosion concerns. Scavengers bind the H ₂ S in a form that is stable in the liquid phase. They can be added at oil production facilities or in transit in a pipeline or tanker.	Stabilizer
(j) Mercaptan Scavengers	Low molecular weight (C1-C3) mercaptans have offensive odors and are toxic. It is necessary to remove and neutralize them. Mercaptan scavengers either oxidize the offending species or convert them to less volatile molecules.	Stabilizer
(k) Paraffin Control Agents and Pour Point Depressants	Crude oils may contain varying degrees of long chain paraffins or waxes that tend to form deposits if the oil is subjected to changes in temperature, pressure or other conditions. Dispersants/detergents are used to remove deposits already formed and inhibitors to interfere with wax crystal growth and formation.	Stabilizer
(l) Asphaltene Control Agents	Asphaltenes can destabilize and precipitate out when temperature, pressure or oil composition changes. Chemicals are added to control asphaltene precipitation.	Stabilizer

V. Crude Origin, Trading and Handling

Only about 21% of European crude is sourced from Europe¹. The remaining 79% comes from the former Soviet Union (~46%), Middle East (~25%), Africa (~23%), and western hemisphere (~6%). Much of the crude imported into Europe can be traded several times before entering Europe and its original source may not be completely known as storage and combining may have occurred. Crude oil is handled under strictly controlled industrial conditions, with no widespread consumer use.

VI. Conclusion

The OFCs described above can be considered in two categories: 1) impurities which remain in crude oil resulting from production and 2) stabilizers for transport. Precise concentrations of these chemicals in crude oil arriving at refineries is not known. However, they would be in the ppm range. As such, these OFCs form an integral part of the crude oil substance, which is exempted of Registration as per Annex V Article 2(7)(b). No specific registration is therefore required under REACH for the introduction of such production-related impurities and crude oil stabilizers with the importation of crude oil into the EU.

¹ 2007 information from ExxonMobil