

Paraffins in Personal Care Products

SITARAM DIXIT

Senior Manager — Fragrance Applications, International Flavours & Fragrances India Ltd.

E-mail: sitaram.dixit@iff.com

History records the use of petroleum and informs that the first oil well was drilled in China during the 4th century AD. The oil was initially used to evaporate salt water in order to make common salt. Bamboo pipelines were laid between oil wells and salt water spring sites to produce edible salt.

Petroleum was used by ancient Americans for creating magic potions, medicine and for burning lamps. Europe used petroleum in the 19th century for lighting street lamps. It was also used to coat boat hulls, for wall painting and for making weapons during warfare.

The first breakthrough in petroleum usage began in 1853, when Polish scientist Ignacy Lukasiewicz distilled crude oil into kerosene. He created the first oil mine in Bobrka near Krosno and was also instrumental in setting up the first distillery in Ulaszowice in Poland.

Modern petroleum industry however, is credited to Edwin Drake who, in 1859, drilled the first oil well in Titusville, Pennsylvania, USA. Many oil wells were later drilled, all around the region and petroleum industry slowly grew then onwards. However, the discovery of the internal combustion engine in early 20th century provided the right impetus for the large demand of petroleum and petroleum products and this demand has sustained till today.

BIOGENIC THEORY

Geologists believe that during the past many centuries incompletely decayed remains of prehistoric marine ani-

mals and terrestrial plants mixed with mud became buried under thick layers of sedimentary rocks. The high levels of heat and pressure caused these buried remains metamorphose into waxy kerogen, which ultimately through the process of catagenesis got converted into liquid and gaseous hydrocarbons. The hydrocarbons then migrated through adjacent rock layers to become trapped within and under porous rocks or reservoirs, forming oil fields.

NON-BIOGENIC THEORY

The alternate theory to the biogenic petroleum origin is proposed by Thomas Gold. It suggests that large amounts of carbon exist naturally on earth. Some of them are in the form of hydrocarbons. Hydrocarbons are less dense than aqueous pore fluids and so they migrate in the upward direction. Microbes deep down in these deposits convert them into different types of hydrocarbons.

Thermodynamic calculations and experimental studies carried out prove that n-alkanes do not spontaneously evolve from methane at pressures found in sedimentary rock basins, but gets generated at 200-km or deeper below the earth's surface.

PETROLEUM SCENARIO TODAY

Today, the world is heavily dependent on petroleum for motive power, lubrication, fuel needs, dyes, drugs and for making many synthetic chemicals. Until 1955, coal was the world's foremost fuel; however petroleum has taken over. More than 90% of the world's fuel needs are

now met by petroleum products. It is the base for the manufacture of many industrial chemicals and is the world's most important commodity. Products based on petroleum crude include kerosene, petrol, diesel, ether, benzene, lubrication oil, paraffins, asphalt, etc.

PETROLEUM EXTRACTION

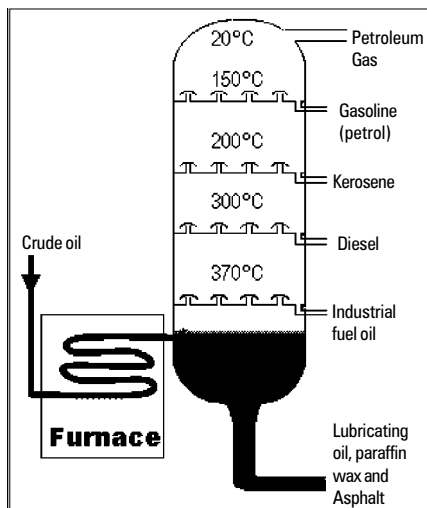
Petroleum extraction from the subterranean region is carried out by drilling a well. Usually, wells are dug several miles deep before petroleum deposits are reached. Petroleum crude is a thick, dark brown or greenish flammable liquid. It is a complex mixture of different hydrocarbon alkanes. Its composition, appearance and purity depend on the locality or area it has been extracted from.

Drilling is fairly complex and risky. Petroleum from a newly dug well comes to the surface under its own pressure. However, as the reservoir gets depleted the pressure falls down. The crude oil now must be forced out, either by pumping or by injecting water, gas or air into the deposit, which, in turn, increases the underground reservoir pressure bringing the crude oil on the top.

PETROLEUM REFINING

Raw unprocessed crude oil as it comes out of the well is not very useful. Crude petroleum, strictly speaking, contains hydrocarbons or compounds made up of hydrogen and carbon and non-hydrocarbon fractions: nitrogen, sulphur, oxygen and trace metals like vanadium and nickel.

The hydrocarbons are of varying chain length and can be paraffins, aromatics, naphthenes or cycloalkanes, dienes and alkynes. It has to be broken down into its different components and refined, before it can be used in various applications like fuel, plastics, chemicals, solvents, etc.



Crude petroleum is separated by fractional distillation. This process is also called refining. The trick of oil refining lies in separating the various hydrocarbons into individual components. Petroleum crude is heated and sent into a tower maintained at different temperatures along its height.

Hydrocarbons are complex molecules having varying chain lengths that lend the various fractions different boiling points. Unique boiling points of the individual components aids in its separation by fractionation. The vapours of the different components get condensed and collect at different heights in the tower. The separated fractions are collected and processed further into various petroleum products.

The hydrocarbon components have differing structures, properties and use. The lighter fraction includes ether, petrol, kerosene, diesel, lubrication engine oil,

etc. The heavier hydrocarbon fractions that emerge from the bottom of the fractioning column are cracked or broken up to make more useful products. Paraffins are one such utility product obtained during petroleum crude refining.

PARAFFIN TYPES & PROPERTIES

The various paraffin types used in cosmetic and pharmaceutical formulations are hard paraffin, soft paraffin and liquid paraffin.

Pure paraffin bases are extremely stable and do not become rancid. Very few chemicals exist that react with paraffin. Cosmetic grade paraffins are considered safe, most non-irritating and moisturising ingredients.

Paraffin bases are not easily absorbed by the skin and do not help in the absorption of actives present in the formulation. Thus they are suitable for superficial or topical skin application products.

Paraffins are chemically & biologically safe, non-comedogenic, do not support growth of pathogenic micro-organisms and do not require antimicrobial preservatives. They are extremely suitable for sterile products, as they can be easily sterilised by heat.

Paraffin restricts loss of moisture keeping skin soft. However, prolonged application can lead to water logging and consequently macerate the skin. It also retains body heat, producing a somewhat uncomfortable warm feeling.

As paraffins are immiscible in water, rubbing and removing paraffin-based product from the skin is difficult. Paraffins are sticky in nature and this makes a formulation stick on to the skin for a longer time than necessary, sometimes spoiling the clothes worn.

HARD PARAFFIN / PARAFFIN WAX

Hard paraffin is a mixture of solid hydrocarbons consisting mainly of n-paraffin, sometimes along with their isomers. It often exists with a crystalline structure. It is translucent, wax-like, greasy, colourless, odourless and slightly unctuous to touch and burns with a luminous flame.

It has a solidification point range between 50°C to 57°C. It is practically insoluble in water and alcohol, but is soluble in ether and chloroform. Hard paraffin is used in hardening paraffin-based cosmetics and pharmaceutical formulations.

SOFT PARAFFIN / PETROLEUM JELLY / VASELINE®

Soft paraffin is a purified mixture of semi-solid hydrocarbons and is available in two varieties namely white and yellow. White petroleum jelly is a bleached variant of the yellow petroleum jelly.

Petroleum jelly consists of a crystalline hydrocarbon matrix embedded in a colloidal gel of liquid and amorphous hydrocarbons. It has a melting point range between 36°C to 56°C. It is practically insoluble in water and alcohol, but soluble in ether and chloroform.

When mixed with light petroleum, fixed oils or volatile oils, soft paraffin sometimes shows a slight opalescence. Soft paraffin is translucent, soft, greasy and odourless.

However their physical properties vary, according to their source of origin, and the quality of the refining and blending process used during its manufacture.

Poor grades of petroleum jelly sometimes may contain hard lumps or even show separation between the crystalline

hydrocarbon matrix and the liquid hydrocarbon portions.

MINERAL OIL / WHITE OIL / LIQUID PETROLATUM

Mineral oil is a chemically inert, transparent, colourless oil, composed mainly of alkenes and cyclic paraffins related to white petrolatum. It has a boiling point ranging between 260°C to 330°C. Mineral oils available for cosmetic uses are heavy liquid paraffin (HLP) and light liquid paraffin (LLP).

HLP has a specific gravity (20°C) range of 0.845 to 0.905 and LLP has a specific gravity range of 0.818 to 0.880. Both HLP & LLP are practically insoluble in water and alcohol. However, they are soluble in ether and chloroform.

Highly refined mineral oil consists of saturated aliphatic and alicyclic non-polar hydrocarbons. They are colourless, tasteless and odourless and do not change colour on storage. White oil thus is an ideal blending base for personal care and pharmaceutical products.

Mineral oil that is inert in nature, lubricate, smoothen, soften and resist moisture in various personal care formulations like body oils, creams, lotions, lipsticks, sunscreen formulations, tissues, etc.

Mineral oils are direct substitutes for high VOC (Volatile Organic Chemical) solvents in various consumer and institutional products, both in aerosol systems (air fresheners, furniture polish, insecticides), and non-aerosol ones (water-free hand soap, floor polishes, nail polish removers, liquid fresheners, candles, etc.).

It is important to note that poorly refined mineral oil is liable to oxidation on very prolonged storage due to peroxide

formation. Addition of an antioxidant like BHT at 10-ppm concentration in the product to arrest this to some extent is necessary.

HARMFUL IMPURITIES IN PARAFFINS

Paraffins are by-products in the distillation of crude petroleum. They are produced in vast quantities and fairly inexpensive. Alkalyted polycyclic aromatic compounds (PAC) are undesirable impurities present in the base oils. PAC not only adversely affects product performance, but is also a potential carcinogen.

During base oil refining, PAC's are reduced by solvent extraction, catalytic hydrotreating or hydrocracking. Continuous exposure to poorly refined mineral oil, which contains aromatics and unsaturated hydrocarbons, has the potential to cause, skin allergy, squamous cell carcinoma or skin cancer. Alkalyted 3-7-ring PACs must be greatly reduced to render the mineral oil non-carcinogenic and safe for use.

Paraffins can have detrimental effects on hormonal secretion and skin's ability to breath. It can slow down cell renewal and cause premature ageing. Sunscreens made using poorly refined paraffins can also induce skin carcinoma as well as colon and breast cancer.

Other impurities present in unrefined or poorly refined paraffins, include sulphur, heavy metals, trace metals vanadium and nickel.

They have to be completely eliminated during the refining process to make it suitable for use in cosmetic formulations.

The refining processes have improved greatly over the years. Currently the processes followed are specific,

stringent and are carried out alternatively both in atmospheric pressure and under vacuum between 370°C to 540°C. Although it is claimed that today base oils undergo many different processes to remove impurities or to improve its physical properties one has to make sure that it is rightly so before selecting it to use in product formulations.

USE ONLY COSMETIC GRADE PARAFFINS IN FORMULATIONS

Paraffins on account of its petroleum crude mineral origin are considered bad for skin. This view has been around for sometime and was very much in news recently.

The reason proffered is that it is used for lubrication and for metal cutting in the industry and so not suitable for use in cosmetic formulations.

However, one forgets that pharmaceutical grade liquid paraffin is prescribed historically during constipation as a laxative. It is taken orally to lubricate digested food and the intestinal mucus membrane and helps in limiting the amount of water being removed from faeces.

To generalise petroleum derivatives as evil and conclude all plant ingredients as holy is incorrect and not in the right perspective. Inferior and superior grade products both co-exist, no matter whether they are obtained from plants or are of mineral origin. Self-discrimination and discipline is the need of the hour.

Paraffin derivatives used in cosmetic formulation should be the ones with the best qualities. Cosmetic manufacturers and marketers should not compromise in using lower available grades to save a couple or more rupees and to make larger profit margins, disregarding the consumer's health and well being.