# Severely Hydrotreated Naphthenics –
# Today's Proven Electrical Insulating Oil for Tomorrow's Transformers

E. CASSERLY, J. RASCO, K. PATRICK
Ergon Refining, Inc., United States
N. HERLENIUS
Ergon Europe MEA, Inc., Belgium
Edward.Casserly@Ergon.com

For over a century, naphthenic mineral oils have been proven as the electrical insulating oil for electrical apparatus. Mineral oil quality has improved as refining technology has improved. In the first half of the 20th century, simple refining techniques such as solvent extraction, filtration and acid treatment produced products that were adequate for the times. The requirements for transformer oil have become more stringent over time, requiring a higher quality, more stable oil. Fortunately, over the last half of the 20th century and into the 21st century, refining technology has been advanced through the use of catalytic hydroprocessing technology. This technology uses a metal catalyst, high pressure hydrogen and elevated temperatures to chemically react with and convert unwanted molecules into smaller molecules which can be removed by distillation or into useful molecules that remain in the oil. This leads to many benefits, including (1) higher product quality, (2) more stable products, (3) higher yields, (4) lower costs and (5) oils which meet ever stringent governmental health, safety and environmental laws and regulations.

This paper will review the various technologies used to produce mineral transformer oils and demonstrate how the inherent properties of naphthenic mineral oils make them uniquely suited to be not only the proven electrical insulating oils for the last century but also the workhorse for decades to come.

## INTRODUCTION

Crude oil is found throughout the world although the type and quality varies considerably. There are two basic types of crude oil, paraffinic and naphthenic. Paraffinic crudes contain waxes and naphthenic crudes are wax deficient. Naphthenic crude oil only comprises about 5% of the total crude oil; however, recently new naphthenic fields have been found off the west coast of Australia and the east coast of Brazil. Crude oil contains literally thousands of molecules, from the very lightest hydrocarbon, methane, to the heaviest hydrocarbons found in asphalt. The molecular weight distribution of the hydrocarbons varies with the crude source. Some crudes are light and are useful for producing fuels, while others are heavier and are useful for lubricants and heavier products. The crudes will contain varying amounts of impurities such as sulfur (S), nitrogen (N) and oxygen (O) containing compounds or various metals such as nickel (Ni), vanadium (V) and iron (Fe). The amounts of these impurities determine the refining techniques best suited for those crudes and the types of products that can be economically produced.

Modern petroleum refining has changed dramatically over the last 30 to 40 years. Improved technology, specifically catalytic hydroprocessing, has brought many benefits and efficiencies to petroleum refining. These include (1) the ability to upgrade poorer quality crudes, (2) larger refineries, (3) higher lubricant yields, (4) higher product quality and (5) lower cost. In addition to this technology advance, the size of the refinery industry changed. The global petroleum refining industry is designed to produce fuels. Lubricants comprise only about 1% of total refining output. Over the last 15 years, the total number of refineries has decreased (from 705 refineries world-wide in 1995 to 655 in 2011) while the total production has increased (from over 74.5 million barrels per day (bpd) of crude in 1995 to over 88 million bpd of crude in 2011) [Oil & Gas Journal Surveys, 1995 – 2011]. The smaller, less efficient refineries have closed. The end result is that only the larger, more efficient refineries remain. While fuel refineries are very large, averaging about 160,000 bpd with the largest over a million bpd, lubricant refineries are much smaller, averaging about 6,600 bpd in Europe and 14,000 bpd in the US, with the largest about 40,000 bpd. Naphthenic refineries are generally smaller, averaging about 8,000 bpd in the US with the largest at 23,000 bpd.

A natural consequence of the reduction in the number of refineries and the increase in the average size of the refineries is that the refined products from these large refineries are viewed as commodities and not specialty products. As a result, naphthenic base oils, which are about 10% of total lubricant production, are no longer manufactured by most independent major oil manufacturers. Naphthenic base oils are generally manufactured in smaller refineries by independent manufacturers. Naphthenics are a specialty or niche product for these manufacturers. They are also a core business for them. For example, since the 1970’s at least 14 naphthenic refineries have closed. Today, there are only 16 naphthenic refineries in the world with 6 in the US and only 2 in Europe. Naphthenics are specialty products that often go into highly technical applications such as electrical insulating oils or rubber extender oils. Naphthenic specialty manufacturers combine the unique properties of naphthenics with excellent customer service and technical support to service these and other industries.

## REFINING TECHNOLOGY

The petroleum refining industry begins with crude oil and refines it, or purifies it, into usable petroleum distillates. Mineral transformer oil manufacturing is a minor subset of the overall global petroleum lubricant industry. However, advances in general refining techniques for lubricants have proven valuable in the manufacture of mineral transformer oils.

The first step in refining is to use a combination of atmospheric and vacuum distillations to fractionate the crude oil into discreet petroleum distillates which can be separately processed. The petroleum distillates are themselves complex mixtures and will distill over a range of temperatures, unlike a pure chemical which will have a very narrow boiling range. The distillation process determines the initial boiling point and the final boiling point of the distillate. The boiling range will ultimately define many of the physical properties of the final oil, such as the flash point, viscosity and density.

The next step in refining is to purify the petroleum distillates, i.e., to remove the unwanted compounds. For most of the $20^{th}$ century, refining was limited to separation techniques. Solvents or adsorbents were used to physically separate the unwanted compounds from the desirable compounds. The desirability of the compounds depends on the ultimate end use. For example, normal paraffins or wax are undesirable in motor oil. Solvents can be used to remove normal paraffins from distillates (this process is referred to as solvent dewaxing) and different solvents can be used to remove certain aromatics and polars from distillates (this process is referred to as solvent extraction). Alternatively, adsorbents can be used to selectively remove aromatics and polar compounds from distillates. In the case of solvent dewaxing, the wax can be recovered and converted to a potentially high valued product, such as wax for food or cosmetic applications. In the case of solvent extraction, the aromatic extract is not a valuable product and is by definition carcinogenic [IARC, 1984]. Currently, the use of aromatic extracts is limited and heavily regulated. The use of aromatic extracts in tire formulations has been prohibited in the European Union since 2010 due to health and environmental concerns [Regulation (EC) No 1907/2006, 2006]. Since solvent processing, both solvent extraction and solvent dewaxing, represents an effective loss in yield of valuable lubricant products, the refining industry has looked to other processes to increase both yields and quality.

Solvent refining, including both solvent extraction and solvent dewaxing, is a physical separation technique and not a chemical conversion process (acids have been used to chemically react with aromatics, but are not further discussed here). The compounds in the petroleum distillate partition between the oil phase and the solvent phase. The solvent is chosen to effectively remove only the unwanted compounds, either aromatics and polar compounds or normal paraffins. Extraction is an equilibrium process and the desired and unwanted compounds will equilibrate between the oil phase and the solvent phase. Therefore, some desired compounds will be extracted and some unwanted compounds will remain in the oil. After extraction, the solvent must be removed from both the raffinate (oil components insoluble in the solvent) and the extract (oil components soluble in the solvent) so that they can be further processed. Solvent removal is an energy intensive process. By contrast, hydroprocessing is a chemical conversion process. Unwanted compounds are either converted to lighter materials, such as gas or fuels, which are distilled from the oil or are converted to wanted compounds that remain in the oil. The net effect of hydroprocessing over solvent refining is an increase in the lubricant yield and no side products, such as aromatic extract or wax, other than gases and fuels.

Catalytic hydroprocessing which uses metal catalysts, high pressure hydrogen gas and temperature to refine petroleum distillates has progressed tremendously over the last several decades. This technology has revolutionized the lubricant and fuels industries. Essentially all new refineries use this technology and many refineries which had relied on solvent technology have converted to catalytic hydroprocessing. As with any technology, there are degrees of sophistication. The International Agency for Research on Cancer (IARC) has concluded that mildly hydroprocessed mineral oils are carcinogenic [IARC, 1984] and IARC later defined mild hydroprocessing as using pressures of 800 psig or less and temperatures of 800°F or less, independent of other process parameters [Federal Register, 1985]. For this reason, severe hydroprocessing will be defined in this paper as > 1200 psig hydrogen.

NAPHTHENIC MINERAL OIL REFINING

A modern state-of-the-art naphthenic refinery will generally use two refining processes to produce high quality naphthenic base oils, distillation and severe hydroprocessing. Through the judicial practice of using only wax-free naphthenic crude oil, there is not the need for a refining process (dewaxing) to remove the wax to improve the low temperature properties of the oil. Naphthenic oils have inherently excellent low temperature properties since they are wax-free and have a higher concentration of cycloparaffinic or naphthene rings than more paraffinic oils. However, if needed, dewaxing via hydroprocessing is an efficient method and it is readily coupled with other hydroprocessing units.

As noted, the first step in the refining process is distillation or fractionation. The crude oil is distilled using a combination of atmospheric and vacuum distillation. Atmospheric distillation removes gases and light hydrocarbons. The use of vacuum distillation allows the refiner to distill the higher boiling fractions at a lower temperature without degrading them. These intermediate fractions are referred to as either atmospheric gas oils or vacuum gas oils. A typical cut for transformer oil is similar to a light gas oil or heavy diesel, with a typical distillation range of 300 – 370°C (572 – 698°F). The distillation range will define many of the physical properties such as viscosity, flash point and density. The distillation range can also affect the chemical composition as well. Since the distillation range for transformer oils is relatively low compared to typical mineral oil lubricants, the petroleum distillate fraction does not contain the heavier polynuclear aromatics which are found in the heavier distillate fractions.

The second step in the refining process is severe hydroprocessing. This process is designed to remove and/or convert unwanted compounds. Distillation will remove light and/or heavy impurities, leaving only compounds within the specified distillation range. Severe hydroprocessing will (1) remove unwanted compounds via cracking or breaking down the compounds to smaller molecules which can then be removed by distillation or (2) convert the unwanted compounds to useful molecules such as the saturation of an olefin to a paraffinic molecule or an aromatic molecule to a saturated cycloparaffin (naphthene). Even after processing, transformer oils are very complex. A recent report analyzed 15 samples [Kaplan et al, 2010]. These included North Sea crude oil, naphthenic base oils, isoparaffinic base oils, uninhibited transformer oils and inhibited transformer oils. Using gas chromatography – mass spectrometry, they identified 180 different hydrocarbon structures found in naphthenic and isoparaffinic transformer oils. These structures included normal paraffins, isoparaffins, one to four ring cycloparaffins, steranes, aromatic steranes and aromatics. Not all structures were found in all samples and not all structures in the oils were ultimately identified.

The goal of a refiner is to produce high quality base oils at the lowest cost. Quality can be defined by various physical parameters such as flash point or viscosity. It can also be defined by stability. In addition to electrical insulating oils, base oils are used in a multitude of applications, often under severe conditions. For base oils derived from petroleum crude oil, the most stable chemical structures are saturated hydrocarbons. Molecules that contain any unsaturation tend to be less stable, either thermally or oxidatively. This unsaturation can be in the form of olefins, aromatics or any polar constituents containing sulfur, nitrogen or oxygen. The more unstable molecules are also the most reactive molecules. These unstable molecules react the fastest during hydroprocessing and are converted/removed first. The more stable molecules react slower and are converted/removed at a slower rate. The end result is that after severe hydroprocessing, the more unstable, more reactive molecules are removed leaving behind the more stable, higher quality molecules. This is in direct contrast to solvent refining where the unwanted molecules are removed by solubility differences and not reactivity. Unstable and reactive molecules can remain in the oil after solvent extraction.

## THE CHEMISTRY OF NAPHTHENICS

The chemistry of naphthenics makes them particularly suited for many technical applications, from metal working fluids, to rubber extender oils, to electrical insulating oils. By nature, naphthenics generally do not contain any significant amounts of normal paraffins which have high pour points. The lack of normal paraffins gives naphthenics their inherently low pour points, thereby eliminating the need for a dewaxing step in the refining process. Only recently have catalytic dewaxing processes produced paraffinic oils with pour points comparable to naphthenics. Pour point depressants are generally not required to lower the pour point of naphthenic mineral insulating oils.

Another important property is solvency which depends on chemical composition. Aromatics have a higher solvency than saturated cycloparaffins (naphthenes) which have a higher solvency than paraffins. Today’s naphthenic oils have been severely hydroprocessed to remove the polynuclear aromatic compounds which are carcinogenic. The remaining aromatics are the smaller ringed aromatics which are not carcinogenic. The remaining aromatics, along with the naphthenes, provide increased solvency which is important for many lubricant applications. Most additives are polar compounds and solvency is required to ensure that the additives are soluble in the oil. During normal use, the oil can become oxidized. The oxidized oil is more polar than the unoxidized oil and solvency is necessary to ensure that the oxidized oil remains in solution and does not create sludge.

A primary function of insulating oils is cooling. In operating transformers, a temperature gradient develops as the core and windings heat up. The heat must be distributed throughout the transformer, most importantly via convection, and eventually dissipated to the outside environment via conduction. Transformers can be designed with natural oil flow, that is, without a pump, or with assisted flow using a pump. In the absence of a pump, the movement of the oil throughout the transformer occurs via convection which depends on the density gradient produced by the less dense hotter oil and the more dense cooler oil. The viscosity is also important as it is easier for oil to flow through a thinner oil than through a more viscous oil. The lower viscosity aids in the convection and also assists in moving the oil in and out of narrow passages and the paper insulation. In larger transformers, pumps will provide additional circulation of the oil, however, less viscous oils are still desired since they are easier to pump and provide the best flow.

Due to their structure, a naphthenic oil is denser than a corresponding paraffinic oil of the same viscosity. In addition, the naphthenic oil has a lower viscosity index (VI). At elevated temperatures, an oil with a low VI will become less viscous than an oil with a higher VI. In other words, as the temperature changes, a higher VI oil will maintain its viscosity more than a lower VI oil. The higher density of the naphthenic mineral oil facilitates the natural convection process. The efficiency of the heat exchange between the oil and the windings or between the oil and the wall of the radiators is determined by the viscosity of the oil. The lower the viscosity, the greater the heat exchange. Since naphthenic oils have a lower VI than paraffinic oils, the naphthenic oils become thinner, less viscous, at the elevated operating temperatures and theoretically provide increased heat exchange.

Of course, other parameters such as the heat capacity and thermal conductivity play a role in cooling efficiency. These parameters vary with the chemical composition of the oil with naphthenic oils having slightly lower heat capacities and thermal conductivities than corresponding viscosity paraffinic oils. However, the viscosity of the oil is the dominant factor in cooling efficiency.

## BLENDING AND FORMULATIONS

The modern-day formulator has many tools to assist the refiner. Additives are almost always used to enhance the performance of base oils. For industrial lubricant applications, these additives can be pour point depressants to improve the low temperature properties, antioxidants to improve the oxidative stability, dispersants to improve the sludge dispersant properties, antifoams to improve the foaming properties, viscosity index improvers to improve the viscosity/temperature response, etc. For electrical insulating oils, the formulation possibilities are limited and are defined by the international standards regulating the products. In addition, many utilities and manufacturers have internal specifications which are often more stringent than the standards.

There are basically three types of electrical insulating oils, (1) uninhibited, (2) trace inhibited, and (3) inhibited. For uninhibited oil, synthetic antioxidants are not allowed. The uninhibited oils rely solely on the natural inhibitors, generally sulfur containing compounds, which remain in the oil after solvent refining to provide minimal oxidation stability.

Two primary phenolic antioxidants are approved for use in inhibited electrical insulating oils. These are 2,6-di-tert-butyl-p-cresol (DBPC or more commonly BHT) and 2,6-di-tert-butylphenol (DBP). Depending on the standard, these can be used at concentrations of up to 0.08% (800 mg/kg) for trace inhibited oils in both ASTM D3487 [ASTM D3487-09, 2009] and IEC 60296 [IEC 60296-4, 2012] or up to 0.30% (3000 mg/kg) for inhibited oils in ASTM D3487 or up to 0.40% (4000 mg/kg) for inhibited oils in IEC 60296.

Severely hydroprocessing, which effectively removes the natural contaminants and pro-oxidants such as sulfur, nitrogen and oxygen compounds and some aromatics, enhances the response of added synthetic antioxidants [Wiklund, 2007]. The antioxidants perform better in these cleaner oils since they do not have to counteract the negative aspects of these contaminants. The cleaner the oil, the better the antioxidant response and the longer the life of the transformer.

The oxidative testing requirements are different for the different types of transformer oils. For example, in the ASTM oils defined in ASTM D3487, the allowable limits of oxidation products, i.e., acid and sludge, for trace inhibited oils (ASTM Type I, 0.08% antioxidant) are generally 1.5 times the allowable limits for the inhibited oils (ASTM Type II, 0.30% antioxidant). The inhibited Type II oil is oxidatively more stable than the trace inhibited Type I oil. The same is seen with the IEC oils defined in IEC 60296. The allowable limits for acid and sludge in the IEC Uninhibited, IEC Trace Inhibited and IEC Inhibited are the same but the duration of the test increases. The more stable oil lasts longer in the test. IEC 60296 also has a Special Applications oil in which the allowable limits are greatly reduced and the test time is increased to 500 hours. These limits are given in Table I.

Table I - Oxidation Stability Requirements for Various Transformer Oils

| | ASTM Type I | ASTM Type II | IEC Uninhibited | IEC Trace Inhibited | IEC Inhibited | IEC Special Applications |
|---|---|---|---|---|---|---|
| Antioxidant, wt% max | 0.08 | 0.30 | Nil | 0.08 | 0.40 | 0.40 |
| Oxidation Stability: Total Acid Number, mg KOH/g, max | | | | | | |
| 72 Hrs | 0.5 | 0.3 | -- | -- | -- | -- |
| 164 Hrs | 0.6 | 0.4 | 1.2 | -- | -- | -- |
| 332 Hrs | -- | -- | -- | 1.2 | -- | -- |
| 500 Hrs | -- | -- | -- | -- | 1.2 | 0.3 |
| Oxidation Stability: Sludge, wt%, max | | | | | | |
| 72 Hrs | 0.15 | 0.1 | -- | -- | -- | -- |
| 164 Hrs | 0.3 | 0.2 | 0.8 | -- | -- | -- |
| 332 Hrs | -- | -- | -- | 0.8 | -- | -- |
| 500 Hrs | -- | -- | -- | -- | 0.8 | 0.05 |

Other additives have been used to improve the performance of the oil. For example, metal passivators have been used to coat the copper metal surfaces to reduce the catalytic effects of the copper. While this may prevent or slow down future corrosion, it is not known to reverse corrosion which may already be present. The concentration of passivators in the bulk liquid has been shown to decrease over time as the passivators react with the copper metal or are absorbed by the paper insulation. The concentration should be monitored and adjusted as needed.

## SULFUR AND CORROSION

Crude oil will contain many types of sulfur compounds. Some sulfur compounds are known to be highly reactive and corrosive, such as elemental sulfur, mercaptans (thiols) or sulfides (thioethers). These reactive compounds can be “pro-oxidants”, that is, they promote the oxidation of the oil. By removing these compounds, the oxidation stability of the oil is enhanced. Other sulfur compounds, such as disulfides and thiophenes (aromatic sulfur) are more stable and can actually be “beneficial sulfur”. Many sulfur compounds, such as disulfides and thiophenes, are known to be antioxidants or antiwear additives for industrial lubricants [Dong et al, 2009]. The hydroprocessing conditions can be varied depending on the crude oil and the needs of the refiner. In general, the refiner will strike a balance to ensure the removal of the reactive and potentially corrosive sulfur and not over process the rest of the transformer oil. The total sulfur content of base oils used in electrical insulating oils is generally in the 150 – 250 mg/kg (ppm) range.

IEC 60296, Edition 4.0, was published in February 2012. It includes new specifications for corrosive sulfur compounds that can lead to copper sulfide deposition, including dibenzyl disulfide (DBDS), and new definitions of additives, including antioxidants, inhibitors and passivators. Most importantly, it requires the declaration of the generic type and the concentration of any antioxidant additive and passivators.

A naphthenic base oil manufacturer, using severe hydroprocessing, will produce corrosion-free naphthenic oils. The small amounts of sulfur that remain in the oil are sterically hindered sulfur compounds that are not corrosive. The instances of sulfur corrosion in transformers over the last decade have been attributed to the use of DBDS as an antioxidant additive. While there remains many transformers filled with potentially corrosive transformer oil, there does not appear to be an ongoing issue of recently produced oil containing corrosive sulfur. Advanced analytical techniques, especially the updated corrosive sulfur tests in the ASTM and IEC standards, and the on-going research of independent laboratories have ensured the world-wide supply of corrosive-free transformer oils.

## CONCLUSION

Naphthenic mineral oils have been used in electrical apparatus for over a century and they have a long and proven track record. During this time, refining processes have improved and advances in catalytic hydroprocessing have revolutionized the industry over the last several decades. Today’s oils are cleaner and more stable, leading to higher quality products. Severe hydroprocessing will effectively remove all corrosive sulfur, producing corrosive-free transformer oil and decades of corrosive-free service in the transformer, without the addition of additives other than BHT..

To ensure the highest quality product, the standard specifications must be followed, including the declaration of any and all additives. The end-user should have a trusting relationship with the original transformer oil manufacturer as the oil will be in the transformer for decades to come.

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