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Mineral Insulating Liquids

Where They Are From, Where They Are Going

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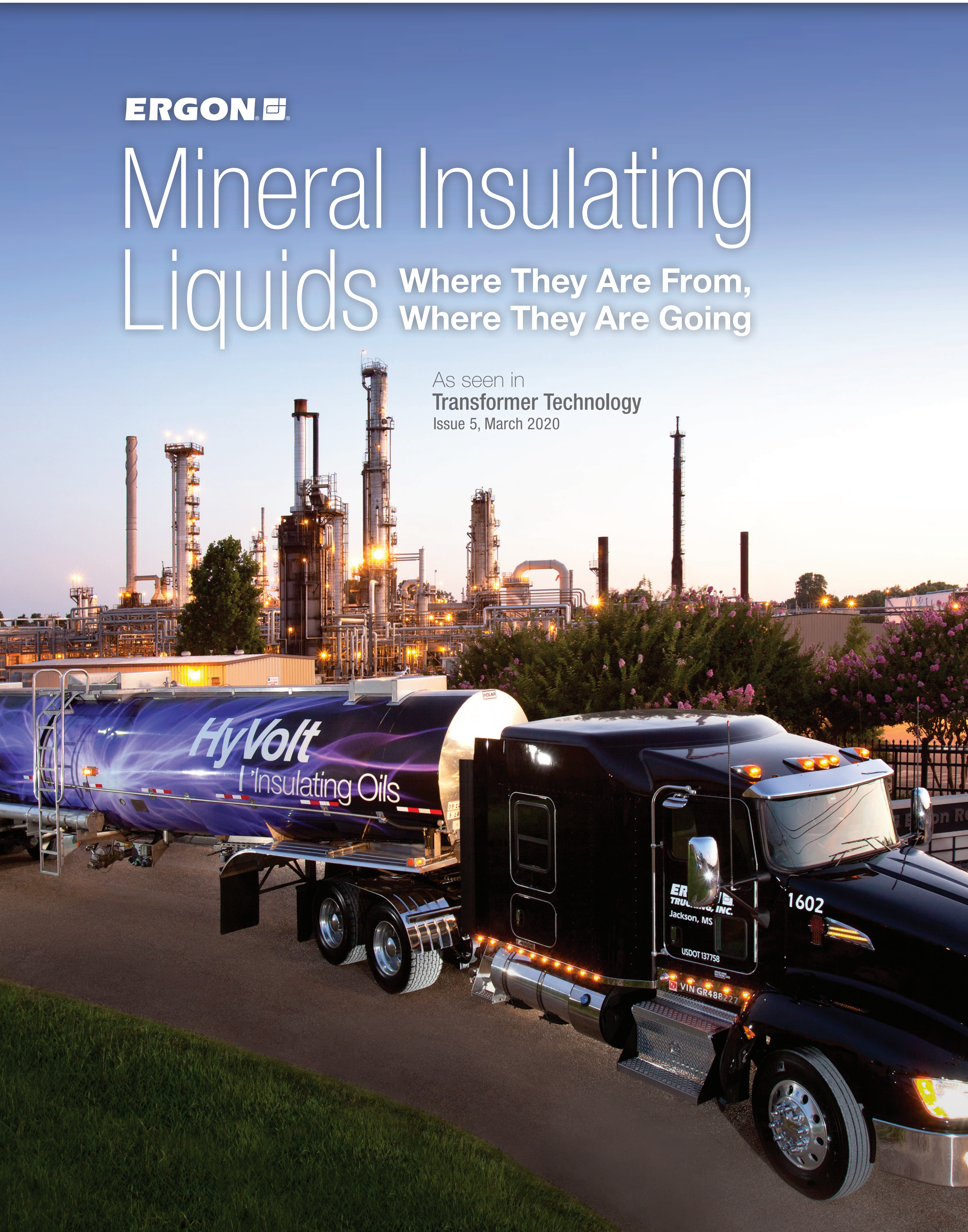

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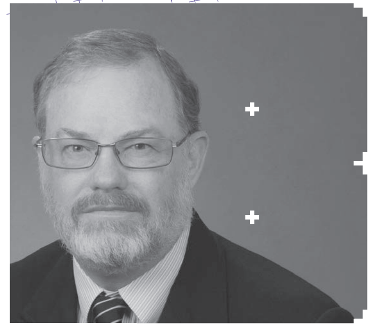
Mineral Insulating Liquids – Where They Are From, Where They Are Going

by **Edward Casserly**



Ed Casserly received his B.A. in Chemistry from the University of St. Thomas and his Ph.D. in Organic Chemistry from Rice University, both in Houston, Texas. He began his career as a research chemist with Pennzoil and Penreco, a specialty hydrocarbon producer. Ed has been involved with R&D and technical support for specialty petroleum products for 35 years. He is a co-inventor on seven U.S. patents on synthetic hydrocarbon fluids and has published numerous technical papers. Ed is currently Senior Scientist at Ergon Refining, Inc., in Jackson, Mississippi. He is a member of IEEE, Cigre USNC, IEC TC10/TC14, and ASTM D27 (Vice-Chair).

Photo: Ergon

Dielectric mineral insulating liquids have changed dramatically over the decades due to advances in refining technologies. The original oils were refined at a lower severity compared to today's mineral oils, but they met the basic requirements as understood at the time. Due to higher power requirements, higher loads, and smaller footprints, today's insulating liquids must meet the more stringent requirements in today's standards. The refining processes used to manufacture these liquids, as well as the specifications in the standards and how they relate to performance, will be discussed in this article.

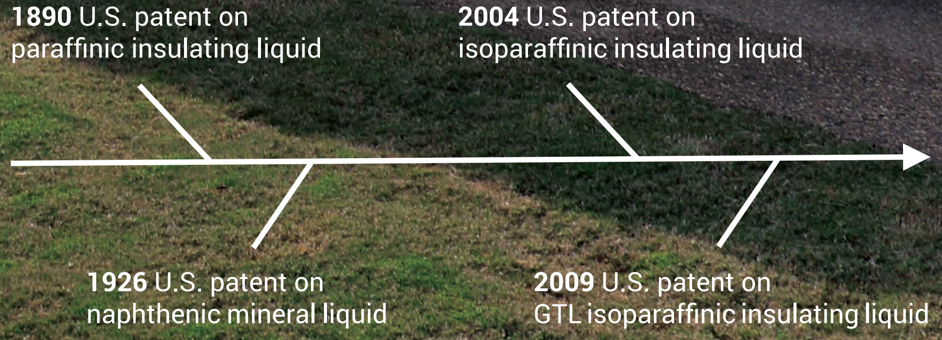
> WHILE THERE IS NO MAGIC LIST OF PROPERTIES OR VALUES THAT DEFINE AN INSULATING LIQUID THAT WILL ULTIMATELY PERFORM FOR 30 YEARS OR MORE, MANY DECADES OF EXPERIENCE HAVE SHOWN WHAT HAS WORKED OVER THE YEARS.

Introduction

Dielectric mineral insulating liquids have been around since the dawn of transformers. The first U.S. patent which disclosed the use of waxy paraffinic mineral oil, wherein the wax was considered an asset since it absorbed the heat from the core as the wax melted, was granted to Elihu Thomson of the Thomson-Houston Electric Company in 1890 [1]. The first U.S. patent which disclosed the use of naphthenic mineral oil was granted to Harold Maitland of Sun Oil in 1926 [2].

Insulating liquids from paraffinic mineral oils could only be used in tropical climates since the residual wax resulted in high pour points. The isoparaffinic insulation liquids [3] with acceptably low pour points were available after the development of new catalysis technologies which were commercialized in the 1980s and 1990s. More recently, gas-to-liquid (GTL) insulating liquids [4, 5], which are highly isoparaffinic, have been produced from natural gas.

Figure 1.
Timeline of the development of mineral insulating liquids

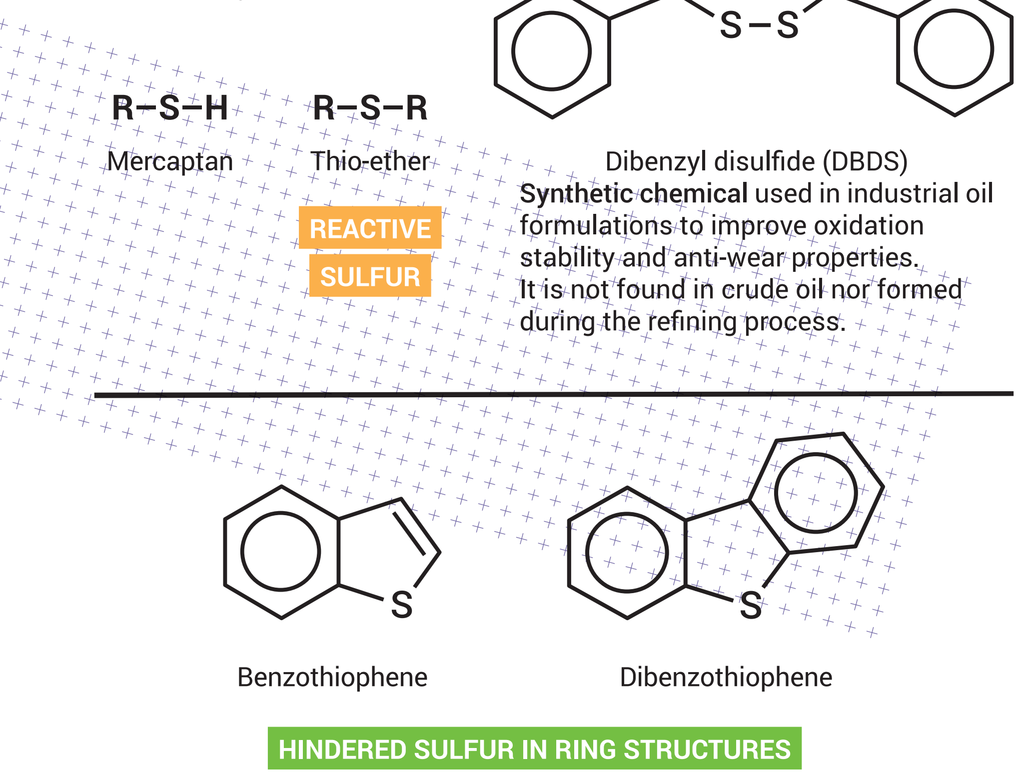


These hydrocarbon liquids have some inherent chemical differences, but all must meet the same international specifications: ASTM D3487 [6] or IEC 60296 [7]. These specifications have been developed and revised over the decades by international committees of chemists and engineers. ASTM D3487 was last revised in 2016, and IEC 60296 is currently under revision with an expected publication date in 2020. The standards list the properties considered relevant to adequately describe the physical, chemical, and electrical properties of the insulating liquid as they relate to the performance in the transformer. While there is no magic list of properties or values that define an insulating liquid that will ultimately perform for 30 years or more, many decades of experience have shown what has worked over the years. The Technical Committee 14 (Power Transformers) of the International Electrotechnical Commission (IEC) has produced a technical report, IEC TR 60076-26 ED1, which describes the requirements of insulating liquids for use in power transformers [8]. This is especially important as new technologies may require the development of new international standards specific to those technologies.

Refining Technologies

In the early 20th century, simple refining techniques such as clay adsorption, acid treatment, and solvent extraction were utilized to remove impurities from the distillates derived from crude oil. These refining techniques physically removed the more polar components and some aromatics to produce mineral oils of adequate purity and stability for that time in history. In addition, solvent dewaxing was utilized to remove the wax in order to lower the pour point. The oxidation stability of these oils was enhanced by the presence of hindered sulfur compounds, which are natural antioxidants. These naturally occurring hindered sulfur compounds remain in the oil after processing and are distinct from the other sulfur compounds which can be corrosive. Corrosive and potentially corrosive sulfur compounds include elemental sulfur, mercaptans (including hydrogen sulfide), sulfides, and disulfides, Figure 2 [9]. Processing had to be balanced to remove the corrosive compounds but leave the non-corrosive sulfur compounds. This facilitated the production of uninhibited transformer oil, i.e., transformer oil without any added synthetic antioxidants.

Figure 2.
Sulfur containing compounds



Synthetic chemical used in industrial oil formulations to improve oxidation stability and anti-wear properties.
It is not found in crude oil nor formed during the refining process.

Photo: Ergon

THE PURITY AND STABILITY OF MINERAL OILS IMPROVED WITH THE DEVELOPMENT OF HYDROPROCESSING OR HYDROTREATING. TODAY, THE MAJORITY OF MINERAL OIL IS PRODUCED VIA SEVERE HYDROPROCESSING.

THE FUNCTIONAL PROPERTIES OF MINERAL INSULATING LIQUIDS ARE DEFINED BY TWO SIMILAR, BUT NOT EXACTLY THE SAME, INDUSTRY STANDARDS: ASTM D3487 AND IEC 60292. THEREFORE, IT IS IMPORTANT TO SPECIFY WHICH STANDARD IS BEING USED AND WHICH TEST METHODS ARE USED IN THE CHARACTERIZATION.

The purity and stability of mineral oils improved with the development of hydroprocessing or hydrotreating. In this technology, the oil is treated at elevated temperatures in the presence of high-pressure hydrogen and an active metal catalyst. This effectively removes polar compounds and saturates aromatic compounds to saturated hydrocarbons called naphthenes. This was first used to process fuels to remove the olefins, in order to make the fuel more stable and less likely to form gum. It was applied to mineral oils in the 1960s and 1970s. When this process is taken to the extreme, the end product is 100% saturated hydrocarbons which can be certified for use in food and pharmaceuticals. Since food and pharmaceuticals are low-volume specialty applications, most mineral oils are produced to conform to industrial applications. Today, the majority of mineral oil is produced via severe hydroprocessing. One consequence of hydroprocessing is the removal of all or nearly all the sulfur compounds in the oil, including the hindered sulfur compounds which are natural inhibitors. The removal of most, if not all, the sulfur makes it easier to produce an inhibited oil but more challenging to produce an uninhibited oil.

Naphthenic mineral oils are produced via the distillation and hydroprocessing of naphthenic crudes which are wax-free, i.e., devoid of normal paraffins and specifically chosen to have inherently low natural pour points. Naphthenic refineries typically do not have refining processes to remove residual wax contamination since they have been selectively chosen.

Isoparaffinic mineral oils are produced from paraffinic crudes via distillation and a series of hydroprocessing techniques called hydrocracking, hydroisomerization, and hydrofinishing. The hydrocracking process opens up aromatic rings so that the sulfur and nitrogen can be effectively removed. Hydroisomerization will isomerize the normal paraffins to isoparaffins, and the hydrofinishing will saturate remaining aromatics and any olefins generated in the other processes. While it sounds complicated, it is highly efficient and has relatively high yields since the aromatics are converted to naphthenes and the normal paraffins are converted to isoparaffins. Earlier refining techniques physically removed the aromatics and normal paraffins; they did not convert them to usable products.

The GTL mineral oils start with methane, i.e., natural gas. Through the Fischer-Tropsch process, methane is converted first to carbon monoxide and hydrogen, which is then converted to normal paraffins or wax. The wax is then converted to isoparaffins via hydrocracking, hydroisomerization, and hydrofinishing. The GTL is different from the other isoparaffinic mineral oils in that it is nearly all isoparaffinic with minimal amounts of cycloparaffins or aromatics.

Functional Properties of Dielectric Mineral Insulating Liquids

The functional properties of mineral insulating liquids are defined by industry standards: ASTM D3487 and IEC 60292. The specifications in the two standards are similar, and the test methods used to characterize the oils are also similar, but they are not exactly the same. Therefore, it is important to specify which standard is being used and which test methods are used in the characterization.

As noted, there are two main types of mineral insulating liquids: naphthenic and isoparaffinic, Figure 3 [10]. While the names imply different chemical compositions, the differences are more of kind rather than type [11].

Naphthenic mineral oils contain cycloparaffins, isoparaffins, and aromatics. Isoparaffinic mineral oils contain the same chemical structures but in different ratios. None of the oils contain straight chain normal paraffins or wax since that leads to high pour points. It is these differences in the chemical composition which determine some of the physical properties. Carbon-type analysis, as defined in ASTM D2140 [12] or Brandes IR [13], can be used to differentiate naphthenic and isoparaffinic mineral oils. Per the ASTM method, the percentage of aromatic carbons ($\%C_A$), the percentage of naphthenic carbons ($\%C_N$), and the percentage of paraffinic carbons ($\%C_P$) are determined from the physical properties of the oil, i.e., the viscosity, density, relative density, and refractive index. In the Brandes IR method, the percentages are determined by the intensities of the infrared absorptions at about 1,600 cm^{-1} and 720 cm^{-1}. A naphthenic mineral insulating liquid is generally defined as one where the $\%C_N$ is greater than 40 and the $\%C_P$ is less than 50. An isoparaffinic mineral insulating liquid is generally defined as one where the $\%C_P$ is greater than 50. This further illustrates that the different mineral oils share many of the same chemical structures.

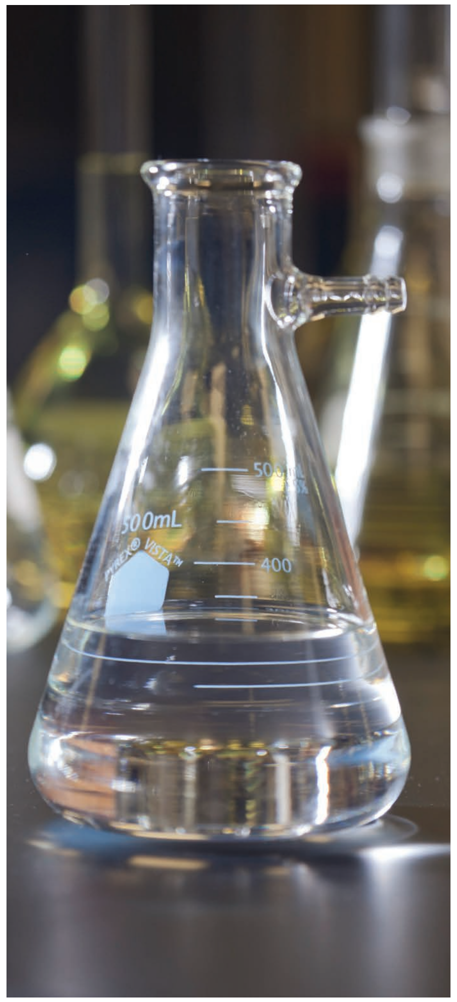
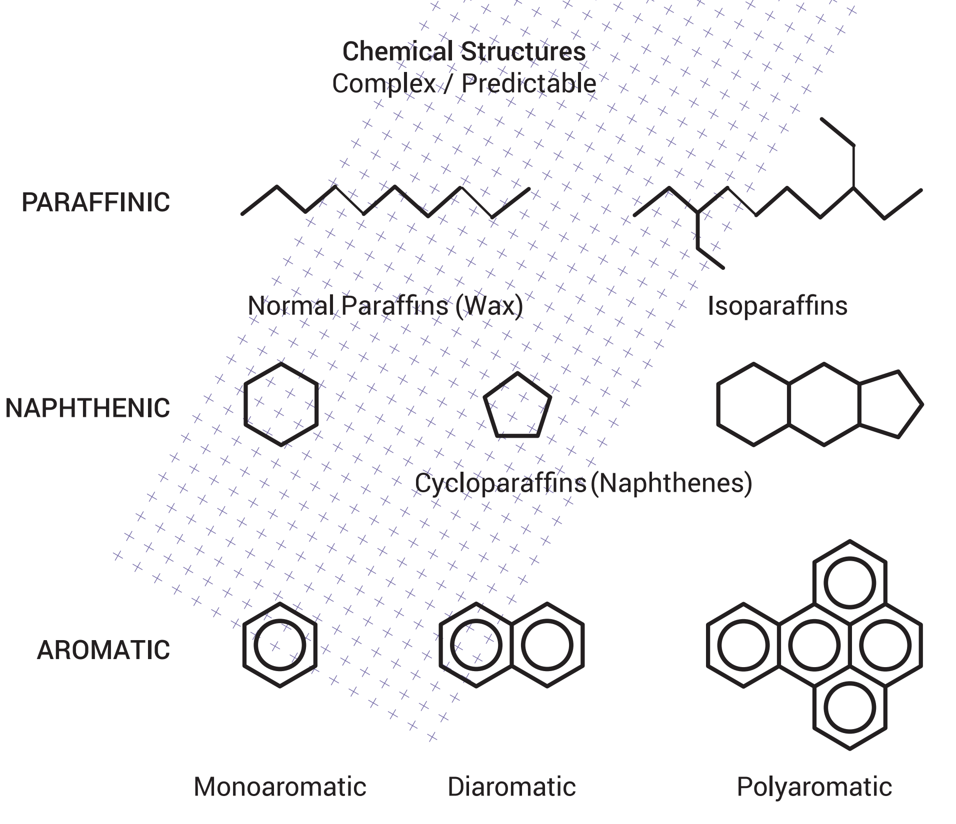


Figure 3.
Basic chemical structures found in mineral insulating liquids



The viscosity of the oil is determined mostly by the distillation range, but the chemical composition has some influence. Isoparaffins have a lower viscosity than the corresponding cycloparaffins of the same distillation range. This is especially evident at very low temperatures. The same is true of density and relative density, where isoparaffins have a lower density than the corresponding cycloparaffins.

The flash point of the oil is determined by the distillation range, specifically the beginning of the distillation range.

The pour point of mineral oils is determined mostly by the ratio of the chemical structures, but the distillation range has some influence. Since the isoparaffins are derived from paraffinic crude, it is imperative that all the normal paraffins be converted to isoparaffins. For this reason, naphthenic mineral insulating liquids generally have lower pour points than isoparaffinic insulating liquids. Even residual amounts of normal paraffins can raise the pour point.

TWO MAIN TYPES OF MINERAL INSULATING LIQUIDS ARE NAPHTHENIC AND ISOPARAFFINIC, WHICH CONTAIN THE SAME CHEMICAL STRUCTURES BUT IN DIFFERENT RATIOS. IT IS THESE DIFFERENCES IN THE CHEMICAL COMPOSITION THAT DETERMINE SOME OF THE PHYSICAL PROPERTIES.

Table 1.
Comparative properties of mineral insulating liquids

	Naphthenic	Isoparaffinic	GTL
Viscosity, mm²/s, 100°C	2.4	2.2	2.6
Viscosity, mm²/s, 40°C	9.8	7.8	9.4
Viscosity, mm²/s, 0°C	66.7	36.2	46.3
Density, kg/m³, 20°C	0.8826	0.8299	0.8049
Relative Density, 15.6/15.6°C	0.8863	0.8335	0.8085
Aniline Point, °C	75	98	112
Refractive Index, 20°C	1.4830	1.4571	1.4502
Flash Point, COC, °C	154	174	190
Color, ASTM	0.1	0.1	0.1
Pour Point, °C	-56	-40	-41
Water Content, mg/kg	16	17	14
Interfacial Tension, mN/m	42	40	51
Viscosity-Gravity Constant	0.857	0.801	0.768
Gassing Tendency, µL/min	+12	+25	+54

OILS THAT HAVE BEEN SEVERELY HYDROPROCESSED AND CONTAIN FEWER AROMATIC STRUCTURES ARE MORE STABLE AND RESPOND MORE EFFECTIVELY TO SYNTHETIC ANTIOXIDANTS.


Photo: Ergon

THE DIELECTRIC PROPERTIES ARE GENERALLY DETERMINED BY THE LEVEL OF MOISTURE, SOLUBLE POLAR CONTAMINANTS, OR SOLID CONTAMINANTS.

The solvency of mineral oils is determined mostly by the ratio of the chemical structures, but the distillation range has some influence. Aromatic structures have the highest solvency, then cycloparaffins, then isoparaffins, and then normal paraffins. Since naphthenic minerals have higher concentrations of aromatics and cycloparaffins than the isoparaffinic mineral oils, they have a higher solvency, i.e., lower aniline points. These differences, while not extreme, could lead to differences in compatibility with materials of construction, such as gaskets and seals. It is important to be cognizant of these differences, especially when retrofilling.

The oxidation stability of the bulk oil is determined by the oxidation stability of the individual chemical structures. With respect to the chemical structures found in petroleum mineral oils, the oxidation stability is generally in the following order: isoparaffinic first, then naphthenics, then aromatics, and finally polars. It is the ratio of the chemical structures which determine the overall stability of the oil. It is known that oils that have been severely hydroprocessed and contain fewer aromatic structures are more stable and respond more effectively to synthetic antioxidants [14, 15]. Phenolic antioxidants, such as 2,6-di-tertiary-butyl-para-cresol (DBPC), which has the common name of butylated hydroxytoluene (BHT), and 2,6-di-tertiary-butylphenol (DBP), have historically been used in transformer oil. While other antioxidants could theoretically be used, there are no current standard methods for the analysis of other antioxidants in transformer oil [16]. The standards for mineral insulating liquids require that all additives and the concentrations of antioxidants and passivators be disclosed.

The presence of aromatics is important for gassing tendency. Certain aromatics are known to lower the gassing tendency, and these can be added to the insulating liquid. Examples of some aromatics are described in IEC 60296. Isoparaffins, without added aromatics, have high gassing tendency values, some higher than the +30 specified in ASTM D3487, and there is no general requirement in IEC 60296. While this is ultimately a decision made by end-users based on their preference, at this time, the correlation of gassing tendency and equipment performance is limited. The dielectric properties are generally determined by the level of moisture, soluble polar contaminants, or solid contaminants. As long as the oil is properly dried, filtered to remove particulates, and devoid of polar contaminants, the insulation liquid should have acceptable dielectric properties.

Conclusion

Dielectric mineral insulating liquids have proven robust and effective for over a century. From early iterations as acid-treated or solvent-extracted insulating liquids to today's severe hydroprocessing, naphthenic mineral insulating liquids have been the primary insulating liquid for decades. In the past 25 years, isoparaffinic mineral insulating liquids have been available due to new refining hydroprocessing, and, more recently, GTL mineral insulating liquids have been developed. These hydrocarbon liquids all meet the same stringent requirements defined in the international standards and meet the functional requirements for use in today's transformers.

AS LONG AS THE OIL IS PROPERLY DRIED, FILTERED TO REMOVE PARTICULATES, AND DEVOID OF POLAR CONTAMINANTS, THE INSULATION LIQUID SHOULD HAVE ACCEPTABLE DIELECTRIC PROPERTIES.

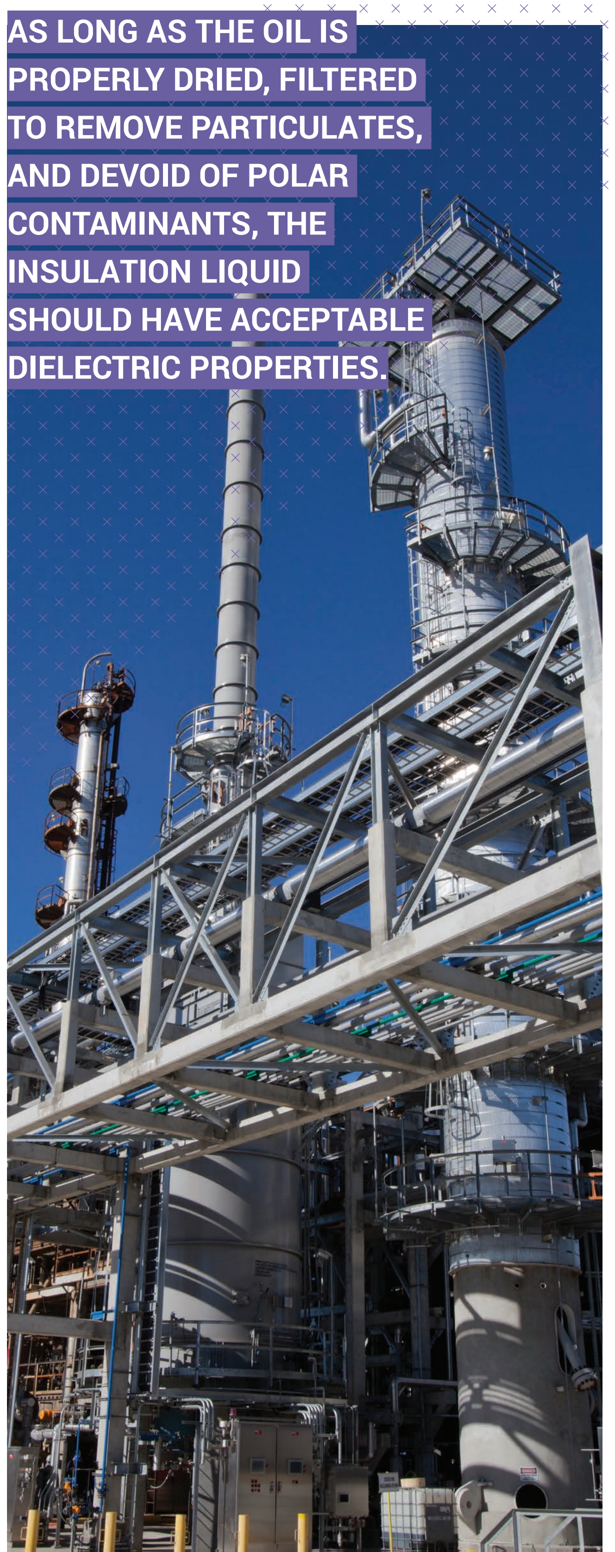


Photo: Ergon

References

[1] E. Thomson, "Casing for induction-coils," U.S. Patent 428,648, May 27, 1890.

[2] H. T. Maitland, "Process of manufacturing a nonemulsifiable mineral oil of high dielectric strength," U.S. Patent 1,605,046, November 2, 1926.

[3] M. Fefer and R. Tomoki, "Dielectric fluid," U.S. Patent 6,790,386, September 14, 2004.

[4] J. M. Rosenbaum, N. L. Yenni and J. M. Pudlak, "Dielectric fluids and processes for making same," U.S. Patent 7,510,674, March 31, 2009.

[5] A. Hilker and V. K. Null, "Electrical oil formulation," U.S. Patent 7,846,882, December 7, 2010.

[6] ASTM D3487, "Standard specification for mineral insulating oil used in electrical apparatus," *Annual Book of ASTM Standards*, Vol. 10.03, Electrical Insulating Liquids and Gases, 2016.

[7] IEC 60296, "Fluids for electrotechnical applications – unused mineral insulating oils for transformers and switchgear," 2012.

[8] IEC TR 60076-26 Ed1, *Power transformers – Part 26: Functional requirements of insulating liquids for use in power transformers*, in press.

[9] M. C. Bruzzoniti, R. M. De Carlo, C. Sarzanini, R. M. Maina, and V. Tumiatti, "Stability and reactivity of sulfur compounds against copper in insulating mineral oil: definition of a corrosiveness ranking," *Industrial & Engineering Chemistry Research*, 53(21), 8675-8684, 2014.

[10] *Paraffinic oils derived from classical, older Group I technology, as opposed to the isoparaffinic oils derived from the newer Group II technology, have historically been used in the tropics where extreme cold temperatures are not seen and low pour points are not required.*

[11] I. R. Kaplan, J. Rasco, and S. T. Lu, "Chemical characterization of transformer mineral-insulating oils." *Environmental Forensics*, 11(1-2), 117-145, 2010.

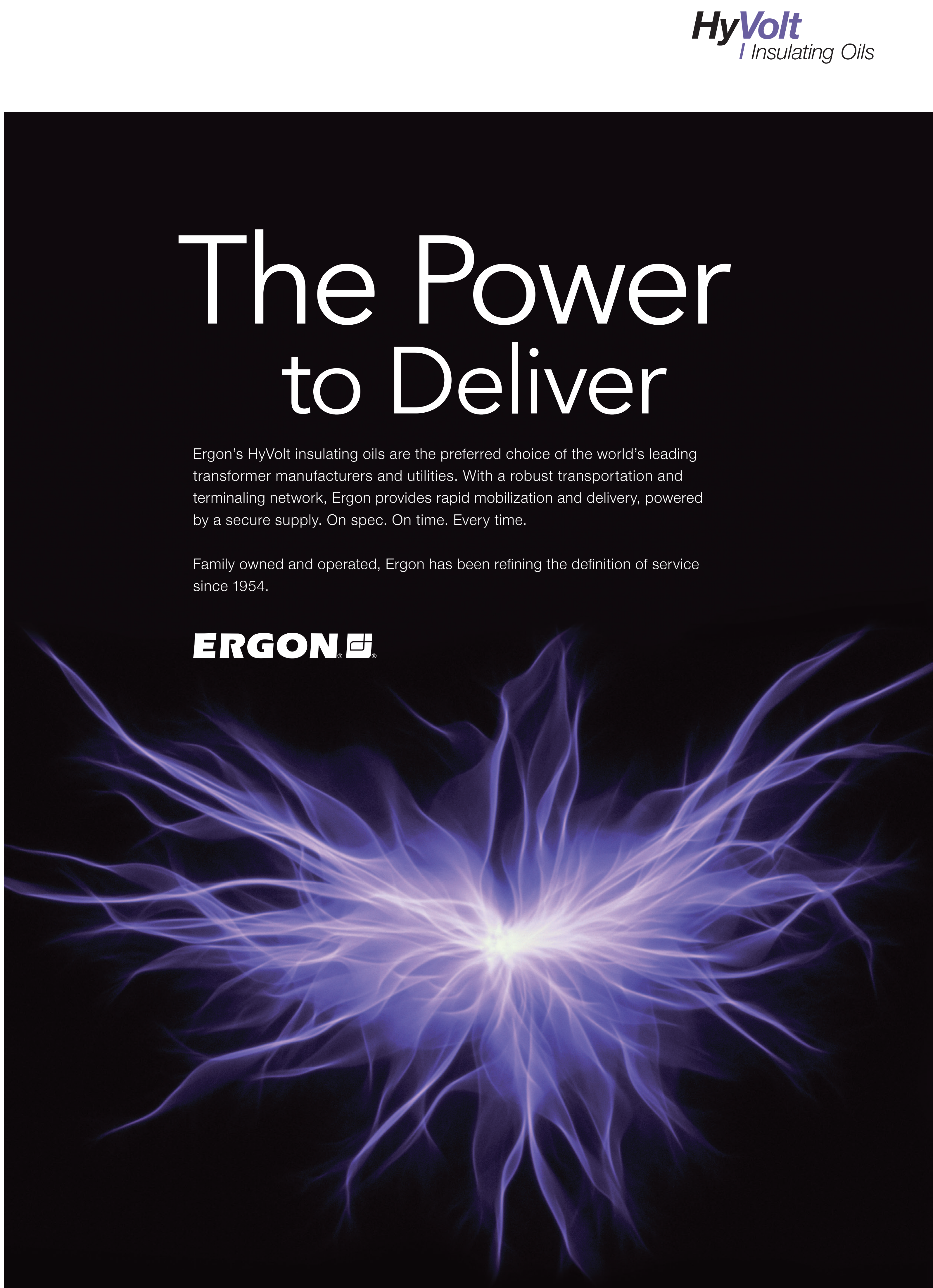
[12] ASTM D2140, "Standard practice for calculating carbon-type composition of insulating oils of petroleum origin," *Annual Book of ASTM Standards*, Vol. 10.03, Electrical Insulating Liquids and Gases, 2017.

[13] Ministry of Defence, Defence Standard 05-50 (Part 65), "Methods for testing fuels, lubricants and associated products Part 65: Determination of hydrocarbon types in mineral oils by infrared spectroscopy," 1995.

[14] P. Wiklund, "The response to antioxidants in base oils of different degrees of refining," *Lubrication Science*, Vol. 19, pp. 169-182, 2007.

[15] V. J. Gatto, M. A. Grina, T. L. Tat and H. T. Ryan, "The influence of chemical structure on the physical properties and antioxidant response of hydrocracked base stocks and polyalphaolefins," *Journal of Synthetic Lubrication*, 19(1), 1-18, 2002.

[16] *There are efforts within CIGRE Working Group D1.70 to develop standard HPLC methods for the determination of other antioxidants.*



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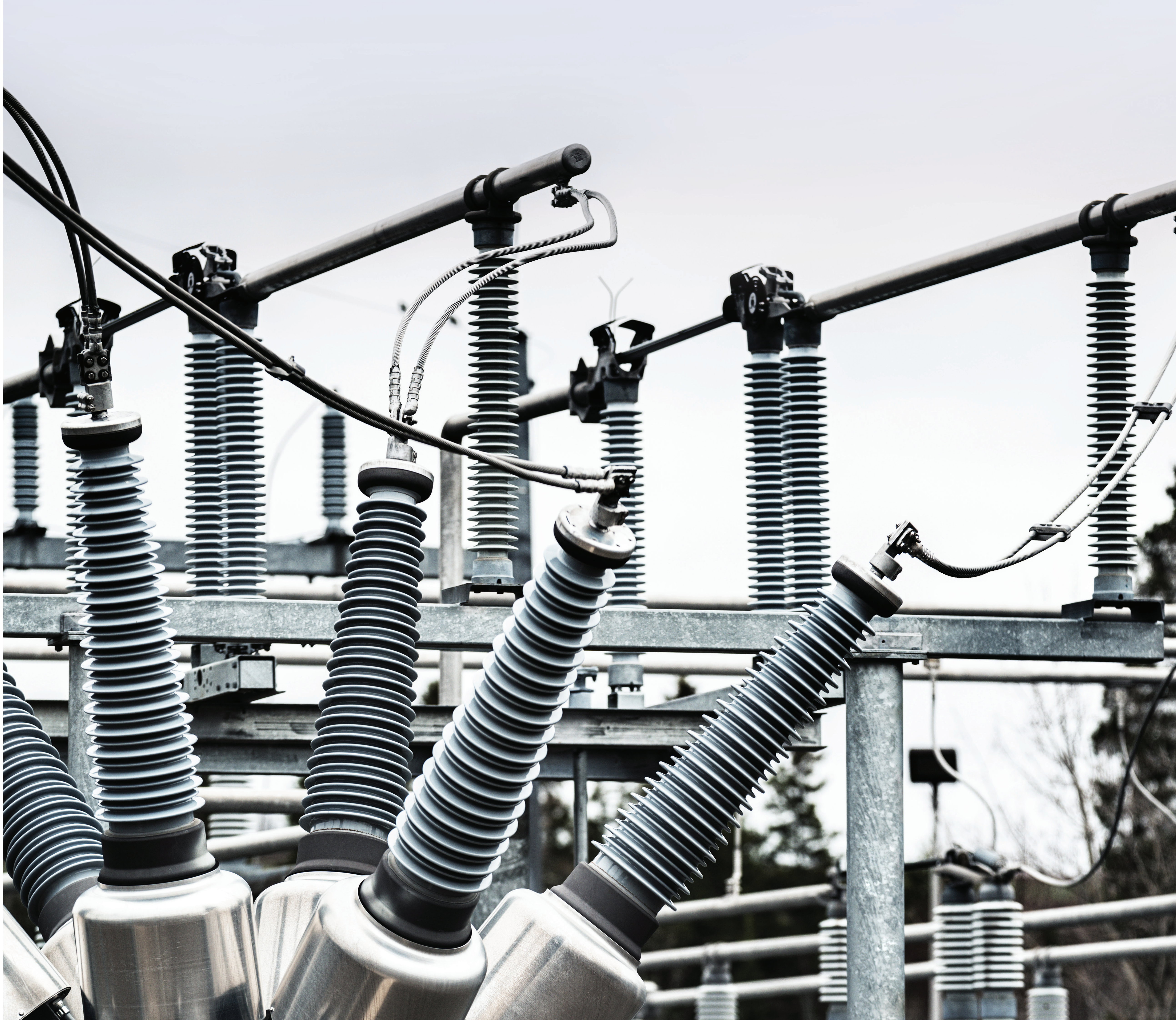

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