

PRODUCTION OF CORROSIVE SULPHUR FREE TRANSFORMER FLUIDS vs. COMMON NAPHTHENIC MINERAL OILS

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ABSTRACT

This paper focuses on the technology currently available for the production of severely refined, corrosive sulphur free base fluids used in the formulation of high quality transformer fluids. It will discuss the formulation, evaluation and performance characteristics of transformer fluids manufactured from corrosive sulphur free, iso-paraffin base fluids. It has been shown that these fluids can pass the latest corrosive sulphur test methodology without the use of passivation additives (eg. copper passivators). In addition, it will cover increased oxidative stability, heat transfer and biodegradability characteristics as compared to common naphthenic mineral oils.

INTRODUCTION

Corrosive sulphur in transformer oils has been a growing concern for the electrical transmission industry for the past few years. There have been a number of documented cases of transformer failures which are believed to be due to corrosive sulphur compounds contained in the transformer oils. This has led to an industry-wide investigation into the causes and possible remedies for these transformer failures [1,2,3,4].

From this investigative work, new or updated test methods have been, or are being developed to help detect corrosive sulphur species in transformer oil. The updated ASTM 1275B and proposed CIGRE Covered Conductor Deposition (CCD) test methods are a direct result of this work. Some naphthenic transformer oil suppliers have chosen to address this corrosive sulphur problem by using additives called passivators to help try and slow down the effects of corrosive sulphur in their oils. However, even with the field addition of passivators to transformer oils known to contain corrosive sulphur, failures related to corrosive sulphur have still been reported [5].

The electrical industry has been asking transformer oil manufacturers to come up with better technologies to resolve this issue. Passivators may only be a “quick fix” for the short term and

may have long term implications that are not yet fully understood [6]. Transformer oil manufacturers are taking this issue seriously as the liability of supplying corrosive transformer oil is a significant consideration for all. Most manufacturers understand that eliminating corrosive sulphur through more thorough refining and purification of the base oils used to manufacture the transformer fluids is a key to preventing corrosive sulphur related failures [7].

Corrosive sulphur free base oils that do not require the use of passivators to manufacture a transformer fluid are not a new development, and in fact have been commercially available for over ten years. These iso-paraffin base oils are produced using state-of-the-art refining instead of the conventional methods used to process some naphthenic based transformer oils.

REFINING BASICS

Crude oil as it comes out of the earth contains molecules made up of mostly carbon and hydrogen. Relatively smaller, but significant, amounts of other undesirable substances such as sulphur, oxygen, nitrogen, inorganic salts, metals and aromatic compounds can also be found in the crude [8,9]. The purpose of refining is to remove these undesirable constituents, as required, to develop the desired range of products with the necessary properties. The rest of this section will focus on the manufacture of lubricant base oil stocks (from which transformer oil is made) and the treatment methods involved.

In the early days of refining, chemical or clay treatment was the best technology for removing unwanted compounds from base oil stocks. In the late 1920's to early 1930's, an alternative method was developed known as Solvent Refining or Solvent Extraction. By contacting the base oil with an extraction solvent, such as furfural or phenol, increased removal of aromatics and other undesirable species could be achieved that led to a more thermally stable (higher viscosity index) and moderately higher quality of base oil.

Around the same timeframe (mid to late 1930's) another process called Hydrogen Refining (commonly called Hydrocracking or Hydrotreating) was being considered. The main benefit over solvent extraction was that the undesirable constituents in the feed were converted into desirable lubricant base oil components or other substances that could be readily removed. It never really caught hold in the industry since hydrogen at that time was expensive, and the overall cost of solvent refining was more economical. However, in the early 1970's there was a resurgence of this technology due to the poorer quality of crude slates available and the difficulty of processing them with conventional solvent refining techniques. The issue of

expensive hydrogen was also alleviated by use of a cheaper source of hydrogen from catalytic reformers.

Finally in the early 1990's, the latest version of Hydrogen Refining was introduced, called Severe Hydrocracking/Hydroisomerization. Instead of using a "chill dewaxing" step to remove wax from the base oil, this process converts the wax to oil by passing it over a catalyst at high temperatures and very high pressures which selectively cracks and recombines the molecules resulting in a water-white, corrosive sulphur free base fluid [10]. It is this technology that the iso-paraffin transformer oils are based upon.

BENEFITS OF ISO-PARAFFIN TRANSFORMER OIL

As mentioned above the state-of-the-art technology for making iso-paraffin base oils is known as Severe Hydrocracking/Hydroisomerization. Some of the main benefits of this technology for producing transformer fluid base oils are:

- Water-white colour
- Virtually no sulphur, nitrogen, aromatics or other impurities
- No corrosive sulphur
- Excellent response to oxidation inhibitors
- Fully saturated iso-paraffin and cyclo-paraffin content
- Increased thermal stability
- Excellent cold temperature properties

What does this mean to a transformer oil user?

A significant benefit of using iso-paraffin base oils to manufacture transformer oils is the fact that it has no corrosive sulphur. The description "virtually no sulphur" above indicates that if sulphur content was analyzed using sophisticated equipment capable of measuring sulphur with extremely low detection limits, there may be trace amounts (< 1 ppm) of sulphur in the oil. However, due to the severe nature of the refining process, this remaining sulphur would be non-corrosive in nature. While the typical high pressure hydrotreating and hydrocracking processes operating at >1,200 psig may be the minimum level necessary to remove many of the corrosive sulphur compounds [7], the Severe Hydrocracking / Hydroisomerization process operates around 2,500 psig to ensure that iso-paraffin base oils used for transformer fluids can consistently provide corrosive sulphur free performance.

Many corrosive sulphur studies and tests have been performed on the iso-paraffin transformer oils in the past few years. Some of these include:

- ASTM D1275 and ASTM D1275B
- A major industry investigative study on Corrosive Sulphur (including copper strip in oil tests and covered conductor deposition studies).
- ABB and Siemens evaluations (varying versions of a Covered Conductor Deposition or CCD test which uses copper and paper in oil). The Siemens version is currently under review by CIGRE committee A2.32 for adoption as a standard.

In all cases to date, test results have reported that the iso-paraffin base transformer fluids successfully provided non-corrosive performance. What is important to note is that all of these were achieved without the use of a copper passivator additive.

Iso-paraffin base oils used for manufacturing transformer oil are also water-white. Some conventional naphthenic transformer oils have a pale yellowish colour to them, which is a result of the aromatic compounds left in the oil after refining. Sometimes, various aromatics can impart specific properties that a refiner may want for blending products, such as motor oil or hydraulic fluid. In a transformer oil, small amounts of certain types of aromatics can aid in providing negative gassing tendencies. However, too many aromatic compounds or the wrong types of aromatic compounds can have a detrimental effect on the biodegradability and toxicity of the oil. Although this is not a typical requirement for a transformer oil today, it is a concern that is continuously being raised in the industry.

Figure 1 below shows the results of the Modified Sturm Test (OECD 301B) that measures the amount of oil degraded by microbes after a set period of time. For the “Readily Biodegradable” zone, a major threshold that the oil must achieve is 60% degradation in 28 days. Although an oil based on natural esters or vegetable oil may be able to achieve this rapid rate of biodegradation it is also subject to hydrolysis leading to poor in-use fluid stability. Iso-paraffin based transformer oils can approach this higher rate of biodegradation without loss of fluid stability. Compared to the conventional naphthenic transformer oil in this chart, the iso-paraffin based transformer oil showed very good results and achieved a level known as “Inherently Biodegradable”.

OECD 301B Testing

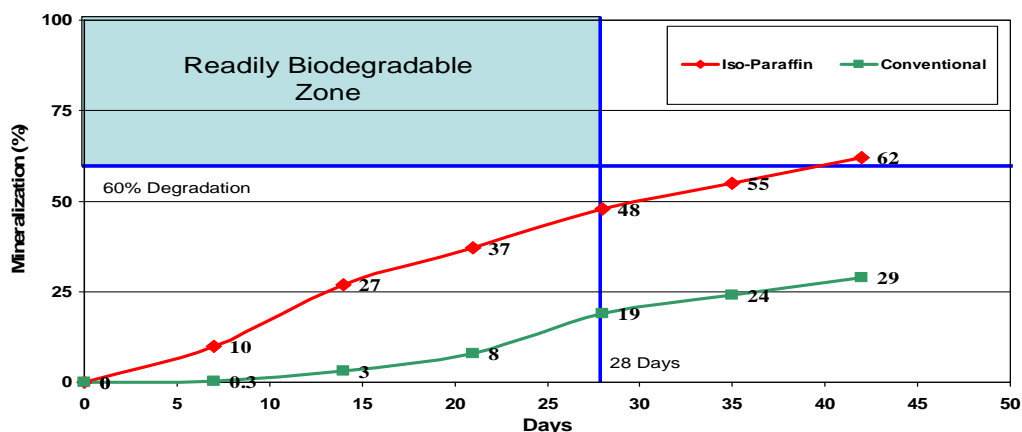


Figure 1 – Biodegradability Data – Modified Sturm Test

Another benefit of the Severe Hydrocracking/Hydroisomerization technology is that of stability and the response to oxidation inhibitors. When a transformer oil oxidizes and breaks down, it will form harmful oxidation byproducts, such as acids, varnish, and sludge. The industry combats oxidation by adding oxidation inhibitors to the oil formulation at specified concentration limits.

Since there are various reaction mechanisms by which oxidation can occur, this is not a fool-proof solution and some oxidation of the oil can still happen. This effect has been shown in lab tests (see Figure 2 below) as well as tests run by Canadian Utilities [11]. Relative to conventional naphthenic products, iso-paraffin based transformer oils have demonstrated excellent response to oxidation inhibitors to provide outstanding oxidation stability.



- Severe oxidation stability testing
- ASTM D2440, modified
- Temperature raised to 120 °C
- Duration extended to 500 hours

Iso-paraffin Conventional Oils
Naphthenic

Figure 2 – Oxidation Stability – Modified ASTM D2440

The final benefit of the iso-paraffin transformer oil that will be covered in this paper is its heat transfer property. Heat transfer is essential in a transformer to take the heat generated at the core and windings and move it to the outer shell where it can be dissipated. Qualities such as improved heat capacity and thermal conductivity have lead to direct comparisons of the iso-paraffin oil with typical naphthenic oil. Figure 3 below shows this comparison during a temperature rise test:

Temperature Rise Test

Copper Conductor, 800 Amperes

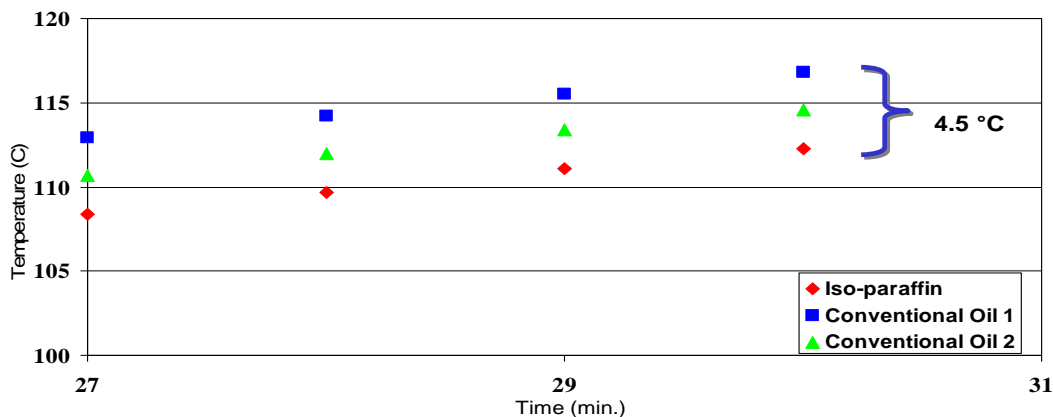


Figure 3 – Temperature Rise Test
(Measuring the temperature of the copper conductor in various transformer oils)

The lower temperature of the copper conductor is a good indication that the iso-paraffin oil could keep a transformer cooler than the conventional naphthenic oils tested. Based on these and other lab tests of a similar nature, a study was conducted by a U.S. electric utility company that showed improved heat transfer with the iso-paraffin [12].

STANDARDS

The industry has a number of key standards and specifications (including ASTM D3487-00, CAN/CSA C50-97, Doble TOPS 2006, and IEC 60296:2003) that buyers of transformer oil can use as a basis for their purchases [13,14,15,16]. The iso-paraffin transformer oils have been tested and were found to meet or exceed the inhibited and/or uninhibited (trace) oil performance requirements for each of these standards.

SUMMARY

The transformer industry has been trying to resolve the issue of corrosive sulphur in transformer oils for a number of years. The “quick fix” that some transformer oil manufacturers are promoting is the use of copper passivators to try and slow down the effects of corrosive sulphur in their oil. From industry investigations, it is becoming more apparent that copper passivators may not be the long term answer. Better refining technology is required to lower or eliminate the corrosive sulphur content of transformer oils.

A state-of-the-art manufacturing technology has been in place for several years that addresses the issue of corrosive sulphur without the use of copper passivators. The very high pressures used in the Severe Hydrocracking/Hydroisomerization refining process produces an iso-paraffin base oil which is corrosive sulphur free and virtually free of any aromatic compounds or other contaminants. This process also imparts qualities to the iso-paraffin transformer fluid that give exceptional areas of performance such as oxidation stability, heat transfer, and biodegradability when compared to the conventional naphthenic transformer oils tested and reported in this paper.

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AUTHOR

Steve Krawiec graduated from the University of Waterloo with a Bachelor of Applied Science degree in Chemical Engineering in 1994. He has 13 years experience in research / manufacturing of base oils with Petro-Canada and has been involved with the analysis of and enhancements to both the severe hydrocracking and severe hydrocracking / hydroisomerization processes for base oil production. Steve is currently a Senior Technical Service Advisor for Petro-Canada working out of the Lubricants Refinery in Mississauga, Ontario. He is a registered Professional Engineer and is presently licensed in the province of Ontario.