

COMPARISON OF COMMON ANALYTICAL TECHNIQUES TO VOLTAMMETRIC ANALYSIS OF ANTIOXIDANTS IN INDUSTRIAL LUBRICATING OILS

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A commercially available Voltammetric instrument designed to measure the antioxidant additive concentrations in lubricating oils was employed for this comparison. The subject oils used in this comparison were industrial lubricating oils analyzed before, during and after laboratory stressing by ASTM D-943, Turbine Oxidation Stability Test (TOST). The Voltammetric data was compared to common methods of lubricant analysis in order to evaluate the usefulness of the Voltammetric technique in determining the antioxidant additive levels in new and used industrial lubricants.

INTRODUCTION

Analytical Voltammetry had its origin in the 1920's with the work of Heyrovsky using a dropping mercury electrode. In the United States, the major research in the 1930's and 1940's was done by Kolthoff and his students. Over the next 20 years, Cyclic Voltammetry, the three-electrode system and other technological advances were developed. Since 1970, other major advances have been made including use of computer methodology, glassy carbon and chemically modified electrodes.

The performance of engine oils, turbine, pump, hydraulic and other industrial lubricants is improved by the addition of specific kinds of chemicals. These oil soluble chemicals are added to prevent the following (2,4,8):

- Formation/deposition of insoluble material

- Oxidation of the lubricant
- Metal corrosion
- Other harmful effects due to oil use, or caused by extended storage

The additive concentration decreases with time due, for example, to a reaction with dissolved atmospheric oxygen. Data which relates the additive concentration in the lubricant to a function of time are therefore very valuable in judging both the remaining useful life of the lubricant, and for determining the benefits of adding antioxidant (3).

Lubricant Additives

Electrooxidized additives are phenols, amines and the anti-wear compound zinc dialkyldithiophosphate (ZDDP). In addition, calcium phenate with the formula $\text{Ca}(\text{OC}_6\text{H}_5)_2$ which is an oil detergent and emulsifier (5), if present, could also be oxidized at a glassy carbon electrode (6). A lubricant can have more than one antioxidant. Phenolic additives can have sulfide/ sulfur groups (4).

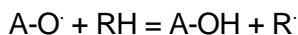
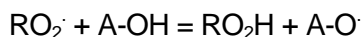
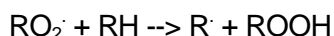
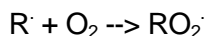
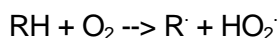
There are three main kinds of antioxidants (4):

1. Hindered and/or aromatic amines.
2. Hindered phenols.
3. Dithiophosphate derivatives.

Most oil antioxidants function by either decomposing peroxides, or by reacting with free radicals (4). Hindered phenols such as

2,6-di-tertiary-butyl-p-cresol (BHT) react with free radicals in the oil and prevent polymerization reactions which would otherwise form insoluble gums.

The reaction mechanism can be written schematically as (12,16):

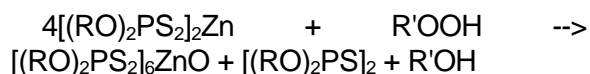


where the symbol " \cdot " identifies a free radical, "A" is an aromatic compound and "R" is an aliphatic compound. Early studies include investigation of peroxy radicals reacting with hindered phenols (25,26).

Hindered and/or aromatic amines such as phenyl-a-naphthylamine function similarly to prevent polymerization of free radicals, but the mechanism differs. For example, the hydrogen which is bonded to the nitrogen is readily removed to generate a stable free radical. A combination of phenolic and amine antioxidants in an additive package enhances the overall antioxidant effect (4). The reaction between alkoxyperoxy radicals and N-alkyloxy hindered amines has been studied using isotopic labeling techniques (22). Earlier work showed oxidation of diphenylamine produced a stable intermediate which was identified as diphenyl nitric oxide (23).

Zinc dialkyldithiophosphate (ZDDP) is both an antioxidant and an anti-wear additive. It decomposes peroxides which form in the oil (4). Selected publications are given in

References 17-19. It is not possible to discuss the action of ZDDP in detail in this paper. The ZDDP anti-wear and peroxide decomposer has been used in lubricating oils for over 50 years (17). The reaction between ZDDP and a hydroperoxide is complex at 95°C, the reaction is (17):



If the peroxide R'OOH is cumene hydroperoxide, then reaction under laboratory conditions is second order (17). At 30°C and 50°C, the kinetic data were interpreted as trapping of peroxy radicals, thus terminating any further reaction (17).

Anti-wear properties of additives such as ZDDP stems from formation of low shear films which adhere to the metal surface (4).

Electroanalysis

The electroanalyzer forces an electrochemical reaction to take place at an otherwise unreactive glassy carbon electrode by application of a sufficient voltage to the electrode. This applied voltage causes the antioxidant, or other electroactive chemical, to oxidize at the carbon electrode surface. The electrooxidation reaction releases electrons to the electrode and the magnitude of the resulting current is linearly related to the additive concentration in the solution. The higher the concentration of additive, the greater will be the current.

However, only a relatively small background current will be found until a specific voltage is reached, or in the absence of additive. This voltage depends on a number of parameters which are held constant.

The electroanalyzer used measured the concentration of electrooxidizable additives in

less than 1 ml of the oil sample. The method involved the extraction of the additive(s) into a solvent which contained a dissolved electrolyte, followed by electroanalysis using linear ramp Voltammetry at a glassy carbon electrode which was immersed in the solution (2,3).

Linear Ramp Voltammetry

The voltage-time signal to the glassy carbon electrode was in the form of a ramp. When a linear ramp is applied to the carbon electrode, the voltage of the electrode becomes increasingly more positive. If the rate of voltage scan is 0.1 volt/sec, then one volt is scanned in 10 sec.

The single scan with a linearly increasing positive voltage in an unstirred solution resulted in typically peak-shaped curves. The solution was not shaken or otherwise stirred while the analysis was being carried out. It was found that a stirred solution gives erroneously high readings.

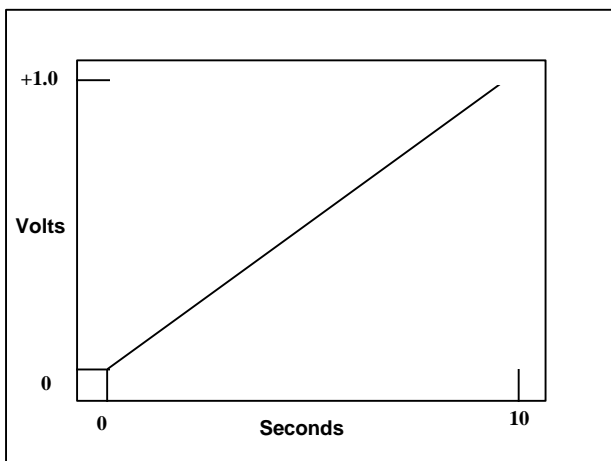


Figure 1 - Single scan linear ramp voltage-time function for the "A" setting, 0 to +1.0 volts, 10 sec.; "V" setting, 0 to 1.5 volts, 15 sec.

Analysis Measurement

The parameter of analytical importance was the peak height. In the electroanalyzer, the

peak heights were automatically calculated and displayed as a digital readout. The net peak heights were calculated as the difference between the height of the peak, and the background (blank) current obtained from a solution without additive, Figure 2.

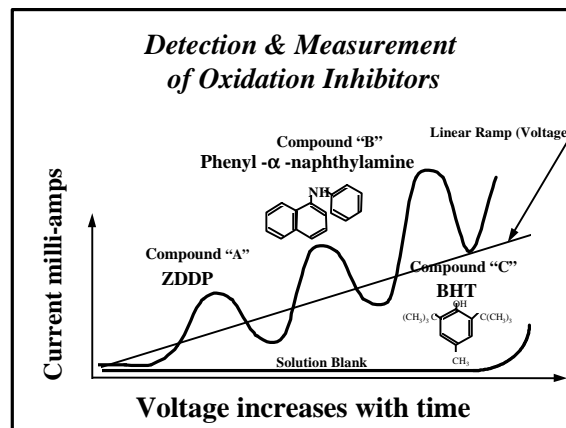


Figure 2 - Example of three additives and Voltammeter response.

If there was a second peak, the peak height was measured in the same manner (7). The peak height(s) were then related to the additive concentration by calibration with known standards. The known standards were the new base oil containing the additive(s), and known dilutions of the base oil with mineral oil.

Three Electrode System

The Voltammeter employed utilized a three-electrode system. All three electrodes were flush with the bottom of the electrode probe. The glassy carbon working electrode had a diameter of about 5 mm, while both the Pt reference and Pt auxiliary electrodes were about 0.3 mm each (6). The voltage-time signal was applied automatically to the glassy carbon electrode and to the Pt reference electrode. The current path was between the glassy carbon and the Pt auxiliary electrodes, and passed through a resistor which created a voltage that was measured as an analog output. Glassy

carbon electrodes are commonly used for electroanalysis of organic compounds (27).

SAMPLE PREPARATION TESTS

Six industrial lubricating oils were made available for the evaluation. They consisted of:

- 1 - Synthetic Hydrocarbon ISO 46
- 1 - Industrial Circulating Oil ISO 46
- 1 - Hydraulic Oil ISO 46
- 3 - R&O Turbine Oils ISO 46

10 different, 300 ml aliquots of each lubricant were placed into an ASTM D-943 TOST apparatus per the procedure for laboratory stressing. The lubricant suppliers estimated time of TOST life was divided by 10 to space the sampling interval so that 5 samples would be taken prior to the estimate TOST life and 5 after the estimated life. The 5 samples before and 5 samples after method was chosen in an attempt to ensure that the "end-of-life" of the lubricating oils was not missed.

The evaluation process consisted of periodically withdrawing a TOST test cell containing 300 ml of the selected lubricant. Then perform a series of analysis to measure the physical and chemical changes in the lubricant, evaluating the relationship of these analysis to that of the Voltammetric technique.

Although a variety of analyses were performed on each sample, the relevant analyses to this paper were the methods of analysis that are commonly used to evaluate the lubricants serviceability.

Rotating Bomb Oxidation Stability (RBOT)
Differential Scanning Calorimetry (DSC)
Voltmmetric Analysis
Total Acid Number (TAN)
Viscosity @ 40 C cSt

RESULTS AND DISCUSSION

Oxidation Inhibitor Reserve

Comparison of the Voltammetric technique to RBOT and DSC can be seen in the correlation coefficient data in Table 1. Chart numbers 1 through 6 graphically depict the relationship between the three methods.

The Voltammetric technique as compared to the RBOT the three turbine type R&O lubricants and the mineral circulating lubricant had an average correlation coefficient of 0.89. The same four lubricants had an average correlation coefficient of 0.95 between the DSC and the Voltammetric technique.

The synthetic hydrocarbon lubricant has historically responded poorly to the RBOT analysis. The DSC and the Voltammetric technique showed much better correlation (0.77 correlation coefficients) and the poor correlation was attributed to the RBOT characteristic as opposed to the Voltammetric technique.

The hydraulic oil showed excellent relationship to the Voltammetric technique after the first two samples which actually showed an increase in additive for the Voltammetric technique.

Subsequently, we determined that a change in the solvent used in the Voltammetric analysis resolved this problem.

OIL TYPE	RBOT	
DSC		
High Performance Turbine	.85	1.00

Circulating Oil	.95	.87
Turbine Oil #4	.84	.95
Turbine Oil #5	.92	.96
Synthetic Hydrocarbon	-0.15	.77
Hydraulic Oil	.36	.18

characteristics quickly and accurately on-site. Changes in the acidity and the viscosity can be predicted using the antioxidant level as a tool for the evaluation of the remaining useful life of the lubricant.

Table #1 - Correlation Coefficients for RBOT and DSC data compared to the Voltammetric technique.

Total Acid Number (TAN)

As depicted graphically in Charts # 7 through #12 the TAN in the lubricants tested showed no significant increase prior to a substantial decrease in the antioxidant concentration of the lubricating oil.

The notable exception to this characteristic was found in the synthetic hydrocarbon lubricant which began to increase at the first sampling and continued to increase throughout the aging process.

In the case of the high performance turbine oil the acid number substantially decreased from a 0.29 TAN to a .025 for over 280 days of aging.

Viscosity

As shown graphically in Chart #13 through # 18 the viscosity value for most of the lubricating oil tested remained relatively constant until the antioxidant additives in the lubricants were depleted. The two exceptions to this were the synthetic hydrocarbon lubricant and the high performance turbine oil which steadily increased throughout the evaluation.

Conclusion

The Voltammetric technique used for the analysis of the antioxidant levels in industrial lubricants showed it to be highly reliable and correlate well with conventional techniques. The method offers industry an opportunity to measure this critical

COMPARISON OF METHODS FOR MEASURING ANTIOXIDANT ADDITIVES LEVELS IN INDUSTRIAL LUBRICATING OILS

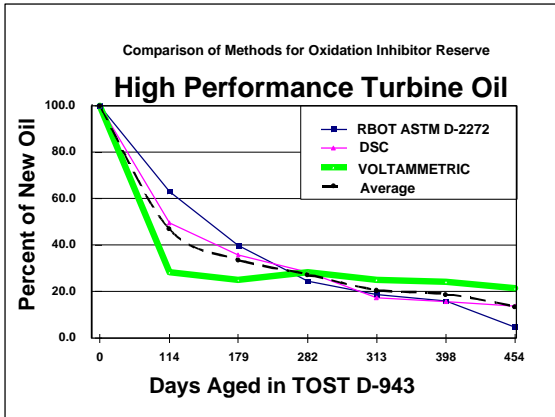


CHART # 1

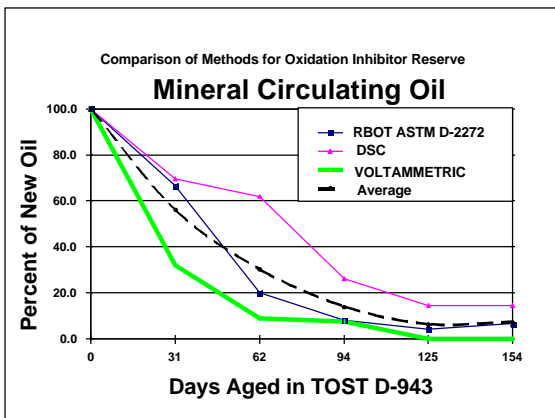


CHART # 2

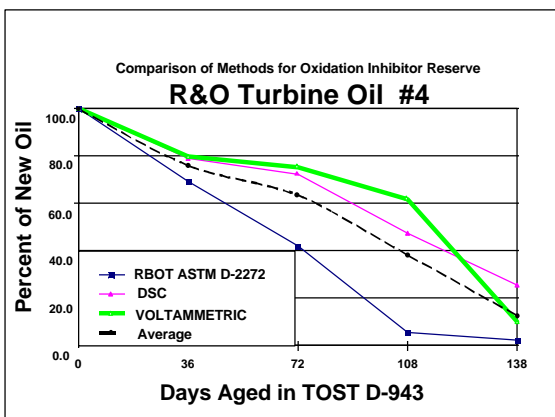


CHART # 3

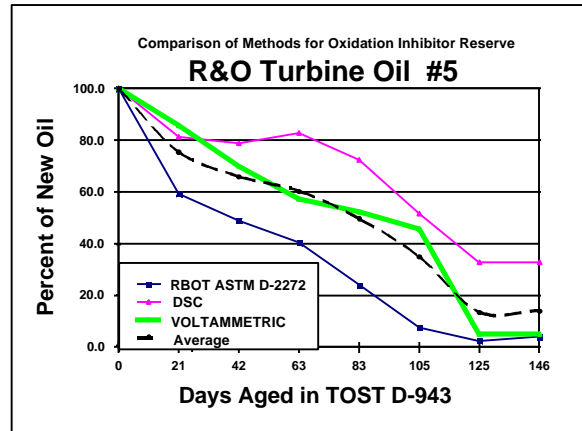


CHART # 4

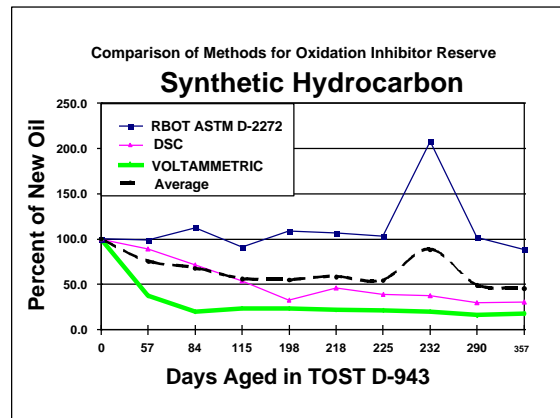


CHART # 5

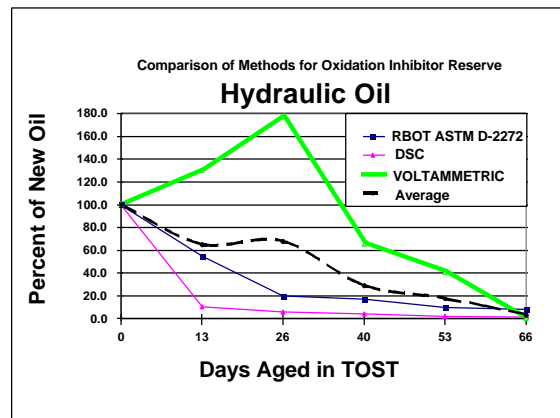


CHART # 6

**COMPARISON OF ACID CONCENTRATION TO ANTIOXIDANT ADDITIVES LEVELS
IN
INDUSTRIAL LUBRICATING OILS**

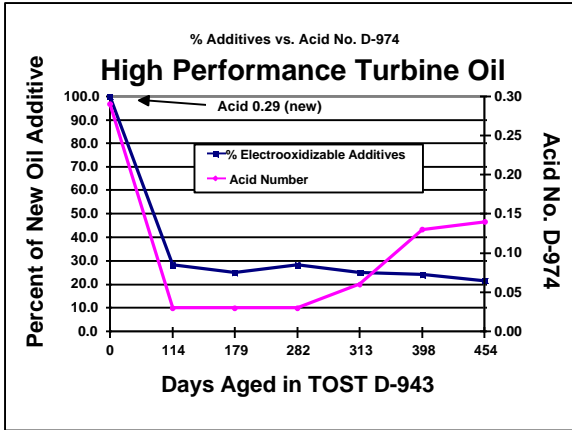


CHART # 7

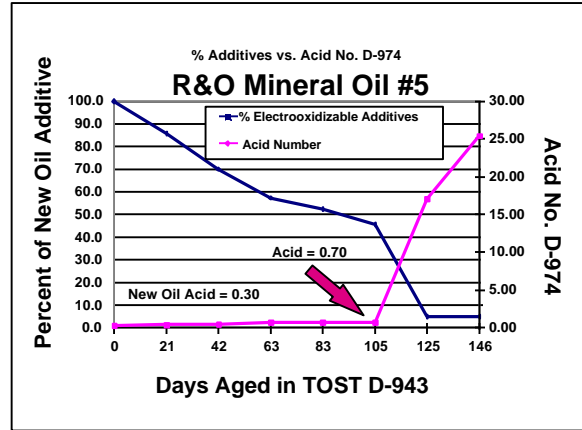


CHART # 10

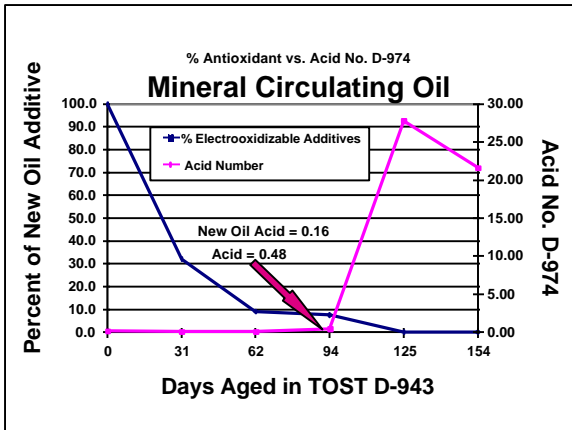


CHART # 8

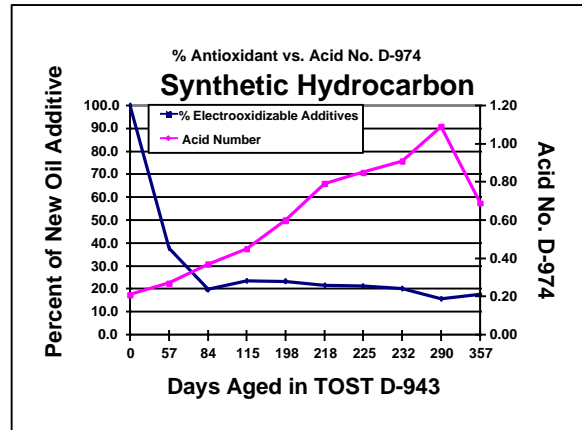


CHART # 11

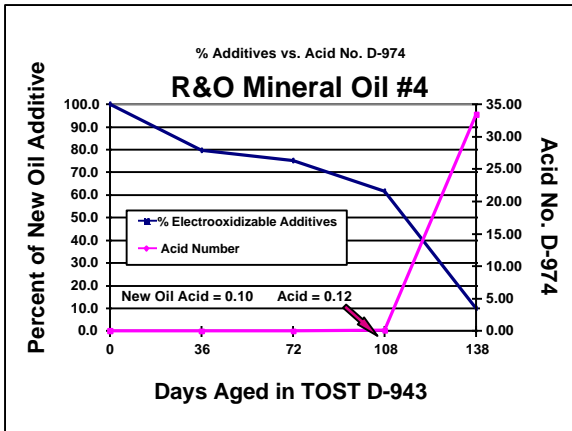


CHART # 9

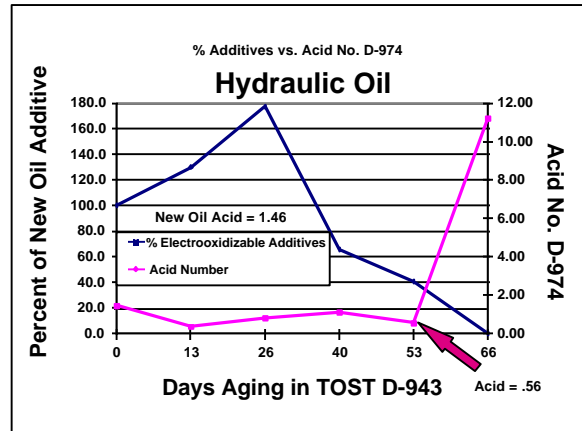


CHART # 12

**COMPARISON OF CHANGE TO ANTIOXIDANT ADDITIVES LEVELS
IN
INDUSTRIAL LUBRICATING OILS**

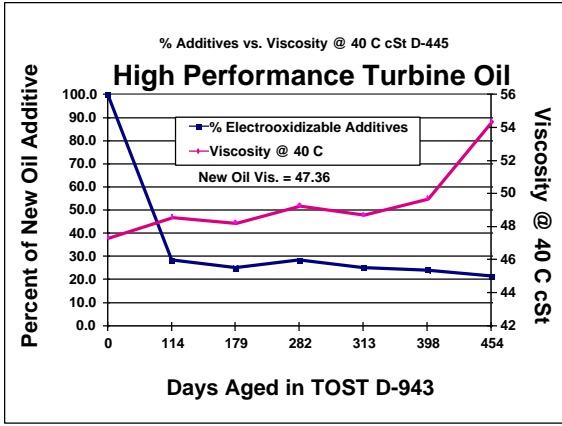


CHART # 13

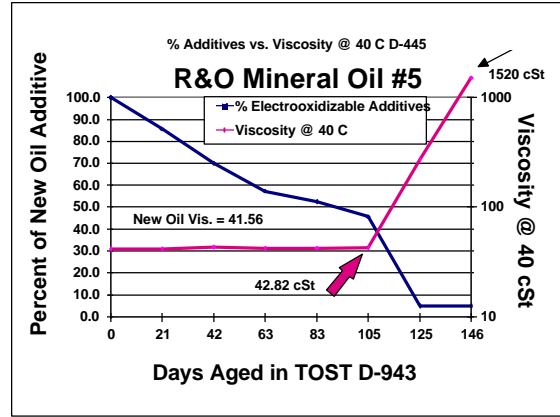


CHART # 16

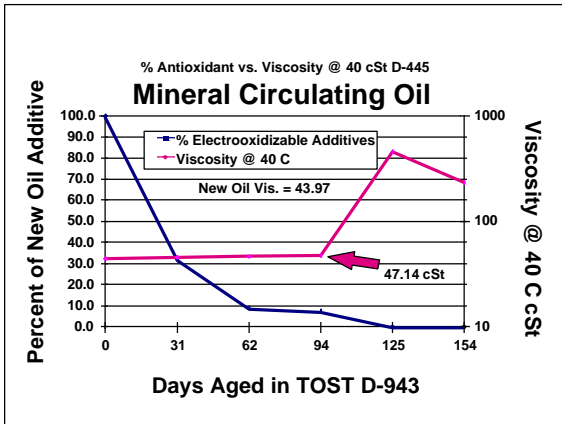


CHART # 14

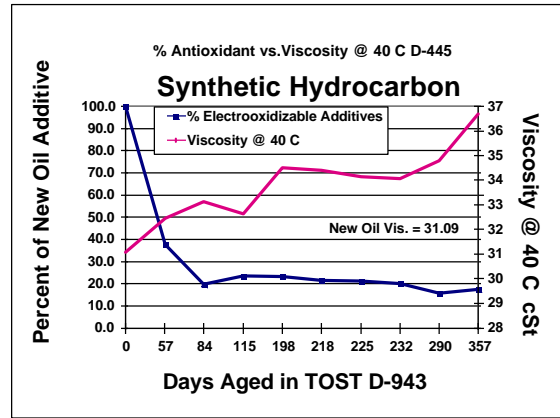


CHART # 17

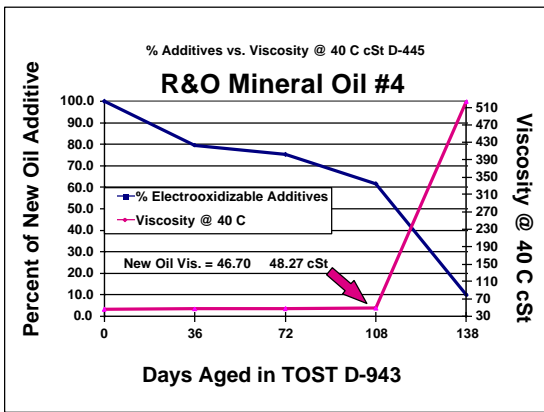


CHART # 15

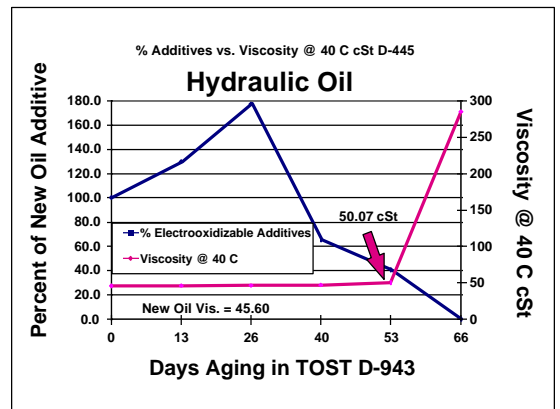


CHART # 18

Acknowledgment

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