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Title: Coking Tendency of Dielectric Fluids at Contact Surfaces – Phase I: Constant Current

Background: Field returns of mineral oil immersed switches show that carbon deposits can form on overheated electrical contacts by a process commonly called coking. Another process that takes place prior to coking is thermal cracking or the breaking up of larger hydrocarbon molecules into smaller ones. Some higher boiling materials are also produced. The smaller primary products react further in a variety of ways to eventually form coke. Thus, the formation of coke is step-wise and depends on a breakdown and a building-up process. The process depends upon the temperature at which thermal decomposition of the oil molecules takes place. Significant thermal decomposition could be expected at 340-370°C. Several characteristics of thermal cracking and coking are summarized. First, the terms are normally associated with petroleum-based oils and their inherent chemistry, so a review of their chemistry is warranted.

Today, transformer oils are vacuum distilled from both naphthenic and paraffinic-based crude stocks. The type of crude is based on the API Gravity of key fractions given by the U.S. Bureau of Mines. Naphthenic oils are derived from crudes with a very low content of straight chain saturated hydrocarbons (n-paraffins). Paraffinic oils contain substantial quantities of n-paraffins, also called waxes, which raise pour point temperatures and require removal. In general, the same types of compounds are present in all crudes, but vary in relative percentage and type of substitution on the ring structures. Table 1 shows the boiling ranges of distillates of both types, which are used to produce finished transformer oil.¹

Table 1: Comparison of naphthenic and paraffinic distillates boiling ranges.

	Naphthenic	Paraffinic
Initial boiling point, °C	271	239
5 % distilled, °C	283	306
50 % distilled, °C	330	372
95 % distilled, °C	384	419
Final boiling point, °C	429	531

Taken from Lipscomb, Mineral Insulating Oil Manufacture and Safekeeping, 1988, reference 1.

The composition of transformer oil is predominately saturated hydrocarbons with 15 to 30 carbons. Unsaturated compounds are kept to a minimum to improve the oils' stability and lower the tendency to form sludge. Aromatic hydrocarbons make up the remainder of the composition of transformer oil. Generally, the aromatics are substituted with alkyl groups and other ring structures. Transformer oils contain small amounts of other compounds, such as oxygen, nitrogen, and sulfur containing heterocyclics, which contribute to oxidative instability. Table 2 below summarizes the compositional breakdown of a naphthenic and a catalytically dewaxed paraffinic transformer oil.² The detailed results were obtained from mass spectrometric analysis.

¹ Erdman, H.G., Electrical Insulating Oils, ASTM STP 998, 1988 pps 5-24.

² Bartnikas, R., Electrical Insulating Liquids, ASTM vol III, 1994 pg 321

Table 2: Mass spectrometer analyses of naphthenic and paraffinic oils.

Hydrocarbons (% by weight)	Paraffinic Oil		Naphthenic Oil	
Total paraffins	80.3		70.6	
Iso- (branched)	23.0		11.4	
Cyclo- (naphthenes)	57.8		59.2	
1-ring	23.3		16.3	
2-ring	16.0		16.8	
3-ring	11.7		12.2	
4-ring	6.8		10.0	
5-ring	0.0		3.9	
6-ring	0.0		0.0	
Total aromatics	19.2		29.4	
Mono-	12.6		18.3	
alkylbenzenes	4.5		4.9	
naphthene benzenes	4.0		6.0	
di-naphthene benzenes	4.0		7.4	
Di-	4.8		8.7	
naphthalenes	2.2		4.1	
acenaphthenes, dibenzofurans	1.5		2.5	
fluorenes	1.1		2.1	
Tri-	0.4		0.7	
phenanthrenes	0.4		0.6	
naphthene phenanthrenes	0.0		0.0	
Tetra-	0.4		0.3	
pyrenes	0.3		0.1	
chrysenes	0.2		0.2	
Penta-	0.0		0.0	
Sulfur heterocyclics	0.8		1.2	
benzothiophenes	0.6		0.6	
di-benzothiophenes	0.1		0.6	
naphthene benzothiophenes	0.0		0.0	
Unidentified	0.2		0.2	
Polar compounds	0.0		0.0	

Table reproduced from Bartnikas, R., Electrical Insulating Liquids vol III ASTM, pg 321

Generally the thermal cracking process is initiated by high temperature and results in the breaking of a carbon-carbon or a carbon-hydrogen bond (homolysis) to form two fragments, each a free radical. The smaller hydrogen, methyl, and ethyl free-radicals are relatively stable compared to the larger radicals, which break down immediately to form an unsaturated compound (olefin) and a smaller, more stable radical. Free radicals are very reactive and propagate through a chain event, or are terminated by reacting with another free radical. The products of the free radical chain reactions are lighter, lower boiling unsaturated compounds, combustible gases, and additional free radicals.

The eventual coking results from polymerization of the unsaturated compounds (olefins) and condensation of aromatics. During these processes, compounds referred to as asphaltenes (aromatic tar) are formed, which become insoluble in the oil phase. This asphaltene rich phase has little or no abstractable hydrogens to propagate the free radical chain event. As a result, asphaltene free radicals combine to form high molecular weight and insoluble coke. The coking tendency increases with increased molecular weight of the oil and increased quantity of multi-ring aromatics and/or cyclic paraffinic compounds.

The degree of thermal cracking of oil and the eventual formation of coke are directly related to temperature and contact time. In a switch, the temperature of the metal conductor in contact with the oil, as well as the composition of the oil, will influence the coking tendency. Likewise, the element temperature of an immersion heater, used to heat fluid in a tank, will influence the breakdown of the fluid. This breakdown has been referred to as scorching. All the breakdown processes that take place at high temperature are commonly called pyrolysis. For the purposes of this and subsequent studies, the term coking will be used to describe the pyrolysis of a fluid and the formation of insoluble by-products from the fluid breakdown upon a metal contact or conductor surface.

Other possible mechanisms exist for the formation of insoluble deposits on high temperature contact surfaces, such as copper. Oxidation of copper metal to either of the oxides (I or II) is a function of time, temperature and concentration of oxygen. The prevalent oxide film formed up to 400°C is red Cu₂O, while at higher temperatures black CuO is formed.³ Copper reacts with hydrogen sulfide, which is released when oil containing organosulfur compounds, is thermally cracked to form the black sulfides CuS and Cu₂S. However, CuS decomposes at 220°C. As can be seen in Table 2, both naphthenic and paraffinic transformer oils contain about 1 % sulfur heterocyclics.

This project was initiated to derive a test procedure to measure the coking tendencies between various dielectric fluids at a high temperature metal surface. Since electric current was the source of heating to coking temperature, the electrical characteristics of the circuit were correlated with the coking observations and the temperature.

To accomplish the goal, phase 1 efforts concentrated on developing both a test apparatus and a test method. There were several key points that were important in test development. First, the design of the copper conductor or element had to allow for both a small bench top test and have sufficient visibility. Secondly, it was desired that the amount of time required to develop coking deposits would be within 8 hours. The above test criteria relies upon the available electric current, which was set at 150 amps in Phase I testing, and the cross-sectional area of the copper conductor, which was sized to carry the current. Together, the test variables required accurate control and measurement in order to compare each of the fluid's tendency to coke and form coke deposits.

Conclusions: The results obtained in this study demonstrate that a viable method to produce and measure coking deposits from various dielectric fluids was attained. The developed method used 150 amps of current applied across a standardized copper strip for a five hour time period. The coking tendency and thermal characteristics of five different dielectric fluids were studied. The results indicate that coking can be expected with any effective dielectric coolant if given enough time at high temperature.

The results show that Rtemp fluid produced the largest amount of coking deposits on a high temperature copper surface, while silicone fluid produced the least. The fluids listed in the order of decreasing coking tendency under the conditions used in this study are: Rtemp > mineral oil > E-200 > FR3 > silicone. The tendency of dielectric fluids to coke was due to a combination of factors that included temperature, time, chemical composition and thermal efficiency. If only the conductor temperature and the thermal efficiency of the fluid were responsible for coking, mineral oil would have the lowest tendency to coke, while Rtemp would have the highest. Using the average strip temperature to judge the cooling efficiency of the fluids, the fluids in the order of decreasing efficiency are mineral oil > E-200 > FR3 > silicone > Rtemp.

The results indicate that the chemical composition of a fluid is a key parameter as to its tendency to coke. Petroleum based fluids contain sulfur compounds that make up about 1 % of their composition. Analysis of the coking deposits showed a direct and positive correlation between quantity of coking deposits and the sulfur content of the deposits. The results suggest that the higher the sulfur content of a dielectric fluid, the greater the coking tendency at higher temperature. It is probable that there exists a threshold temperature for each fluid, at which point sulfur compounds convert from stable to reactive. The fluids listed in the order of decreasing tendency to coke based on chemical interaction with a copper strip are: Rtemp > mineral oil > E-200 > FR3 > silicone.

The chemical reactions between the high temperature copper strip and the various fluid components resulted in coking deposits on and around the strip. SEM/EDX showed that the deposits contained high concentrations of copper, thereby suggesting that copper base metal was both altered and depleted. This study measured the net change in strip resistance due to the combination of temperature and other factors. However, the reference resistance of the strip after the coking trials

³ Holm, R., Electric Contacts: Theory and Application, Springer-Verlag, NY, 1967 pp 112

was not measured, which could have indicated the extent of the change in cross-sectional area of the copper strip due to copper depletion. Future coking studies can be improved by incorporating this R_0 measurement into the procedure.

The results of this study showed that a copper conductor, under short term high current conditions, is not effectively cooled by silicone fluid and will open at a current at least 41 % lower than a mineral oil cooled conductor. In comparison, FR3, Rtemp and E-200 fluid cooled conductors opened with at least 14 % lower current than mineral oil cooled conductors.

Collectively, the results from the coking study showed that an FR3 fluid insulated conductor would generate less coking deposits, would maintain its integrity longer and would carry higher current than a silicone insulated conductor or at least as high as Rtemp and E-200 fluids. Thus, the results indicate that the coking tendency combined with the thermal capability of FR3 fluid is superior to E-200, mineral oil, Rtemp and silicone fluids.

Materials Tested & Purpose: The dielectric fluids evaluated in this study consist of 1) Petroleum based transformer oils, Equilon Diala AX and Ergon Hyvolt II, both naphthenic distillates. 2) Envirottemp FR3 fluid, a natural mix of fatty acid triglycerides. 3) Rtemp fluid, a petroleum based, heavy paraffinic distillate. 4) Envirottemp E-200 fluid, a synthetic, pentaerythritol ester of heptanoic and isononanoic acids. 5) Dow Corning Silicone DC #561 fluid, a polydimethylsiloxane. The fluids were new, freshly degassed and dried in all cases. Certain fluids were tested in a used and unprocessed condition. The fluids were tested under an air and a dry nitrogen headspace.

The electrical conductor material consisted of electrical tough pitch (ETP) copper strip (CDA 110) with dimensions of 0.003 in. thick x 0.187 in. wide (0.00762 cm x 0.475 cm), and cut to lengths of approx. 3 in. A fixture was used to punch holes at both ends of the strip, to allow for placement into a mica holder containing two threaded studs. The effective distance between current and voltage carrying leads was 1.97 in. (5 cm). The cross-sectional area (thickness x width) of the strip was 0.000561 in² (0.00362 cm²). The complete test set-up with a close-up of the copper strip under FR3 fluid is displayed in **Figure 1**.

The purpose of the phase I work was to develop a test method to evaluate the coking tendency of various dielectric fluids used to insulate and cool an energized copper strip. Furthermore, measurement and comparison of the coking deposits and the copper strips was desired to assess the relative tendency of dielectric fluids to form deposits on or react with hot conductor surfaces.



Figure 1a: Coking tendency test set-up.

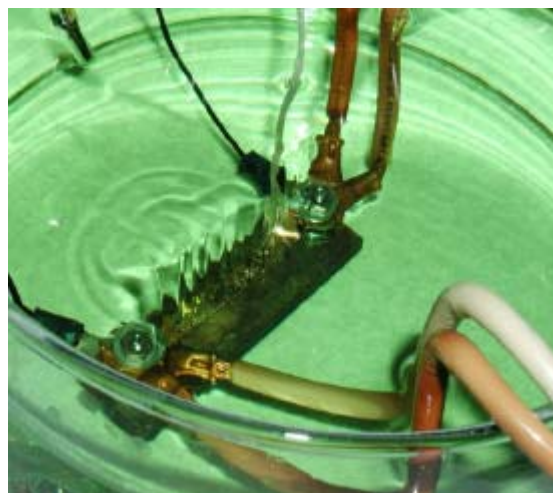


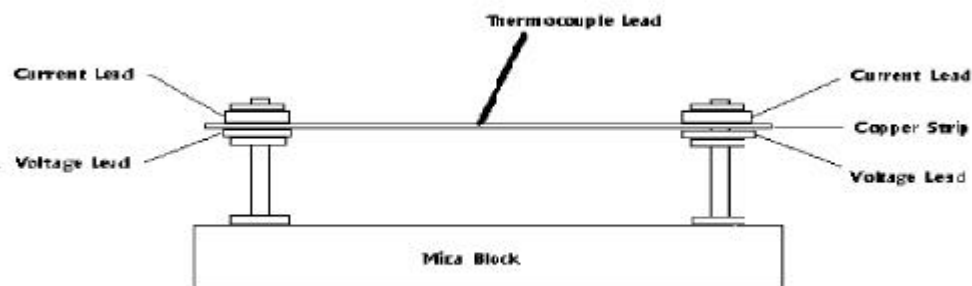
Figure 1b: Energized Cu strip in mica fixture.

Methods Used: The equipment and specifications used to construct the test set-up shown in **Figure 1** are summarized in **Table 3**. Additionally, the pyrex crystallizing dish of fluid was placed in an ice bath in order to cool the oil below its flash point. Even in an ice bath, the fluid temperature increased to between 80 and 140°C depending on the fluid type.

Table 3: Equipment and Specifications used for Coking Tendency Testing

Item	Description
Test vessel	Pyrex crystallizing dish #3140, 170 x 90 size, about 2 liter volume
Ice bath	Aluminum pan 9 in. x 13 in.
Current transformer	120/5 volt, 250 amps output
Current shunt	R = 0.000668 ohms
Current leads (doubled 20 inch long)	#8 AWG 600v type MTW or THHN or THWN
Variac	0 to 140 v
Voltage leads	22 AWG
Multimeters	Fluke models 85 and 87III
Thermocouple meter	Fluke model 52 type K
Hg thermometer for oil	ASTM 1C, 76mm
Strip holder	Mica block 2.75 in. x 0.75 in. x 0.25 in. thick
Strip	ETP Copper CDA 110, 3 in. x 0.187 in. x 0.003 in. thick

The copper strip was connected in a studded mica test fixture per the diagram in **Figure 2** below. The voltage leads were placed directly under the strip, while the current leads were placed directly on top of the strip, both at the studs. The leads were in direct contact with the strip and were attached to the studs with steel washers/nuts. A type K thermocouple was set on top of the middle of the strip using the springiness in the thermocouple wire to apply a slight downward force. The thermocouple wire was clamped above the strip.

**Figure 2: Copper strip test fixture**

Coking Tendency Procedure

- 1) Place 0.187 in. x 0.003 in. copper strip stock in hole punch fixture and punch a 1/8 in. hole at each end, about 1.97 in. (5 cm) apart.
- 2) Weigh and record strip mass to 0.00001 g.
- 3) Obtain resistance of strip with an ohmmeter by placing Kelvin clips across strip over the holes.
- 4) Assemble coking fixture at each stud (4-40 x 1 in. machine screw) by placing down in order the nuts, washers, voltage leads, copper strip, double current leads, washers, and tightening nuts. (Note: Double current leads are already attached to transformer).
- 5) Place connected coking fixture in crystallizing dish, which is to be placed into ice bath pan, and set thermocouple on top of the center-most spot on the copper strip using flex bend to apply down force.
- 6) Add 1500 ml of selected fluid (new, vacuum degassed/dried or used) to crystallizing dish.

- 7) Add water and ice to ice bath pan surrounding the dish.
- 8) Lower Hg thermometer into top layer of fluid.
- 9) Lower small hood over experimental set-up if using nitrogen blanket and start gas flow.
- 10) Turn on all meters, variac, and adjust current to apply 150 amps continuous (use clamp-on CT).
- 11) Verify current by recording voltage across shunt and divide by the shunt resistance (0.000668 ohms).
- 12) Apply current for five hours (300 min) continuous.
- 13) Record elapsed time, CT current, shunt voltage, strip voltage, K-type thermocouple, top oil temperature, and any observations made on the condition of the strip.
- 14) Take readings immediately after starting coking experiment and after 1, 5, 10, 20, 30, 60, 100, 120, 140, 160, 180, 200, 220, 260, 280, & 300 minutes of operation.
- 15) Add ice when necessary and record additions on log.
- 16) After 5 hrs completion, allow fluid and strip to cool, then carefully remove the fixture from the fluid bath and carefully disassemble fixture.
- 17) Place copper strip in small beaker of degreasing solvent (heptane) to collect any dislodged particles.
- 18) Weigh final mass of strip and add any particle weight, filtered from the solvent, to the weight of the strip. (Note: if particles dislodged into the fluid, the fluid requires filtering and the particle weight from the fluid will be added to the strip weight).
- 19) Calculate weight of coking deposits or loss of strip mass.
- 20) Verify composition of coking deposits by SEM-EDX.

Multiple coking experiments were performed with each fluid using a new copper strip and fresh fluid for each experiment. In most cases the fluid was new, dried and degassed, but used FR3 fluid and used mineral oil (not dried or degassed) were studied. Headspace atmospheres of room air and dry nitrogen were also compared for each fluid type.

The CDA 110 copper strips used for the coking work are specified as 99.90 % min copper + silver with some sulfur and oxygen listed as impurities. A copper strip was analyzed for sulfur content using a Leco Analyzer.

Strip Temperature Measurement

The development of a procedure to measure the coking tendency of a fluid upon a metallic conductor or contact requires a means to accurately measure the temperature of the conductor over a wide temperature range. The fact that the coking procedure is accomplished under nonequilibrium conditions, coupled with probable depletion and alteration of the metallic conductor by oxidation and other reactions with the fluid and fluid by-products, adds several degrees of difficulty and uncertainty to the temperature measurement procedure. It was a relatively straightforward task to produce and measure coking deposits on a metallic contact. However, a viable method for producing coking by-products from differing fluid compositions required an understanding of the temperature at which it happens and why it happens. Four methods to measure the strip temperature were investigated and are described below.

1) Thermocouple Procedure: A thermocouple wire placed down lightly on the strip to measure the strip temperature is not accurate. The thermocouple tends to get displaced or lifted slightly during the violent boiling of the fluid at the hot strip surface. To remedy this, the thermocouple was epoxied to the strip. The epoxy did not adhere after the strip temperature increased and after the oil began to boil. Using a plain or epoxied thermocouple to measure the strip temperature is not accurate under the conditions used for the coking study, however the thermocouple readings were recorded to show the large temperature gradient that existed near the strip surface.

2) Linear Temperature Coefficient of Resistance: The strip temperature was calculated using the average temperature coefficient of resistance (TCR) of CDA 110 copper (100% conductivity), which is 0.00393 per degree C (at 20°C) within a fairly linear temperature range of -100 to 200°C. For many engineering calculations, this method is adequate. However, the 1000°C temperature range required for the coking study demanded a more rigorous technique where the TCR and resistance function with higher temperatures becomes increasingly nonlinear. The nonlinear TCR method will be explained in the next section. Either TCR calculated method gives the average

temperature of the entire cross-section of the strip. It is based on the change in resistance of the metal conductor with change in temperature. The formula to calculate the temperature from the measured resistance, using an average TCR that is based on a narrow and somewhat linear temperature range is:

$$\frac{R - R_o}{R_o} = \alpha_o(T - T_o) \quad , \text{ which converts to } T = \frac{(R - R_o)}{\alpha_o(R_o)} + T_o$$

where α_o is the temperature coefficient of resistance at the reference temperature T_o , R is the resistance at temperature T ($^{\circ}\text{C}$), and R_o is the resistance at the reference temperature T_o ($^{\circ}\text{C}$). The reference resistance of each copper strip was measured at room temperature with an Electro Scientific Industries ohmmeter 1701B using Kelvin clips. The clips were attached across the strip at the two holes made to fit over the studs.

The coking strip temperatures, calculated from the above equation using the linear TCR value ($0.00393/^{\circ}\text{C}$), are included in the results of this report to show the inaccuracy that is obtained when applying the linear equation over a wide range of temperature.

3) Nonlinear Calculated TCR from Theory: Over wide ranges of temperature, the linear relationship of the above formula is not applicable. In addition, as the temperature increases, the dimensions of the copper strip change, which changes the absolute resistance of the strip. To account for the nonlinear changes in the TCR values, resistances and dimensions over the wide temperature range encountered in this work, a multi-step procedure was developed. This procedure uses a series of equations to calculate changes in TCR values, dimensions and resistances with increasing temperature to 1000°C . The relationships were derived and reported by J.H. Dellinger in NBS Bulletin vol 7, 1911, pp 71 to 101⁴. Dellinger's work was done in the linear temperature region between 20 and 100°C , thus the equations were intended for use in this temperature range. None the less, the equations gave a means to calculate new TCR values and resistances of copper at any temperature and any percent conductivity. Plots of this data versus temperature and calculation of the resulting non-linear regression equations gave a method that could finally be used to calculate a reasonably accurate strip temperature. However, it should be noted that as the temperature of copper rises to an increasingly non-linear portion of the curve, the calculation of the Cu strip temperature from its resistance and TCR becomes less accurate.

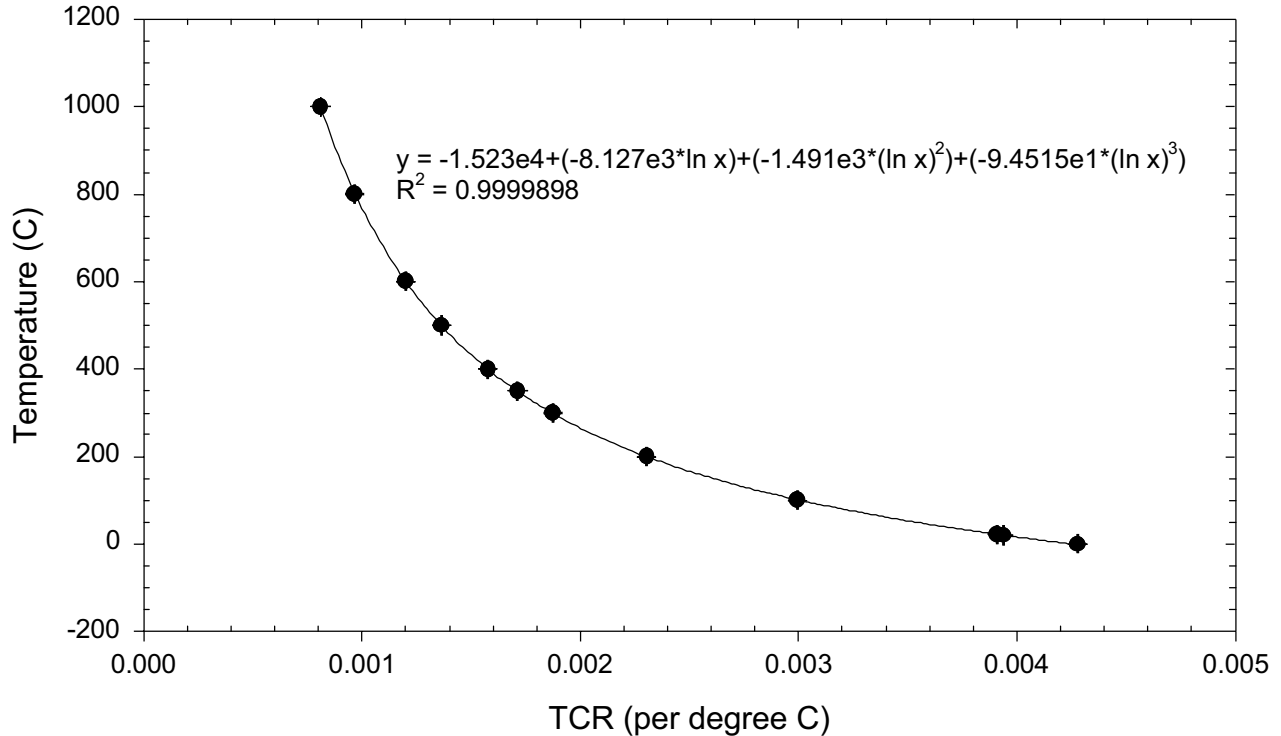
The TCR was calculated at each 100°C interval up to 1000°C with the following relationship:

$$TCR(t) = \frac{1}{\frac{1}{n(0.00394)} + (t - 20)}$$

n = decimal equivalent of the conductivity of the Cu metal used (e.g. 100% conductive Cu = 1.0) and t = the new temperature. The TCR was plotted versus temperature in $^{\circ}\text{C}$ up to 1000°C . The plot follows as **Figure 3**, which displays the equation of the non-linear function.

⁴ Dellinger, J.H., "The Temperature Coefficient of Resistance of Copper" NBS Bulletin vol 7 1911, pp71-101.

Figure 3-TCR vs Temperature of Copper Strip

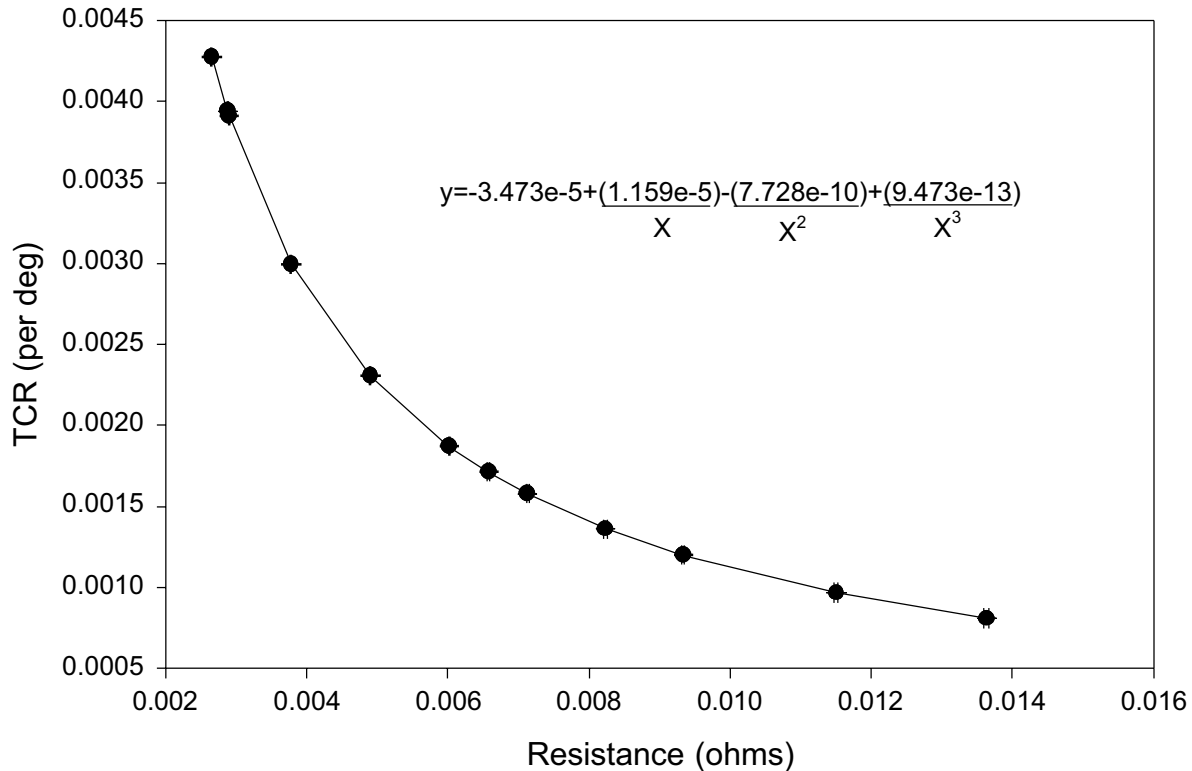


The resistance of copper (C=100%) was calculated at each 100°C interval up to 1000°C using an equation from the NBS document. The calculated resistances were adjusted with a dimensional change factor that compensates the resistance for the thermal expansion of the metal at high temperatures. The coefficient of thermal expansion (CTE) at each temperature was obtained from the Metals Handbook 9th Edition, vol 2, 1979. A plot of the CTE versus temperature is attached to this report in the appendix. The resistance of the copper strip at each temperature was calculated with the following equation.

$$R_t = (R_{t=22C} (1 + TCR_{t=22C} [t - 22])) \times \left(\frac{1}{(1 + [CTE \times t])} \right)$$

The reference temperature for the above equation was 22°C and t = the new temperature. The calculated resistance at each temperature was plotted versus the calculated TCR at each temperature to derive an equation. This equation, combined with the equation from Figure 3, was used to calculate the strip temperature from the observed resistance. It should be mentioned that this equation assumes that the change in strip resistance is due to strictly temperature and CTE, not cross-sectional area change of the strip due to alteration of the copper. The plot of resistance versus TCR is shown in **Figure 4** below:

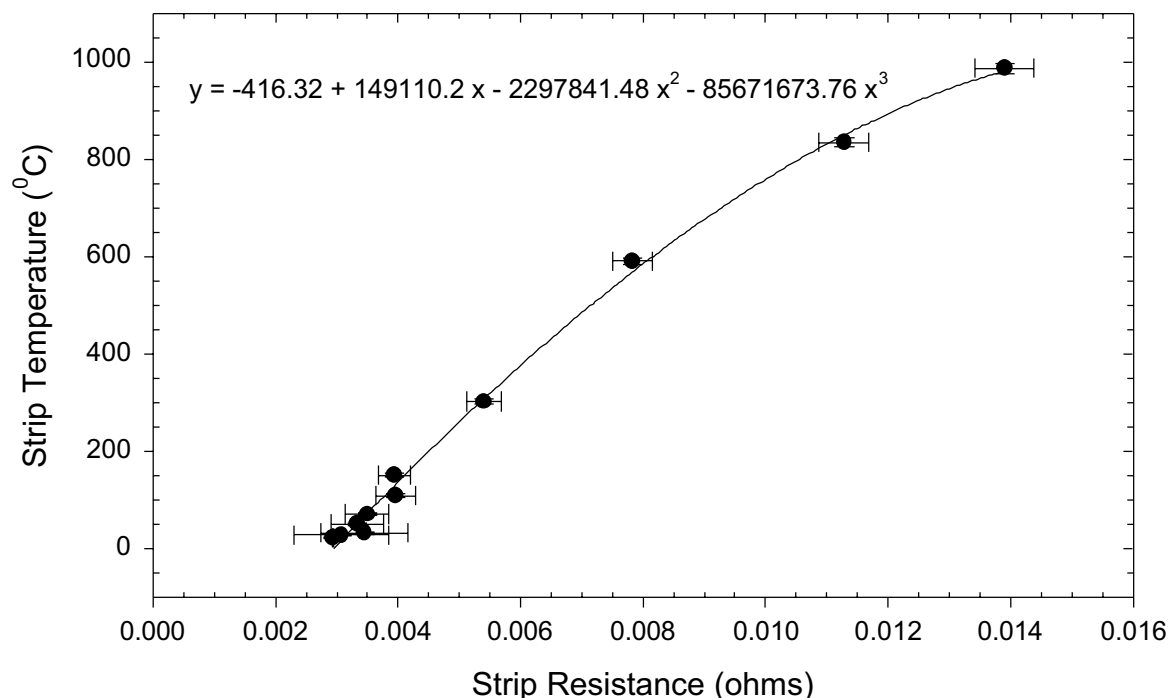
Figure 4 - Resistance vs TCR of Copper



4) Ceramic Embedded Thermocouple Model: The optimum method to determine the strip temperature from observed resistance readings was to first develop a model. A typical copper strip, as used for all the coking experiments, was connected in the cell as explained previously. A micro-thermocouple (Omega #CO2-K) was set into a tiny bead of Omega CC high temperature ceramic cement placed at the center-most spot on the copper strip. Care was taken that the metal thermocouple was not in direct contact with the surface of the copper strip. The high temperature cement was a two part mixture; 3 parts of powder to 1 part liquid binder. The cement was cured for 24 hours at room temperature. The cell was connected to the coking circuit and current was applied to the strip in small increments in air. The voltage and current across the strip were recorded, as well as the temperature of the strip via the K-type micro-thermocouple. The resulting strip resistance, which was calculated from the applied current and voltage, versus the measured temperature of the strip in air became the thermal model for all the coking experiments. A second thermal model was built and tested for verification. The resistance versus temperature was measured up to the melting point of the copper.

The strip resistance versus the strip temperature of the model was plotted and a relationship was determined. The graph containing the function ($R^2=0.99706$) is displayed below as **Figure 5**.

Figure 5
Calibrated Coking Strip Resistance versus Temperature

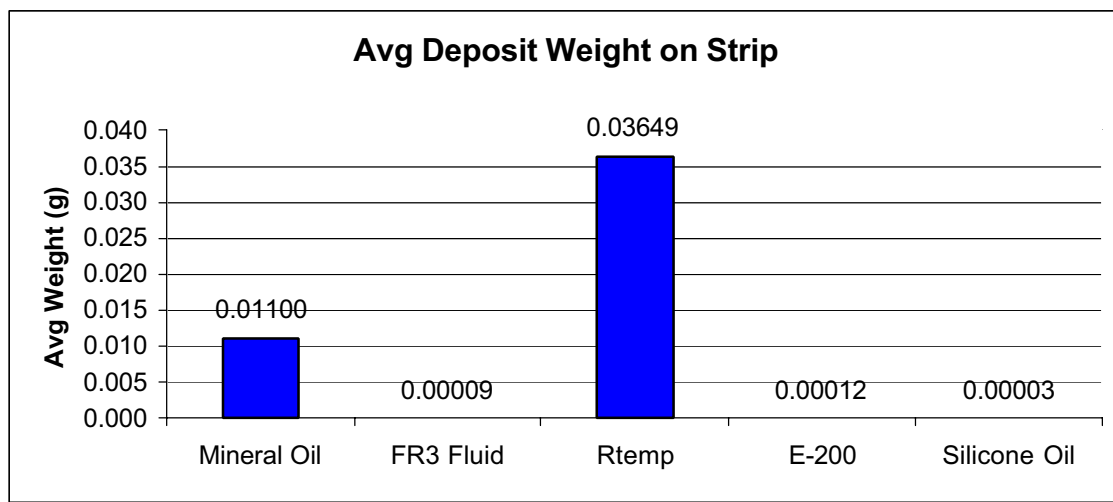


Current vs Resistance (Temperature) of Coking Strip

The resistance of a coking strip with varying current was measured to study the cooling characteristics of mineral oil, FR3 and silicone fluids and to record significant observations at the strip/fluid interface. The measurement and observations were important to not only determine the strip temperature with varying current, but to develop an understanding of the physical phenomena that influence electrical conductors in various dielectric fluids.

The coking fixture was assembled per the procedure above and the strip was placed into 1500 ml of fluid. No ice bath was used. The strip voltage, shunt voltage, K-type thermocouple reading, and top oil temperature were recorded at every 5 to 10 amp interval from about 90 amps up to the maximum capacity of the transformer, or until the strip opened. At each interval, the current was applied, the above readings were recorded, then the strip was allowed to equilibrate at 0 amps applied for ~20 sec. Changes in the strip appearance and observed changes at the strip/fluid interface were noted. The data was used to plot applied current versus strip temperature, where the strip temperature was derived from the thermocouple model detailed in (4) above. The strip temperatures were also calculated by the methods detailed in (2) and (3) above and are included for comparison.

Results & Discussion: A summary of the experimental results for the coking tendency of dielectric fluids on a copper strip surface is compiled in **Table # 4** in the appendix. The results show that the dielectric fluids derived from petroleum crudes, such as Ergon II transformer oil and Rtemp fluid, produce the greatest amounts of coking deposits on an electrically heated copper strip. **Figure # 6** below compares the average weight of the coking deposits from each of the five fluids studied. Figure # 6 is also included in the appendix.

Figure 6 – Coking Deposits after 5 hrs at 150 amps

Rtemp fluid and mineral oil produced the greatest quantity of deposits on a heated strip, amounting to 122 and 405 times the quantities produced by FR3 fluid respectively. For Rtemp, the high amount of deposits correlate with the highest average strip temperature over the five-hour length of the test. The results show that Rtemp was the least efficient coolant that was tested. The average strip temperature in Rtemp was above the observed average 679°C boiling temperature of the fluid at the strip interface.

Mineral oil was the most efficient coolant tested with an average strip temperature of 353°C, slightly below an observed boiling temperature of 366°C. However, the comparatively reduced strip temperature in mineral oil was still beyond the temperature at which coking occurred. Petroleum-based oils are known to coke at 340°C.⁵ The four mineral oil trials showed that there was a high negative correlation between average strip temperature, total energy, and coking deposits with the initial weight of the copper strip. There was variability in the weight of the copper strips in all fluids, which caused some scatter in the total energy and temperature. Each strip was cut to an approximate length after the holes were punched with a die. The method could be improved by maintaining a closer tolerance on strip length and distance between the holes.

In plots of the measured strip resistance over time in the appendix, the copper strips in both mineral oil and Rtemp were in thermal run-away. **Figure # 7** for mineral oil and **Figure # 9** for Rtemp fluid display both the increasing resistance and temperature over the five hours of coking time. The strip resistance in Rtemp increased about 58 % compared to about 9 % in mineral oil. The large difference in the percent increase in resistance between mineral oil and Rtemp fluid can be partially explained by the quantities of coking by-products adhering to the strips. The coking deposits act as thermal insulation around the strip. The high levels of copper in the deposits indicate that copper depletion of the cross-sectional area of the strip is another contributing factor to changes in strip resistance. The total energy plots, shown in the appendix as **Figure # 8** for mineral oil and **Figure # 10** for Rtemp fluid, help explain the variability in the resistances and temperatures between the individual trials for each fluid. For example, the high total energy of the strip in Trial # 22 for Rtemp fluid, which opened after 130 minutes at the lead connection, showed the steepest increase in the measurements. The data suggests that the lead connection was faulty.

In direct contrast to the petroleum oils, both natural and synthetic ester-based fluids and silicone oil had a significantly reduced tendency to coke. In fact, in three out of seven trials in **Table # 4** with ester-based fluids, the copper strips contained no coking deposits and actually lost weight. With silicone fluid, there was a slight weight

⁵ Schabron, J.F., Characterization of Residua During Pyrolysis, Petroleum Chemistry Div. Preprint, 2002, 47(1), 17-21.

gain, but the strips appeared shiny and new looking. The strips from the silicone trials were not observed under a microscope. For purposes of cooling efficiency, the esters and silicone fluid fell between mineral oil and Rtemp as follows:

Most efficient coolant: mineral oil > E-200 > FR3 > silicone > Rtemp least efficient coolant

The average strip temperature in silicone fluid was higher than the observed 577°C boiling temperature at the surface of the strip. There was no observed boiling at the surface of the strips in either E-200 or FR3 fluids during the experiments with constant 150 amps applied. The average temperature of the strips in FR3 fluid was 540°C and the resistance was fairly stable over the five hours of the test. The average temperature of the strips in E-200 fluid was 471°C and the resistance actually decreased about 9 % from start to finish. The resistance measurements have a 2 % RSD. The strip resistance and temperature plots with coking time for FR3, E-200, and silicon fluids are located in the appendix as **Figures 11, 13, and 15** respectively. The total energy plots of each fluid follow the resistance plots as **Figures 12, 14 and 16** respectively.

Figure 17 in the appendix is a photo summary of several coking strips after individual trials in each of the fluids. The trials done under an air blanket were compared to those done under a nitrogen blanket. There was no correlation found between either an air or a nitrogen blanket and coking deposits. The coking deposits were analyzed for the elemental composition using SEM-EDX. A summary of the elemental composition of the coking deposits is listed in **Table # 5** in the appendix. All the trials in mineral oil, FR3 and Rtemp fluids are compared to the coking deposits from a 17- year old LTC, which was removed from a mineral oil transformer that was retrofilled with FR3 fluid (minimal effort unit). Large chunks of black coke were adhering to the LTC at the location of a copper contact that was completely burned and eroded away. The results show that the LTC coking deposits contain a high carbon and oxygen content. A comparison of the carbon to oxygen ratio of the coking deposits indicates that the coking deposits from the trials in mineral oil have about the same ratio as the actual coke from the LTC.

The results in **Table # 5** show that all fluids, except silicone fluid, have at least some tendency to coke. This was suggested by the carbon level of the coking deposits removed from each of the strips. Even though the ester fluids showed a low tendency to coke, deposits will build up over time if the condition of high temperature is present. A close-up comparison of the coking deposits from the strips in mineral oil and FR3 fluid are highlighted in **Figures # 18 and # 19** in the appendix. These photos gave a good perspective as to the condition of the strips at 10x magnification. The photos were obtained from the same general location on the strips.

The coking deposits from mineral oil and Rtemp fluid contained a high sulfur content. Even the deposits from E-200 fluid contained high sulfur. The results indicate that there is a close correlation between high amounts of coking deposits and high sulfur. **Table # 2** shows that both paraffinic and naphthenic oils contain about 1 % sulfur compounds. A Leco analysis of the copper strip base metal showed that the CDA 110 copper contained 17 ± 6 ppm sulfur. There is no doubt that some of the sulfur originates from the base metal of the strip, but the amount is low and should be nearly constant throughout the study. The high temperatures generated at the strip surface cause sulfur compounds to become reactive, which helps to produce coking deposits. It is also likely that reactive sulfur compounds destroy the metal conductor surfaces, which promotes the run-away resistance and temperature condition displayed in **Figures # 7 & # 9** for mineral oil and Rtemp fluid. The strips that were energized in mineral oil in particular were observed to delaminate, peel and self-destruct. It is probable that oxidation processes are also responsible for the overall poor condition of the copper strips in mineral oil. **Figure # 21** in the appendix displays photomicrographs of a copper strip energized in mineral oil and one in FR3 fluid. The strip after an experiment in mineral oil is at the top and shows the poor condition of the conductor near the end of the strip. The bottom photo shows the strip to be in good condition after Trial # 17 in FR3 fluid. It is interesting to note that the black particles near the edge of the strip from Trial # 17 consisted of about 60 % carbon, 7 % oxygen, 1 % sulfur and eight other elements.

The coking deposits generated from Rtemp fluid were unique in that they were fibrous in nature and not typical particles. SEM photomicrographs of the deposits from Rtemp Trials # 21 & 23 are shown in **Figure # 20** in the appendix. The 700x photos show how coiled and fibrous the Rtemp deposits are. This condition was not observed with any of the other fluids tested. A 10x photo is also shown, which displays the overall deposit loading on the two

strips. There exists evidence in the literature that coke formation is triggered by liquid-liquid phase separation of asphaltene rich cores.⁶ This asphaltene rich phase is present as spherical liquid crystalline coke, which remains liquid enough to be thrust or spun into fibers. The overall process is caused by thermal cracking and insolubility at high temperatures.

The coking strip after Trial # 28 in E-200 fluid was the only strip in E-200 fluid that contained deposits. The other two strips actually lost weight and were not looked at under a microscope. The deposits that formed on the strip after Trial # 28 were concentrated in dark blotchy areas. Under the microscope, these areas contained a large number of circular pits with particles condensed around the perimeter of the hole. **Figure # 22** in the appendix shows both a 10x mag photo of the overall area and a photomicrograph from the SEM at 150x magnification. An elemental analysis using SEM-EDX of the hole showed about 87 % copper, 2 % carbon, 9 % sulfur, 2 % tin and minor amounts of oxygen, silicon, iron and zinc. The observed pitting and observed particle distribution were unique to E-200 fluid in Trial # 28. The results suggest that the level of sulfur from either the copper strip, the synthetic ester E-200 fluid or both, under high thermal conditions, caused pitting and erosion of the copper conductor. However, the results could not be verified since the other E-200 coking strips were not analyzed. It is shown that in Trials # 29 & 30, the net effect of coking was loss of strip weight, but the discoloration on the strips, as shown in **Figure # 17**, leads to the conclusion that deposits were produced from E-200 fluid.

Figure # 23 in the appendix displays a graph of applied current versus strip temperature for mineral oil, FR3 fluid and silicone oil. In this separate experiment, the current was applied incrementally from about 90 amps up to the capacity of the current transformer. A comparison of the plots shows the relative cooling capacity of the fluids at high currents. Silicone oil was not able to cool effectively beyond 160 amps, while FR3 fluid maintained cooling to 240 amps, after which, the strips opened. Rtemp and E-200 also maintained effective cooling to about 240 amps before the strips opened, however these were not incrementally plotted. The results with silicone fluid were verified by a second run which again showed the strip opening at greater than 160 amps applied. Mineral oil maintained cooling throughout the range of the current transformer. Each of the plots show an inflection point where the rapidly rising temperature of the strip levels off. The inflection points correspond closely with observed bubbling at the surface of the strips in this experiment. It is most likely that the inflection point of each of the three curves defines the boiling points of the fluids. The boiling temperatures obtained from the plots in **Figure # 23** are close to those observed during the individual coking trials summarized in **Table # 4** for mineral oil and silicone fluid. There was no observed boiling of the FR3 fluid during the constant current trials detailed in **Table # 4**.

The data that was plotted in **Figure # 23** is summarized in **Figure # 24** for mineral oil, **Figure # 25** for FR3 fluid and **Figure # 26** for DC 561 Silicone fluid. These data summaries show the range of temperatures calculated from the different methods detailed as (2), (3) and (4). The temperatures highlighted in green were calculated from the thermal model as described in method (4) and were used for the plots in **Figure # 23**. A comparison of the temperature data from the three calculation methods shows that the thermal model of (4) predicts temperatures between the two other methods. In general, using the linear TCR (0.00393) method (2) predicts strip temperatures nearly 100 or more degrees low.

The calculated errors in metering at higher currents of 90 amps and above were reasonably low at 2 to 3% RSD. However, at lower currents from 5 to 50 amps, the metering errors became unreasonable with RSD's near 50 % at 5 amps. Any data that was generated at lower currents was deemed unreliable and was not used. Future work at lower currents will require improved metering methods. This would also help to improve the thermal model of the strip that will more accurately predict strip temperature.

⁶ <http://www.solublesolutions.com/ResTutorial.html>, Resid Conversion Tutorial, 7/11/2002

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Key Terms:

1822	Coking
789	Degradation/ thermal
1427	Envirotemp E-200 Flui
1850	Envirotemp FR3 Fluid
69	Oxidation
441	Polymerization
1388	Rtemp Fluid
778	Resistivity/ electrical
1261	Silicone Fluid
262	Sulfur Content
972	Temperature/ measurement
357	Thermal properties
1440	Oil/ mineral

Figure # 6

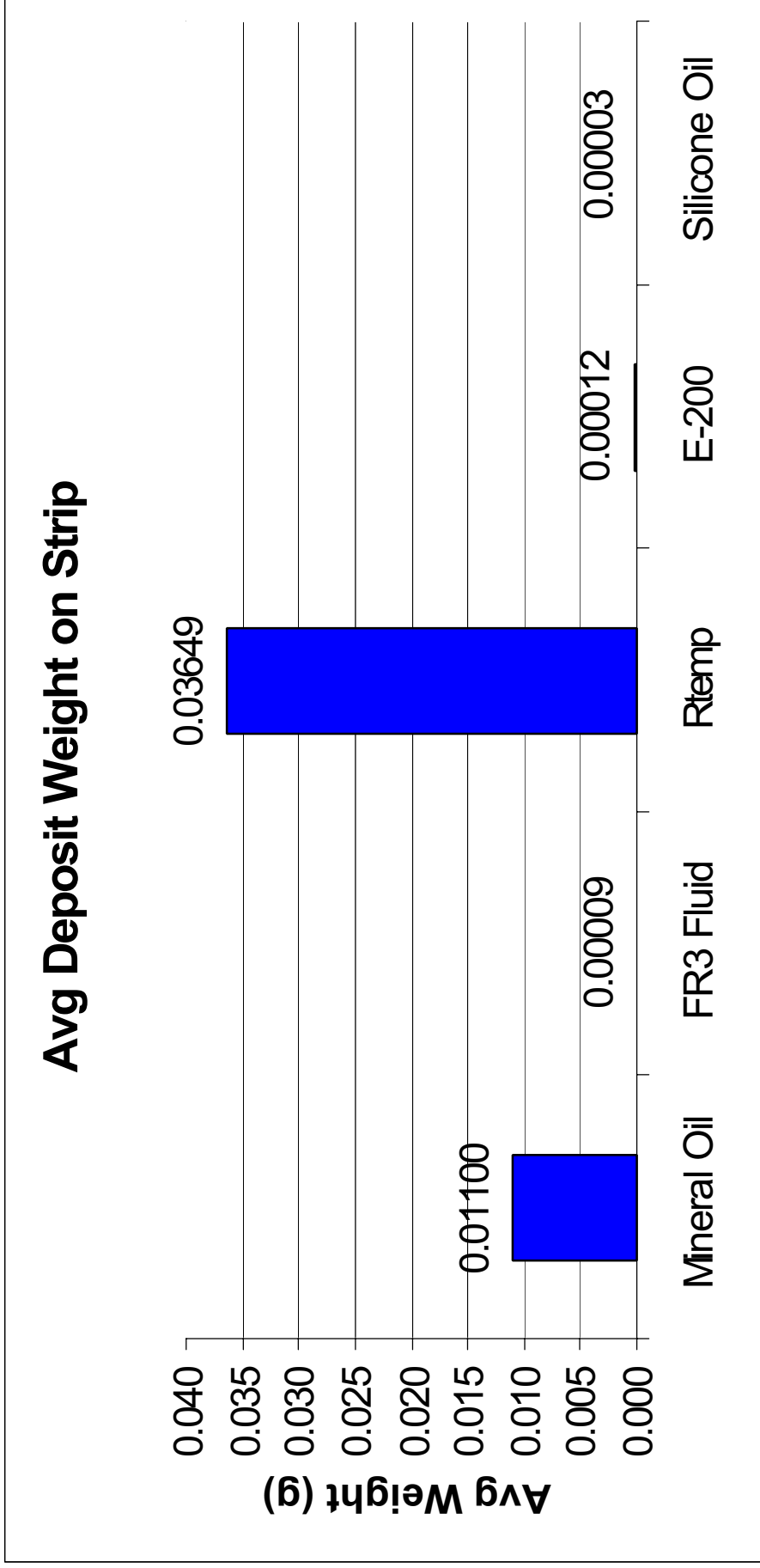


Figure # 9

Copper Strip Resistance and Temperature in RTemp with Coking Time

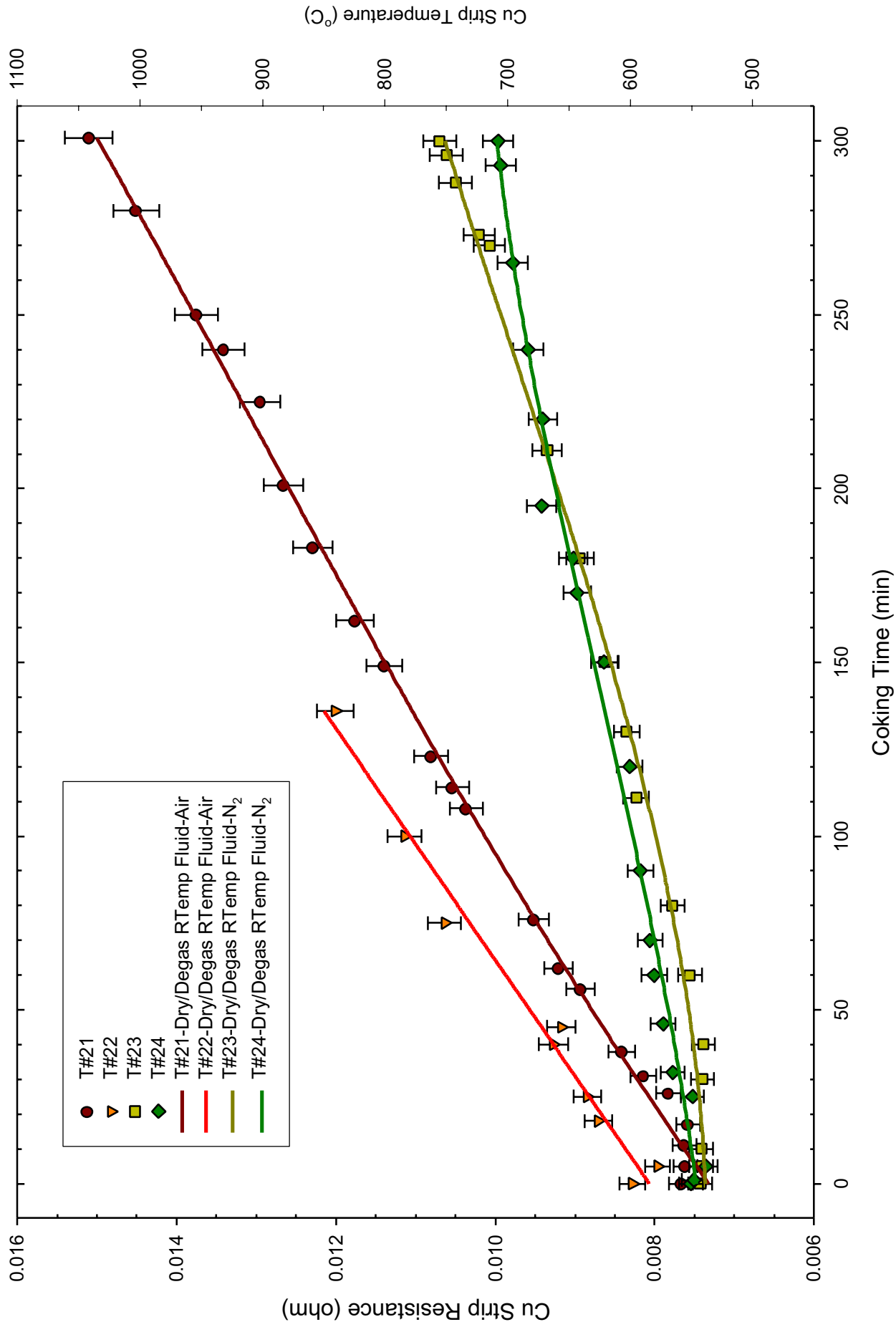


Figure # 10

Total Energy Dissipated by Strip in RTemp with Coking Time

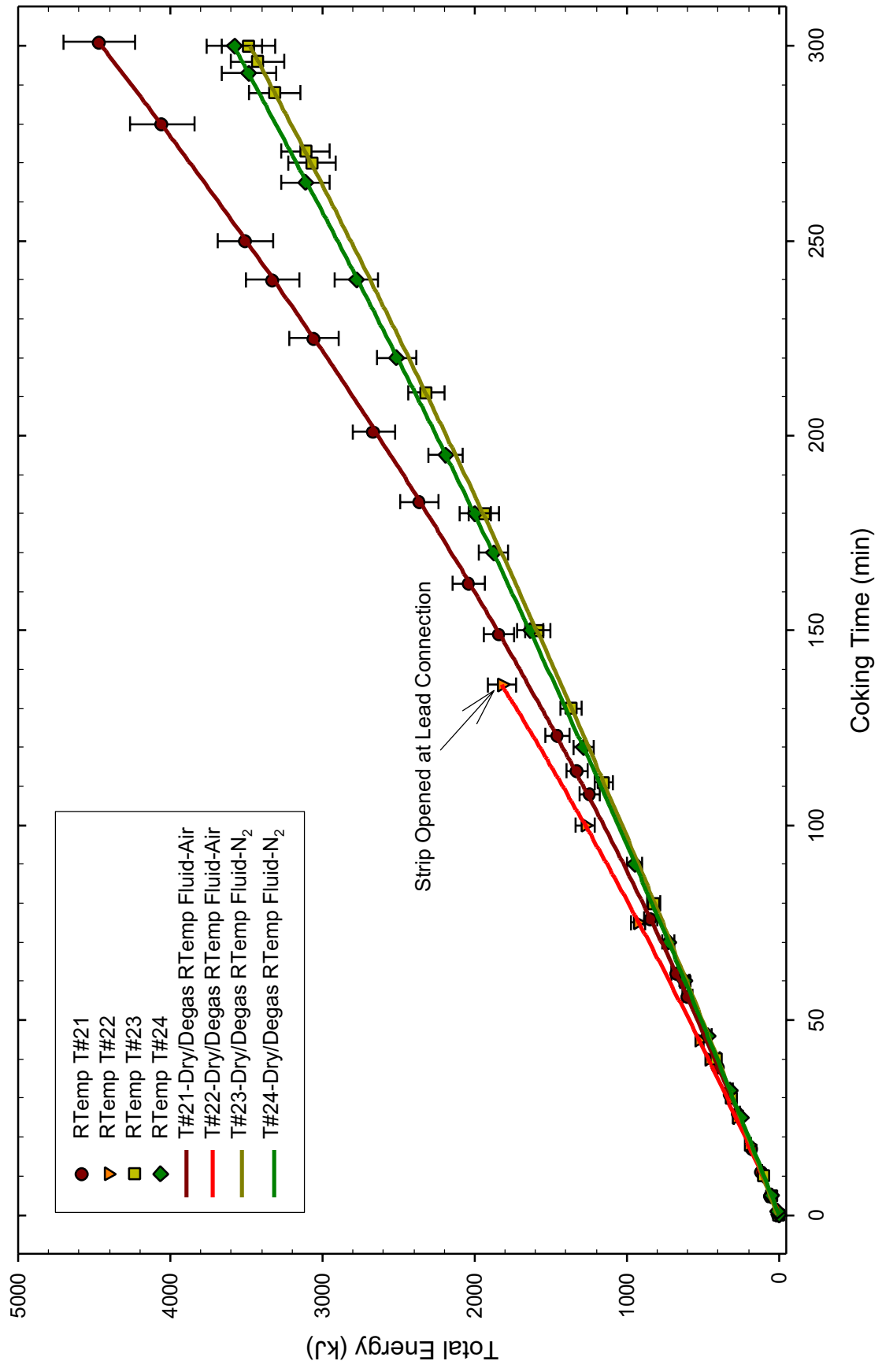


Figure # 11

Copper Strip Resistance and Temperature in FR3 Fluid with Coking Time

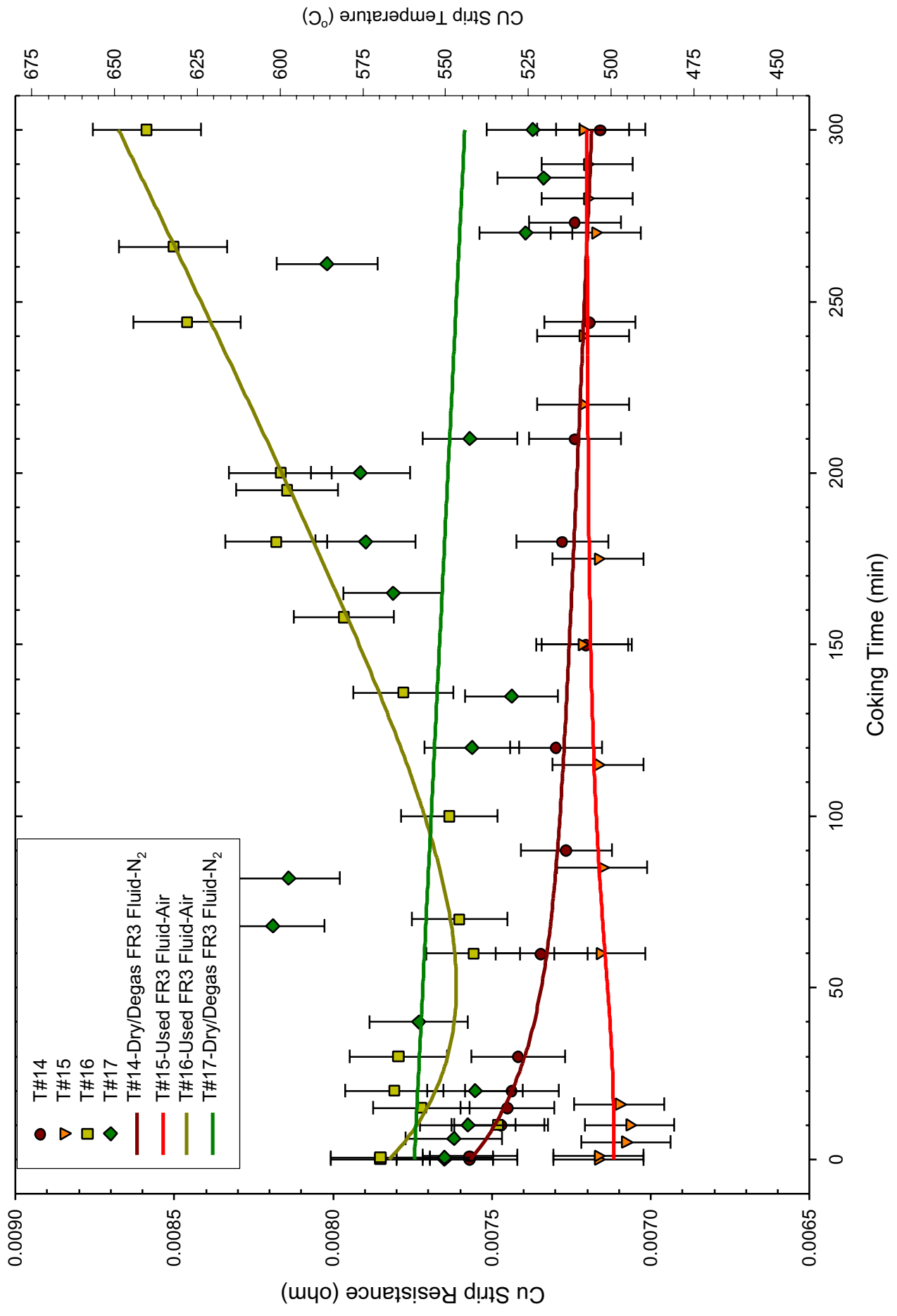


Figure # 13

Copper Strip Resistance and Temperature in E-200 Fluid with Coking Time

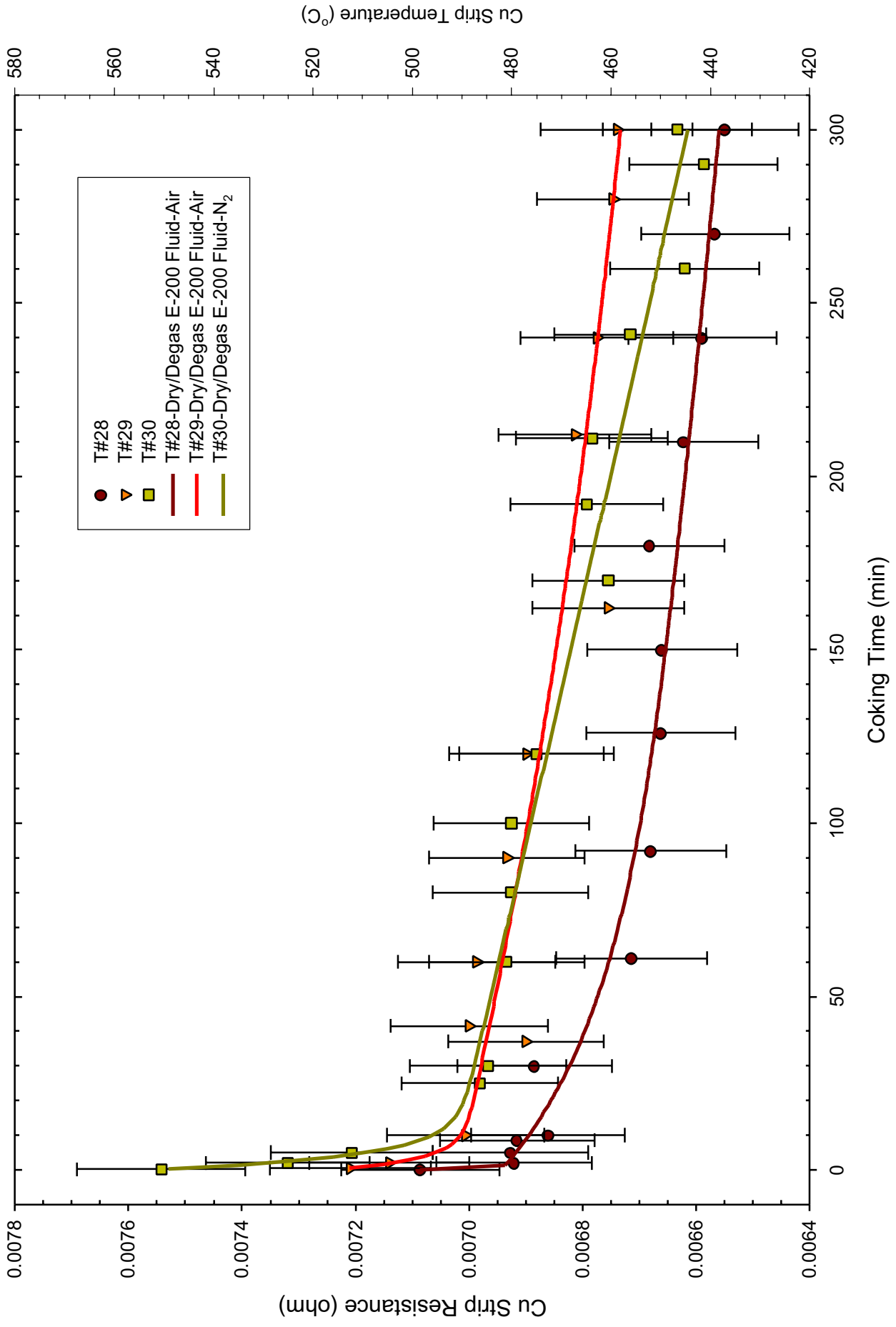


Figure # 14

Total Energy Dissipated by Strip in E200 Fluid with Coking Time

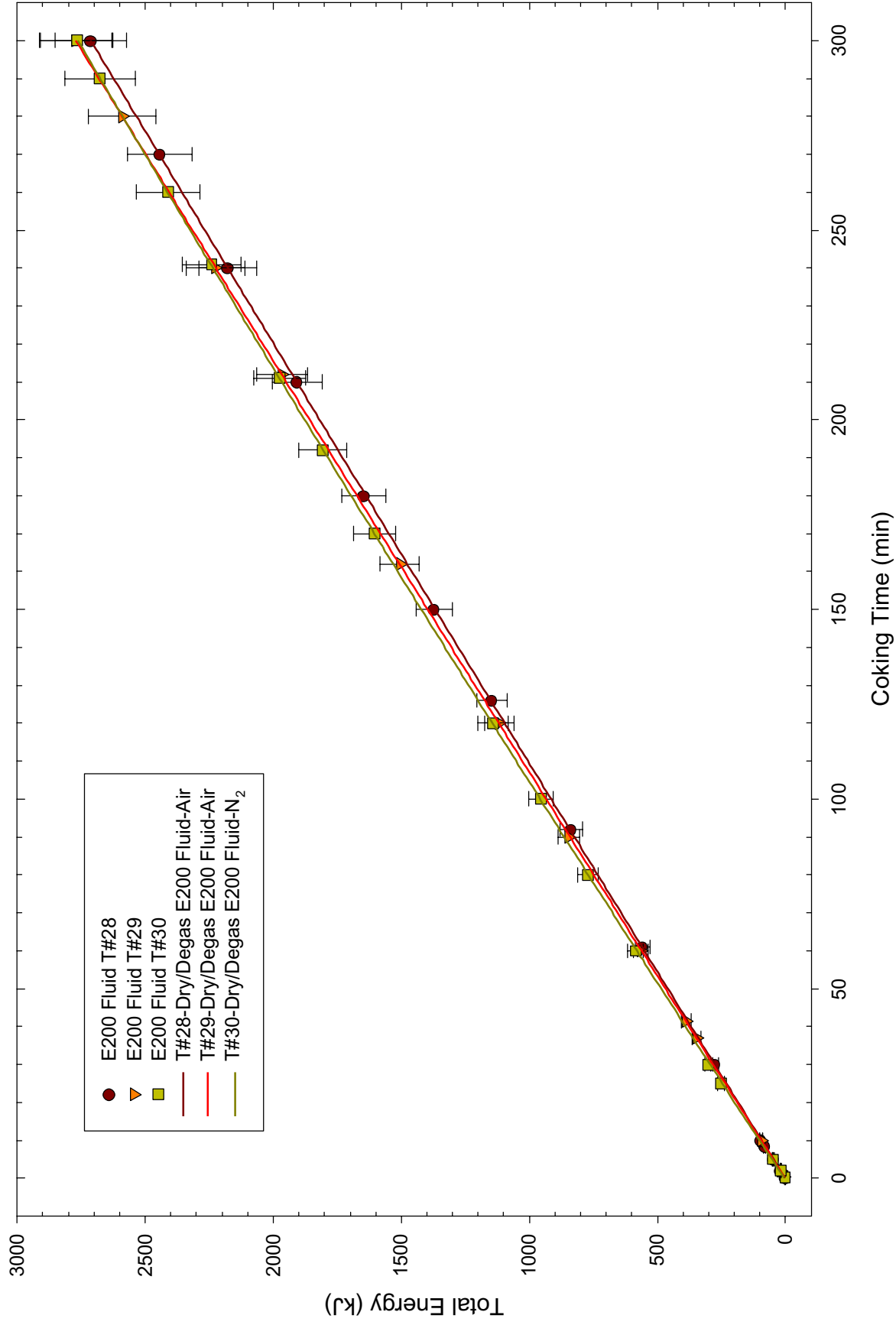


Figure # 15

Copper Strip Resistance and Temperature in Silicone Fluid with Coking Time

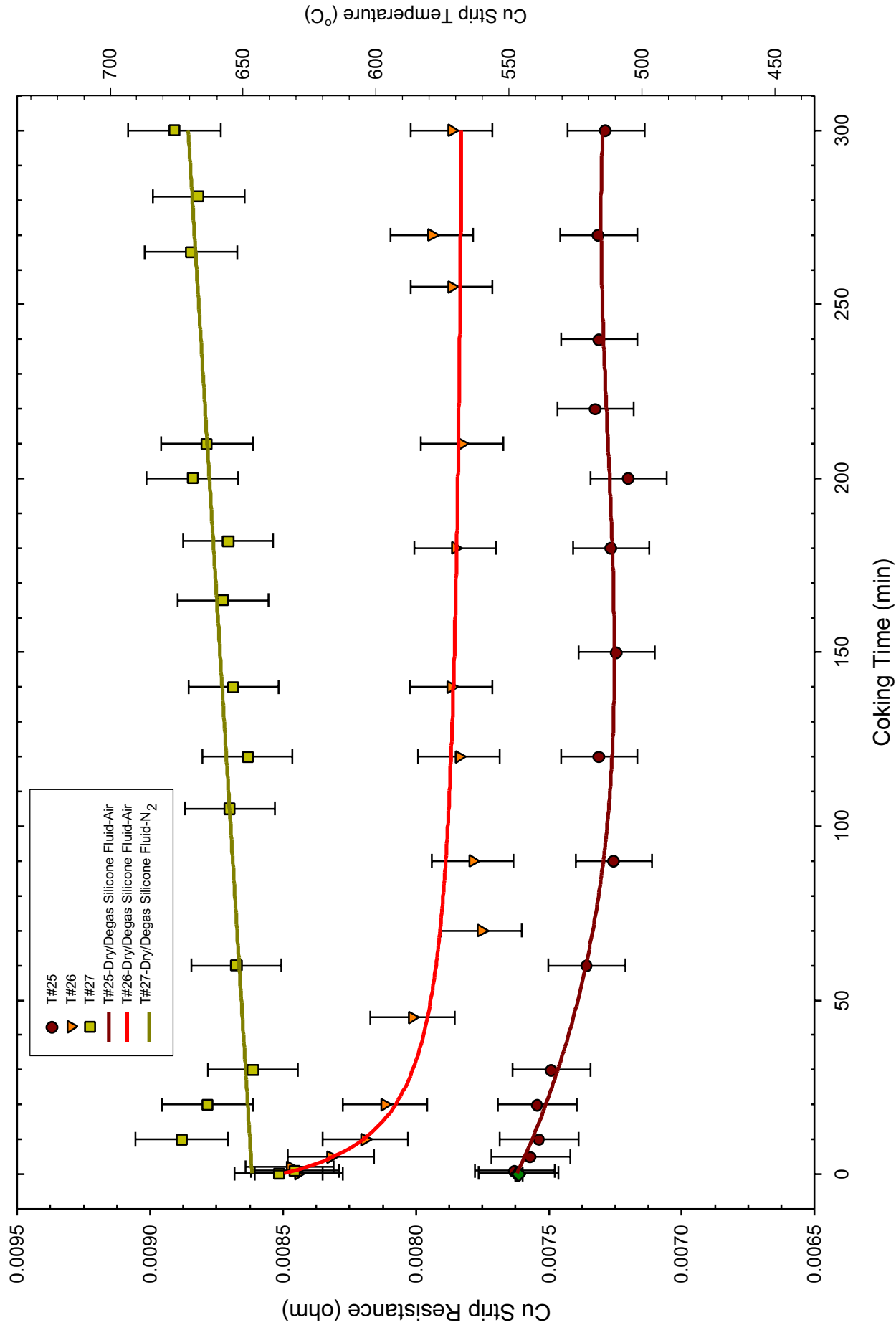


Figure # 16

Total Energy Dissipated by Strip in Silicone Fluid with Coking Time

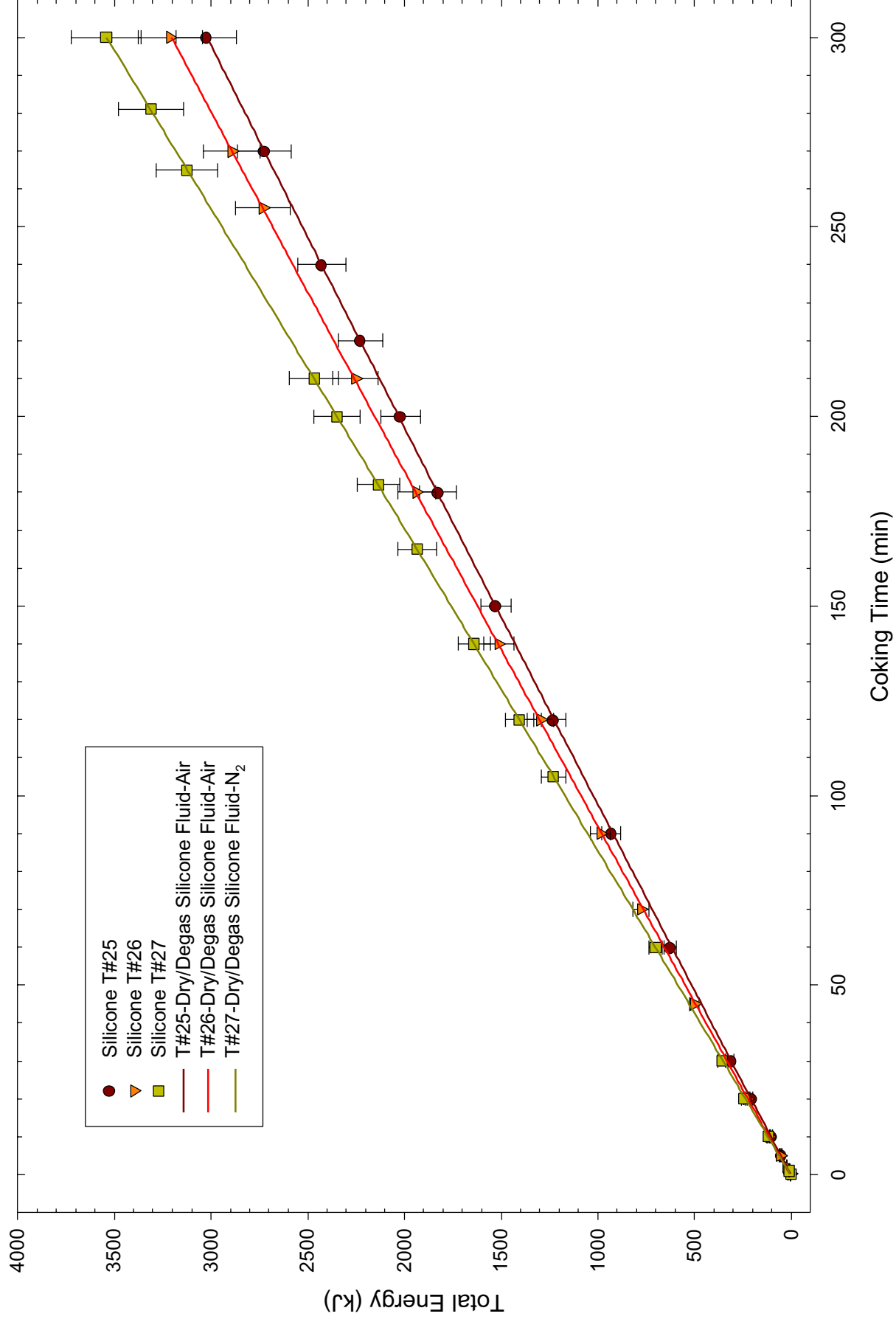


Figure # 17

COKING TENDENCY SUMMARY

Air Blanket

 Mineral Oil Trial #19
3.9 mg - Deposit

 FR3 Trial #16
0.1 mg - Deposit

 R-Temp Trial #21
32.0 mg - Deposit

 E-200 Trial #29
0.01 mg - Wt. loss

 Silicone Trial #26
0.04 mg - Deposit

N₂ Blanket

 Mineral Oil Trial #18
16.0 mg - Deposit

 FR3 Trial #17
0.2 mg - Deposit

 R-Temp Trial #23
18.2 mg - Deposit

 R-Temp Trial #24
68.4 mg - Deposit

 E-200 Trial #30
0.02 mg - Wt. loss

 Silicone Trial #27
0.04 mg - Deposit

Coking Tendency Summary

Figure # 18



AIR

#12 USED OIL

#15 USED FR3



MINERAL OIL

N₂

#13 DRY/DEGAS

#14 DRY/DEGAS



FR3



Coking Tendency Summary

Figure # 19



MINERAL OIL

AIR

N₂

#19 UNPROCESSED OIL

#18 DRY/DEGAS

#16 USED FR3

#17 DRY/DEGAS

FR3



Figure # 20

Photographs of Coking Strips and Deposits from Trials 21 & 23 in Rtemp Fluid

Trial # 21



Trial # 23

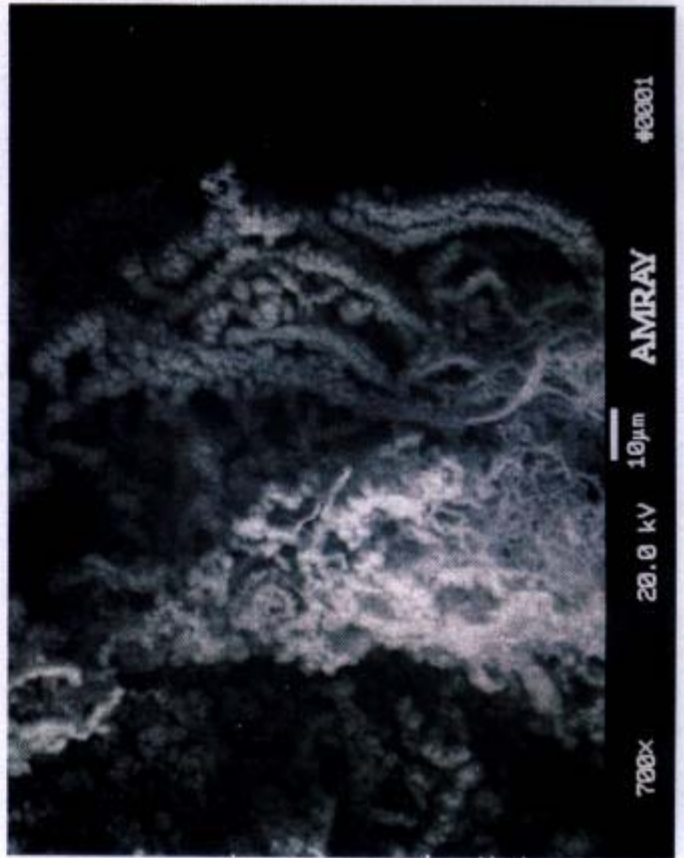


Figure # 21

Photomicrographs Comparing Strips after Trials in Mineral oil (top) and FR3 Fluid

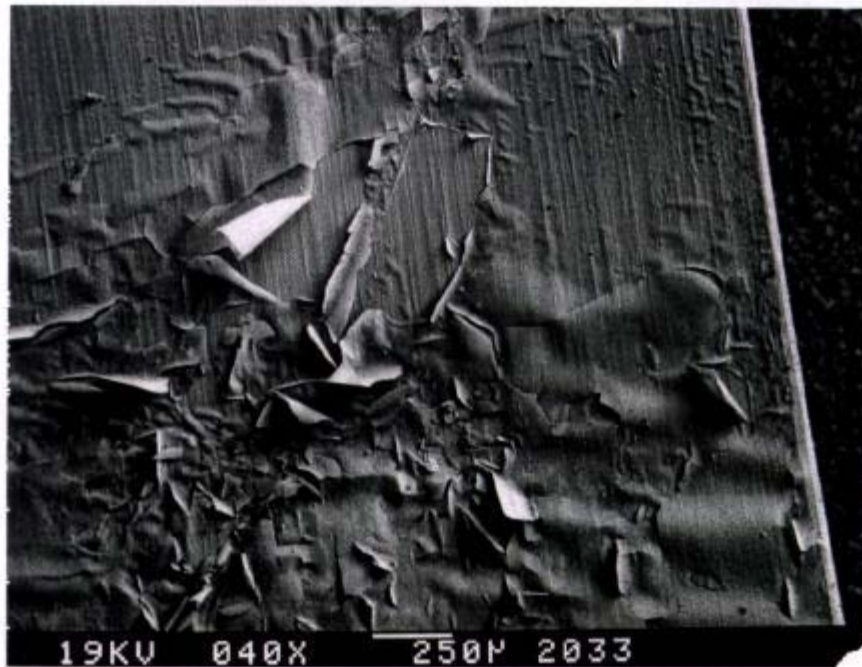


Figure # 22

Coking Strip after Trial # 28 in E-200 Fluid (photo at 10x mag)

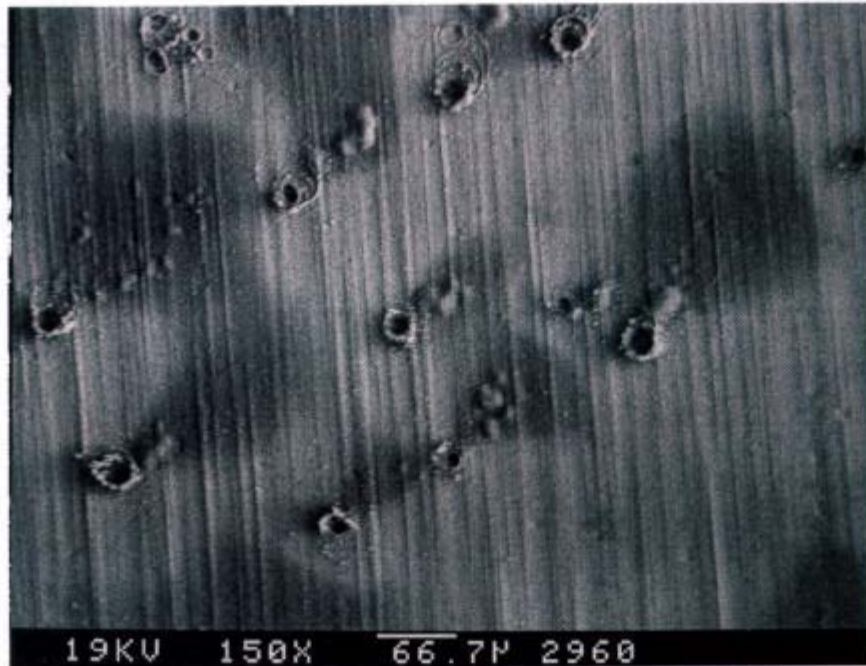
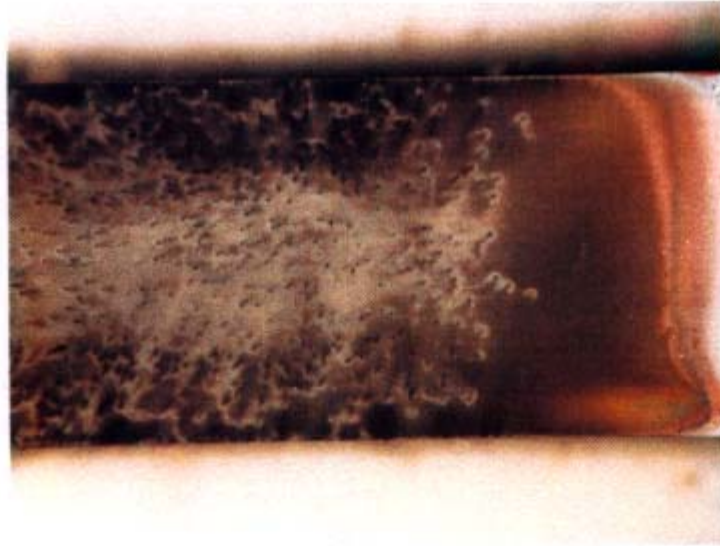
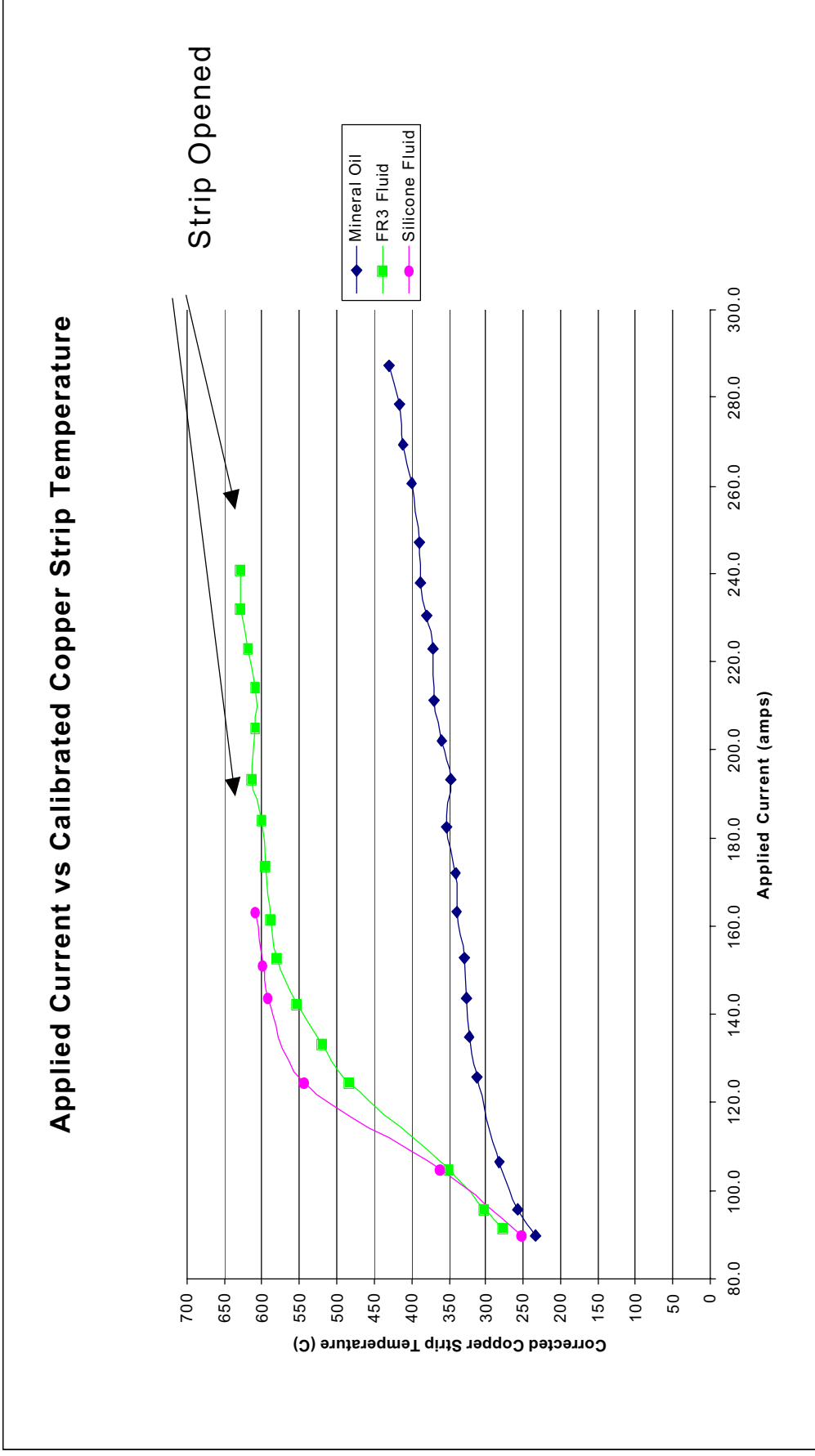


Figure # 23



Applied Current vs Resistance and TCR Calculated Temperature

Ergon Mineral Based Transformer Oil									
CT Current Applied (A)	Measured Shunt Current (A)	Error in Shunt Current (±A)	Measured Strip Resistance (ohm)	Error in Strip Resistance (± ohm)	Calculated TCR from Curve (per C)	Temperature from Calibrated Resistance vs Temp	TCR (0.00393) Calculated Temperature of Strip (C)	Curve Corrected TCR Calculated Temp (C)	
90	89.8	2.0	0.004776	0.000134	0.002367	234.1	188.8	292.2	
95	95.8	2.1	0.004968	0.000133	0.002274	257.3	205.7	310.9	
100	106.3	2.1	0.005175	0.000129	0.002183	281.9	223.9	331.1	
120	125.7	2.3	0.005439	0.000122	0.002076	313.0	247.3	356.9	
130	134.7	2.3	0.005515	0.000118	0.002047	321.7	253.9	364.3	
140	143.7	2.4	0.005546	0.000115	0.002036	325.3	256.7	367.3	
150	152.7	2.4	0.005580	0.000111	0.002023	329.3	259.7	370.6	
160	163.2	2.5	0.005663	0.000109	0.001993	338.8	267.0	378.7	
170	172.2	2.5	0.005687	0.000106	0.001985	341.6	269.1	381.1	
180	182.6	2.6	0.005777	0.000105	0.001953	351.8	277.0	389.9	
190	193.1	2.7	0.005743	0.000101	0.001965	348.0	274.0	386.6	
200	202.1	2.7	0.005839	0.000101	0.001932	358.9	282.5	396.0	
210	211.1	2.8	0.005931	0.000100	0.001902	369.4	290.7	405.0	
220	223.1	2.8	0.005945	0.000098	0.001898	370.9	291.9	406.3	
230	230.5	2.9	0.006016	0.000098	0.001875	378.9	298.2	413.3	
240	238.0	2.9	0.006092	0.000097	0.001851	387.4	304.8	420.7	
250	247.0	3.0	0.006113	0.000096	0.001845	389.8	306.7	422.8	
260	260.5	3.1	0.006200	0.000095	0.001818	399.4	314.4	431.3	
270	269.5	3.1	0.006305	0.000095	0.001788	411.0	323.7	441.6	
280	278.4	3.2	0.006357	0.000095	0.001773	416.7	328.2	446.7	
290	287.4	3.2	0.006468	0.000095	0.001742	428.8	338.0	457.6	

Figure # 25

Applied Current vs Resistance and TCR Calculated Temperature

Envirotemp FR3 Fluid								
CT Current Applied (A)	Measured Shunt Current (A)	Error in Shunt Current (±A)	Measured Strip Resistance (ohm)	Error in Strip Resistance (± ohm)	Calculated TCR from Curve (per C)	Temperature from Calibrated Resistance vs Temp	TCR (0.00393) Calculated Temperature of Strip (C)	Curve Corrected TCR Calculated Temp (C)
90	91.3	2.0	0.005136	0.000141	0.002200	277.3	220.5	327.3
95	95.8	2.1	0.005354	0.000142	0.002109	303.1	239.8	348.6
100	104.8	2.1	0.005754	0.000144	0.001961	349.3	275.1	387.7
120	124.3	2.2	0.006970	0.000155	0.001615	482.3	382.3	506.9
130	133.2	2.3	0.007325	0.000156	0.001535	519.0	413.6	541.8
140	142.2	2.3	0.007664	0.000157	0.001466	553.0	443.5	575.2
150	152.7	2.4	0.007937	0.000156	0.001415	579.6	467.6	602.1
160	161.7	2.5	0.008022	0.000153	0.001400	587.8	475.1	610.4
170	173.7	2.5	0.008091	0.000148	0.001388	594.3	481.1	617.2
180	184.1	2.6	0.008152	0.000145	0.001377	600.1	486.5	623.2
190	193.1	2.7	0.008290	0.000144	0.001354	613.1	498.8	636.9
200	205.1	2.7	0.008245	0.000139	0.001361	608.9	494.8	632.4
210	214.1	2.8	0.008240	0.000136	0.001362	608.4	494.3	631.9
220	223.1	2.8	0.008339	0.000135	0.001346	617.6	503.0	641.6
230	232.0	2.9	0.008447	0.000135	0.001328	627.6	512.6	652.3
240	241.0	2.9	0.008452	0.000133	0.001327	628.1	513.0	652.7
250	open		open					

Applied Current vs Resistance and TCR Calculated Temperature

DC#561 Silicone Fluid								
CT Current Applied (A)	Measured Shunt Current (A)	Error in Shunt Current ($\pm A$)	Measured Strip Resistance (ohm)	Error in Strip Resistance (\pm ohm)	Calculated TCR from Curve (per C)	Temperature from Calibrated Resistance vs Temp	TCR (0.00393) Calculated Temperature of Strip (C)	Curve Corrected TCR Calculated Temp (C)
90	90	2.0	0.004921	0.000137	0.002297	251.6	206.3	306.3
100	105	2.1	0.005850	0.000146	0.001929	360.2	289.1	397.0
120	124	2.2	0.007565	0.000167	0.001486	543.1	442.0	565.4
140	144	2.4	0.008058	0.000163	0.001394	591.2	485.9	613.9
150	151	2.4	0.008128	0.000160	0.001381	597.9	492.3	620.9
160	163	2.5	0.008243	0.000156	0.001362	608.7	502.4	632.2
170	open		open					

Coefficient of Thermal Expansion of Pure Copper

