

**INFLUENCE OF GROUP II & III BASE OIL COMPOSITION  
ON VI AND OXIDATION STABILITY**

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***Abstract***

Group II and III base oils are high quality oils containing less than 10% aromatics and less than 300 ppm sulfur as defined by API publication 1509. Group II and III base oils made using a hydrocracking/ISODEWAXING®/hydrofinishing catalyst combination typically have about 1% aromatics or less and almost undetectable amounts of sulfur and nitrogen. The virtual absence of heteroatom containing compounds coupled with an inherently low aromatic content gives them superior oxidation stability relative to Group I base oils. The primary factor that influences the oxidation stability of Group II and III oils is the aromatic concentration. But as the aromatic content approaches zero, oxidation stability is influenced more by the saturates composition, particularly the paraffin and polycyclic naphthenes content and distribution. This paper discusses the types and distribution of naphthene and aromatic compounds in highly hydroprocessed Group II/III base oils, and their relative influence on oxidation stability.

***Introduction***

Oxidation stability is one of the most important properties of a lubricating base oil. The more resistant a base oil is to oxidation, the less tendency it has to form deposits, sludge, and corrosive byproducts in grease, engine oil and industrial oil applications, and the more resistant it is to undesirable viscosity increases during use.

Studies have shown that base oil composition can have a significant impact on many traditional aspects of grease performance such as wheel bearing leakage and low-temperature torque<sup>1</sup>. In general, the performance improves with decreasing base oil aromatics content. But the most significant benefit that the relatively new, very-low-aromatic Group II/III base oils brings is improved oxidation and thermal stability.

Many base oil studies have described how an oil's molecular composition influences its physical and chemical properties, particularly its oxidation stability. In general, most of these have shown that nitrogen heterocycles and aromatic compounds have a negative influence on base oil stability. On the other hand, some sulfur containing compounds are viewed as

desirable since they inhibit hydrocarbon autocatalytic oxidation through free-radical chain termination pathways. Of the different saturated hydrocarbons found in mineral oils, paraffins are considered more stable than cycloparaffins (naphthenes) towards oxidation, and therefore, more desirable.

Understanding how the various classes of aromatics and saturates impact oxidation stability helps us focus on appropriate product quality targets and refining strategies to best meet the future needs of our customers.

Compositional (and hence stability) differences between base oils has become an increasingly important issue for customers in recent years as changing engine and industrial oil applications demand higher quality, longer lasting lubricants. For example, new OEM requirements translate into new ILSAC and API categories that call for extended drain intervals in PCMO/HDMO applications with lower viscosity and lower volatility requirements. Automatic transmission fluids are also being designed with fill-for-life applications in mind. Greases must perform at higher loads, higher bearing speeds, and higher temperatures. In the industrial oil area, new EPA requirements for PCB stable paper-machine oils, and enhanced thermal stability for ammonia refrigeration oils demand that low-aromatic catalytically-processed mineral oils be used in place of the traditional solvent refined oils.

The potential health hazards of a base oil are also dependent on the concentration of aromatic compounds, particularly polycyclic aromatic compounds (PACs). Base oils with low concentrations of PACs do not cause skin cancer in chronic mouse studies<sup>2</sup>. The total PAC concentration in these high-purity Group II and III base oils is consistently much less than one percent as measured by the IP346/80 method<sup>3</sup>. Oils with a PAC concentration > 3 percent by this method may be considered potentially hazardous. The Modified Ames Test (ASTM E1687 - 95) measures extractable mutagenic activity in base oils and the results (mutagenicity index) are highly correlated with skin carcinogenicity. Base oils with a mutagenicity index of > 2 are considered hazardous and results between 1 and 2 are suspect. The mutagenicity index of these high-purity Group II and III base oils indicates that biological activity for these oils is negligible.

Historically, formulators sought to meet any new performance requirement by selecting/developing more robust inhibitor and dispersant additive packages for their product lines. This response was due in part to the limited availability of Group II and III base stocks. The API officially classifies base stocks on the basis of their V.I., and sulfur and aromatic content (see **table I**). Until recently, Group I base stocks

represented more than 90% of the total U.S. domestic supply. But these oils have relatively poor oxidation stability because of their high aromatic and nitrogen heterocycle contents. The more stable Group II/III stocks have been limited by supply and consequently additive suppliers have found it uneconomical to develop special packages designed around their exclusive use in automotive, gear, and industrial lubricant applications.

However, with the recent plant expansions of Chevron's Richmond, California Lube Oil Plant, PetroCanada's Lubricants Centre Phoenix Project in Mississauga, Ontario, and Conoco/Pennzoil's Lake Charles, Louisiana Excel Paralubes Plant, and the Motiva plant in Port Arthur, Texas, Group II and III basestocks have now become far more available. In fact Chevron and its licensees now manufacture about one third of the base stocks in North America. Additive suppliers recognized the importance of these new stocks and are developing customized additive systems that take better advantage of the unique properties of these highly hydroprocessed basestocks.

Group III stocks, the most highly hydroprocessed, are now widely available and are emerging as substitutes for current synthetics in formulations requiring high oxidation resistance, wide temperature range viscometrics, and low volatility.

The development of new additive packages for Group II and III base oils is facilitated by a deeper understanding of their molecular composition. Unfortunately, any scheme used to characterize the composition of a base oil is hampered by the vast number of compounds present. High boiling mineral oils are composed of thousands of different hydrocarbons represented by carbon numbers in the range of  $C_{20}$  -  $C_{60}$ .

The methods described in the literature for characterizing base stocks to date have mainly been developed with Group I base stocks in mind. For example, the API defines the dividing line between Group I and Group II stocks by ASTM D 2007, a traditional clay gel chromatography method for determining aromatics and saturates. However this method is not useful for measuring the very low levels of aromatics in modern Group II and III base stocks.

The complex nature of these stocks resulted in the development of multi-step, time-consuming separation schemes that are costly and impractical for routine characterization (e.g. mineral oil nitrogen containing species alone are comprised of different amine, amide, pyrrole, pyrrolidine, pyridine, and piperidine alkyl and aromatic analogs that each require special separation and characterization techniques).

In order to simplify the characterization process, many group type mass spectral techniques were developed to unveil the complex nature of hydrocarbon mixtures using only one analytical technique. These techniques attempt to identify different base oil components by reconstructing the distribution of selected compound classes using empirically derived responsive factor matrices from characteristic fragment ions of standard compounds. However, the applicability of these techniques toward general base oil characterization is only as good as the matrix of compounds used in developing/calibrating the method. Since the compound matrices used were typically patterned after the molecular composition of Group I base stocks, the validity of these methods for characterizing Group II and III base stocks is highly questionable and, in certain cases, actually provides misleading information on the real composition of these oils.

Fortunately, if we ignore isomers of the same molecular formula, the task of characterizing the molecular compositions of Group II and III base stocks is much easier than that for Group I base stocks because of their highly refined nature. Most of the commercially available Group II and III base oils are made from combinations of high pressure catalytic hydrocracking/dewaxing/ and hydrofinishing operations that result in the nearly complete destruction of all heteroatom containing molecules and the saturation of all but a few percent of the most thermodynamically stable aromatic species. This greatly simplifies the job of compositional analysis and renders them more open to single-step analytical techniques like HPLC aromatics characterization with UV diode array detection, and Field Ionization Mass Spectral [FIMS] saturate analysis.

FIMS is especially valuable in determining the distribution of paraffins and naphthenes in Group II base oils since it relies exclusively on the use of molecular ions for compound class identification rather than fragment ion reconstruction.

The purpose of this study is to describe the application of HPLC and NMR analyses for aromatics characterization coupled with FIMS for saturates characterization of commercial Group II and III base oils and use this information to relate their compositional properties to oxidation stability.

## ***Experimental***

Pilot Plant:

Samples of finished 60N, 100N, 150N, 240N, 325N, 500N, and 650N base oils were obtained from various commercial suppliers. [Note that Chevron's new base oil grades 100R, 220R, and 600R were not available when this work was done, but the results and conclusions apply equally well to them.] Special low aromatic Group II and III 100N base oils were prepared from commercial waxy/hydrocracked VGO feeds using the ISODEWAXING and hydrofinishing processes. The special base oils were made in Chevron pilot plants that make oils with properties that closely match those from commercial operations.

#### Aromatics Measurement by HPLC-UV:

The official method used to distinguish between API Group I and Group II base stock categories is D2007. However, this clay gel chromatography method is not useful for measuring aromatics in modern Group II and III base stocks because it is not reliable below about 5%. The published repeatability is 2.3%.

Other popular methods such as n-d-M are not useful for aromatics measurement because modern Group II and III base stocks typically fall below the detection limit.

Therefore, we developed a proprietary analytical method using a Hewlett Packard 1050 Series Quaternary Gradient High Performance Liquid Chromatography (HPLC) system coupled with a HP 1050 Diode-Array UV-Vis detector interfaced to an HP Chem-station. Identification of the individual aromatic classes in these Group II and III base oils was made on the basis of their UV spectral pattern and their elution time. The amino column used for this analysis differentiates aromatic molecules largely on the basis of their ring-number (or more correctly, double-bond number). Thus, the single ring aromatic containing molecules would elute first, followed by the polycyclic aromatics in order of increasing double bond number per molecule. For aromatics with similar double bond character, those with only alkyl substitution on the ring would elute sooner than those with naphthenic substitution.

Unequivocal identification of the various base oil aromatic hydrocarbons from their UV absorbance spectra was somewhat complicated by the fact their peak electronic transitions were all red-shifted relative to the pure model compound analogs to a degree dependent on the amount of alkyl and naphthenic substitution on the ring system. These bathochromic shifts are well known to be caused by alkyl-group delocalization of the  $\pi$ -electrons in the aromatic ring. Since few unsubstituted aromatic compounds boil in the lube range, some degree of red-shift was expected and observed for all of the principle aromatic groups identified. Representative examples of lube oil aromatic molecule UV spectra are

shown in **figures 1 to 3** versus their unsubstituted model compound analogs.

Quantitation of the eluting aromatic compounds was made by integrating chromatograms made from wavelengths optimized for each general class of compounds over the appropriate retention time window for that aromatic. Retention time window limits for each aromatic class were determined by manually evaluating the individual absorbance spectra of eluting compounds at different times and assigning them to the appropriate aromatic class based on their qualitative similarity to model compound absorption spectra. With few exceptions, only five classes of aromatic compounds were observed in all of the Group II and III oils.

These were:

**Alkyl benzenes (1 Ring).** Typically 0.1 – 1.0 wt%. Examples include alkyl-tetralins, alkyl octahydro-phenanthrenes, and alkyl-decahydro-pyrenes. Chromatograms were constructed using the principal peak absorbance at 272nm with a bandwidth of 4nm.

**Alkyl naphthalenes (2 Ring).** Typically 10-200 ppm. Examples include alkyl-naphthalenes, alkyl-tetrahydro-phenanthrenes, and alkyl-hexahydro-pyrenes. Chromatograms were constructed using peak absorbances at 241nm and 290nm with bandwidths of 4nm.

**Alkyl phenanthrenes (3 Ring).** Typically 0-30 ppm. Examples include alkyl-phenanthrenes and alkyl-dihydro-pyrenes. Chromatograms were constructed using the principal peak absorbance at 260nm with a bandwidth of 4nm.

**Alkyl pyrenes (4 Ring).** Examples include alkyl-pyrenes, and alkyl-octahydro-coronenes. Chromatograms constructed using peak absorbances at 283nm and 351nm with bandwidths of 4nm.

**Alkyl coronenes (6 Ring).** Examples include mono-, di-, tri-, and tetra-methyl coronenes. Chromatograms were constructed using the peak absorbance at 312nm with a bandwidth of 8nm.

#### HPLC-UV Calibration

We found that HPLC-UV is a useful tool for identifying these classes of aromatic compounds even at very low levels. However, calibration was the biggest challenge. Multi-ring aromatics typically absorb 10 to 200 times more strongly than single-ring aromatics. Alkyl-substitution also

affected absorption by about 20%. Therefore, you need to know what species you are observing and how efficiently they absorb.

Identifying the five classes of aromatic compounds was the easy part. With the exception of a small overlap between the most highly retained alkyl-1-ring aromatic naphthenes and the least highly retained alkyl naphthalenes, all of the aromatic compound classes were baseline resolved. Integration limits for the co-eluting 1-ring and 2-ring aromatics at 272nm were made by the perpendicular drop method. Wavelength dependent response factors for each general aromatic class were first determined by constructing Beer's Law plots from pure model compound mixtures based on the nearest spectral peak absorbances to the substituted aromatic analogs.

For example, alkyl-cyclohexylbenzene molecules in base oils exhibit a distinct peak absorbance at 272nm that corresponds to the same  $\pi-\pi^*$  (forbidden) transition that unsubstituted tetralin model compounds do at 268nm. The concentration of alkyl-1-ring aromatic naphthenes in base oil samples was estimated by assuming that its molar absorptivity response factor at 272nm was approximately equal to tetralin's molar absorptivity at 268nm, calculated from Beer's law plots. Weight percent concentrations of aromatics were further estimated by assuming that the average molecular weight for each aromatic class was approximately equal to the average molecular weight for the whole base oil sample (determined by FIMS analyses).

We later improved our calibration by isolating the 1-ring aromatics directly from the base stocks via exhaustive HPLC chromatography. As expected, the isolated aromatic sample had a lower response factor than the model compound because it was more highly substituted.

More specifically, we separated the substituted benzene aromatics from the bulk of the base oil using a Waters semi-preparative HPLC unit. 10 grams of sample was diluted 1:1 in n-hexane and injected onto an amino-bonded silica column, a 5cm x 22.4mm ID guard, followed by two 25cm x 22.4mm ID columns of 8-12 micron amino-bonded silica particles, manufactured by Rainin Instruments, Emeryville, California, with n-hexane as the mobile phase at a flow rate of 18mls/min. Column eluent was fractionated based on the detector response from a dual wavelength UV detector set at 265nm and 295nm. Saturate fractions were collected until the 265nm absorbance showed a change of 0.01 absorbance units, which signaled the onset of single ring aromatic elution. A single ring aromatic fraction was collected until the absorbance ratio between 265nm and 295nm decreased to 2.0, indicating the onset of two ring aromatic elution. Purification and separation of the single ring aromatic fraction was made by re-



chromatographing the monoaromatic fraction away from the “tailing” saturates fraction which resulted from overloading the HPLC column.

This purified aromatic “standard” showed that alkyl substitution decreased the molar absorptivity response factor by about 20% relative to unsubstituted tetralin.

#### Confirmation by NMR

We confirmed the aromatic content in our purified mono-aromatic standard via long-duration carbon 13 NMR analysis. NMR is easier to calibrate than HPLC-UV because it simply measures aromatic carbon so the response does not depend on the class of aromatics being analyzed. Also, it was easy to translate % aromatic carbon to % aromatic molecules (to be consistent with HPLC-UV and D 2007) because usually 95-99% of the aromatics in modern Group II and III oils are single-ring aromatics.

The tradeoff is sensitivity. High power, long duration, and good baseline analysis are needed to accurately measure aromatics at 0.2% aromatic carbon (~1% aromatic molecules) or less.

More specifically, we modified the standard D 5292 method to give us a minimum carbon sensitivity of 500:1 (by ASTM standard practice E 386). To do this we needed a 15-hour duration on a 400-500 MHz NMR with a 10-12 mm Nalorac probe. Acorn PC integration software was used to define the shape of the baseline and consistently integrate. Another important “trick” is that we changed the carrier frequency once during the run to avoid artifacts from imaging the aliphatic peak into the aromatic region. By taking spectra on either side of the carrier spectra, we improved the resolution significantly without taking much time. [author’s note: We are seeking partners who would be willing to participate in round robin testing to get ASTM approval for this NMR method. ]

#### Saturates Characterization by FIMS:

Field ionization mass spectra (FIMS) of saturate and aromatic enriched base oil samples were obtained on a VG 70VSE mass spectrometer. The samples were introduced via a solid probe, which was heated from about 40C to 500C at a rate of 50C per minute. The mass spectrometer was scanned from m/z 40 to m/z 1000 at a rate of 5 seconds per decade. The acquired mass spectra were summed to generate one “averaged” spectrum. Each spectrum was C<sub>13</sub> corrected using a software package from PC-MassSpec.

FIMS ionization efficiency was evaluated using blends of nearly pure branched paraffins and highly naphthenic, aromatics-free base stock. We confirmed that the ionization efficiencies of various classes of saturates in these base oils were not dramatically different. N-paraffins, on the other hand, did indeed show a significantly lower (~50% lower) ionization efficiency than branched paraffins or naphthenes. Fortunately, branched paraffins and naphthenes typically comprise more than 99.8% of the saturates in modern Group II and III oils. However, the lower n-paraffin ionization efficiency should be considered when analyzing oils that have not been through the ISODEWAXING process and may have a significant amount of n-paraffins.

Base oil oxidation stability was evaluated using a Chevron proprietary test. The test measured the amount of time it takes 25 grams of oil containing an oxidation inhibitor and an oxidation accelerator catalyst package to react with 250cc of oxygen while being vigorously stirred at 340°F (171°C). The oxidation catalyst (0.2mls) used consisted of selected metal naphthenates dissolved in Pearl oil. The composition of this catalyst mixture was patterned after the normal distribution of metals found in used crankcase engine oils sampled from Chevrolet L-4 engine tests. The oxidation inhibitor used consisted of 1 gram of Oronite lube oil additive (an organic zinc dithiophosphate compound) .

### ***Results and Discussion***

The speciation of aromatics using HPLC analyses for all modern Group II base oils revealed that only five general classes of aromatics were present. Not surprisingly, the most predominant class was represented by the substituted one ring aromatics (0.1 - 1wt%). Lower amounts of substituted 2-ring naphthalenes (10 - 200 ppm), substituted 3-ring phenanthrenes (0-30 ppm), substituted 4-ring pyrenes (<5-10ppm), and substituted 6-ring coronenes (<1-20ppm) were observed.

It is interesting to note that no five ring aromatic compounds have been observed in any of the hundreds of samples analyzed by the authors. Similarly, no evidence exists for the presence of substituted bi-phenyl in these base oils, even though typical hydrocrackate feeds contain considerable quantities of pyrene and coronene analogs, and elimination of these species from the final products is known to occur via a hydrogenation mechanism that proceeds one ring at a time. Evidently, these intermediate aromatic classes are labile enough under the typical hydrofinishing conditions used for Group II manufacture that they rapidly convert to the more stable pyrene, naphthalene, and cyclohexylbenzene classes.

The nature and distribution of substituted benzene analogs in selected 100N, 240N, and 500N oils was further explored by concentrating and isolating them through a multi-step batch separation, GC/MS and FIMS analyses revealed that these aromatic ring cores consist mainly of alkyl-substituted tetralin, octahydro-phenanthrene, and decahydro-pyrene homologs. Alkyl substituted tetralin homologs are entirely consistent with the UV spectra observed during the elution of single ring aromatics in the HPLC analyses. These spectra displayed characteristic major peaks at 202nm and 272nm, with pronounced shoulders at 220nm and 278nm, respectively. A bathochromic shift of ~4nm would be expected in the spectral features of pure tetralin with one ring position alkyl substituent. **Figure 4** shows that unsubstituted tetralin in cyclohexane has peaks at 216nm and 266nm, with a shoulder at 274nm.

Conspicuously absent from the single ring aromatic compounds were any substantial quantities of simple mono-substituted alkyl-benzenes. If present in any sizable concentration, they should have been the first aromatic compound series to elute during the HPLC analyses and should have showed a peak  $\pi$ - $\pi^*$  (forbidden) transition close to 265nm (e.g. hexadecyl benzene). However, close examination of spectra in the leading edge of the single ring elution peak, showed that the 1-ring aromatics present in commercial base oil samples were all similar in character to that of the later eluting alkyl-tetralin aromatics. For all of the above reasons, it appears that the majority of the single ring aromatics are represented by alkyl substituted 1-ring aromatic-naphthenes. This is consistent with FIMS analysis of a single-aromatic-ring rich fraction.

The relationship between aromatic content and base oil oxidation stability for various 100N, 240N, and 500N Group II neutral oils is shown in **figure 5**. Here, only the single ring aromatic concentration was considered since the total polycyclic aromatic hydrocarbon content of most oils was generally less than 2% of the single ring aromatic concentration (in other words, typically <200 ppm multi-ring aromatics in the base stock). This simplification was substantiated in several samples in which the polycyclic aromatics were chromatographically removed from the base oil by silica-gel flash chromatography. These polycyclic aromatic free and its oxidation stability was found to be unchanged with respect to the parent oil. For example, we took one 500N oil with an estimated total aromatic level of ~3% and an oxidation stability of 19.1 hours and chromatographically removed all of the polycyclic aromatics [PAC's]. The resulting oxidation stability of the PAC depleted oil was nearly unchanged at 19.0 hours, while a sample of the original oil spiked with the isolated PAC's was nearly the same within experimental error at 18.7 hours.

The results in **figure 5** show that when the alkyl-1-ring aromatic naphthenes increase from about 18 to 150  $\mu\text{moles/gram oil}$  ( $\sim 1$  to 8.5 wt% for 500N), the oxidation stability of the base oil nearly dropped in half (i.e. the rate of oxygen consumption nearly doubled). Even for base oils with relatively low aromatic contents the effect can be large. For example, a drop in aromatic naphthenes from 2 wt% to 1 wt% for a 500N base oil lead to an increase of 3 hours in oxidation stability (13%). This illustrates that small changes in alkyl-1-ring aromatic naphthene content can lead to relatively large changes in base oil stability.

The role of alkyl-1-ring aromatic naphthenes in base oil oxidation can best be appreciated by considering the mass balance of typical non-additive reactants in the test.

### Mole Content of Reactants in Oxidation Stability Test

	Base Oil [100g]	1-Ring Arom. [per 100g]	Oxygen [1 liter]
100N[MW350]	0.278	0.0024 (1%)	0.0408
240N[MW420]	0.238	0.0100 (2.5%)	0.0408
500N[MW550]	0.182	0.0130 (3%)	0.0408

The oxidation test used to evaluate these oils compares the amount of time it takes 100 grams of oil to react with 1 liter of oxygen. Thus, by the end of the test, a large fraction (from 14-20% on average) of the overall base oil components will have reacted with oxygen. More significantly, however, this represents over four times the total number of alkyl-1-ring aromatic naphthenes present in the most aromatic fraction of the base oils. Given the limited number of 1-ring aromatic molecules present in these Group II oils relative to the quantity of saturate molecules and oxygen reactants, it's hard to reconcile their large impact on overall oxidation stability on the basis of simple first order kinetics. This is in stark contrast to the oxidation behavior of typical Group I base oils, where stability's are typically half the number of hours observed with Group II oils under similar test conditions, and plots of Log[Aromatics] vs. Oxidation stability (hours) are linear and suggest a first order dependence on aromatic content.

Since hydrocarbon oxidation is well known to be a complex autocatalytic process involving multiple free-radical pathways for chain initiation, propagation, and termination, we suspect that the type of alkyl-1-ring-aromatic naphthenes present in Group II base oil have an unusually large influence on bulk oxidation stability possibly because they assist in oxidizing other less reactive base oil saturate molecules.

Assuming that the average rate of oxidation for the various saturate compounds is roughly equivalent, we can write the following general expression for rate of oxygen depletion as:

$$d[O_2]/dt = k_1 [Arom_0 - x_a] + k_2 [Sat_0 - x_b] + k_3 [x_a][Sat_0 - x_b]$$

where  $k_1$ ,  $k_2$ , and  $k_3$  are the rate constants for the reaction between 1-ring aromatics and oxygen, base oil saturates and oxygen, and base oil saturates and oxidized aromatic compounds, respectively. X represents the amount of reacted hydrocarbon. Oxygen does not appear in the

above rate expression since its concentration in the oil is held constant for the duration of the test.

Assuming further that  $k_1 \gg k_2$  or  $k_3$ , and  $[\text{Sat}_0] \gg [\text{Arom}_0]$ , we may simplify the rate expression above by assuming that at the end of the test, 1) virtually all of the aromatic-naphthenes are oxidized, and 2) the quantity and average reactivity of oxidized saturates is essentially constant from oil to oil (denoted S). This allows us to simplify the above expression to the following:

$$\Delta[\text{O}_2]/\Delta t \equiv 1/(\text{Oxidation Stability}) \approx k_2 S + (k_1 + k_3 S)[\text{Arom}_0]$$

Support for these assumptions is shown by the fact that there is good experimental agreement between the inverse oxidation stability of the base oils (essentially the oxidation rate) and their aromatic contents (see **figure 6**).

In short, with 500N the oxidation rate doubled when the wt% aromatic molecules increased from 1% to 8.5%. With 100N it doubled when the wt% aromatic molecules increased from 1 wt% to 6.3 wt%. Note that the difference here was due only to the differences in molecular weight. Light and heavy neutral fall on the same line when presented on a molar basis as per Figures 5 and 6.

The key assumption that the Group II aromatics are highly reactive in nature and oxidize quickly relative to the majority of saturates is also consistent with our finding that these compounds are aromatic naphthenes. Aromatic naphthenes (e.g. tetralin) contain at least 2 benzylic hydrogens per molecule. In free-radical oxidation reactions, benzylic hydrogen abstraction is favored over the more labile than tertiary, secondary, primary, or vinylic hydrogen. The results are also consistent with previous pure compound studies on the oxidation stability of different hydrocarbon compounds (see **table II**).

The large amount of scatter in the oxidation stability results shown in **figures 5 and 6** was partly due to the nature of the test, and partly due to the wide variety of oil samples represented. The reproducibility of the test is highly dependent on making good contact between the reactant oxygen gas and the liquid oil sample through out the duration of the analyses. Since gas/liquid contacting is highly geometry and mixing speed dependent, special care had to be made to ensure that all of the glass stirring equipment was uniform in dimensions and stirring speeds carefully maintained by sensitive electronic controllers. Despite this, the oxidation repeatability was never any better than  $\pm 2$  hours over 20 hours.

Other factors contributing to the scatter in the stability versus aromatic content plots have to do with the relatively wide range of base oil viscosities and V.I.'s. This wide range is possible because the aromatic content of the oil and its VI can be controlled independently in the hydrocracking/ISODEWAXING/hydrofinishing processes.

In general, we've observed that the higher the absolute viscosity (i.e. higher molecular weight) of an oil at a given aromatic level, the higher its measured stability. This is to be expected given the nature of the test since oils were analyzed on the basis of their stability per weight of sample rather than per average number of molecules per sample. For a 25 gram sample, the higher an oil's viscosity, the more exhaustive (in terms of total moles of base oil reacted) the oxidation required to take up 250cc of oxygen. Lastly, most of the oils used in this study had V.I.'s that ranged all the way from 102-108, the significance of which will be discussed in the next section. In spite of all of these sources of variation, the results suggest that the maximum expected base oil stability from 105 V.I. average oils with near zero aromatics is expected to be approximately 25-27 hours.

The validity of the kinetic expression derived above rests strongly on the assumption that the saturate compound reactivity is relatively constant from sample to sample. However, many studies have been published which suggest that significant stability differences exist between naphthenic and paraffinic saturated compounds. Since the distribution of naphthenes and paraffins in any sample will be highly dependent on the V.I. of base oil, we were interested in uncovering the oxidation stability dependence on V.I. in the absence of appreciable aromatics.

At aromatics levels below about 1%, the VI and oxidation stability can be influenced far more by the molecular structure of the saturates than by the aromatics concentration. The effect of molecular composition on V.I. and oxidation stability for a series of near-zero aromatic content 100N base oils is summarized in **tables III**. All of the oils in this set were extensively hydroprocessed and all but one have total aromatic levels less than 0.1% (the lowest V.I. oil has 0.26% aromatics). This greatly reduced the number of compound classes which had to be considered and allowed us to accurately determine the distribution of paraffins and naphthenes from their molecular ion distribution using FIMS (see **tables IV-IX**).

The **table III** data shows that all of the low V.I. base oils contained a substantial fraction of 3+ ring naphthenics with, by default, relatively few alkanes. This situation reverses itself as V.I. increases, such that the alkane and monocyclic naphthene fractions now become the predominant classes.

The strong relationship between ring number and V.I. was established years ago by the American Petroleum Institute Research Project 42<sup>4</sup> on high MW hydrocarbon properties (see **table X**). Since V.I. is a measure of a base oil's rate of viscosity change with temperature (high V.I. denotes relatively little viscosity change) oils made up of molecules which can deform easily under the high shear forces experienced in flowing liquids will have the highest V.I.'s. Paraffins have low conformational activation energies for rotation about their carbon-carbon bonds [3-6 kcal/mol] and consequently exhibit relatively small changes in viscosity with temperature. Cycloparaffins or naphthenes, on the other hand, are relatively rigid molecules with much higher conformation activation energies [e.g. monocyclic naphthenes require 11 kcal/mol just to make the conversion between chair and boat conformations]. Therefore, when heat energy is imparted to highly naphthenic base oils, the ability of the molecules to bend and accommodate fluid movement changes more rapidly than the more paraffinic base oils.

The one interesting anomaly in the 100N V.I. series of **table III** concerns the two base oils with the highest V.I. Even though the 120 V.I. sample contained a slightly higher alkane and monocyclic naphthene content than the 124 V.I. sample, its higher percentage (by 0.4 wt%) of low V.I. pentacyclic and hexacyclic naphthenes was apparently large enough to lower its V.I. by four numbers. This minor difference in molecular composition is not an artifact or consequence of the reproducibility of the FIMS analysis. Replicate FIMS analyses were performed on both samples and the 5+ ring number distributions agreed with another by  $\pm 0.05$  wt%. Evidently, even though the 120 V.I. sample contained a slightly higher alkane and monocyclic naphthene content than the 124 V.I. sample, its higher percentage of low V.I. pentacyclic and hexacyclic naphthenes was enough to lower its V.I. by four whole numbers.

The influence of V.I. [i.e. multi-ring naphthene content] on oxidation stability for the low-aromatic 4 cSt base stocks is illustrated in **figure 7**. This figure shows that, in general, base oil oxidation stability increases with increasing V.I. However, from the scatter in the data, it is evident that other factors are also involved.

Previously we discussed how the oxidation stability of aromatic-naphthenes was low because of the labile nature of their benzylic hydrogen toward free-radical oxygen attack. The aromatic-naphthenes present in the Group II and III base oils examined were found to be predominately alkyl substituted tetralin (2 ring) and octahydro-phenanthrene (3 ring) analogs. Although relatively low in total concentration, their mere presence must none-the-less be considered an influencing factor governing base oil stability. In FIMS analysis, these



compound classes occur in Z-series -6 and -8, the same Z-series that contain the pentacyclic and hexacyclic naphthene homologs. Since 5 & 6 ring naphthenes also contain a relatively high number of labile hydrogens in tertiary carbon positions, these compounds are also likely to be more susceptible to oxidation than the bulk of the base oil molecules made up of lower ring-number naphthenes. Plotting the total concentration of 5 + 6 ring polycyclic naphthenes together with the concentration of 2 + 3 ring aromatic naphthenes as measured by FIMS Z-series -6 and 8 improved the correlation. (see **figure 8**).

## **Conclusions**

The composition and distribution of aromatics and, to a lesser extent, polycyclic naphthenes have a significant influence on the oxidation stability of Group II and III base oils.

The oxidation stability of these oils was primarily governed by their aromatic content. Most of the aromatic compounds in these oils appear to contain 1 aromatic ring attached to one or more naphthene rings and one alkyl-substituted chain. The labile benzylic hydrogens in these compounds make them highly susceptible to free-radical oxygen attack. Once oxidized, the products appear to accelerate the oxidation of the remaining base oil saturates.

As an illustration, we found that an increase in 500N aromatic naphthenes from 1 wt% to 2 wt% increased the base oil oxidation rate by about 13%. An increase from 1 wt% to 8.5 wt% doubled the oxidation rate. On a wt% basis, the impact of aromatic molecules is slightly greater in lighter base oils simply due to their lower molecular weight. With 100N, for example, an increase in aromatic naphthenes from 1 wt% to 6.3 wt% doubled the oxidation rate.

Multi-ring aromatics did not have a measurable impact on oxidation presumably because the concentration was so low.

Below 1% aromatics, the oxidation rate was influenced more by the saturates composition than the aromatics content. Below 1% aromatics, the most effective way to further improve oxidation stability was to increase VI. As VI increased, the paraffin content increased and the polycyclic naphthene content decreased which increased stability by about 60%.

The subtle influence of polycyclic naphthenes on oxidation stability was examined with base oils having nearly zero aromatic content which were manufactured via an all catalytic hydrocracking/ISODEWAXING/

hydrofinishing processing route. In general, the lower the concentration of polycyclic naphthenes in an oil, the higher its V.I. and oxidation stability. But 5-ring and 6-ring naphthenics seem to play a disproportionately large role since they contain a relatively high number of labile hydrogens in tertiary carbon positions.

For low-aromatic Group II oils in the 98 to 105VI range, the oxidation stability did not vary significantly (<5% increase from 98 to 105VI) because the concentration of polycyclic naphthenes did not vary significantly. But for base oils in the 115-125VI range, there were significantly fewer polycyclic naphthene compounds so higher oxidation stability was achieved provided aromatic levels were limited to about 1%.

### **References**

1. Beret, Samil, Impact of Base Oil Changes on Grease Performance, 59<sup>th</sup> NLGI Annual Meeting, October 25-28, 1992.
2. Blackburn, G.R., Roy, T.A., Bleicher, W.T.Jr., Reddy, M.V., and Mackerer, C.R. Comparison of Biological and Chemical Predictors of Dermal Carcinogenicity of Petroleum Oils. Polycyclic Aromatic Compounds 11:201-210 (1996).
3. Institute of Petroleum, Methods for Analysis and Testing, 2, pp. 346.1-346.6 (1985).
4. American Petroleum Institute Research Project 42, API Proceedings, Vol. 26 (III), p. 254, 1946.

Table I

## API BASE OIL INTERCHANGE GUIDELINES

Base Oil Category	% Saturates		% Sulfur	Viscosity Index
Group I	< 90	and/or	> 0.03	80 - 119
Group II	≥ 90	and	≤ 0.03	80 - 119
Group III	≥ 90	and	≤ 0.03	≥ 120
Group IV	All Polyalphaolefins (PAO's)			
Group V	Anything Not Covered in Groups I - IV			

**Table II**  
**Time to Absorb 2 Liters Oxygen per Mole-Hr**  
**for Various Hydrocarbons<sup>21</sup>**

**Paraffinic Hydrocarbons [110°C]**

n-Decane	47 hrs
Cetane	45

**Naphthenic Hydrocarbons [110°C]**

Decalin	27
Dicyclohexyl	28
Octadecyldecalin	24
Octadecylcyclohexane	37
Perhydroanthracene	12

**Monocyclic Aromatics [110°C]**

n-Amylbenzene	28
tert-Amylbenzene	80
Diphenylmethane	>70
Hexaethylbenzene	23
Hexadecylbenzene	12

**Polycyclic Aromatics [150°C]**

Naphthalene	>150
$\alpha$ -Methylnaphthalene	62
$\beta$ -Methylnaphthalene	>150
Isoamyl-naphthalene	55
Fluorene	26
Diisobutylanthracene	90
Phenanthrene	>50

**Aromatic-Naphthenes [110°C]**

Tetralin	2
Octadecyl tetralin	4
Octahydroanthracene	2
5-Isobutylacenaphthene	8

<sup>21</sup> Alan C Nixon 'Autoxidation and Antioxidants of Petroleum,' Table XXVII, in 'Autoxidation and Antioxidants,' Vol. II, p 795. W.O. Lundberg ed., Interscience, New York, 1962.

**Table III**  
**100N Base Oil Sample Properties**

	OIL A	OIL B	OIL C	OIL D	OIL E	OIL F
API Gravity			35.40	38.00	38.20	37.80
Viscosity Index	98	103	109	116	120	124
Viscosity @ 40 °C (cSt)	20.14	19.17	19.79	18.79	17.32	16.56
Viscosity @ 100 °C (cSt)	4.055	3.987	4.119	3.789	3.900	3.828
UV 272 Absorbance (Absxccc/gxmm)	0.37112	0.13780	0.12900	0.17961	0.11826	0.01100
UV 310 Absorbance (Absxccc/gxmm)	0.05687	0.00470	0.03112	0.06537	0.02971	0.00370
UV 348 Absorbance (Absxccc/gxmm)	0.00815	0.00020	0.00600	0.01625	0.00989	0.00050
UV 384 Absorbance (Absxccc/gxmm)	0.00182	0.00000	0.00120	0.00108	0.00117	0.00050
Est. Aromatic Conc. (wt%)	0.259	0.108	0.085	0.106	0.083	0.007
Saturate Distribution (wt%)						
Alkanes	6.54	10.50	14.58	20.60	34.75	33.27
1Ring Naphthenes	25.90	32.90	33.07	45.37	39.54	38.02
2Ring Naphthenes	31.18	31.07	26.88	23.68	17.54	19.57
3Ring Naphthenes	23.07	17.12	16.44	7.44	5.64	6.72
4Ring Naphthenes	10.67	6.85	7.11	1.90	1.43	1.72
5Ring Naphthenes	2.43	1.49	1.79	0.74	0.66	0.56
6Ring Naphthenes	0.22	0.07	0.11	0.27	0.43	0.14
Ave. Molecular Wt.(gm/mole)	346.9	354.7	354.5	386.2	390.1	377.9
Oxidator BN (hrs.)	23.40	27.65	23.70	33.51	29.42	38.65
	23.48	24.49	24.70	33.22	25.50	44.68
	22.72	22.56	23.58	29.57	25.50	37.01
Average	23.19	24.90	23.99	32.10	26.81	40.11
Std. Dev.	0.41	2.57	0.61	2.20	2.26	4.04
Simulated Distillation, D2887 (wt. %, °F)						
IBP	614	574	517	642	682	583
5	652	650	648	686	709	673
10	671	672	673	701	721	697
20	699	700	706	723	739	725
30	720	722	729	742	754	745
40	738	741	751	758	768	763
50	755	789	770	774	782	781
60	772	777	789	790	797	798
70	789	795	808	807	813	817
80	809	817	827	828	832	840
90	838	845	850	856	859	871
95	862	867	867	880	881	898
99.5	924	906	924	952	951	977
Pour Point, (°C)		-12	-23	-21	-13	-14
Cloud Point, (°C)		-9	-20	-16		-7

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# Oil A

V.I. = 98

Carbon#	Alk.MW	Alkanes	MN.MW	MonoN	DN.MW	DiNaph	TN.MW	TriNaph	TN.MW	TetrNaph	PN.MW	entaNap	HN.MW	HexaNaph
16	226	0.01	224	0.01	222	0.01	220	0	218	0	216	0.01	214	0
17	240	0	238	0.01	236	0.02	234	0	232	0.03	230	0	228	0
18	254	0	252	0.02	250	0.07	248	0.21	246	0.43	244	0.03	242	0.02
19	268	0	266	0.21	264	0.69	262	1.22	260	0.66	258	0.27	256	0.03
20	282	0	280	0.87	278	1.97	276	2.1	274	0.99	272	0.38	270	0.03
21	296	0.12	294	1.65	292	2.82	290	2.51	288	1.05	286	0.35	284	0
22	310	0.3	308	2.07	306	3.11	304	2.43	302	1.03	300	0.29	298	0.04
23	324	0.58	322	2.35	320	3.04	318	2.16	316	0.89	314	0.24	312	0.08
24	338	0.58	336	2.45	334	2.8	332	1.94	330	0.79	328	0.22	326	0
25	352	0.68	350	2.37	348	2.64	346	1.88	344	0.69	342	0.18	340	0
26	366	0.72	364	2.29	362	2.43	360	1.49	358	0.59	356	0.15	354	0
27	380	0.78	378	2.14	376	2.15	374	1.4	372	0.55	370	0.06	368	0
28	394	0.59	392	1.87	390	1.79	388	1.1	386	0.43	384	0.03	382	0
29	408	0.52	406	1.54	404	1.47	402	0.95	400	0.38	398	0	396	0
30	422	0.42	420	1.23	418	1.12	416	0.68	414	0.37	412	0.01	410	0
31	436	0.3	434	0.93	432	0.82	430	0.48	428	0.26	426	0.01	424	0
32	450	0.21	448	0.68	446	0.61	444	0.32	442	0.19	440	0	438	0
33	464	0.12	462	0.47	460	0.4	458	0.24	456	0.13	454	0	452	0
34	478	0.08	476	0.3	474	0.27	472	0.13	470	0.07	468	0	466	0
35	492	0.04	490	0.19	488	0.16	486	0.09	484	0.04	482	0	480	0
36	506	0.01	504	0.09	502	0.09	500	0.04	498	0.02	496	0	494	0
37	520	0	518	0.03	516	0.03	514	0	512	0	510	0	508	0
38	534	0	532	0	530	0	528	0	526	0	524	0	522	0
39	548	0	546	0	544	0	542	0	540	0	538	0	536	0
40	562	0	560	0	558	0	556	0	554	0	552	0	550	0
41	576	0	574	0	572	0	570	0	568	0	566	0	564	0
42	590	0	588	0	586	0	584	0	582	0	580	0	578	0
43	604	0	602	0	600	0	598	0	596	0	594	0	592	0
44	618	0	616	0	614	0	612	0	610	0	608	0	606	0
45	632	0	630	0	628	0	626	0	624	0	622	0	620	0
<b>Wt. Percent</b>		<b>8.54</b>		<b>25.90</b>		<b>31.18</b>		<b>23.07</b>		<b>10.67</b>		<b>2.43</b>		<b>0.22</b>
<b>Ave MW =</b>	<b>345.9</b>													

Table IV

## Oil B

V.I. = 103

Carbon#	Alk.MW	Alkanes	MN.MW	MonoN	DN.MW	DiNaph	TN.MW	TriNaph	TN.MW	TetrNaph	PN.MW	entaNap	HN.MW	HexaNaph
16	226	0	224	0	222	0	220	0	218	0.01	216	0.01	214	0.02
17	240	0	238	0.02	236	0.02	234	0	232	0.07	230	0	228	0.01
18	254	0.05	252	0.05	250	0.07	248	0.1	246	0.2	244	0.01	242	0
19	268	0.08	266	0.18	264	0.35	262	0.36	260	0.31	258	0.15	256	0.01
20	282	0.15	280	0.58	278	1.04	276	0.84	274	0.39	272	0.25	270	0.01
21	296	0.34	294	1.44	292	1.99	290	1.33	288	0.52	286	0.19	284	0
22	310	0.61	308	2.34	306	2.65	304	1.58	302	0.57	300	0.16	298	0.01
23	324	0.88	322	3.01	320	3.24	318	1.71	316	0.61	314	0.16	312	0
24	338	1.16	336	3.41	334	3.37	332	1.83	330	0.63	328	0.17	326	0
25	352	1.19	350	3.32	348	3.17	346	1.65	344	0.58	342	0.15	340	0
26	366	1.21	364	3.28	362	2.78	360	1.57	358	0.5	356	0.12	354	0
27	380	0.99	378	2.93	376	2.52	374	1.35	372	0.51	370	0	368	0
28	394	0.79	392	2.52	390	2	388	1.01	386	0.37	384	0	382	0
29	408	0.67	406	1.97	404	1.71	402	0.81	400	0.29	398	0	396	0
30	422	0.51	420	1.56	418	1.16	416	0.62	414	0.25	412	0	410	0
31	436	0.39	434	1.25	432	0.88	430	0.4	428	0.22	426	0	424	0
32	450	0.26	448	0.86	446	0.6	444	0.25	442	0.13	440	0	438	0
33	464	0.16	462	0.6	460	0.41	458	0.16	456	0.06	454	0	452	0
34	478	0.1	476	0.38	474	0.26	472	0.09	470	0.03	468	0	466	0
35	492	0.07	490	0.26	488	0.16	486	0.03	484	0.01	482	0	480	0
36	506	0.01	504	0.13	502	0.08	500	0	498	0	496	0	494	0
37	520	0	518	0.04	516	0.03	514	0	512	0	510	0	508	0
38	534	0	532	0	530	0	528	0	526	0	524	0	522	0
39	548	0	546	0	544	0	542	0	540	0	538	0	536	0
40	562	0	560	0	558	0	556	0	554	0	552	0	550	0
41	576	0	574	0	572	0	570	0	568	0	566	0	564	0
42	590	0	588	0	586	0	584	0	582	0	580	0	578	0
43	604	0	602	0	600	0	598	0	596	0	594	0	592	0
44	618	0	616	0	614	0	612	0	610	0	608	0	606	0
45	632	0	630	0	628	0	626	0	624	0	622	0	620	0
<b>Wt. Percent</b>		<b>10.50</b>		<b>32.90</b>		<b>31.07</b>		<b>17.12</b>		<b>6.65</b>		<b>1.49</b>		<b>0.07</b>
<b>Ave MW =</b>	<b>354.7</b>													

Table V

## Oil C

V.I. = 110

Carbon#	Alk.MW	Alkanes	MLMW	MonoN	DN.MW	DiNaph	TN.MW	TriNaph	TL.MW	TetrNaph	PL.MW	entaNap	HL.MW	HexaNaph
16	228	0	224	0.02	222	0.02	220	0	218	0	216	0	214	0
17	240	0.07	238	0.12	236	0.06	234	0.04	232	0.01	230	0	228	0.01
18	254	0.12	252	0.19	250	0.19	248	0.12	246	0.12	244	0	242	0
19	268	0.19	266	0.4	264	0.45	262	0.33	260	0.21	258	0.07	256	0.04
20	282	0.32	280	0.77	278	0.91	276	0.75	274	0.37	272	0.18	270	0
21	296	0.61	294	1.54	292	1.62	290	1.1	288	0.49	286	0.22	284	0
22	310	1.05	308	2.29	306	2.06	304	1.36	302	0.57	300	0.2	298	0.03
23	324	1.24	322	2.89	320	2.55	318	1.48	316	0.62	314	0.16	312	0.02
24	338	1.67	336	3.14	334	2.51	332	1.45	330	0.6	328	0.16	326	0
25	352	1.72	350	3.19	348	2.46	346	1.31	344	0.56	342	0.14	340	0
26	366	1.45	364	2.93	362	2.26	360	1.24	358	0.53	356	0.16	354	0
27	380	1.22	378	2.79	376	2.14	374	1.31	372	0.6	370	0.14	368	0
28	394	1.01	392	2.5	390	1.88	388	1.14	386	0.45	384	0.07	382	0
29	408	0.89	406	2.14	404	1.59	402	1.08	400	0.48	398	0.1	396	0
30	422	0.85	420	1.81	418	1.27	416	0.82	414	0.36	412	0	410	0
31	436	0.43	434	1.24	432	0.9	430	0.54	428	0.21	426	0	424	0
32	450	0.27	448	0.83	446	0.57	444	0.35	442	0.11	440	0	438	0
33	464	0.09	462	0.43	460	0.33	458	0.17	456	0.05	454	0	452	0
34	478	0.02	476	0.23	474	0.15	472	0.08	470	0.01	468	0	466	0
35	492	0	490	0.07	488	0.06	486	0.01	484	0	482	0	480	0
38	506	0	504	0.01	502	0	500	0	498	0	496	0	494	0
37	520	0	518	0	516	0	514	0	512	0	510	0	508	0
38	534	0	532	0	530	0	528	0	526	0	524	0	522	0
39	548	0	546	0	544	0	542	0	540	0	538	0	536	0
40	562	0	560	0	558	0	556	0	554	0	552	0	550	0
41	576	0	574	0	572	0	570	0	568	0	566	0	564	0
42	590	0	588	0	586	0	584	0	582	0	580	0	578	0
43	604	0	602	0	600	0	598	0	596	0	594	0	592	0
44	618	0	616	0	614	0	612	0	610	0	608	0	606	0
45	632	0	630	0	628	0	626	0	624	0	622	0	620	0
<b>Wt. Percent</b>		<b>14.58</b>		<b>33.07</b>		<b>26.88</b>		<b>16.44</b>		<b>7.11</b>		<b>1.79</b>		<b>0.11</b>

Ave MW = 354.5

Table VI



## Oil D

V.I. = 116

Carbon#	Alk.MW	Alkanes	MM.MW	MonoN	DN.MW	DINaph	TM.MW	TriNaph	TM.MW	TetrNaph	PN.MW	entaNap	HM.MW	HexaNaph
16	226	0.01	224	0.11	222	0	220	0	218	0	216	0	214	0.05
17	240	0.06	236	0.13	236	0.02	234	0	232	0	230	0.01	228	0
18	254	0.07	252	0.2	250	0.08	248	0	246	0.04	244	0	242	0
19	268	0.17	266	0.29	264	0.11	262	0.15	260	0.07	258	0.1	256	0.02
20	282	0.22	280	0.42	278	0.26	276	0.33	274	0.1	272	0.2	270	0
21	296	0.4	294	0.66	292	0.7	290	0.48	288	0.11	286	0.18	284	0
22	310	1.03	306	1.87	306	1.39	304	0.54	302	0.18	300	0.09	298	0.06
23	324	2.09	322	3.09	320	1.83	318	0.57	316	0.17	314	0	312	0
24	338	2.4	336	3.74	334	1.93	332	0.52	330	0.15	328	0	326	0.08
25	352	2.39	350	3.82	348	1.9	346	0.49	344	0.14	342	0	340	0
26	366	2.03	364	3.75	362	1.73	360	0.55	358	0.11	356	0	354	0
27	380	1.88	378	3.3	376	1.62	374	0.4	372	0.15	370	0	368	0
28	394	1.26	392	3.06	390	1.48	388	0.4	386	0.07	384	0	382	0
29	408	0.9	406	2.6	404	1.28	402	0.4	400	0.07	398	0	396	0
30	422	0.6	420	2.19	418	1.12	416	0.32	414	0.08	412	0	410	0
31	436	0.4	434	1.85	432	0.85	430	0.23	428	0.03	426	0	424	0
32	450	0.23	448	1.42	446	0.7	444	0.17	442	0.01	440	0	438	0
33	464	0.12	462	1.1	460	0.58	458	0.13	456	0	454	0	452	0
34	478	0.01	476	0.73	474	0.41	472	0.08	470	0	468	0	466	0
35	492	0	490	0.49	488	0.27	486	0.04	484	0	482	0	480	0
36	506	0	504	0.25	502	0.17	500	0	498	0	496	0	494	0
37	520	0	518	0.1	516	0.06	514	0	512	0	510	0	508	0
38	534	0	532	0.02	530	0	528	0	526	0	524	0	522	0
39	548	0	546	0	544	0	542	0	540	0	538	0	536	0
40	562	0	560	0	558	0	556	0	554	0	552	0	550	0
41	576	0	574	0	572	0	570	0	568	0	566	0	564	0
42	590	0	588	0	586	0	584	0	582	0	580	0	578	0
43	604	0	602	0	600	0	598	0	596	0	594	0	592	0
44	618	0	616	0	614	0	612	0	610	0	608	0	606	0
45	632	0	630	0	628	0	626	0	624	0	622	0	620	0
Normalized		20.60		45.37		23.68		7.44		1.90		0.74		0.27

Ave MW = 366.2

Table VII

# Oil E

V.I. = 120

Carbon#	AR.MW	Alkanes	MN.MW	MonoN	DN.MW	DINaph	TN.MW	TriNaph	TN.MW	TetrNaph	PN.MW	entaNap	HN.MW	HexaNaph
16	226	0	224	0.04	222	0	220	0	218	0	216	0	214	0.01
17	240	0.01	238	0.09	236	0	234	0	232	0	230	0	228	0.02
18	254	0	252	0.11	250	0.01	248	0.03	246	0.03	244	0.03	242	0.02
19	268	0.05	266	0.13	264	0.02	262	0.01	260	0.02	258	0.02	256	0.02
20	282	0.08	280	0.19	278	0.06	276	0.02	274	0.01	272	0.11	270	0.04
21	296	0.11	294	0.3	292	0.14	290	0.1	288	0.06	286	0.13	284	0.01
22	310	0.21	308	0.53	306	0.43	304	0.24	302	0.1	300	0.07	298	0.05
23	324	0.66	322	1.25	320	0.96	318	0.37	316	0.1	314	0.04	312	0.04
24	338	2.04	336	2.35	334	1.32	332	0.42	330	0.1	328	0.04	326	0.01
25	352	3.41	350	3.15	348	1.4	346	0.39	344	0.1	342	0.03	340	0.02
26	366	3.79	364	3.35	362	1.43	360	0.41	358	0.16	356	0.03	354	0.12
27	380	4.16	378	3.6	376	1.51	374	0.44	372	0.07	370	0.02	368	0
28	394	3.58	392	3.4	390	1.34	388	0.4	386	0.07	384	0	382	0
29	408	3.06	406	3.16	404	1.26	402	0.41	400	0.08	398	0.03	396	0
30	422	2.38	420	2.81	418	1.19	416	0.39	414	0.08	412	0	410	0
31	436	1.78	434	2.36	432	0.96	430	0.29	428	0.07	426	0	424	0
32	450	1.78	448	1.91	446	0.79	444	0.23	442	0.05	440	0	438	0
33	464	0.8	462	1.62	460	0.63	458	0.19	456	0.05	454	0	452	0
34	478	0.53	476	1.12	474	0.48	472	0.16	470	0.03	468	0	466	0
35	492	0.32	490	0.7	488	0.35	486	0.1	484	0.01	482	0	480	0
36	506	0.2	504	0.46	502	0.21	500	0.06	498	0	496	0	494	0
37	520	0.07	518	0.23	516	0.09	514	0.03	512	0	510	0	508	0
38	534	0.04	532	0.12	530	0.06	528	0.02	526	0	524	0	522	0
39	548	0	546	0.02	544	0	542	0	540	0	538	0	536	0
40	562	0	560	0	558	0	556	0	554	0	552	0	550	0
41	576	0	574	0	572	0	570	0	568	0	566	0	564	0
42	590	0	588	0	586	0	584	0	582	0	580	0	578	0
43	604	0	602	0	600	0	598	0	596	0	594	0	592	0
44	618	0	616	0	614	0	612	0	610	0	608	0	606	0
45	632	0	630	0	628	0	626	0	624	0	622	0	620	0
<b>Wt. Percent</b>		<b>34.75</b>		<b>39.54</b>		<b>17.54</b>		<b>5.64</b>		<b>1.43</b>		<b>0.66</b>		<b>0.43</b>

Ave MW = 390.1

Table VIII

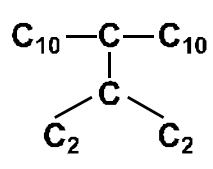
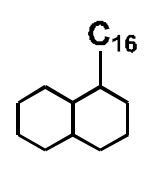
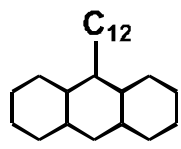
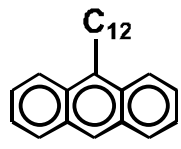
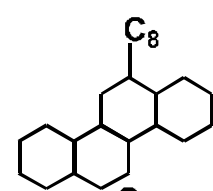
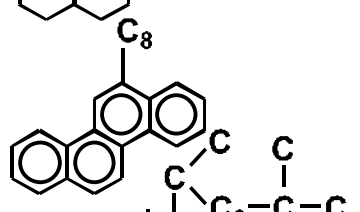
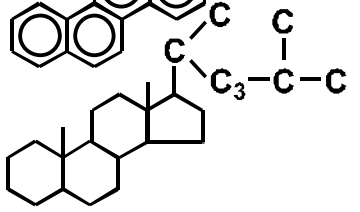
## Oil F

V.I. = 124

Carbon#	Alk.MW	Alkanes	ML.MW	MonoN	DN.MW	DiNaph	TN.MW	TriNaph	TN.MW	TetrNaph	PN.MW	entaNap	HN.MW	HexaNaph
16	220	0.09	224	0.09	222	0.01	220	0.01	218	0	216	0	214	0
17	240	0.26	238	0.23	236	0.05	234	0.03	232	0.04	230	0	228	0
18	254	0.46	252	0.38	250	0.17	248	0.07	246	0.12	244	0	242	0.02
19	268	0.86	266	0.5	264	0.29	262	0.14	260	0.09	258	0.09	256	0.02
20	282	0.79	280	0.66	278	0.43	276	0.21	274	0.09	272	0.16	270	0.01
21	296	0.85	294	0.86	292	0.84	290	0.31	288	0.1	286	0.08	284	0
22	310	1.04	308	1.21	306	0.89	304	0.38	302	0.09	300	0.05	298	0.02
23	324	1.56	322	1.74	320	1.14	318	0.42	316	0.09	314	0.03	312	0.02
24	338	2.27	336	2.23	334	1.23	332	0.41	330	0.11	328	0.02	326	0.01
25	352	2.74	350	2.7	348	1.35	346	0.42	344	0.11	342	0.01	340	0.02
26	366	2.97	364	2.73	362	1.33	360	0.42	358	0.08	356	0.02	354	0
27	380	3.08	378	2.73	376	1.34	374	0.48	372	0.09	370	0	368	0
28	394	2.82	392	2.72	390	1.27	388	0.39	386	0.09	384	0.01	382	0
29	408	2.38	406	2.59	404	1.18	402	0.4	400	0.07	398	0	396	0
30	422	1.77	420	2.3	418	1.06	416	0.36	414	0.08	412	0	410	0
31	436	1.4	434	1.94	432	0.91	430	0.29	428	0.08	426	0	424	0
32	450	1.02	448	1.7	446	0.79	444	0.25	442	0.06	440	0	438	0
33	464	0.89	462	1.37	460	0.66	458	0.2	456	0.03	454	0	452	0
34	478	0.44	476	1.09	474	0.52	472	0.15	470	0.03	468	0	466	0
35	492	0.3	490	0.81	488	0.42	486	0.12	484	0.01	482	0	480	0
36	506	0.18	504	0.54	502	0.28	500	0.09	498	0	496	0	494	0
37	520	0.15	518	0.33	516	0.2	514	0.07	512	0	510	0	508	0
38	534	0.07	532	0.21	530	0.13	528	0.03	526	0	524	0	522	0
39	548	0.04	546	0.11	544	0.06	542	0.01	540	0	538	0	536	0
40	562	0	560	0.04	558	0.02	556	0	554	0	552	0	550	0
41	576	0	574	0	572	0	570	0	568	0	566	0	564	0
42	590	0	588	0	586	0	584	0	582	0	580	0	578	0
43	604	0	602	0	600	0	598	0	596	0	594	0	592	0
44	618	0	616	0	614	0	612	0	610	0	608	0	606	0
45	632	0	630	0	628	0	626	0	624	0	622	0	620	0
<b>Wt. Percent</b>		<b>33.27</b>		<b>38.02</b>		<b>19.57</b>		<b>6.72</b>		<b>1.72</b>		<b>0.56</b>		<b>0.14</b>
<b>Ave MW =</b>	<b>377.9</b>													

Table IX

**Table X**  
**Viscosity Index (V.I.) of Selected Petroleum CPD's**

	$nC_{26}H_{54}$	170
	$C_{26}H_{54}$	141
	$C_{26}H_{50}$	133
	$C_{26}H_{48}$	77
	$C_{26}H_{34}$	28
	$C_{26}H_{46}$	-18
	$C_{26}H_{28}$	-57
	$C_{27}H_{48}$	-73

The pure compound values listed above were taken from the American Petroleum Institute Research Project 42 on high MW hydrocarbon properties [API Proceedings, Vol. 26 (III), p. 254, 1946]

\*High V.I. = Small Viscosity/Temperature Slope

Figure 1

# Representative UV Spectra Model (Low Res.) Compounds Versus Lube Aromatics

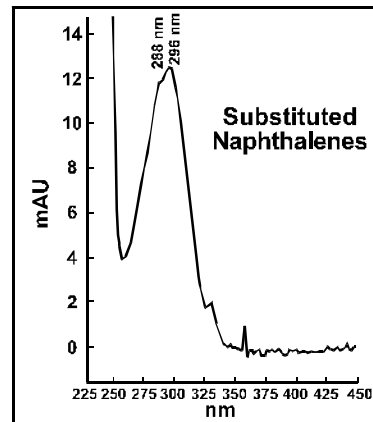
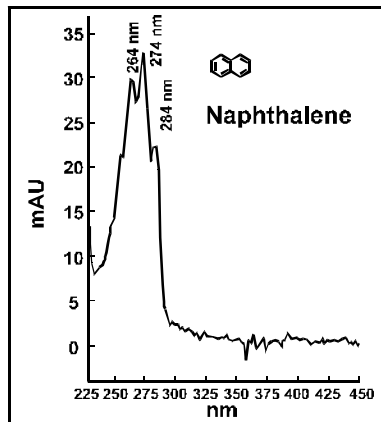
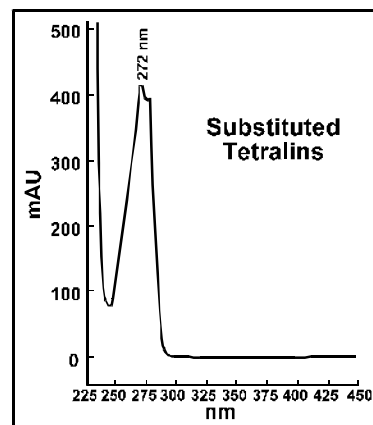
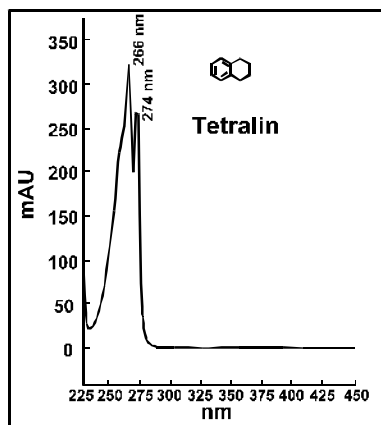


Figure 2

# Representative UV Spectra Model Compounds Versus Lube Aromatics

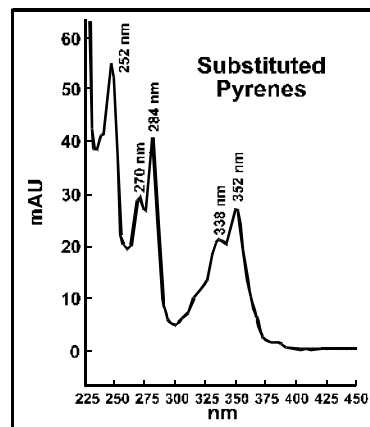
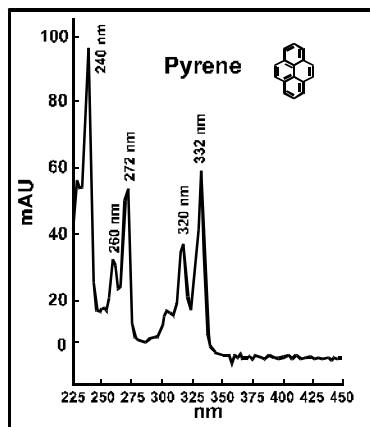
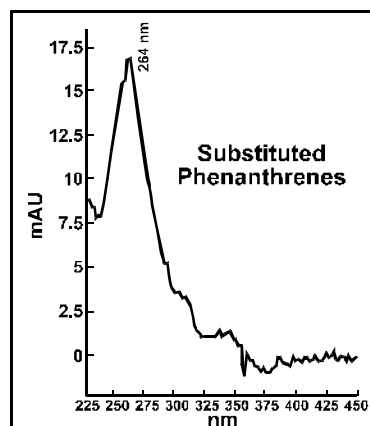
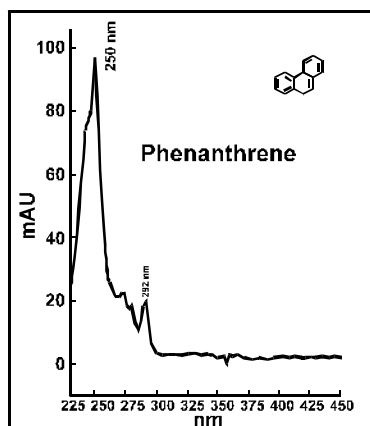


Figure 3

# Low Resolution UV Spectra

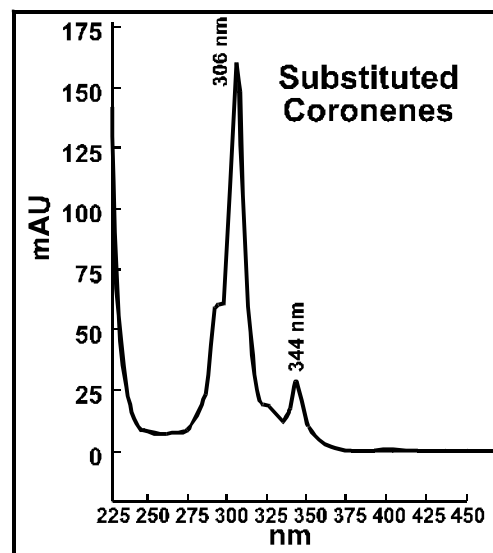
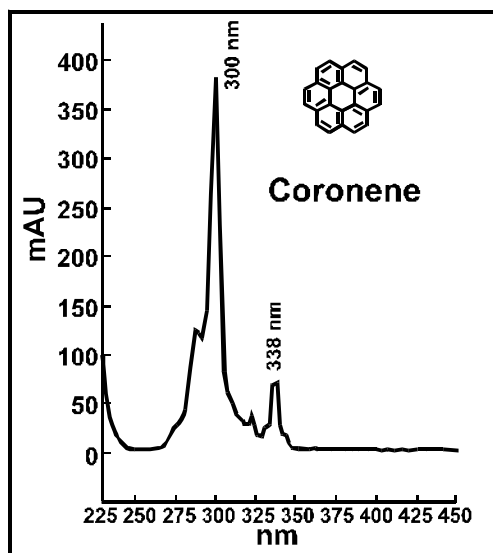


Figure 4

# Tetraline UV Absorbance Spectra

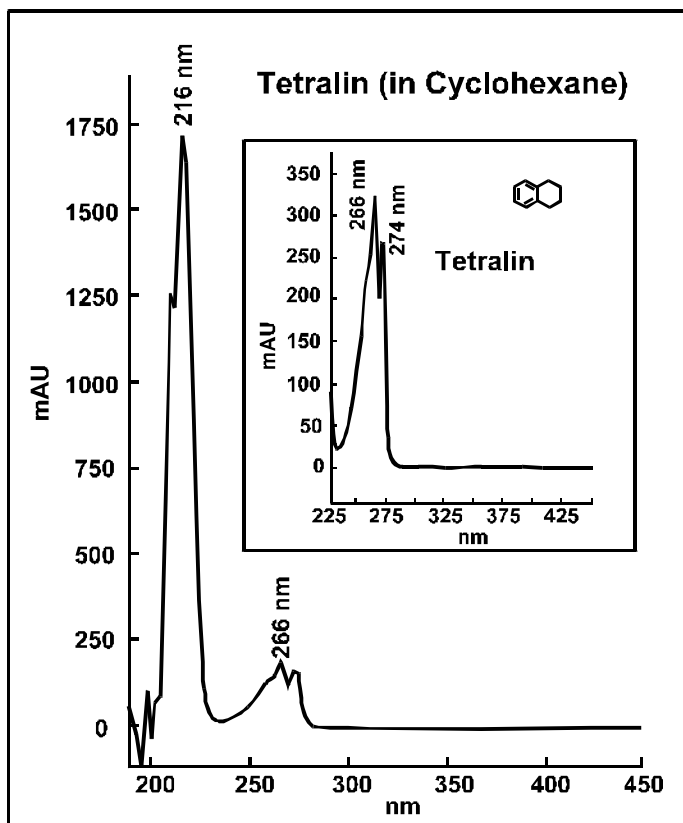




Figure 5

# Relationship Between Base Oil Oxidation Stability and (1-Ring) Aromatic-Naphthene Content

*98-105 V.I. Group II Neutral Oil*

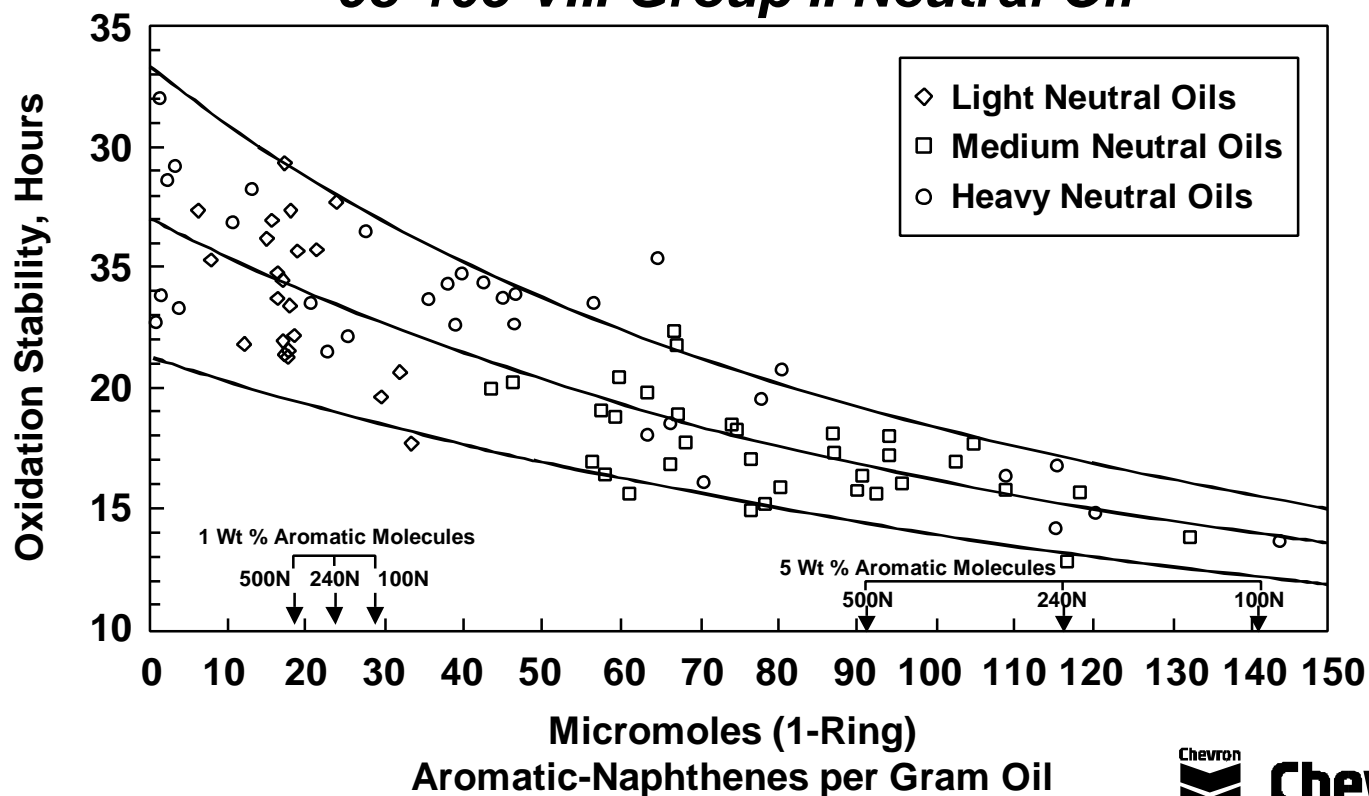


Figure 6

## Inverse Relationship Between Base Oil Oxidation Stability and (1-Ring) Aromatic-Naphthene Content

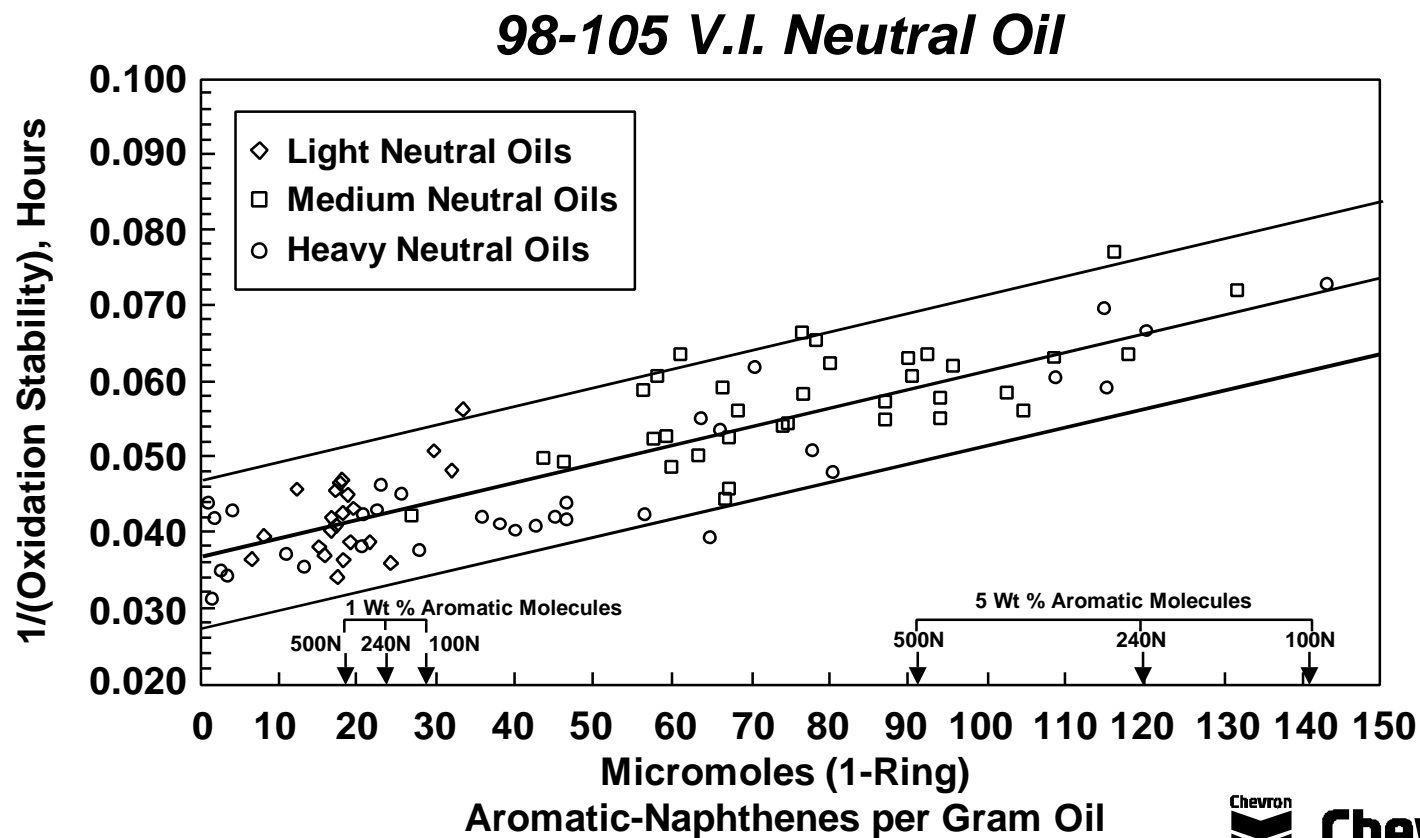


Figure 7

# Change in 4 cSt Group II/III Base Oil Oxidation Stability With Viscosity Index

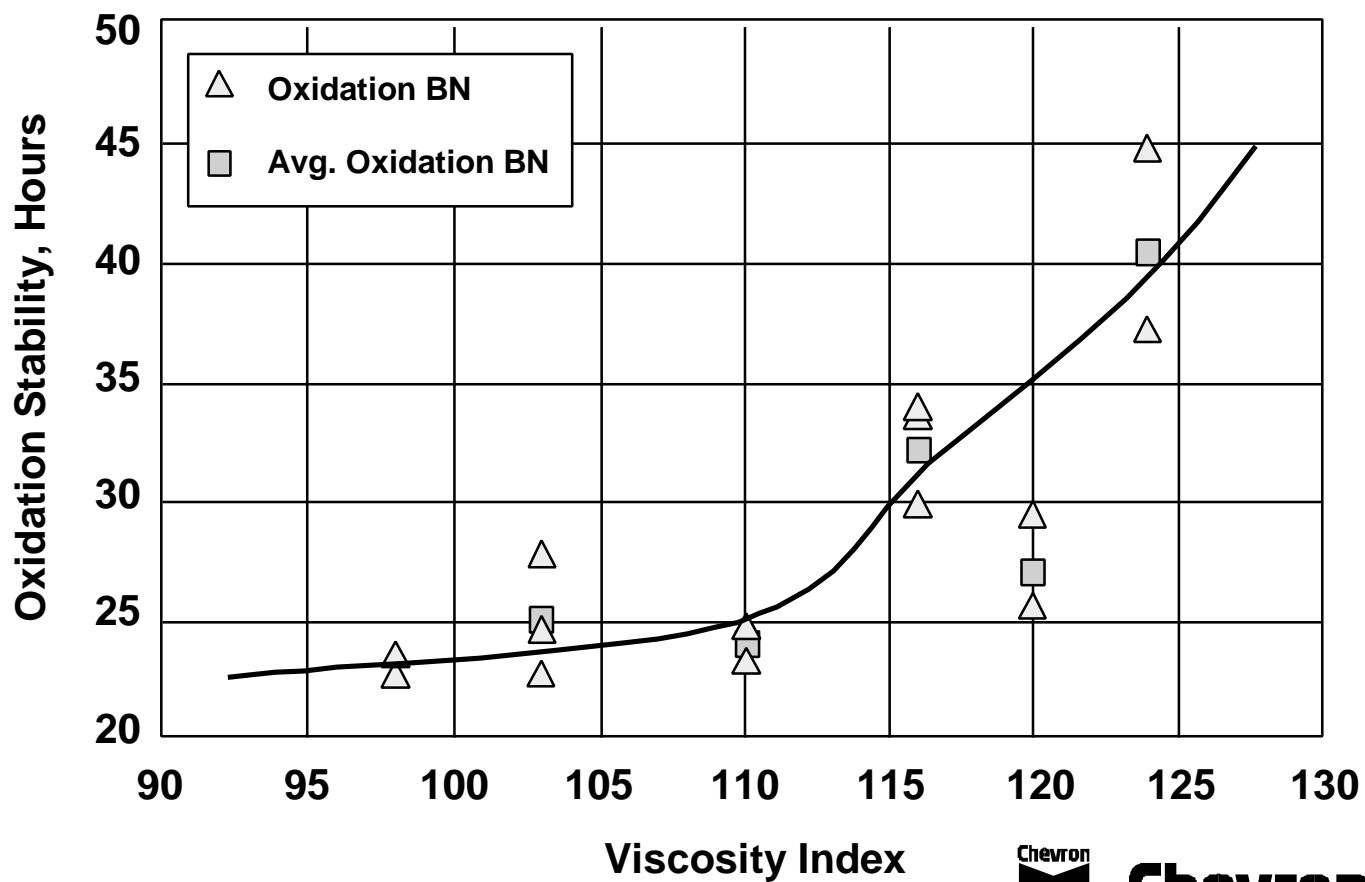


Figure 8

## Change in 4 cSt Group II/III Base Oil Oxidation Stability With Polycyclic Naphthene and Aromatic-Naphthene Content

