DEMYSTIFYING AND UNDERSTANDING YOUR LUBRICANTS USING FT-IR SPECTROSCOPIC ANALYSIS

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ABSTRACT

We're all aware of various advertising mediums flogging super-excellent lubricants with outrageous claims that–if you buy lots of them- will solve all your lubrication woes (whether you have them or not)! Just take a look around your local super big box automotive/hardware store. Does anybody buy that stuff? They sure do! Check out the costly floor-space allocated to all these magic lubricant potions. Check out the infomercials. If nobody bought them, they wouldn't be there, and media advertising is not cheap. Do they work? Well, that's another story and the answers can be highly subjective.

In the field of lubricant analysis, 'condition monitoring' is a general term used to describe analyses of in-service lubricants. Fourier Transform Infra Red (FT-IR) spectroscopy is an analytical tool that may be used to provide an indication of the quality of a particular fluid before, during, and after its designated functional service life.

KEY WORDS: Condition monitoring, ICP spectroscopy, FT-IR spectroscopy, ASTM, lubricant analysis, Aftermarket Lubricant Additives (ALA).

INTRODUCTION

Historically, lubricant testing was accomplished by colour, taste and smell. Modern lubricant data is collected and processed ensuring accurate, reproducible data in accordance to relevant industry recognized standards, such as one prescribed by the American Society of Testing Materials International (ASTM); The American Petroleum Institute (API); The Society of Automotive Engineers (SAE) etc. Only the strict adherence to respected peer reviewed test procedures should be used to verify the validity of these so called 'super excellent lubricants/lubricant additives'. Anecdotal claims without scientifically proven facts are just a marketer's way of 'fooling the public' and getting rich.

Of the many different proven technologies available to the modern tribologist, spectroscopy has always played an important role in both lubricant formulations as well as in service lube analysis. The detailed information on the chemical composition it provides is reliable, repeatable and totally non subjective. Although there are many types of IR spectrometers used in the lubricant industry, the following two instruments are most widely used in lubricant formulation and in service lube analysis:

1) Inductively Coupled Plasma (ICP) spectroscopy. This is a process where an argon plasma, a very hot flame-like source, is created by pumping energy into a stream of argon through high-energy radio waves and a sample solution is aspirated into it[1]. ICP spectroscopy measures the concentration of wear metals, contaminant metals, and additive metals in a lubricant.

   Significance: This information assists decision makers in determining the oil and machine condition.

Table-1 identifies the types of elements that may be identified by this test procedure as well as provides a brief description explaining where the metal comes from for engines, transmissions, gears, and hydraulics.[2]

Table -1 Spectrometer Metals Guide

Metal	Engines	Transmissions	Gears	Hydraulics
Iron	Cylinder liners, rings, gears, crankshaft, camshaft, valve train, oil pump gear, wrist pins	Gears, disks, housing, bearings, brake bands, shaft	Gears, bearings shaft, housing	Rods, cylinders, gears
Chrome	Rings, liners, exhaust valves, shaft plating, stainless steel alloy	Roller bearings	Roller bearings	Shaft
Aluminum	Pistons, thrust bearings, turbo bearings, main bearings (cat)	Pumps, thrust washers	Pumps, thrust washers	Bearings, thrust plates
Nickel	Valve plating, steel alloy from crankshaft, camshaft, gears from heavy bunker-type diesel fuels	Steel alloy from roller bearings and shaft	Steel alloy from roller bearings and shaft	
Copper	Lube coolers, main and rod bearings, bushings, turbo bearings, lube additive	Bushings, clutch plates (auto Power-shift), lube coolers	Bushings ,thrust plates	Bushings, thrust plates, lube coolers
Lead	Main and rod bearings bushings, lead solder	Bushings (bronze alloy), lube additive supplement	Bushings (bronze alloy), grease contamination	Bushing (bronze alloy)
Tin	Piston flashing ,bearing over lay, bronze alloy, Babbitt metal along with copper and lead	Bearing cage metal	Bearing cage metal, lube additive	
Cadmium	N/A	N/A	N/A	N/A
Silver	Wrist pin bushings (EMDs), silver solder (from lube coolers)	Torrington needle bearings (Allison transmission)		Silver solder (from lube coolers)
Titanium	Gas turbine bearings/hub blades, paint (white lead)	N/A	N/A	N/A
Vanadium	From heavy bunker-type diesel fuels	N/A	N/A	N/A
Contaminant Metals				
Silicon	Dirt, seals and sealants, cool-ant inhibitor, lube additive (15 ppm or less)	Dirt, seals and sealants ,coolant inhibitor, lube additive (15 ppm or less)	Dirt, seals and sealants, coolant additive, lube additive (15 ppm or less)	Dirt, seals and sealants, coolant additive, lube additive (15 ppm or less)
Sodium	Lube additive, coolant inhibitor, salt water contamination wash detergents	Lube additive, coolant inhibitor, salt water contamination wash detergents	Lube additive, salt water Contamination airborne contaminate	Lube additive coolant inhibitor, salt water contamination, airborne contaminate
Multi-Source Metals				

Molybdenum	Ring plating, lube additive coolant inhibitor	Lube additive, coolant inhibitor	Lube additive, coolant inhibitor grease additive	Lube additive, coolant inhibitor
Antimony	Lube additive	Lube additive	Lube additive	Lube additive
Manganese	Steel alloy	Steel alloy	Steel alloy	Steel alloy
Lithium	N/A	Lithium complex grease	Lithium complex grease	Lithium complex grease
Boron	Lube additive, coolant inhibitor	Lube additive, coolant Inhibitor	Lube additive coolant inhibitor	Lube additive coolant inhibitor
Additive Metals				
Magnesium	Detergent dispersant additive. airborne contaminant at some sites	Detergent dispersant additive, airborne contaminant at some sites	Detergent dispersant additive, airborne contaminant at some sites	Detergent dispersant additive, airborne contaminant at some sites
Calcium	Detergent dispersant additive airborne contaminant at some sites, contaminant from water	Detergent dispersant additive, airborne contaminant at some sites contaminant from water	Detergent dispersant additive, airborne contaminant at some sites contaminant from water	Detergent dispersant additive, airborne contaminant at some sites contaminant from water
Barium	Usually an additive from synthetic lubricants	Usually an additive from synthetic lubricants	Usually an additive from synthetic lubricants	Usually an additive from synthetic lubricants
Phosphorus	Anti-wear additive (ZDP)	Anti-wear additive (ZDP)	Anti-wear additive Anti-wear additive (ZDP), EP additive (extreme pressure)	Anti-wear additive (ZDP)
Zinc	Anti-wear additive (ZDP)	Anti-wear additive (ZDP)	Anti-wear additive (ZDP)	Anti-wear additive (ZDP)

2) Fourier Transform Infrared (FT-IR) Spectroscopy – Measures the chemical composition of a lubricant. FT-IR spectroscopy is used as a condition monitoring tool[3] with its inherent advantage over conventional IR instrumentation includes simpler instrumentation, faster spectral acquisition, and spectral data manipulation capabilities.

    Significance: Molecular analysis of lubricants and hydraulic fluids by FT-IR spectroscopy produces direct information on molecular species of interest, including additives, fluid breakdown products, and external contamination[4].

Table-2 depicts parameters measured using this test procedure[5].

Table-2 Petroleum Lubricant Condition (e.g. Crankcase oils) Monitoring Parameters – Direct Trending

Component	Measurement Area, cm^{-1}	Baseline Point(s), cm^{-1}	Reporting
Water	Area 3500 to 3150	Minima 4000 to 3680 and 2200 to 1900	Report Value as Measured
Soot Loading	Absorbance intensity at 2000	None	Value x 100
Oxidation	Area 1800 to 1670	Minima 2200 to 1900 and 650 to 550	Report Value as Measured
Nitration	Area from 1650 to 1600	Minima 2200 to 1900 and 650 to 550	Report Value as Measured
Antiwear Components (Phosphate based, typically ZDDP)	Area 1025 to 960	Minima 2200 to 1900 and 650 to 550	Report Value as Measured
Gasoline	Area 755 to 745	Minima 780 to 760 and 750 to 730	Report Value as Measured
Diesel JP-5 JP-8	Area 815 to 805	Minima 835 to 825 and 805 to 795	(Value + 2) x 100
Sulfate by-products	Area 1180 to 1120	Minima 2200 to 1900 and 650 to 550	Report value as measured
Ethylene Glycol Coolant	Area 1100 to 1030	Minima 1130 to 1100 and 1030 to 1010	Report value as measured

For in-service lubricants, most of the early work on condition monitoring was related to observing bulk spectral changes in the fluid, usually associated with additive depletion or gross oxidative changes in the oil.[6,7,8] Condition monitoring can include measurements of oil viscosity, wear metals, particle count, acid number (AN), base number (BN), moisture (H_2O), soot, nitration, sulfation, glycol contamination, oxidation, additive depletion, diesel or gasoline contamination, etc. This information can then be correlated to equipment performance and wear. Regular monitoring of oil can often predict machinery and component failures and ensure that lubricants are changed only when required.

For crankcase lubricants, generally the critical parameters are AN (indicative of oil oxidation), BN (measure of reserve alkalinity used to counteract acidity developed by oxidative processes), moisture (resulting in corrosion and/or lubricant failure) and soot load (resulting in increased wear and viscosity). In other mechanical systems, such as compressors, wear metals and AN are crucial, especially in relation to bearing wear and corrosion. For synthetic ester based hydraulic oils, ester breakdown byproducts and moisture are the critical parameters.

ASTM has standardized analytical procedures designed to determine condition monitoring parameters associated with more common conventional lubricant quality. The ASTM sub committee D02.96-III is currently writing new analytical standards for ‘in service lubricants’ using FT-IR spectroscopy. Although generally applicable to petroleum hydrocarbons[9], only the FT-IR condition monitoring of petroleum hydrocarbons is relatively well defined. The methodology becomes more tenuous as synthetic oils, esters and glycols come into play in many versions and combinations as indicated in Table 3.

Table 3

Hydrocarbon Based	
Ground Petroleum	CH
Synthetic Polyalphaolefins	CH
Alkylated Aromatics	CH, $CH_{(aromatic)}$
Monoalkylbenzenes	CH, $CH_{(aromatic)}$
Dialkylbenzenes	CH, $CH_{(aromatic)}$
Ester Based	
Carboxylic Acid Esters	
Dicarboxylic Acid Esters (Diesters)	CH, (O-C=O)
Dimer Acid Ester	CH, (O-C=O)
Polyols	CH, (O-C=O)
Polyoleates	CH, (O-C=O)
Phtalate	CH, $CH_{(aromatic),}$ (O-C=O)
Trimellitate	CH, $CH_{(aromatic),}$ (O-C=O)
Pyromellitate	CH, $CH_{(aromatic),}$ (O-C=O)
Phosphate Esters	
Trialkyl Phosphates	CH, O-P=O
Triaryl Phosphates	CH, $CH_{(aromatic),}$ O-P=O
Alkyl Aryl Phosphates	CH, $CH_{(aromatic),}$ O-P=O
Polyalkylene Glycols	
Monoalkyl ethers	CH, C-O-C, OH
Diol/Triol ethers	CH, C-O-C, OH
Silicone Based	
Silicone Oils	CH, Si-O-Si
Polysilicone oils (siloxanes)	CH, Si-O-Si
Silicate esters	CH, O-Si=O
Polyphenylethers	CH, $CH_{(aromatic),}$ C-O-C
Polyfluoroalkylethers	CF, C-O-C
Chlorofluorocarbons	CF, CCl
Polymethacrylate/polyalphaolefin cooligomers	CH, O-C=O

METHODOLOGY

A spectral snapshot of the ‘fingerprint region’ for most common ‘in service’ mineral oil lubricants is depicted below in Figure 1. The defined spectral regions (on the horizontal axis) for performance additives hardly change from lubricant to lubricant. The amount present will however affect the amplitude of the peaks (on the vertical axis). In lubricant analysis, it is normal for additives to deplete over time, while new bands will be created depending on the oxidative state of the lubricant. Figure 2[10] depicts the graphical (on the vertical axis) remnant of an antioxidant in mineral oil over time (on the horizontal axis). Its accompanying spectral degradation is indicated on the right where each amplitude depicts remaining antioxidant correlating to the vertical axis, and each curve superimposed equates to time (horizontal axis).

Figure 1

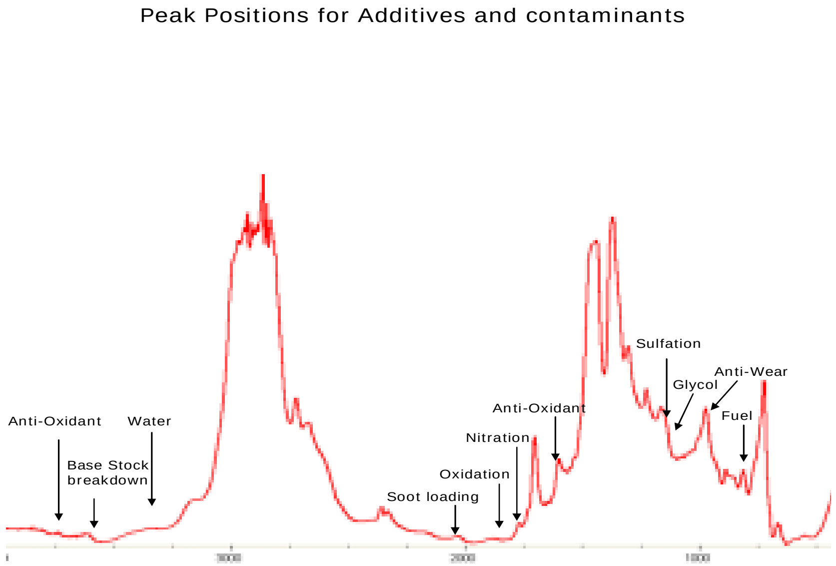


Figure 2

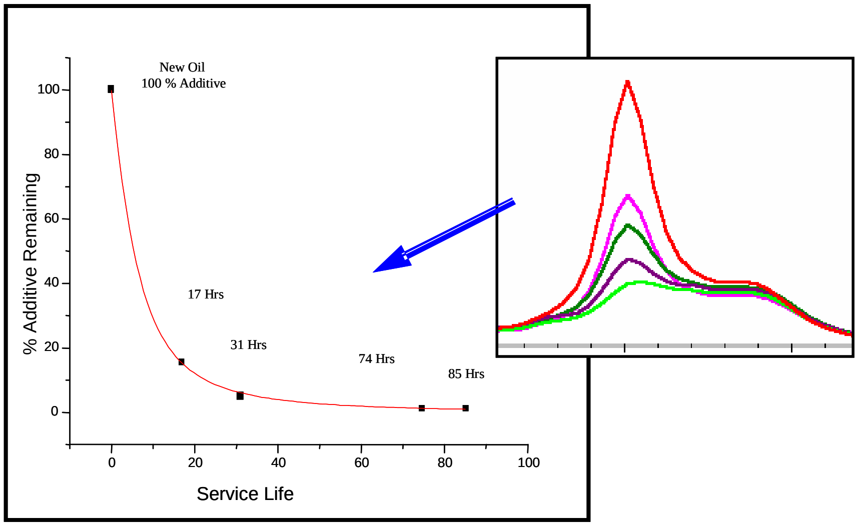
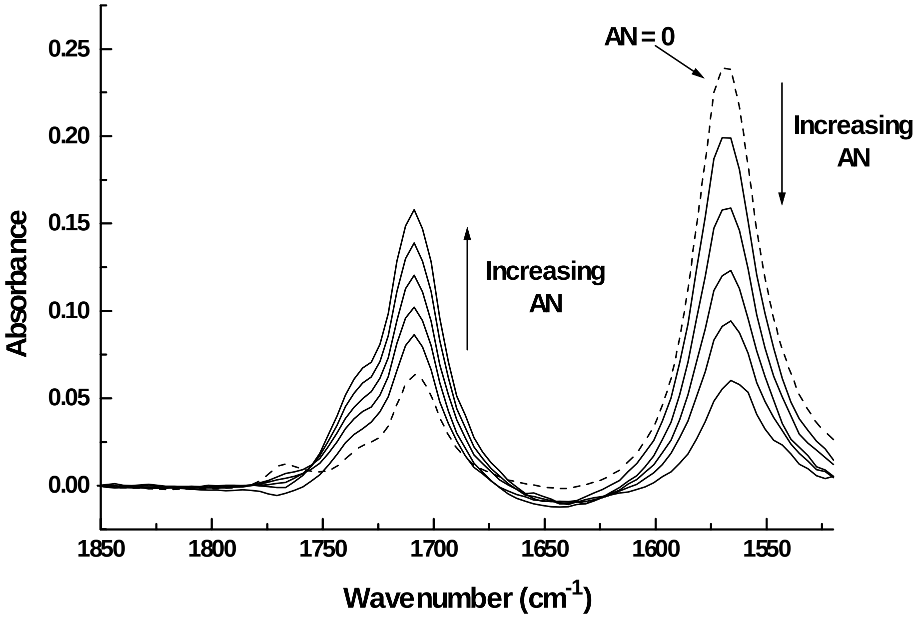


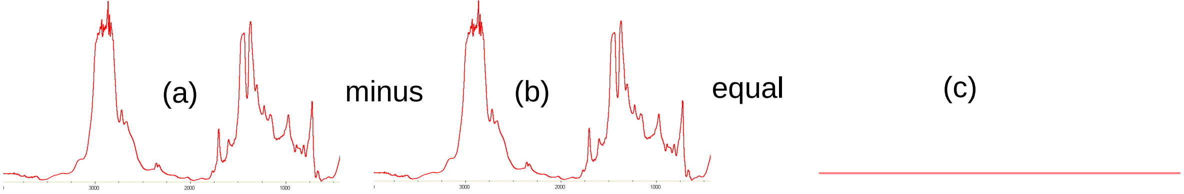
Figure 3 shows fluid degradation using two peaks that correlate to AN after the fluid was dosed with a titrating reagent.

Figure 3



One of the most versatile advantages of FT-IR spectroscopy is the fact that the spectra themselves can be added or subtracted from each other. For example, if we use the sample spectra in Figure 1 as a (a) “benchmark” oil and then subtract (b) the “candidate” oil (which, in this case, is the same as (a)), we will generate (c) a ‘flat-line’ Figure 4 . The resultant ‘flat-line (c)’ proves (b) to be a perfect clone of (a).

Figure 4



In reality, this would be pretty difficult to accomplish, as any ‘blip’ in (c) will indicate a differential of a component succinctly identified by its horizontal axis position and its relative quantity depicted by the vertical axis amplitude –on the positive side or negative side- of the horizontal ‘flat-line’. Lubricant manufacturers may use this methodology as part of their quality control system where (a) will be stored in a data library as the targeted lubricant, and (b) will be the production lot manufactured. (c) will then indicate any components deviating from the original formulation.

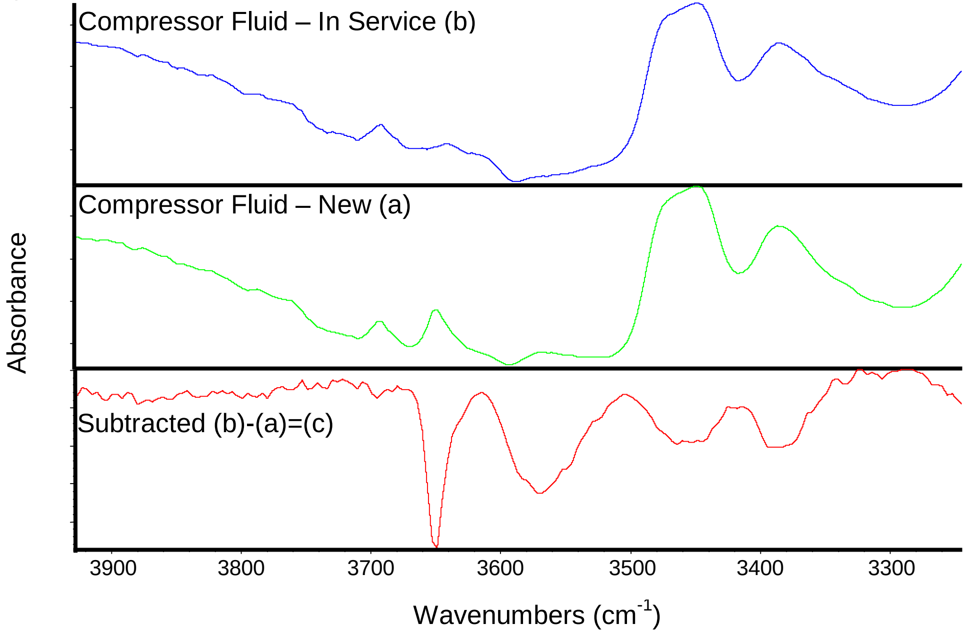
In this context, the FT-IR spectrometer[11] (Figure 5) with or without an auto-sampler has become increasingly prominent in lubricant identification and analysis. Its power is based on the fact that specific molecular functional groups absorb in unique regions of the mid-infrared spectrum, allowing identification of base oils, additives, contaminants and breakdown products.

Figure 5

EXAMPLES

#1-- An example of a spectral subtraction for a New and an In Service Compressor Lubricant is given in Figure 6. The New spectrum (a) was pulled from the COAT®[12] System spectral library of benchmarked oils, and the In Service spectrum (b) –from the customer's compressor- was analyzed and subtracted from spectrum (a). It is beyond the scope of this paper to determine the specific causes for 'blips' in the subtracted spectrum (c), however simple comparisons to regions in Figure 1 would be a good visual start. Computer software programmed with the correct algorithms using peak height and/or peak area and/or and other mathematical derivatives will instantly crunch the data and report the actual lubricant 'condition'.

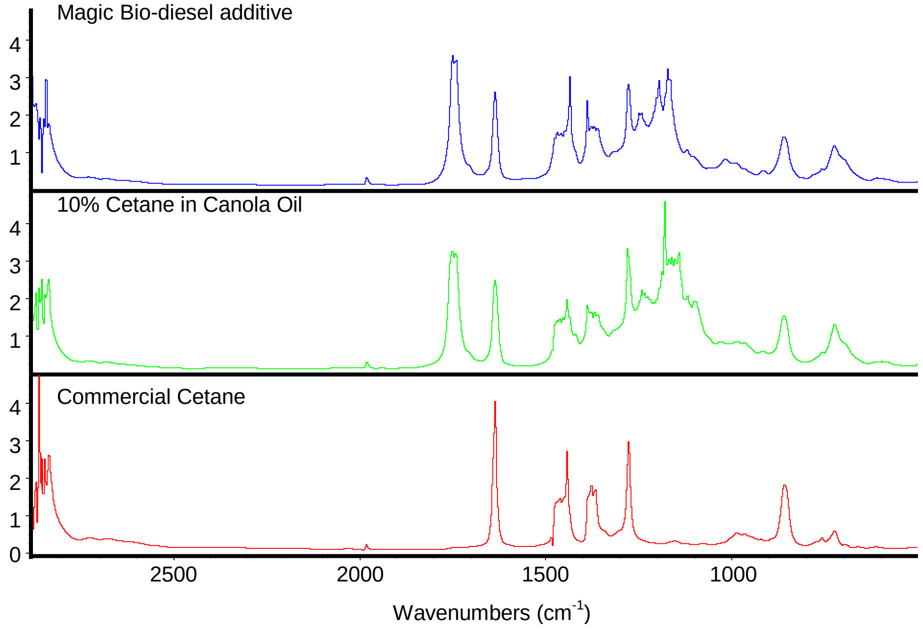
Figure 6



Using powerful software and an expansive spectral library of known fluids and commercially available additives, an ‘unknown’ fluid can be identified with reasonable accuracy using techniques such as classification algorithms and dendrograms. Spectral subtraction can then be employed to weed out the similarities, leaving to focus on the ‘blips’. In the following (Figure 7) scenario below, an unknown ‘magic’ fluid was being marketed as a ‘biodegradable non-toxic diesel fuel conditioner and power booster’. A simple visual analysis of the spectra de-mystifies most of the magic. Further computerized analysis will break down the actual formulation.

The FT-IR analysis determined this to be an oil based on fatty acid methyl esters (FAME) of vegetable oils, such as Canola oil with a cetane improver (alkylated nitrate) in the range of 5-10%.

Figure 7



#2 -- An Aftermarket Lubricant Additive (ALA) marketed as a Metal Conditioner (even though this product is added to a lubricant) and retails for ~$85.00 for an 11oz. bottle boasts the following performance benefits:

I. Provides a lubricity between moving components, which improves tolerances to their correct degree and increases efficiency with less wear
II. Penetrates metal to form a tough, slippery, residual coating to all friction points
III. Eliminates the rapid oxidation of motor oils
IV. Prevents buildup of engine contaminants and actually *prepares deposits* to be entrapped by the motor oil filter
V. Gas mileage *may* be increased by as mush as 8-10% with long term use
VI. Circulates throughout the oil system to seal costly and dangerous leaks…reaches *all* gaskets and increases their seal protection and service life.

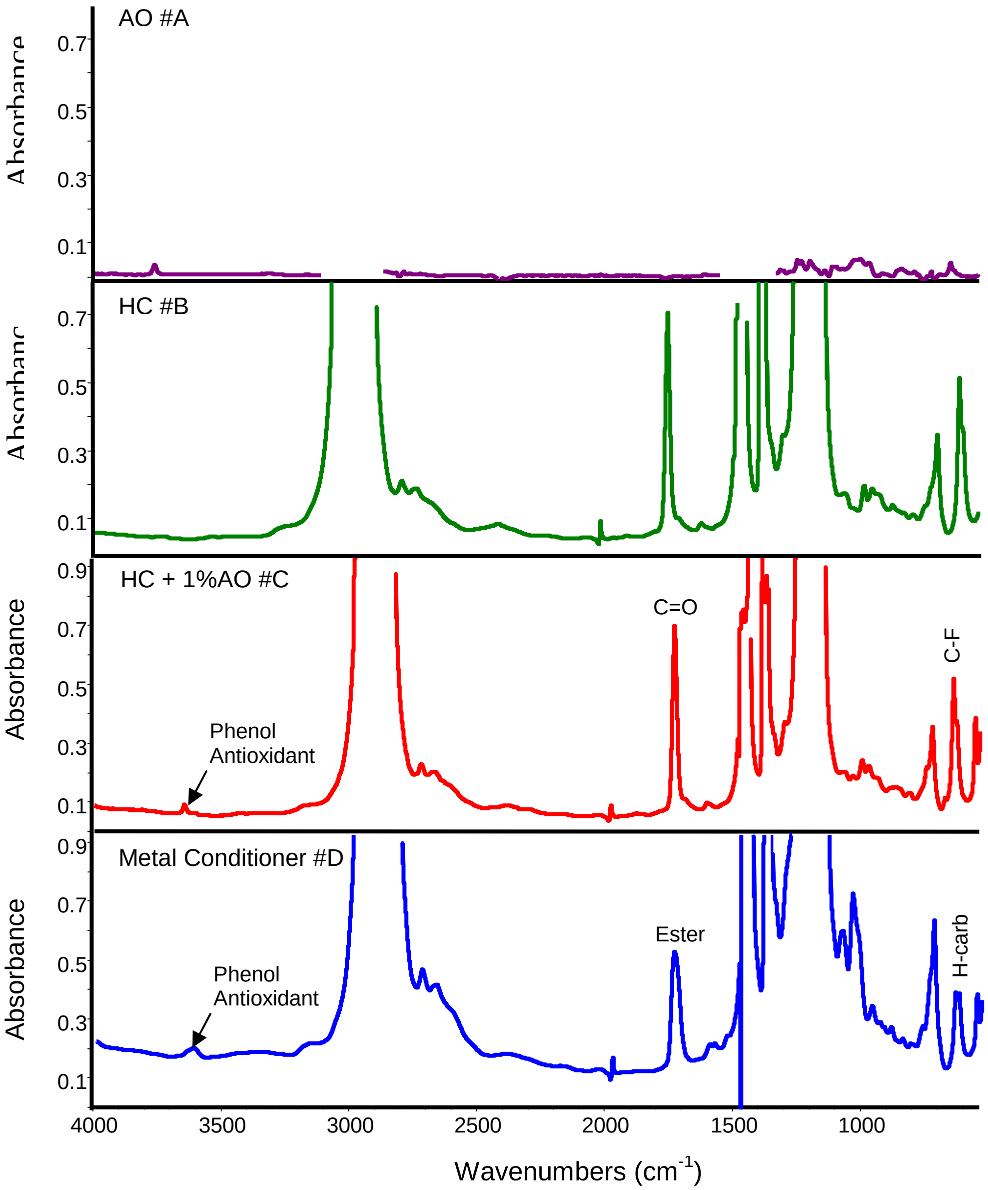
An initial hypothesis was formed based *only* on the performance benefits listed above:

I. Definitely contains oil. Adequate amounts are already in the motor oil.
II. Possibly contains an ester (a polar molecule that adheres to and wets out metallic surfaces) and also possibly PTFE because:
    a. It's considered slippery
    b. The product itself is not black so it eliminates MoS_2 and graphite.
    c. PTFE will *not* form a residual coating. Why should it if it's so slippery? Why only on friction points? Discount this claim!
III. Definitely contains an antioxidant. Adequate amounts are already in the motor oil.
IV. Definitely contains a detergent/dispersant. Adequate amounts are already in the motor oil. It's the job of the filter to eliminate the dispersed contaminants. Nothing unusual about this.
V. Doesn't mean anything. Discount this claim! (Which is really not a claim!)
VI. The esters will wet out and penetrate seals. The product will circulate with the oil and reach whatever the oil reaches. Esters will:
    a. Increase the flexibility of gaskets if they are dried out.
    b. Slightly swell seals & gaskets which *may* stop a leak!

An FT-IR spectrum was taken of the Metal Conditioner and compared to the spectral library of lubricant additives and lubricants in Figure 8 below. Using UMPIRE®[13] software, the program was able to components of the Metal Conditioner on the basis of their spectral "fingerprints".

In Figure 8, specific regions in the spectrum of the Metal Conditioner are indicated in #D. Note the 'phenol antioxidant', 'ester', and 'halocarbon' peaks. These conform to the hypothesis above.
Spectrum #A depicts a commercially available antioxidant which closely matches the peak of #D.
Spectrum #B depicts a commercially available colloidal suspension of PTFE in mineral oil and ester. Notice how the spectrum 'looks like' #D.
Spectra #C is a co-added spectrum of 1% #A and #B.

Dispersants/detergents, rust inhibitors, defoamers, etc. were also found using this methodology, and also co-added to the spectra.
It can now be observed that the fingerprint of #D has been successfully reproduced. A rough costing estimate indicates the material blended in the 11oz container is ~$1.25. However, most of the ingredients in the bottle are already present in the motor oil, and already doing their designated jobs. If we eliminate the duplication, then this 11oz container actually contains ~$0.50 worth of product, which, in essence, is useless and perhaps detrimental to the engine itself.
Figure 8



FT-IR LIMITATIONS AND DISCUSSION

Given the power of FT-IR spectroscopy, one has to question why it is not used more, and more effectively. One of the key limitations in this regard is that the currently accepted methodology is *qualitative* rather than *quantitative*[14]. At issue is the complexity and variability of formulated lubricants, making unambiguous quantitative IR data difficult to obtain. By subtracting the spectrum of the fresh oil from its used or in-service oil counterpart, one can spectrally visualize what has changed at a molecular level, including moisture ingression, additive depletion, oxidation, soot buildup etc. This type of spectral information can be rapidly

collected on an ongoing basis and via trending can be associated with specific lubricant changes (e.g., oxidation, soot buildup).
As such, further refinement and evolution of FT-IR condition monitoring methodology within the ester category (e.g., synthetic phosphate vs. carboxylic esters) is required as it is for glycols. In addition, further basic research is required to both define the condition monitoring parameters of interest to be trended for many of the oil categories outlined.
Although IR spectral information is meaningful to a spectroscopist, its meaning is not necessarily apparent to the non-expert. Even with this limitation, IR spectroscopy is still a very powerful tool, simply because it can provide substantial information about oil condition using a single instrument. Indications about the state of oxidation, nitration and sulfation and levels of soot, moisture, glycol and various additives, among others, are available.

Remember, beauty is only skin deep. You have to look behind the label inside the bottle to understand the true meaning of a ‘super excellent lubricant’.

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