Chapter 18

CHALLENGES IN DETERGENTS AND DISPERSANTS FOR ENGINE OILS

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1. INTRODUCTION

This chapter will focus on the function and chemistries of today's detergents and dispersants, and how they are being transformed to meet increasing performance and cost demands. A significant trend to address market needs by the combination of additive chemistry with additional technologies will also be presented and some examples discussed.

2. ENGINE OIL ADDITIVE AND FORMULATION

Detergents and dispersants are the dominant performance additives components in engine oil formulations. For example, a "typical" gasoline engine oil contains 5-20% of a performance package, which is the largest component, on average, after base oil. The additive supplier supplies the oil marketer with the additive performance package, the pour point depressant, and the viscosity modifier (sometimes known as the viscosity index improver). In a typical crankcase oil the performance package is between 5 and 20% of the formulation. A typical level is about 10%. The viscosity modifier cannot be blended with the performance package and is supplied separately. The performance package is dominated by dispersant and detergent.

The dispersant and detergent together make up about 55-70% of the performance package. Thus, the chemistry of the total package and finished oil is greatly influenced by these two components. As in this example (Figure 1) of a "typical" finished engine oil, the detergent and dispersant must not only perform their intended chemical functions, but must also provide the proper bulk and rheological properties consistent with the application.

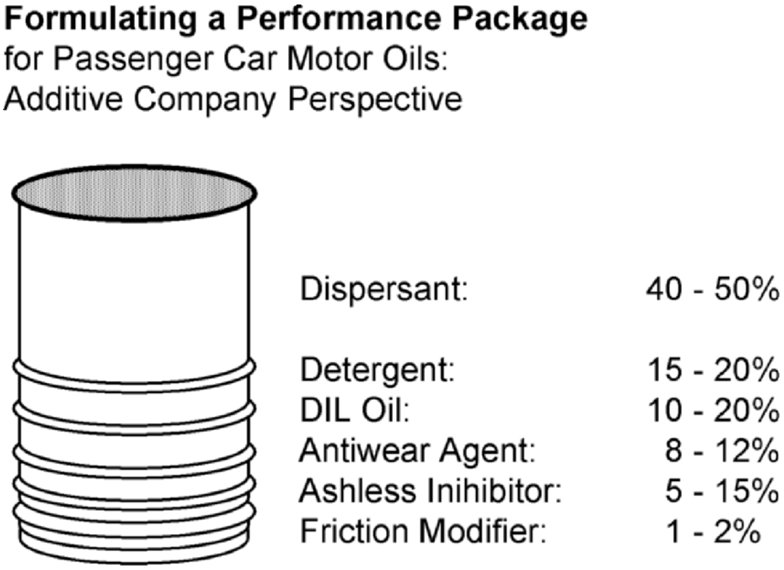
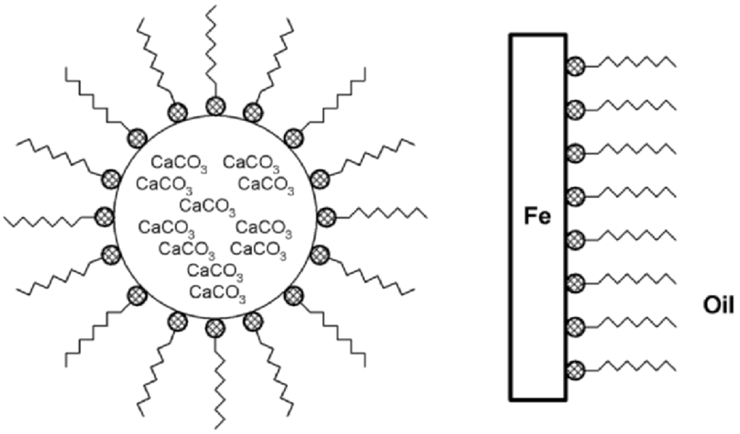


Figure 1. A typical finished engine oil

2.1 Detergents

The detergent functions to solubilize polar components, inhibit rust & corrosion, and prevent high temperature deposits, in part, through neutralization of acids. They are composed of two components, a substrate or surfactant and a colloidal inorganic phase, generally resulting from the overbasing process. The major variables effecting performance are the substrate, which is generally sulfonate, phenate, or salicylate, the metal, which is generally Ca, Mg or Na, the degree of overbasing or conversion, which is the level of basic phase present relative to the amount of surfactant. The structural features of a detergent responsible for these unique properties is shown in Fig. 2.

The combination of a surfactant molecule with a colloidal inorganic core results in a micelluar-type structure as shown in the figure. This gives both the ability to solubilize polar materials in a continuous matrix of oil, and provides acid neutralization capacity, which is also intimately contacted with the oil in a dispersed amorphous colloidal phase, shown in the figure as $CaCO_3$ for a Ca-detergent. This basic colloidal carbonate neutralizes acids formed during the combustion process, such as nitric acid, sulfuric acid, and hydrochloric acid, which lead to metal corrosion and wear, as well as organic acids, which lead to polymerization, viscosity increase and resin formation. Nitro-hydroxy-carbonyl-compounds also form and, if not neutralized, are the precursors of varnish and sludge.



Overbased & surfactant components work in synergy to:

- *Inhibit rust and corrosion*
- *Inhibit oil degradation*
- *Reduce high temperature deposits*
- *Solubilize polar contaminants*

Figure 2. Detergents: Surfactant/base oil synergies

The surfactant component of the detergent can also form a protective layer on metal parts as shown here, resulting in the inhibition of rust and corrosion. Together, the surfactant and the basic components work in synergy to inhibit rust and corrosion and oil degradation, reduce high temperature deposits and solubilize polar components.

This is an idealized representation of a detergent. Calcium carbonate is suspended in oil with a sulfonate or phenate. The excess calcium carbonate provides a base reserve to oils and neutralizes acids that are formed during combustion. Detergents are also effective at keeping surfaces in the engine clean. The metals used to make detergents are typically calcium, magnesium, and sodium. Calcium is the most common.

The need for this acid neutralization capacity is evident from Fig. 3, which shows the continual decrease in total base number (TBN) and increase in total acid number (TAN) for a high- and low-TAN gasoline engine oil. The TBN/TAN equivalence point occurs at around 3000 to 6000 miles. (The metal content in the drain increases after the equivalence point is reached in field testing.) Typically, at this point, acids build up to unacceptable levels, and it is, therefore, desirable to change the oil before the TBN and TAN cross.

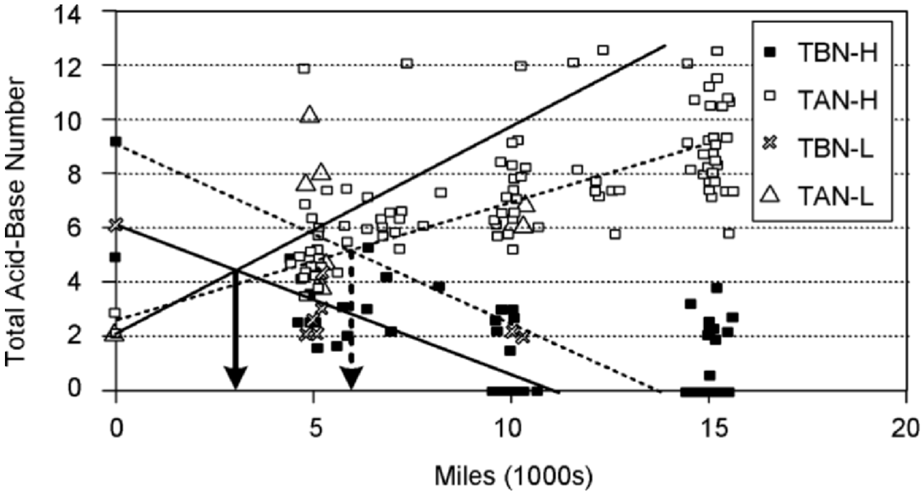


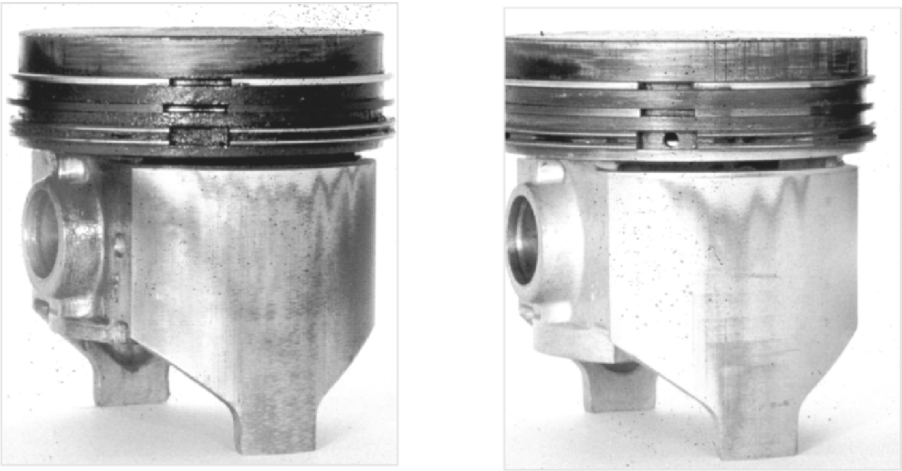
Figure 3. Field testing data demonstrate the need for base capacity (solid lines: TBN, dotted lines: TAN)

These are data from a recent field test showing the decrease in TBN and the increase in TAN with usage. Drain recommendations are often determined by this type of testing. In this example the oil represented by the blue (darker) lines has a lower TBN initially than the oil represented by the pink (lighter) lines. It is not surprising that the cross over point occurs sooner with the lower TBN oil. It is evidence such as this that results in oils with higher TBN being recommended for longer drain intervals.

Another important detergent function is the prevention of high temperature deposit. These deposits, such as the varnish shown in Fig. 4 result, in part, from the acidic precursors formed from high temperature reaction of nitrogen oxides and oxygen with the mixture of fuel and lubricant. The pictures show the effect when these high temperature deposit-forming processes *are* (acceptable) and when they *are not* (unacceptable) sufficiently controlled.

2.2 Dispersants

Dispersants function to suspend soot, thereby mitigating the deleterious effects of large particle agglomerates inside the crankcase. Dispersants include a polymer backbone component, which is predominantly polyisobutylene, or PIB, connected to a polar group, normally an amino group. There are two major classes of dispersants, both of which use PIB and a polar amine group: succinimide dispersants, which use maleic anhydride hook, and Mannich dispersants which use formaldehyde. The major variables affecting performance are the nature of the backbone (composition and structure) and the nature, and relative levels of, the hook and polar group.



Unacceptable **Acceptable**

Figure 4. Detergents prevent high temperature deposits

In practice, the dispersant, like the detergent, also solubilizes polar contaminants, but in this case is designed with a longer tail (M_n = thousands vs. hundreds for detergents) to provide greater steric stabilization to the dispersed carbon (or other contaminant) particle in the micelular structure (Fig. 5). A polyamine head group is used, which is tailored specifically for strong adsorption of soot particles. The nature of the dispersant interactions is tailored to meet the performance characteristics of the particular engine and application. Like detergents, dispersants have been finely tuned over decades to arrive at an optimal structure and composition of the various parameters.

Thus, the combination of the longer hydrocarbon chain and the polar amine head group provides for: (1) the suspension of soot particles (Fig. 6) and the reduction in the corresponding wear and viscosity increases; (2) the solubilization of other polar contaminants; and (3) the prevention of low temperature deposits.

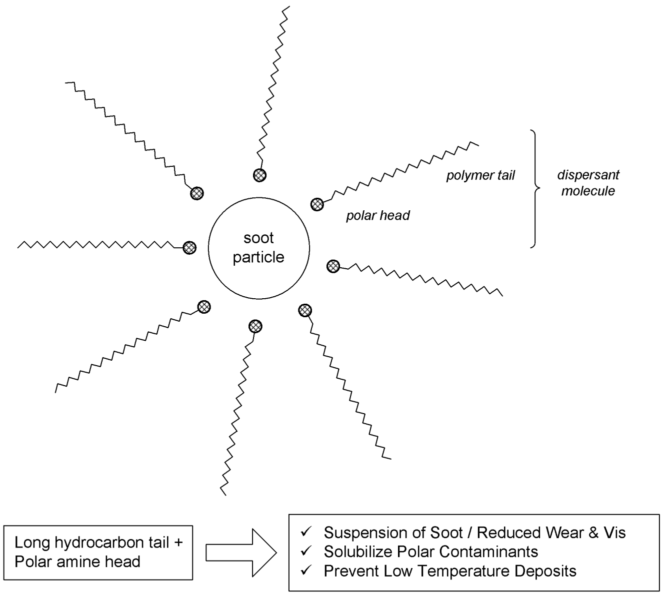


Figure 5. Dispersant chemistry

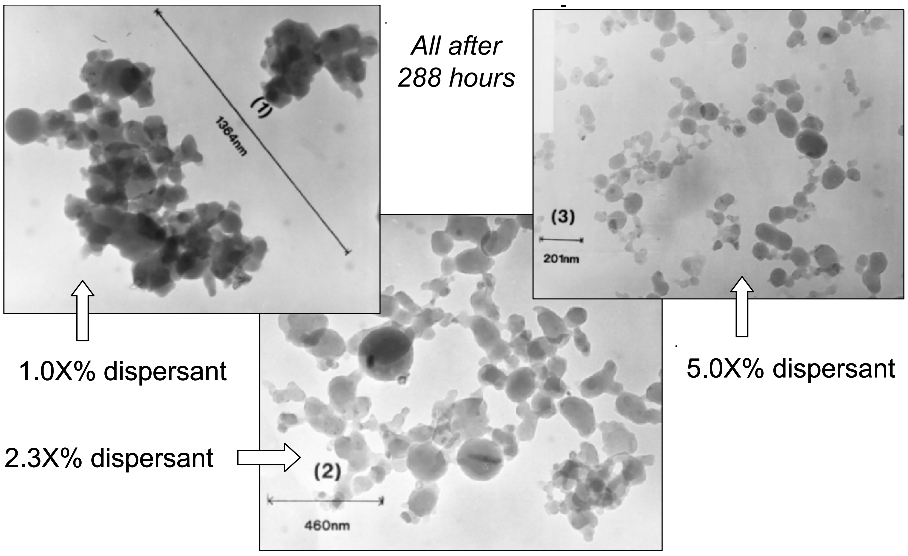
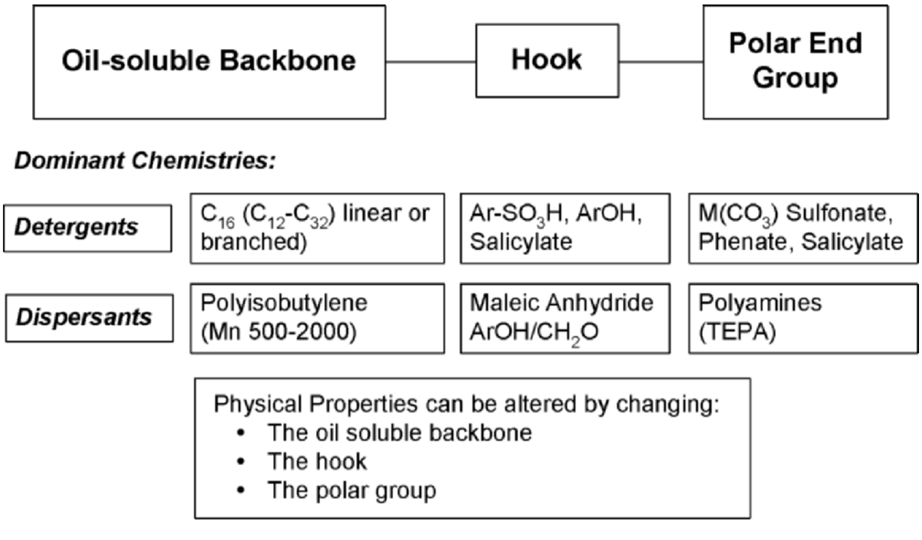


Figure 6. Soot particle growth in a sequence VE test

3. PERFORMANCE CHEMISTRY

The rest of this chapter will discuss the chemistries of these additive systems, the opportunities for performance improvements based on chemistry and incorporation of other technologies with additives. Dispersants and detergents are an important class of performance products made by Lubrizol and other additives suppliers based on alkyl succinimides, succans and phenols. These molecules represent a class of surfactant-type materials which are composed of alkyl chains of varying lengths and polar heads.

The dispersant or detergent molecule can be pictured as a “typical” functionalized molecule with a non-polar tail connected to a polar head via a hook connecting group (Fig.7). Detergents generally employ an alkylated aromatic sulfonate, phenol or salicylate where the hydrocarbon chain is a C_{12}-C_{32}, typically C_{16}, linear or branched alpha olefin or olefin oligomer mixture. These are converted to the corresponding sulfonate, phenate or salicylate salt (usually Ca, Mg or Na) and converted to an “overbased” product with a metal base and CO_2 to incorporate an amorphous carbonate phase which provides base capacity. Again, the short chain and polar head surfactant combination provides the mechanism for solubilization of polars and adsorption/protection of metals. The base capacity neutralizes acid, which can contribute to high temperature deposits.



Detergents	C_{16} (C_{12}-C_{32}) linear or branched)	Ar-SO_3H, ArOH, Salicylate	M(CO_3) Sulfonate, Phenate, Salicylate
Dispersants	Polyisobutylene (Mn 500-2000)	Maleic Anhydride ArOH/CH_2O	Polyamines (TEPA)

Physical Properties can be altered by changing:
- The oil soluble backbone
- The hook
- The polar group

Figure 7. Typical functional molecules

Dispersants, on the other hand, utilize longer alkyl chains, mainly polyisobutylene of 500-2000 Mn. For succinimide-types, these are converted to the succinic anhydride intermediates (or succans) by reaction with maleic anhydride, and subsequently to the final succinimide dispersant by condensation with a polyamine such as TEPA. For Mannich-types, the long-chain alkylphenol is converted with formaldehyde and the amine to the corresponding dispersant. The polyamine end group strongly adsorbs to soot particles as they are formed in the combustion process and the longer tail provides the steric stabilization of the dispersant/soot micelle structure to inhibit agglomeration into larger, more harmful wear particles.

The physical properties of these end products can be tailored by controlling the nature of each component and the relative amounts of hooks and end groups per molecular chain. These have been optimized over several decades, resulting in today's cost effective and high performance products. But despite the large body of knowledge regarding these structure-function relationships, there are only a handful of chemistries commonly in actual commercial use today for production of detergents and dispersants. This is especially true of the "hooks", and "polar end groups", which generally make up only 10% by weight or less of the product, and where the cost effective polyamine succinimides (from maleic anhydride and polyamines) and overbased alkyl sufonates and phenates dominate dispersants and detergents, respectively. While polyisobutylene and aromatic alkylate backbones are most commonly used, there has been a significant emphasis on backbone modifications as a means to greater leverage of chemical and physical properties, for optimal cost and performance, particularly for dispersants.

Table 1. Currently available backbones

Backbones	Sources (Examples)
Conventional PIB	Lubrizol, BP
High vinulidene PIB	BASF, BP, Nippon Petrochemical Co.
Olefnin copolymer (OCP)	Mitsui, ExxonMobil
Poly alpha olefin (PAO)	Mitsui, ExxonMobil

4. CURRENT DISPERSANT AND DETERGENT POLYMER BACKBONES

While dispersant hydrocarbon backbones are currently dominated by conventional polyisobutylene, many more backbones are on the horizon with the potential to provide improved properties, processing, overall performance per cost, and the ability to optimize properties to respond to specific engine performance characteristics. Some of these (Fig. 8) include high vinylidene PIB, olefin copolymers (OCP) and poly-alpha olefins (PAO). Each of these will be discussed in terms of their structure and reactivity, physical properties and how these translate into strengths and weaknesses in the final application.

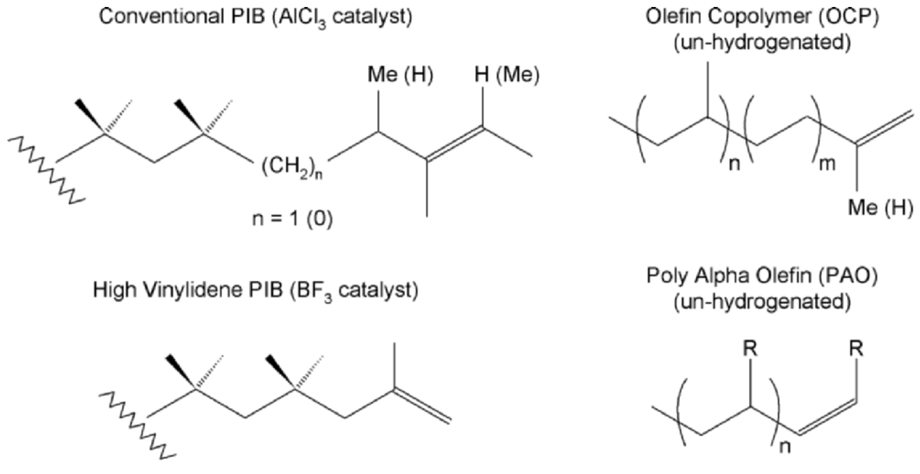


Figure 8. Polyolefin backbone structures

Conventional PIB, made using $AlCl_3$ as the isobutylene polymerization catalyst, has a distinctive 5-carbon end grouping with either a tetra- or trisubstituted terminal olefin. High vinylidene PIB, on the other hand, which can be made from a BF_3-based catalyst, contains a predominance (usually >70%) of the more straightforward gem-disubstituted vinylidene group. These PIB's have similar physical and rheological properties dictated by the common gem-di-methyl groups on every other carbon of the backbone, while the reactivities with the olefinic end groups are very different. Olefin co-polymers and poly alpha olefins, on the other hand, have very different rheological properties than either of the PIB's, but are more similar to high vinylidene PIB in chemical reactivity. These properties are discussed in more detail below, first dealing with their relative reactivities.

Shown here are some representative structures of common backbones and their corresponding succinic anhydrides. Conventional PIB, with multiple allylic carbon atoms, is ideally suited to maleination reaction conditions which promote the formation of diene intermediate, as has been proposed for chlorine-assisted maleination. The diene, once formed, undergoes rapid Diels-Alder reaction with maleic anhydride to form the corresponding polyisobutenyl succinic anhydride, or PIBSA. The vinylidene-type polymers, on the other hand, are more suited to the thermal succination process, thought to proceed by an ene reaction as shown. PAO can also be made with a high degree of vinylidene end groups.

The vinylidene-type containing backbones - that is, high vinylidene PIB, OCP's and PAO's, are also the good reactants for the acid catalyzed alkylation of phenol. The resulting long-chain alkyphenols are intermediates for the Mannich-type dispersants.

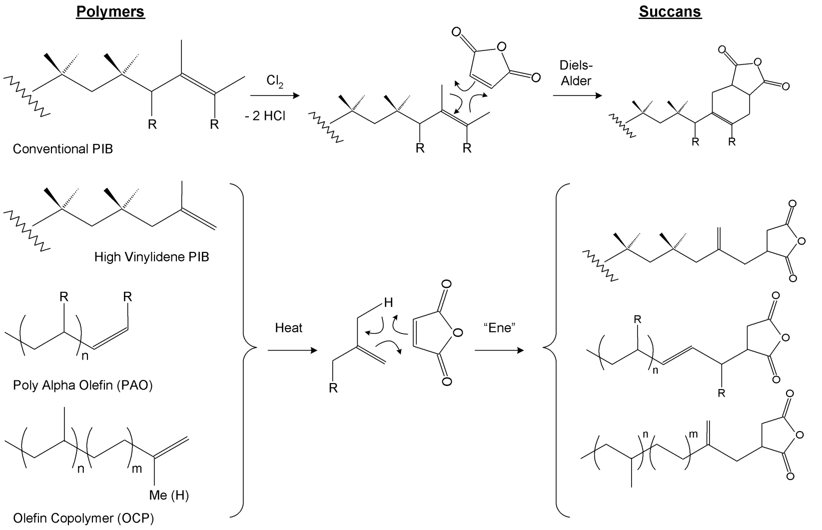


Figure 9. Succination chemistry

5. FUTURE POLYMER BACKBONES

Besides reactivity, there are also a number of other properties that are desirable in an "ideal" polymer backbone for detergents and dispersants. As we have discussed, high reactivity with maleic anhydride and phenol is of course important. For example, conversion to dispersants is also key to achieve high conversions at low temperatures, short reaction times, and with minimal excess and decomposition of maleic anhydride. Good overall viscometrics and low temperature properties are becoming increasingly important, especially in light of high energy efficiency and low emissions formulations. These requirements will also drive changes to other formulation components, making it important to use dispersants and detergents with broad flexibility in formulating. Of course, backbones must be produced at low overall cost with minimal capital outlay by well-developed, commercialized (or at least commercializable) processes.

A summary of the strengths and weaknesses of current backbones against these criteria is presented in Table 2.

Conventional PIB has the advantage of providing very low cost products that utilize tried and true technology and already having large volume capacity in place. However, the process is not amenable to thermal processing technology and the resulting products can limit flexibility in formulating to an optimal elemental composition.

As has been discussed, high vinylidene PIB is more thermally reactive,[3] giving more process and formulation flexibility, but requires more expense and is thinner than conventional PIB. The OCP and PAO's have excellent reactivity and improved low temperature viscometrics, but are even more expensive.

Table 2. Polyolefin backbone alternatives

	Low Overall Cost	Reactive w/MAA (thermal)	Reactive w/Phenol	Low Capital Requirements (mainly succination	Viscosity Credit / Thickening Power	Low Temperature Performance	Low Treat Rate	Process / Formulation Flexibility	Developed Technology	Commercially Available
Conventional PIB (AlCl3)	+	-	-	+	+	-	0	-	+	+
High Vinylidene PIB (BF3)	-	+	+	-	-	-	0	+	+	+
LZ High Vinylidene PIB (developmental)	+	+	+	-	+	-	0	+	-	-
OCP, PAO	--	++	++	-	-	+	+	+	+	+
Branched Polyethylene (potential)	+	++	++	-	-	+	+	+	-	-

This situation leads to several opportunities for improvement, two of which are: (in the shorter term) to reduce the cost of high vinylidene PIB, and, (in the longer term) for maximal performance, to provide a backbone that has OCP/PAO-type performance at PIB cost. The first opportunity is discussed below.

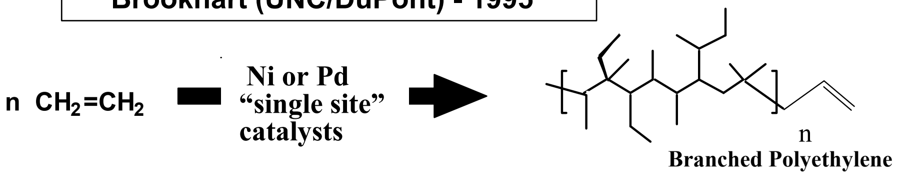
A catalytic process for producing high vinylidene PIB using a non-BF_3 catalyst was discovered and patented at Lubrizol,[1] uses a solid heteropolyacid-based heterogeneous catalyst,[2] and produces PIB form IOB with high >70% terminal olefin content, and thus, has high reactivity with maleic anhydride and phenol. In addition, it has a unique molecular weight distribution, which gives it and the resulting dispersant products unique properties, especially viscometrics. The process is very efficient, with almost no by-products, is amenable to continuous or batch processing and has a simple product recovery stage. At the heart of this process is a heteropolyacid-based catalyst.

Besides reduced overall cost because of the simplified process and materials requirements, it also provides some improvement in thickening power lost from the BF_3-produced material, while maintaining the good reactivity properties. However, this process is not yet fully developed, so the total costs are not yet fully certain.

Another alternative backbone, this time moving to a more OCP/PAO-type architecture, is shown in Fig. 10.

- **Branched Ethylene Oligomers**

Brookhart (UNC/DuPont) - 1995



- **Many variations of catalysts, MW, and branching level/length**
  - ✓ **Grubbs / Caltech**
  - ✓ **Turner / Symyx**
  - ✓ **Others**
- **Terminal olefin: thermal succination reactivity**
- **Potential: PE-like price; PAO-like properties:**
  - ✓ **Low deposit detergents**
  - ✓ **High performance dispersants**
  - ✓ **Alternative to PAO in other additives**

Figure 10. New backbone: branched polyethylene

Branched backbones resulting from polymerization of homopolymerization of ethylene was first reported by Brookhart at UNC/Chapel Hill and co-workers at DuPont in 1995.[4] The discovery generated a flurry of literature reports and patents with many claims around the materials and the catalysts, the majority of which are Ni and Pd systems with diimide ligands. The excitement was based on the possibility of generating branched backbones with broad range of molecular weights solely from ethylene. Since then, many other groups have investigated these so-called "single-site", late transition metal systems for production of branched polyethylenes, including Bob Grubbs at Caltech and workers at Symyx. The latter investigation involved the use of combinatorial-type methods for rapid screening of di and multi-dentate ligands for catalysts for ethylene polymerization activity.

Included in the reported literature of these single-site Ni and Pd catalysts are branched polyethylenes in the dispersant MW ranges and with terminal olefins, which provide thermal succination reactivity to provide PAO-like properties such as low deposits and low temperature performance, at polyethylene-type prices.

These alternate backbones are summarized in the Table 2.

6. FUTURE TRENDS

Besides these new backbones, there are also many other approaches being pursued to improve detergents and dispersants to better address market needs.

Cost reduction activities by reducing treat rate and process improvements are continually occurring, as are formulating approaches to improved compatibility with low friction/fuel economy systems, improved viscometrics and incorporation of EP/antiwear and low S/P/Cl and ashless components.

In the longer term, customers are continually expecting extended life and durability while demanding lower cost, compatibility with catalyst systems and accountability for everything with which the lube comes into contact during its lifetime. These broader and more demanding challenges will be difficult to address with chemistry and formulation technology alone. Presented below is the growing trend to incorporate other technologies and systems to complement the work that detergents and dispersants do as chemical additives.

These trends include:

- Advanced fluids technology
- Technologies for new product introduction, and
- Performance systems

6.1 Advanced Fluids Technology

The evolution of Advanced Fluids Technology through improvements in understanding of compatibility of key components with each other and with base oils is having a significant impact on our ability to predict performance based on high speed computations. Simple empirical models which may have worked in the past are inadequate for today's and future complex formulations. The resulting solutions provide advanced fluids technology not possible even 2-3 years ago. This is described in more detail below.

As an example, some of the major interactions of base oil with additives to be considered in the design of a lubricant package are shown in Fig. 11. This list isn't complete by any means, but it gives a feel for some of the major issues in base oil quality.

The properties are particularly important to dispersant and detergent surface activity, chemical activity, thermal/oxidative stability and solvent power. Furthermore, maximum performance for one test requires very different and frequently conflicting properties.

Before talking about specific issues, it's worth reminding ourselves about the reasons we use additives at all. With respect to our today's oil industry customers, it is suggested if all oils were perfect, then additives would not be so widely needed. Yet today we see great improvements in base oil quality in combination with additive developments which – together – give us outstanding finished lubricant performance. The conflicting requirements for a dispersant formulation are discussed below.

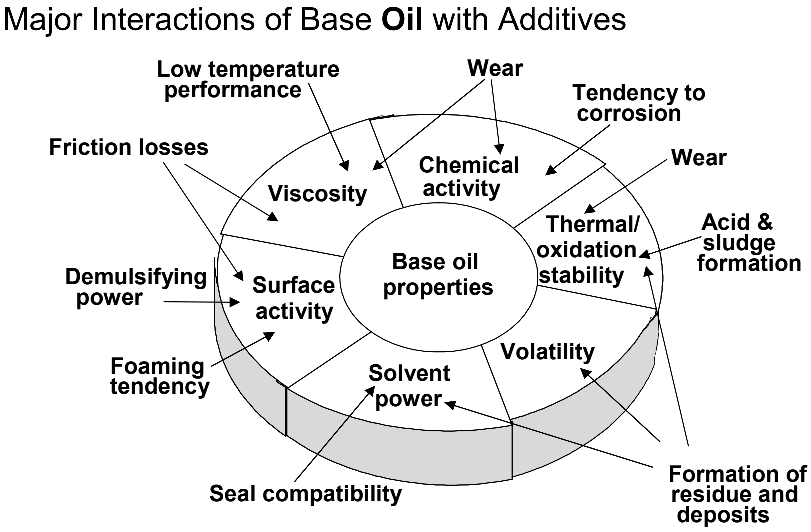

Major Interactions of Base **Oil** with Additives

Figure 11. Major interactions of base oil with additives

Four of the performance criteria for dispersants are shown on each axis of Fig. 12; the higher the performance, the larger the area of the figure. The typical dilemma is represented by the dotted lines. Thermal stability and soot control require high conversion normally and high TBN disperants, which are also the ones which attack seals and give poor VE (sludge) performance. Adjusting the formulation with this conventional wisdom to improve seal compatibility and VE performance results in unacceptable thermal stability. The solid line is a computer-generated formulation, which takes into account many more variables and interactions than would be possible without a very large statistical design and computational power. This design is shown in more detail in Fig. 13.

6.2 Technologies for New Product Introduction

The way in which a thorough understanding of structure-performance relationships is obtained is through statistically designed experiments. This design results in a better balance between the competing requirements by consideration of a large statistically designed matrix of variables, including PIB mol. wt. and mol. wt. cut-off, succination level, amine type, and amine charge. Two new formulations were identified which significantly improved performance (the lower the number the better) over the current baseline. Continued use of these powerful, but computationally demanding statistical models will continue to improve our abilities for formulation to competing requirements.

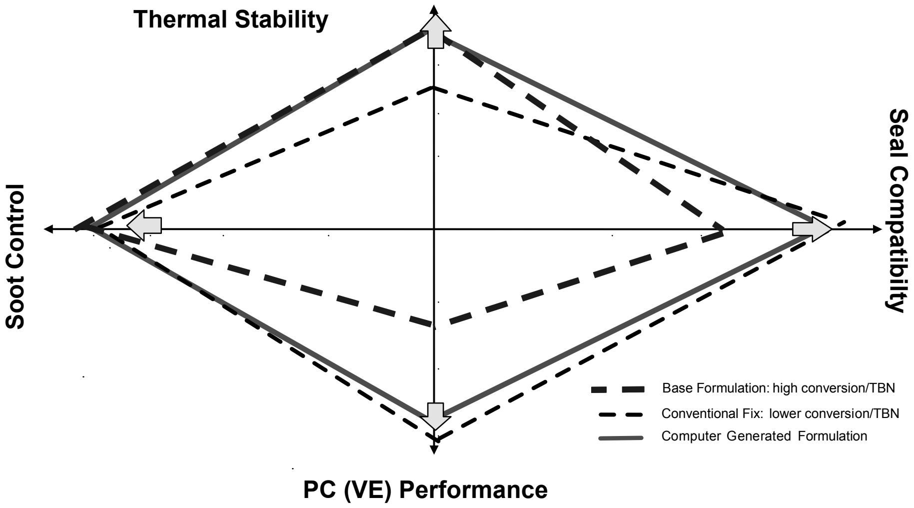
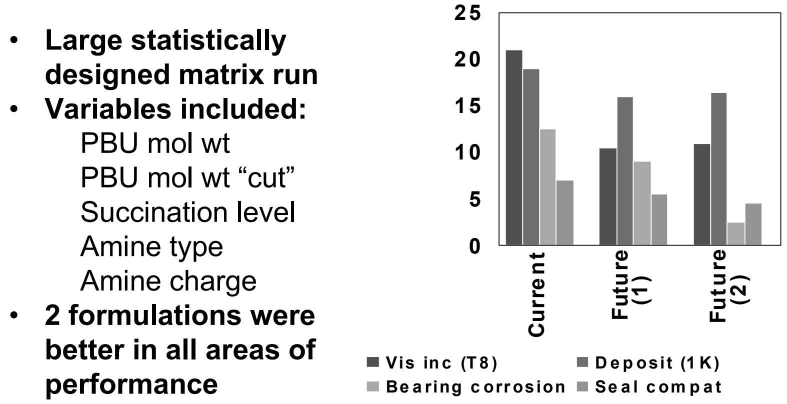


Figure 12. Multiple dispersant requirements



- **Large statistically designed matrix run**
- **Variables included:**
  - PBU mol wt
  - PBU mol wt "cut"
  - Succination level
  - Amine type
  - Amine charge
- **2 formulations were better in all areas of performance**

Figure 13. Balance between competing requirements

6.3 Performance Systems

Performance Systems integrate mechanical, chemical and electronic technologies. An example is Lubrizol's water-blended emulsion fuel system called PuriNOx.[5] PuriNOx is a fill-and-go solution for the simultaneous reduction of both particulate and NOx without the need for engine modifications. Typical results are 50% particulate reduction and 30% NOx reduction by simply switching to PuriNOx fuel, with no other modifications.

The system is composed on the additive package, which includes dispersant-type chemistry, water, diesel fuels and season components, and a blending unit, which includes the mechanical and electronic components necessary to provide a stable water-fuel emulsion, the final PuriNOx fuel product. The system is currently being used in several key cities in North America and Europe with emissions problems for both off and on-road applications.

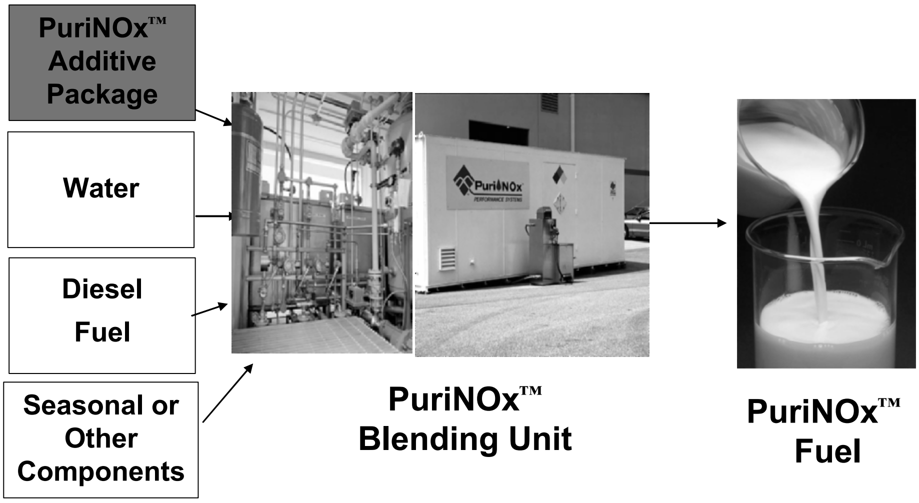


Figure 14. PuriNOx water blended fuel

7. SUMMARY AND CONCLUSIONS

In summary, dispersants and detergents perform critical functions in lubricants, and the chemistry has been well-optimized over the years for existing PIB backbones. However, new backbones provide the potential for beyond-incremental improvements in performance and cost. Integration of additives chemistry with artificial intelligence, and mechanical and electronic systems will provide the technological basis for future step changes in performance.

8. ACKNOWLEDGEMENTS

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