Base Oil Oxidation – The Importance of Prevention

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Base oil oxidation, or more especially its resistance to oxidation, is probably the most important factor in the lifetime of a lubricant. In the oxidation of a hydrocarbon base stock, oxygen is incorporated into the base oil molecules. If sufficiently extreme, oxidation can result in the molecules becoming so polar and polymerized that they are no longer soluble in the remaining mass of nonoxidized, nonpolar base oil molecules.

The result is separation of the oxidized molecules from the lubricant as a distinct solid phase; that is, a sludge. Equally important, though, and even before any separation occurs, the oxidized hydrocarbons take on an acidic character and become a corrosive actor within the lubricant.

From the viewpoint of hydrocarbon base oil chemistry, what causes oxidation and what prevents it are pretty well understood. There is a rank order of the ease with which hydrogen atoms detach from the hydrocarbon molecular frame, which is the first stage of oxidation and known as lability. This detachment results in a hydrocarbon free radical – one of the oxidation intermediates before oxygen incorporation.

Base stock molecules containing a disproportionate amount of the most readily detachable or labile hydrogen atoms tend to be the most oxidatively unstable. This is a gross simplification of a complex family of oxidation reactions, which is beyond the scope of this article, but it is a useful working concept. It is perhaps more relevant to understand what steps can be taken in both base oil production and lubricant formulation to minimize the chances of base oil oxidizing in the first place.

The first thing to understand is the intrinsic tendency of a particular base oil type, or API group, to oxidize. This understanding involves both uninhibited and inhibited oxidation. Uninhibited oxidation is the natural tendency of a base oil to oxidize when no additive antioxidants are present – such as might be triggered by heating a neat base oil to reduce its viscosity through a loading manifold to a ship. Inhibited oxidation is the tendency of the base stock to oxidize when an antioxidant, usually a synthetic molecule, has been added.

The rank order of uninhibited oxidation stability can be the reverse of that for inhibited oxidation stability. For example, most people tend to assume that API Group I base oil is always the most oxidatively unstable. In fact, uninhibited oxidation stability of a Group I is more often greater than

Continued on page 8

Continued from page 6

that of Group II or Group III base stocks. This is mainly due to residual sulfur in the oil acting as a secondary antioxidant that Group II and Group III base oils lack. Of course, if a Group I base stock is processed to drive out the residual sulfur, say by hydrofinishing to improve color, it loses this benefit and probably has lower uninhibited oxidation stability than Group II and Group III.

In addition, higher paraffinic content and lower polynaphthenic or polyaromatic content correlate with both the viscosity index of the base stock and a decreasing content of labile hydrogen. Therefore, a higher viscosity index base stock will have higher inhibited oxidation stability in a finished lube; hence, Group III base oils outperform Group II in antioxidant response.

There are many variants in the main chemical families of synthetic antioxidants that allow formulators to tune the overall oxidation performance of lubricant base oils. But one should not overlook the fact that some additives can be dual-functional – such as certain overbased detergents that can have primary antioxidancy as well as their main acid-neutralizing powers. Also zincs or ZDDPs have secondary antioxidancy as well as antiwear functionality by virtue of their sulfur and phosphorus content.

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In the simplest terms, a primary antioxidant interferes with and inhibits the primary phases of oxidation, which is the incorporation of oxygen into a preformed hydrocarbon free radical. A secondary antioxidant acts to defuse certain oxidation products, which if they don't remain stable, can break down suddenly, leading to a chain reaction that forms many reactive oxygenated species. These compounds cause runaway oxidation, high oxygen consumption and a sudden end to the effective life of a finished lubricant.

A good lubricant formulation will ensure an appropriate balance between the two types of antioxidant. Neither primary nor secondary antioxidants on their own provide optimal performance. This is where the formulator's skill and understanding becomes such an important factor in long term lubricant performance.

Also, the molecular characteristics of the base oil feedstocks and the type of base oil produced must not be overlooked. As noted above, the more paraffinic and the less polynaphthenic or polyaromatic content, the better the oxidation performance in additized finished lubricants. Feed stock characteristics tend to remain broadly intact through processing and contribute to completed base stock characteristics in some form. This despite the fact that most base stock molecules from modern hydroprocessing plants will have undergone some chemical transformation.

However, hydrocracking can improve the balance of labile and less-labile hydrogen types, to the benefit of oxidation stability. This is also why fuel hydrocracker bottoms or waxy crudes are excellent feedstocks for Group III base oil production and provide global supply of high quality base stocks for ever more demanding performance categories. □

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