

Those darn polys!

At one time or another, lube formulators have had to deal with aromatics – whether when agreeing to a performance specification for a base stock, wanting to develop an additive package or just wishing for a bit more solvency. Aromatics at some level are a feature of almost all hydrocarbon base stocks made from crude oil or when other hydrocarbon feedstocks are subject to hydroprocessing.

In their place, aromatics can have benefits for lubricant and process oil base stocks. However, one subclass of aromatics, the polyaromatics or “polys” for short, has few, if any, saving graces.

Aromatics can be classified as mono-, di- and polyaromatic depending on whether they have one, two or three plus fused cyclic aromatic rings. In all cases, the aromatic head group is molecularly flat – unlike their naphthenic ring equivalents – and also pretty reactive.

In hydroprocessing of crude cuts, tunes can be played on the aromatics

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to balance paraffinic content, mainly through control of hydrogen pressures and catalyst temperatures as well as catalyst type. In base stock manufacture, aromatics are typically removed from feedstocks to produce API Group II or Group III stocks by catalytically saturating aromatics with hydrogen through to naphthenics and then cracking rings open to form paraffinics.

However, the opposite can also be done, and hydrogen can effectively be extracted from the molecular system to create aromatics. This is done every day in refineries where so-called platformers – or platinum reformers – put more aromatics into naphtha cuts to produce higher octane gasolines.

Get the hydroprocessing conditions wrong, and exactly the same thing can

be done with the base stocks. Even base stocks starting life as predominantly paraffinic cuts can contain aromatics, including polys, created under adverse hydroprocessing conditions.

Returning to the mono-, di-, polyaromatics issue, monos and dis are tolerable. In fact in some cases, they are beneficial to base stock performance. This is evidenced by the offerings of synthetic aromatic base stocks such as alkyl naphthalenes, which are specifically diaromatics.

But when it comes to polyaromatics, there is no such synthetic offering because it's all bad news. Base stocks containing significant polyfused (three or greater) aromatic rings are inherently oxidatively unstable. Also, in the lighter base stock distillation range,

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they are inherently unsafe with respect to health, safety and environmental criteria.

Really heavy polyaromatics in residual base stocks have one saving grace, in that once molecules become larger than a critical size, they cease to be so toxic. Hence, residual aromatic extracts from solvent-based bright stock production, which are rich in polyaromatics, are relatively HSE benign and make good process oils.

In simplistic terms, this is because the larger polyaromatic molecules are too large to penetrate tissue membranes; whereas, their lighter cousins from untreated distillate aromatic

extracts can penetrate tissue membranes and enter cells and do their worst. In fact, a specific test method, IP-346, addresses the levels of polys in distillate base stocks. In this method, polys are extracted into a polar solvent (DMSO), then weighed.

In essence, all distillate base stocks should have a DMSO extract level of less than 3 percent mass. Otherwise the EU requires labeling the product as "potentially carcinogenic." For Group II and Group III stocks, which usually have a total aromatics content, including monos and dis, of around 1 percent, the "less than 3 percent rule" is not an issue. But it could potentially be an issue for poorly

processed Group I stocks.

We should not, however, assume that polys are unimportant, even in highly saturated Group II and Group III stocks. Excessive poly content is one of the prime causes of photochemical instability in the Group II and Group III supply chain, even in a small total aromatics population.

So what can we do to rid ourselves of polyaromatics in base stock production? There are two approaches: One is mechanical, where they are adsorbed onto solid polar substrates; the other is chemical conversion to something more benign like polynaphthenics. Polynaphthenics will still maintain the basic poly-ring structure, but they are much less reactive and hazardous.

In removing polys by adsorption onto a solid substrate, the conventional approach is to percolate the partially finished stock through a bed of specific clay types. Here, the highly polar heads on the polyaromatic molecules adsorb or stick to the highly polar surface of the clay. The eluted base stock will be essentially free of polyaromatics. It will be lower in the other aromatics as well because the polys preferentially stick to the clay. This is a regular process in the production of naphthenic or paraffinic base oils to meet either oxidation criteria or to meet "readily carbonizable" criteria for higher-tier white oils.

More usually though, hydrofinishing is used as

the last step in the hydro-processing run to seal in the performance characteristics of a base stock. It has to be the last step because all other hydroprocessing steps have the potential to recreate polys.

Hydrofinishing uses variants on the hydrocracking catalysts, but in a lower temperature environment mode and with suitably adjusted throughput rates. This approach favors the conversion of refractory polyaromatics to more hydrogen-saturated species.

To conclude, polyaromatics are an issue for all main mineral base stock groupings, and they must be appropriately addressed to get the best out of any base stock. They can't be ignored just because they may be present at low concentrations because they are a potential catalyst for instability. □



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DAVID WEDLOCK

retired from Shell Lubricants after more than 10 years as global technology manager for finished lubricants and base oils. Before that he worked in R&D for Shell Additives International. He is now an independent consultant. He can be contacted at david.wedlock@live.co.uk