Refrigerant Acids in HFC/POE Systems
and How They Differ from HCFC System

by

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We all know that the development of acids in the refrigerant of air conditioners, refrigerators or heat pumps can severely shorten the life of the system. But did you know the source of the problem and the chemistry is quite different with HFC refrigerants. That is the “Old-School” practices may have to be changed when dealing with HFC’s or do they?

First let’s recall that acids are typically formed by chemical reactions with components and/or materials of construction, lubricating oils, and/or impurities. Elevated temperatures and moisture can accelerate the instability of the refrigerant or the oil and cause the formation of acids. This may be the result of improper operation, such as a failed condenser fan or a clogged airflow path. Checking for acid and water is a common maintenance recommendation since problematic conditions can be easily cleaned up before a system failure. This all remains true regardless of the system, now lets look at the differences.

The refrigerants in the new hydrofluorocatrbon/Polyol ester (HFC/POE) systems are much more thermally stable than the older chlorofluorocarbon (CFC) or hydrochlorofluorocarbon (HCFC) refrigerants. However the new POE oils are less stable that the mineral oils used in CFC or HCFC systems. That is where as the refrigerant would breakdown in the CFC or HCFC and mineral oil systems, now it is the oil that is breaking down in the HFC/POE systems. POE oils are manufactured from organic acids and, in an ideal world without additives, it is the hydrolytic decomposition of the POE lubricants with water (reverse esterification) that reverses this reaction and produces mild organic acids usually carboxylic acids. To explain this another way, POE oil is made from acid in an esterification reaction and when exposed to water the POE lubricant decomposes back to the acid. The amount of acid generated from POE hydrolysis is primarily dependent on the amount of water available, more water means more acid is formed. Unfortunately POE (Polyol ester), PVE (polyvinyl ether), and PAG (polyalkylene glycols) are very hygroscopic with saturation values of 2500, 6500, and 10000 parts per million (ppm) water compared to 25 ppm for mineral oil (Thomas and Pham 1989, Hiodoshi et al 1999). While PVE and PAG are not subject to hydrolysis they are prone to oxidative degradation which also forms acidic by products.

The hydrolysis of POE is worse with improper evacuation. Cavestri et al (2000) showed that in POE systems, low levels of organic acid and water both contributed to system corrosion but the degradation process was greatly accelerated in the presence of air. That means good system evacuation is even more critical in these newer HFC systems.

These mild organic acids typically do not directly damage compressor windings leading to a burn-out. Rather these carbolic acids react with metals in the system (that is they are neutralized) to form carbolic metal salts and the resulting sludge clogs the narrow passages of expansion devices and oil lubrication channels. Tazaki et al (1998) has shown that capillary plugging is more predominate in HFC/POE systems. This hydrolysis reaction can be stopped by removing the water from the system. The addition of additional "Acid Neutralizers" to clean up the acid is exactly the wrong thing to do since the formation of the salt, which is a product of the neutralization reaction, is the failure mode in these POE systems.

If this were an ideal world, then for POE systems, water (and air) and the resulting formation of a precipitate or sludge would be the problem. Corrosion of motor winding by the acid would not be the problem because the system would plug up well before the insulation on the motor windings would be etched away. In this ideal world, simply get rid of the water and the resulting sludge (from the reaction of the mild acid with metal) will not be a problem. The problem solved if you believe only pure POE oil and HFC refrigerant are in your system, unfortunately there is a lot more "stuff" in the system.

Before we proceed to discuss the other things in the system, lets talk about the Critical total acid number (TAN). The Critical TAN is the acid level at which remedial action should be taken to prevent the onset of rapid acid formation which will rapidly destroy the system. The destruction mechanism for strong mineral acids is etching of the insulation off the motor windings and motor burnout. The destruction mechanism for weak organic acids is the chemical reaction (neutralization) with metals to from a precipitate sludge which clogs small passages leading to excessive pressures or loss of lubrication and compressor failure. For HCFC or CFC systems operating with mineral oil, the critical TAN is well established as 0.05 mg KOH per gram of oil. Unfortunately there is no consensus in the industry what the Critical TAN number for HFC/POE systems should be, however all agree that it should be much higher since the organic acids formed in the HFC/POE systems are much weaker. While an exact value for the Critical TAN in HFC systems has not been established it is clear that for the organic acids the critical TAN should be about 0.3 KOH/g (others recommend values as low as 0.05 and as high as 1.5, but most agree to the 0.2 to 0.3 range). Unfortunately, we started this POE acid discussions with the caveat that in an "ideal world", yet the world is far from ideal!

The discussion to date has centered on the fact that, in an "ideal" system, mineral acids would not be found in HFC/POE systems. This is not exactly correct, because POE oil contains many oil additives that are added to improve performance. One common additive is phosphorus, which is added to POE, PVE, and PAG oils as an antiwear additive. Lilje (2000) examined the effect of various phosphorus antiwear additives on different POE lubricants containing 2000 ppp water and found after one week the TAN had increased to 6 mg KOH/g, which is much higher than the critical TAN for POE systems (0.3 suggested by Mainstream) or mineral oil systems (0.05). Since a corrosive mineral acid, not a mild organic acid, is formed from the reaction, the critical TAN is only 0.05, so this acid level is 120-times the critical TAN. A "conventional" mineral-acid (strong-acid) burnout would probably occur in about 40 hours of run-time for this situation. Conclusion: even in POE systems, strong mineral acids and burn-outs can occur, however once again, without the water, this problem is dramatically reduced.

There are many contaminants in a typical system, Cavestri and Schooley (1996) investigated the effects of 64 fluids typically used in the manufacture of systems and found as a residue in actual operating systems. They showed that the TAN values were generally 4-5 times higher due to these fluid contaminants and in some cases acid levels above 1.0 mg KOH/g were found.

Clearly mineral acids can also be a problem in HFC/POE systems. It is also clear that these acids need to be removed but not neutralized, since the precipitate is even more of a problem in these HFC/POE systems. Unfortunately, changing the refrigerant and oil in a system still leaves trace amounts of the existing highly acidic oil throughout the system.

Whenever acid or water is present in either a HCFC or HFC system, the recommended procedure should be to replace the filter/drier. If the acid level is very high, above 0.3 mg KOH/g for HFC systems or above 0.05 mg KOH/g for HCFC systems, then the oil and refrigerant should also be replaced. It is also a good idea to add a suction line filter-drier to trap any acid lodged in the system before it can flow back to the compressor. The purpose of this filter-drier is to keep the return flow to the compressor as acid-free as possible, therefore, the filter should be located as close to the compressor suction as practical (since these suction lines could also be contaminated with residual acid).

Even with new refrigerant, oil, and a new liquid-line filter-drier supplemented with a new suction line filter-drier, there still must be some method of removing or flushing the residual acid and water from the system (note that I said *removing* or *flushing,* and not *neutralizing* the acid). Some ill-informed technicians often make the costly error of believing that the addition of a foreign substance (which forms a chemical reaction to neutralize the acid) will solve the acid problem. This is not the case. Remember that every neutralization reaction must follow the basic laws of chemistry--acid and base react to form salt and water. The salt that forms is a corrosive metallic salt sludge, which remains in the system to corrode components and potentially clog small passageways (such as bearing oil feed lines and expansion devices). As we know, every acid neutralization reaction leaves a residue. However, some manufactures have created a formulation where the solid residue is dissolved in another foreign substance to form a liquid residue (instead of a solid residue). This is not a better situation. Adding more foreign substances will simply cause corrosive salt to dissolve into a corrosive liquid form, and the solids can still precipitate to clog small passages. Unfortunately, this method allows manufacturers to deceptively claim it “leaves no SOLID residue.” With HFC/POE systems there is already a potential sludge problem, use of an acid neutralizer can only make matters worse. Tazaki et al (1998) found that capillary tube plugging is worse in HFC systems! Stay away from neutralization reactions.

The corrosive salt residue of the neutralization reaction is not the only problem with neutralization acid treatments. Another severe problem is that to neutralize the acid you must add the correct amount of base. But exactly how much are you supposed to add? Too much base leaves a residual base, a caustic residue that is much more corrosive than the salt residue. Adding too little base and you still have remaining acid, which will accelerate the formation of additional acid. In my experience, this is an overlooked problem with neutralization reactions. It's nearly impossible to add the correct amount of base into a system without knowing the exact amount of acid in the system. I recommend that you read the neutralization instructions, which typically suggests adding the entire contents of the bottle. But common sense will tell you that a whole bottle can't be the correct amount of base for a high acid situation *and* a mild acid problem!

So, how *do* we deal with acid and water? Filter-driers do an excellent job of removing any acid or moisture passing through them. But without any way to accelerate the rate at which the acid or water is flushed into the filter-drier, the system might fail before the filter-drier can remove all the acid from the compressor's oil. Lilje's experiments showed that the TAN increased from 0.3 (mild organic acid)to about 6 mg KOH/g (stong mineral acid) in only one week due to the phosphorus antiwear additive and water in the system. This is a strong mineral acid, namely phosphoric acid that is formed. Our tests have shown that with a strong mineral acid level of 0.133 mg KOH/g and only a filter drier to remove the acid, it took 32 hours for the acid level to drop to 0.073 mg KOH/g. While this may sound great, since the filter-drier is clearly removing the acid, the bad news is that the compressor burned out after 32 hours. However, if we could speed the acid removal, we could avoid a compressor burn out. In comparison, an essentially identical system with 0.133 mg KOH/g acid was tested after one percent (by weight) of **QwikShot® Acid Flush™** was added. After 20 minutes, the oil containing QwikShot was tested for acid and it was determined that 100% of the acid was removed from the oil. Remember, without the addition of QwikShot, the acid level only dropped 45% in 32 hours

QwikShot is also adsorbed into the filter-drier and *leaves no residue*! The exact rate at which QwikShot is adsorbed in the filter-drier depends on the system flow rate and drier type. Experiments with an R-22 system have demonstrated that more than 60 percent of the QwikShot is removed from the oil in less than six minutes and all of the QwikShot is normally removed in less than 15 minutes of operation in a typical system.

In conclusion, while the chemistry of HFC/POE systems is clearly different from HCFC/mineral oil systems, the treatment is the same: Namely keep the water and air out and monitor the acid level. Mineral acids can be present in either system, however strong mineral acids are less likely in the new HFC systems, where oil sludge is more of a problem and the more likely failure mechanism. In either case, avoid neutralization reactions which can increase the formation of sludge in the system.

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