Effect of Metal Alloys, Degradation Inhibitors, Temperatures on Thermal Oxidative Stability of CF₃O(CF₂O)ₓ(CF₂CF₂O)ᵧCF₃ Fluids

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**CF$_3$O(CF$_2$O)$_x$(CF$_2$CF$_2$O)$_y$CF$_3$ Fluids**

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Degradation-promoting action of a series of ferrous and titanium alloys on CF$_3$O(CF$_2$O)$_x$(CF$_2$CF$_2$O)$_y$CF$_3$-based Z25 fluids and the inhibition effectiveness of several classes of additives were investigated. Four types of additives—phosphines, phosphates, phospha-s-triazines, and diphasphetraazacyclooctatetraene—were studied in two batches of Z25 fluid, P28 and P151. In the absence of inhibitors, titanium alloys were more detrimental than the ferrous metals, but the additives were more effective in the presence of titanium alloys. Phosphate esters totally inhibited the decomposition of P151 at 330 °C over 24 h in both types of alloys. The other additives were effective at lower temperatures. The responsiveness of fluid to an additive was found to be batch dependent.

**Introduction**

The copolymers CF$_3$O(CF$_2$O)$_x$(CF$_2$CF$_2$O)$_y$CF$_3$ due to the presence of −CF$_2$− units in particular when $x > y$ possess low temperature and viscosity/temperature characteristics (viscosity index) superior to that of any other industrial or experimental poly(perfluoroalkyl ether) fluid (Sianesi et al., 1971; Gumprecht, 1966; Ohsaka, 1985; Jones et al., 1993). Yet, these compositions exhibit the lowest thermal oxidative stability in the presence of metals (Paciorek and Kratzer, 1994). Recently developed additives (Paciorek et al., 1994, 1996a,b; Paciorek, 1996), especially the phosphate esters, were shown to inhibit the degradation of poly(hexafluoropropene oxide) fluids in oxidizing atmospheres in the presence of metals at least up to 330 °C (Jones et al., 1996). It was thus essential to determine whether these materials would perform equally well in the CF$_3$O(CF$_2$O)$_x$(CF$_2$CF$_2$O)$_y$CF$_3$ copolymers and whether variations within the Z25 family of fluids would affect the additives' behavior. Due to the nature of the polymerization reaction, reaction of CF$_3$ with oxygen under ultraviolet radiation, the relative ratio of CF$_3$O to CF$_2$CF$_2$O units, and their arrangement can vary from batch to batch.

**Experimental Section**

**Fluids.** Fomblin Z25–P151 (Product of Montedison): MW, 9700; viscosity at 100 °C, 42.6 cSt; based on $^{19}$F NMR CF$_3$O(CF$_2$O)$_x$(CF$_2$CF$_2$O)$_y$O, 0.74:1.00. Fomblin Z25–P28 (Product of Montedison): MW, 9750; viscosity at 100 °C, 47.3 cSt; based on $^{19}$F NMR CF$_3$O(CF$_2$O)$_x$(CF$_2$CF$_2$O)$_y$O, 0.68:1.00.

**Alloys.** Six metal alloys were studied: M-50 steel, 440C steel, Pyrowear 675, Cronidur 30, Ti(4Al,4Mn), and Ti(6Al,4V). The alloys M-50, 440C, Ti(4Al,4Mn), and Ti(6Al,4V) were in the form of coupons of 1.67 cm$^2$ surface area. Pyrowear 675 and Cronidur 30 were in the form of bearing balls of 9.58 and 1.50 cm$^2$ surface area, respectively.

**Inhibitors.** These included three hindered phosphas-triazines [CF$_3$F$_4$(OCF(CF$_3$)CF$_2$)CN]$_2$(C$_6$H$_5$)$_2$PN (I), [CF$_3$F$_4$(OCF(CF$_3$)CF$_2$)OC(CF$_2$)CN][(C$_6$H$_5$)$_2$PN] (II), and [CF$_3$F$_4$(OCF(CF$_3$)CF$_2$)OC(CF$_2$)CN][(C$_6$H$_5$)$_2$PN] (III), a monophospha-s-triazine [CF$_3$F$_4$(OCF(CF$_3$)CF$_2$)OCF(CF$_2$)CN][(C$_6$H$_5$)$_2$PN] (IV), phosphines [CF$_3$F$_4$(OCF(CF$_3$)CF$_2$)OC(CF$_2$)CN]$_2$P (V), and [CF$_3$F$_4$(OCF(CF$_3$)CF$_2$)OCF(CF$_2$)CN]$_2$P (VI), four phosphates 

**Results and Discussion**

The low thermal oxidative stability of the Z25 fluids in the presence of metals is clearly evident from the Figure 1 data. All the ferrous alloys over an 8 h exposure at 316 °C caused approximately 50% volatilization into primary and secondary decomposition products such as CO$_2$, COF$_2$, and SiF$_4$ in the case of both of the fluid batches (Kratzer et al., 1979; Paciorek and Kratzer, 1994). However, the extent of degradation promoted by the titanium alloy, Ti(4Al,4Mn), as measured by volatiles produced, was higher by a factor of 2 in the case of P151 compared to P28 over the 8 h exposure at 288 °C. This is contrary to what would be expected based on the higher ratio of CF$_3$O to CF$_2$CF$_2$O in P28 (1.00:0.74 versus 1.00:0.68 in P151). It has been clearly shown by (Kasai et al., 1991) that segments of...
(CF$_2$O)$_n$ provide the most reactive sites in -(CF$_2$O)$_m$(CF$_2$CF$_2$O)$_n$- copolymers. The higher the CF$_2$O to CF$_2$CF$_2$O ratio, the greater the extent of (CF$_2$O)$_m$ segments. Apparently, differences other than the content of CF$_2$O moieties are responsible for the observed behavior. In both fluids the action of the titanium alloys was found to be more detrimental than that of the ferrous metals, in agreement with past findings (Paciorek and Kratzer, 1994). Surprisingly, there was no difference between the action of Ti(4Al,4Mn) and Ti(6Al,4V) alloys in the case of P151. In analogy with poly(hexafluoropropene oxide) fluids, Ti(4Al,4Mn) would be expected to be more detrimental. On the other hand, in view of the essentially total volatilization no meaningful conclusions can be drawn. To detect differences, it would be necessary to perform tests either at lower temperatures or for shorter periods. Thermal stability evaluations performed to date on additives alone showed C$_2$PN$_3$, I, C, and V to be stable at 316 °C over a 24 h exposure; compounds II and III under these conditions volatilized 48 and 62%, respectively (Kratzer et al., 1979; Paciorek, 1996).

As shown by the data presented in Figure 2, in the P151 batch the majority of the additives tested (A, B, C, D-2, D-4, II, V, and PH-3) were fully effective in arresting its degradation in the presence of ferrous alloys at 316 °C over a 24 h period. The exceptions were monophospha-s-triazine I (3.4 mg/g) and possibly diphospha-s-triazine III (0.9 mg/g). The volatile production does not correspond to the relative stability of the
additives themselves. As noted above, I was found to be stable at 316 °C, whereas III was extensively degraded at 316 °C. The acceptable inhibition performance is based on a volatile production limit of 0.5 mg/g (Paciorek et al., 1996b). Phosphate C was fully effective (0.5 mg/g) even at 330 °C; V was unexpectedly less effective at 330 °C (1.4 mg/g). Based on the comparisons given in Figure 3, the P28 batch is definitively less susceptible to additive action than the P151 material, which would be in agreement with its higher content of CF₂O units. This is shown by the action of M-50, 440C, and Ti(4Al,4Mn) alloys in the presence of additives I, PH-3, and phosphate A. As pointed out earlier, in the absence of an additive the extent of degradation of P151 at 288 °C over 8 h in the presence of Ti(4Al,4Mn) was higher by a factor of 2 compared to P28.

The additives C, V, D-2, and PH-3 were fully effective in arresting the degradation of Fomblin Z25–P151 at
316 °C in oxygen in the presence of Ti(4Al,4Mn) alloy, as shown by the Figure 4 data. The hindered diphsosa-s-triazines, compounds II and III, were only marginally inferior in performance (0.9–1.0 mg/g). The value for monophospha-s-triazine I (1.9 mg/g) is, however, definitely higher.

It is of interest that, although the action of titanium alloys is much more detrimental than that of the ferrous alloys in the absence of inhibitors, the additives are more effective with titanium alloys, at least in the case of P151. This is shown by the complete degradation inhibition by additives V and C at 330 °C over 24 h, in the presence of Ti(4Al,4Mn) and Ti(6Al,4V).

As illustrated in Figure 5, neither the phosphines PH-3 and P-3 nor the hindered monophospha-s-triazine I and the monophospha-s-triazine C2PN3 provided acceptable degradation arresting action, based on the 0.5 mg/g limit, for P28 in the presence of M-50 at 316 °C. Over the shortened 16 h exposure, PH-3 exhibited the best performance, 1.1 mg/g of volatiles. The monophospha-s-triazines had limited action, decreasing the volatiles production only to 108–142 mg/g. However, at 300 °C I was almost fully effective (0.7 mg/g). It must be emphasized that in the absence of an additive over only an 8 h period, at 316 °C under otherwise identical conditions, Z25–P28 fluid produced 337 mg/g of volatiles; the value for the P151 batch was higher, 482 mg/g. Although M-50 does not promote the fluid's degradation to as high a degree as Ti(4Al,4Mn), the latter is significantly more receptive to inhibition by additives, which as noted earlier applies also to the other ferrous and titanium alloys.

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Literature Cited


Jones, W. R., Jr.; Bierschenk, T. R.; Juhlke, T. J.; Kawa, H.; Lagow, R. J. Physical and Chemical Properties of Some Perfluoropoly-


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