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Stability of perfluoroalkylethers

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Abstract

The thermal and thermal oxidative behavior of perfluoroalkylethers alone and in the presence of metals, metal alloys, oxides and halides is reviewed. The correlation between processes at elevated temperatures and under boundary lubrication conditions and the effect of structural arrangements on stability and ease of reaction with metals are discussed. Additives effective in arresting the perfluoroalkylether degradation and their action are also included.

Introduction

In view of their physical and chemical properties perfluoroalkylethers are used as vacuum pump oils [1], as lubricants for magnetic recording media [2] and for space applications [3, 4]. Currently, these materials are being investigated as lubrication systems for the next generation of aircraft [5, 6].

Perfluoroalkylethers exhibit wide liquid ranges and depending on structural arrangements possess high viscosity indices. Owing to the absence of C−H bonds, these materials are oxidatively stable at elevated temperatures and are chemically inert as compared to hydrocarbon-based systems, in particular to oxidizing agents and reactive gases such as, for example, chlorine and fluorine. The highly desirable viscosity/temperature characteristics combined with high molecular weights provide for low volatility at elevated temperatures with good performance at very low temperatures. The major shortcomings of perfluoroalkylethers are caused by the high free energy of formation of M−F bonds which renders these compositions relatively unstable in the presence of metals, metal salts and oxides at elevated temperatures.

Perfluoroalkylether fluid types and syntheses

There are basically four commercially available perfluoroalkylether fluids. Poly(hexafluoropropene oxide), $C_3F_7O[CF(CF_3)CF_2O]_nC_2F_5$, a product of Du Pont (Krytox series of materials) prepared by the anionic polymerization of hexafluoropropene oxide followed by transformation of the original acid fluoride end-groups to C_xF_{2x+1} moieties [7, 8]. This synthesis procedure essentially assures the head-to-tail arrangement and does not allow for structure irregularities with the exception of the terminal hydrogen impurity; this aspect will be discussed in later portions of this review. A related composition manufactured by Montefluos (Fomblin Y), via the O_2/C_3F_6 reaction performed under ultraviolet irradiation [9], has the general structure $CF_3O[CF(CF_3)CF_2O]_{40x}(CF_2O)_xCF_3$. Due to the method of synthesis, head-to-head and tail-to-tail arrangements of the $-$ $CF(CF_3)CF_2O$ $-$ segment cannot be ignored. The relative ratio of $CF(CF_3)CF_2O$ to CF_2O translates to about one CF_2O unit per molecule.

Another product of Montefluos, Fomblin Z, is obtained by reaction of C_2F_4 with oxygen again carried out under ultraviolet radiation. The general structure of this series of materials is $CF_3O(CF_2CF_2O)_{0.6x}(CF_2O)_xCF_3$ [10]. The relative proportion of CF_2O to CF_2CF_2O units provides for the presence of segments having adjacent CF_2O moieties.

The Demnum series of fluids, of the general composition $C_3F_6O(CF_2CF_2CF_2O)_xC_2F_5$, is produced by Daikin Industries using the Lewis acid-catalyzed ring-opening polymerization of 2,2,3,3-tetrafluorooxetane followed by direct fluorination under ultraviolet light to convert CH_2 groups to CF_2 entities [11].

Thermal and thermal oxidative stability in the absence and presence of metal alloys

This review pertains to the four commercial fluids listed below:

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Fluid K	$C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$
Fluid Y	$CF_3O[CF(CF_3)CF_2O]_{40x}(CF_2O)_xCF_3$
Fluid Z	$CF_3O(CF_2CF_2O)_{0.6x}(CF_2O)_xCF_3$
Fluid D	$C_3F_7O(CF_2CF_2CF_2O)_xC_2F_5$

Poly(hexafluoropropene oxide) telomers exhibit extremely high thermal stabilities with incipient decomposition temperatures in the vicinity of 410 °C [7, 8]. More recent investigations using a tensimeter and hydrogen-free material point to a thermal stability of *c.* 370 °C [12]. Based on the stability decrease with increase in the molecular weight, these authors postulate unzipping as the degradation mechanism. The thermal stability is essentially unchanged by oxidizing media represented by air or pure oxygen, which contrasts with the behavior of hydrocarbons. This is not surprising if one considers that the oxidative instability of hydrocarbons is due to the high free energy of formation of water and the propensity to form OH radicals. No such mechanism exists in perfluorinated systems since neither OF nor OF_2 are thermodynamically favored species. On the other hand, the formation of MF, wherein M is a metal, is a thermodynamically favored process reflected by the thermal instability of fluorinated materials in the presence of metals, their salts and oxides. In the commercial K fluids, the presence of impurities [13], viz. hydrogen-terminated chains, $C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)H$, results in a significant lowering of the thermal oxidative stability [14, 15]. However, these materials were found to be thermally stable in inert atmospheres in the presence of M-50 steel and titanium alloys, at least up to 343 °C and 316 °C, respectively.

Oxidation of the hydrogen-terminated chains takes place below 300 °C; however, the rate is low. Prolonged treatment of the commercial fluids at 343 °C in an oxygen atmosphere gives hydrogen-free materials of unchanged molecular weight [14, 15]. In oxidizing atmospheres, the hydrogen-terminated chains, following initial hydrogen abstraction, degrade by unzipping giving as the primary products COF_2 and CF_3COF in the ratio of 2 to 1 [7, 8]. In Pyrex glass, using a sealed tube assembly [14, 15], the major volatile products are SiF_4, BF_3 and CO_2 due to reactions of CF_3COF and COF_2 with the silica and boric oxide present in glass. The BF_3/SiF_4 ratio observed is significantly higher than the B/Si content of Pyrex in agreement with the higher free energy of formation of BF_3 as compared to SiF_4.

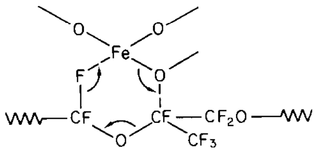
The commercial Fluid K degrades at a faster rate in oxygen at 316 °C in the presence of M-50 steel than in its absence. Based on the quantity of the volatiles evolved, the process is limited exclusively to hydrogen-terminated chains, showing that at 316 °C neither iron oxides nor fluorides promote bond scissions. An increase of temperature to 343 °C causes scissions to occur, as evidenced by the increased production of volatiles and the rate increase with time of exposure [14, 15]. These results are in agreement with the findings of Carre' and Markowitz [16] who did not observe decomposition of Fluid K at 300 °C in the presence of FeF_3. The effect of metal alloys on the degradation of perfluoroalkylether fluids was also investigated by Snyder *et al.* [17, 18] employing a flow system wherein air was passed into the hot fluid in the presence of several different alloys. This approach permitted an assessment of the combined action of the alloys, but did not differentiate between the effects of specific alloys. Studies carried out using different metals and metal alloys in oxidizing atmospheres show that vast differences in activity do exist [14, 15, 19–21].

As mentioned, the degradation of commercial Fluid K at 316 °C in the presence of M-50 steel was limited only to hydrogen-terminated chains. But in the presence of Ti(4Al, 4Mn) alloy, even at 288 °C a large increase in the production of volatiles with length of exposure was recorded. This was accompanied by a drastic decrease in viscosity [19, 20]. The latter, in conjunction with a decrease in the molecular weight, points to bond scissions, not unzipping, as the rate-determining step. Hydrogen-free Fluid K, when exposed to Ti(4Al, 4Mn) at 316 °C, under otherwise identical conditions, exhibited a degradation rate which was lower by a factor of 30 [14, 15]. These results indicate that metal fluorides, namely AlF_3 and/or TiF_4 (MnO_2 is not considered based on Fluid Y data [9]) formed by reactions of the oxides Al_2O_3 and TiO_2 with the primary fluid degradation products COF_2 and CF_3COF, are the catalysts for chain scissions even at 288 °C.

The ready transformation of metal oxides to metal fluorides by COF_2 was demonstrated by Zehe and Faut [22]. Titanium metal itself promoted oxidative degradation at 316 °C. The degree of degradation was lower by a factor of three compared to Ti(4Al, 4Mn) alloy, with a significant rate increase with length of exposure [13, 14]. Under identical conditions degradation by aluminum metal was negligible [13]. Based on Carre' and Markowitz [16] data, AlF_3 has no effect on Fluid K at 250 °C. At 350 °C, bond scissions are observed. It is of interest that alloys such as Ti(6Al, 4V) and Ti(8Mn) promote the degradation of the fluid to a much lower extent than Ti(4Al, 4Mn) [20]. Thus, it is apparent that $C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$ is unaffected, even under oxidizing conditions, at least up to 316 °C, by Fe_2O_3, FeF_2/FeF_3, Al_2O_3 and AlF_3. However, Ti and its compounds promote degradation of this fluid in oxidizing atmospheres below 316 °C; there are no data for a low temperature limit.

The behavior of the different alloys points to a synergistic action [7, 8, 12–21]. Gumprecht [7, 8] proposed a general complex **I** followed by fluorine-atom transfer to the metal and a metal oxygen to carbon.

In view of the presence of metal oxyfluorides and other intermediates, any postulation of the subsequent steps would be highly speculative. Contrary to the theories advanced by many workers (to be discussed in latter sections), we also believe that it is fluorine and not oxygen atoms which are transferred from the perfluoroalkylether chain to the metal. In the case of metal fluorides, the breakdown of the complex **II** leads to the formation of $-COF$ and $-CF_3$ terminated chains.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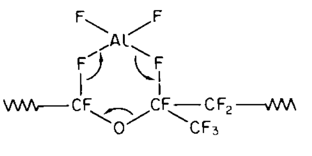

II

The weaker the C−F bond, the more readily the M−F bond will be established. The recent studies of Smart and Dixon [23] show the CF bonds in the $-OCF_2O-$ arrangement to be significantly weaker than other C−F bonds in perfluoroalkylethers. The relative instability of $-OCF_2O-$ segments containing compositions, in the presence of metals and their compounds, supports these findings.

Owing to the presence, however low, of the $-OCF_2O-$ linkages, Fluid Y exhibits somewhat lower thermal oxidative stability than the commercial Fluid K. The difference becomes much more pronounced compared to the hydrogen-free $C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$ [21]. Extensive investigations of the behavior of Fluid Y were carried out by Sianesi *et al.* [9]. These workers reported the material to be thermally stable at 400 °C; however, Helmick and Jones [12] using an isoteniscope determined the fluid to be unstable above 340 °C. The thermal oxidative stability, as measured by thermogravimetric analysis, was approximately 375 °C [9]. It is believed that the procedure used by Paciorek *et al.* [21], who found Fluid Y to undergo measurable decomposition at 316 °C in oxidizing media, is more reliable than the TGA approach.

Fluids D, $C_3F_7O(CF_2CF_2CF_2O)_xC_2F_5$, exhibit a thermal stability comparable to that of the isomeric K series $C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$ [12, 21]. The actual degradation temperature was determined to be *c.* 380 °C [12]. These materials were found to be stable at 316 °C in oxidizing atmospheres in the presence of M-50 alloy; however, the Ti(4Al, 4Mn) alloy promoted extensive degradation [21]. The oxidative stability of the fluids at 343 °C in the absence of metals was somewhat lower than that of the hydrogen-free Fluids K [24].

In view of the higher concentration of $-CF_2O-$ than $-CF_2CF_2O-$ units, Fluids Z, $CF_3O(CF_2CF_2O)_{0.6x}(CF_2O)_xCF_3$, contain segments of $-OCF_2OCF_2O-$. The $-OCF_2O-$ groups, and in particular the $-OCF_2OCF_2O-$ segments, provide weak sites for attack by metals, metal alloys and metal compounds. These fluids are remarkably stable thermally to *c.* 360–380 °C [12], with the stability varying with a specific fluid batch. Due to the method of synthesis and the copolymeric nature of the fluid, structural variations are unavoidable. This family of materials exhibits the best temperature/viscosity characteristics and low volatility at elevated temperatures of all the known perfluoroalkylethers.

Fluids Z, even in the absence of metals, metal alloys and compounds, already show some oxidative decomposition at 288 °C [20, 25]. The extent of degradation in oxidizing atmospheres is greatly accelerated by titanium and its alloys, which even at 288 °C cause catastrophic fluid decomposition [13, 19–21, 25]. Steel alloys [13, 17–21, 25] were found to promote the process to a much lesser degree with low degradation at 260 °C [18]. In the absence of oxygen, at least up to 316 °C [21], these fluids appear to be stable in the presence of metals and metal alloys. Cobalt metal did not promote the decomposition of Fluids Z in oxygen at 316 °C [21].

Behavior of perfluoroalkylether fluids under boundary conditions

Boundary conditions prevail in systems such as those encountered in space guidance instrumentation, in computer disc assemblies and aircraft engine operations. At the asperity contacts, hot spots are produced on an essentially molecular level for extremely short periods of time. This occurrence is not amenable to measurement by conventional means. The approach of Hsu and Klaus [26] utilizing reaction rate studies probably provides the most realistic temperature estimations. The derived temperature of 379 ± 28 °C is supported by the results obtained from investigations of the behavior of perfluoroalkylethers under boundary conditions. A number of different assemblies were utilized to simulate these conditions in relatively easy to examine and analyze laboratory set-ups. Extensive investigations in this area were carried out at the NASA Lewis Research Center prompted by problems encountered with space instrumentation [4]. Using 440 C steel under sliding conditions *in vacuo*, Mori and Morales [27] found Fluids Z to degrade extensively with formation of metal fluorides and gaseous products (COF_2). The rate of decomposition increased with increasing loads and sliding speed, with the former having a greater effect. No volatiles were observed in parallel tests using Fluids K and D; however, iron fluorides were formed. The authors claim free metal to be the reactive species, but based on the work performed by Zehe and Faut [22] it is clear that metal oxides, in this case Fe_2O_3, react more readily than metals with, for example, COF_2 to form the degradation catalysts, namely metal fluorides.

One would expect alloys to be more reactive than pure metals, in which the lattice energy provides an extra reaction barrier. Studies discussed in earlier sections above support this; further confirmation is provided by Morales' [28] investigations of the action of clean steel (440C) and iron surfaces on perfluoroalkylether films at 345 °C in inert and air atmospheres. Under these conditions no degradation of Fluid D was apparent; Fluids Z degraded significantly less on iron than on steel. The presence of fluorinated acids was shown by infrared spectral analysis. Fluorinated acids as well as metallic fluorides act as high-temperature lubricants [29]; unfortunately, in the case of perfluoroalkylethers, the latter also act as degradation catalysts.

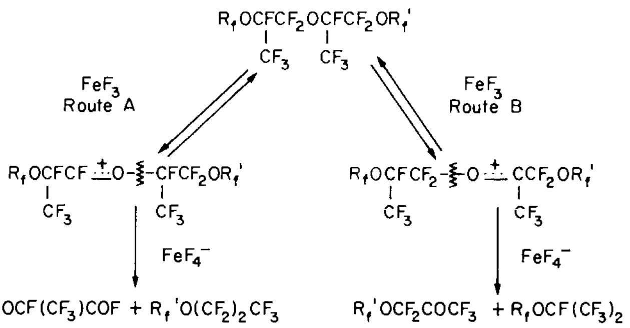
The formation of FeF^+ species by Fluid K under boundary conditions was observed by Carre' [30] using X-ray photoemission spectroscopy (XPS). The author postulates temperatures at the asperity contacts to be of the order of 500 °C and proposes as the initial attack the reaction of the fluid's oxygen atoms with metal. As discussed earlier, on the basis of other experimental data, we believe that temperatures well below 400 °C are sufficient to initiate the degradation, which then becomes autocatalytic. The mechanisms involving the weakest C–F bond were outlined earlier.

As reported by Jones and Snyder [31], Fluid K and a hexafluoropropene oxide-substituted triazine, in a ball-on-disk sliding friction apparatus, not only exhibited lower wear rates than polyphenyl- and C-ethers over the temperature range 100–300 °C but also gave unusually smooth friction–time traces. No debris was observed in the wear tests. This is contrary to the data discussed earlier; however, it must be understood that the extent of formation of FeF_3 and the salts of the fluorinated acids (soaps) is dependent on the test assembly, load, speed and operation duration. Furthermore, in this instance, only visual examination was carried out. Experiments performed using a vacuum four-ball friction rig [32] showed that in air using Fluid D the wear scar increased with load yet the friction coefficient remained constant. In vacuum, both the wear scar diameter and the coefficient of friction increased. Wear increased in air in the order Fluid $D > Z > K$ whereas in vacuum the order was Fluid $Z > D > K$. The authors suggest that low wear by perfluoroalkylethers at atmospheric pressure can be attributed to the formation of iron fluoride which protects the surfaces from local seizure. The reaction in air between fluorine atoms and metal surfaces is controlled, we believe, by the competing oxidation of the reactive fluid species which are transformed into volatiles and thus removed. Under vacuum, there is no ready mechanism to remove the active species by oxidation, which thus react with the metal maintaining low friction but increasing wear.

In view of the affinity of steel or rather iron for fluorine, the use of coated or ceramic components should alleviate these problems. This approach was demonstrated as means of prolonging the operational life of bearings from 3000 h to at least 25,000 h (at 24,000 rpm) by having raceways coated with a thin film of TiC in oil–grease lubricated equipment [33]. In the specific case cited, the actual lubricants were not identified. This concept was found by Carre' [34] to apply to Fluid K both in hybrid silicon nitride/stainless steel and homogeneous titanium nitride systems, extending failure-free operation by a factor of 5–10 as compared to only steel components. We believe the results observed with coated components are partially due to the low coefficient of friction of the ceramic surfaces both in heterogeneous and homogeneous environments. This produces lower temperatures at the asperity contacts and it is the temperature which dictates the production of the catalysts such as FeF_3 and their subsequent action on the perfluoroalkylethers. A number of factors associated with boundary lubrication by perfluoroalkylethers were addressed by Carre' in a recent review [35].

FeF_3 was clearly identified by Zehe and Faut [22] as the primary catalyst in steel systems. Its formation on the contact surfaces under boundary lubrication was fully discussed above, as were the bulk temperatures necessary to promote the degradation process of the different types of the perfluoroalkylethers. It is of interest that exposure of perfluoroalkylethers to XPS over long periods, *c.* 1 h, resulted in fluid degradation as shown by the appearance of carbonyl, the production of COF_2 and crosslinking. The latter was indicated by the molecular weight increase measured by HPLC. Fluid Z showed the highest extent of reaction, whereas Fluid D seemed to undergo crosslinking most readily [36]. The XPS spectra of treated Fluid Z pointed to preferential depletion of the $-OCF_2O-$ linkages.

The action of preformed FeF_3, AlF_3 and $AlCl_3$ upon Fluid K was investigated by Carre' and Markowitz [16]. In inert atmospheres, FeF_3 was inactive at 300 °C; however, at 350 °C definite fluid degradation took place as demonstrated by the formation of acid fluorides, $R_fOCF(CF_3)COF$, and ketones, $R_fOCF_2COCF_3$. Compound identification was by infrared spectral analysis. The mechanisms proposed are depicted below.



The authors claim that both Route A and Route B are being followed. Gumprecht [7, 8] envisioned only Route A in agreement with the early work of Van Dyke Tiers [37]. In the present investigation [16], the actual compounds were not isolated; however, infrared data strongly support the theory advanced. AlF_3 was found to catalyze the degradation of Fluid K at 350 °C; the fluid was stable to AlF_3 at 250 °C. Why intermediate temperatures were not studied is unknown. Our work [13], performed with aluminum metal at 316 °C under conditions established to produce COF_2, viz. the use of hydrogen-containing Fluid K in oxygen atmospheres, failed to result in an autocatalytic process. Actually, the reaction rate decreased with time showing AlF_3 to be inactive as a catalyst at 316 °C. $AlCl_3$ was found to degrade Fluid K at 200 °C [16] forming $R_fOCF(CF_3)COCl$, $R_fOCF_2COCF_3$ and $R_fOCF(CF_3)COF$.

As mentioned earlier, the reactivities of the different perfluoroalkylether fluids are very strongly structure-dependent with Fluid Z, in view of the presence of OCF_2O linkages, exhibiting the lowest stability to metal, metal halide or metal oxide attack. This behavior is clearly illustrated by the investigations of Herrera-Fierro *et al.* [38]. Even at room temperature, a thin film of Fluid Z was found to undergo degradation on aluminum oxide as evidenced by XPS-determined depletion of $-OCF_2O-$ carbon and the appearance of Fls peaks. Of course, the detrimental action of XPS itself cannot be fully ruled out. On the other hand, no such effect was observed on the surface of clean sapphire, showing that here the crystal lattice energy was sufficient to prevent reaction. The authors studied the desorption characteristics of Fluid Z (at *c.* 150 °C) from the surfaces of aluminum and aluminum oxide. In both instances degradation took place. Under boundary lubrication conditions, Fluid Z was degraded on sapphire surfaces and peaks due to aluminum fluoride and aluminum oxyfluoride were detected by XPS.

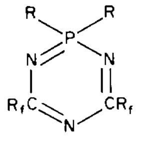
A very elegant series of experiments was performed by Kasai and co-workers [39, 40] analyzing the action of aluminum oxide and aluminum fluoride on Fluids K, Y, D and Z. At 200 °C, Al_2O_3 powder did not affect Fluids K, Y and D. In the case of Fluid Z, following an induction period of *c.* 1 h, vigorous reaction commenced. Using AlF_3, the induction period was essentially absent. These results parallel the behavior of Fe_2O_3 [22]. It was confirmed by ^{19}F NMR spectroscopy of the partially degraded fluid that the susceptibility to attack follows the series $-OCF_2OCF_2OCF_2O- > -CF_2CF_2OCF_2OCF_2O- > -CF_2CF_2OCF_2OCF_2CF_2-$ Decomposition is accompanied by the formation of $CF_3OCF_2CF_2O-$ groupings in the residue and the evolution of COF_2. Fluid Y was unaffected by exposure to Al_2O_3 for 6 h at 200 °C. Treatment with $AlCl_3$ at 200 °C resulted in depletion of the $-OCF_2O-$ units and what was believed to be $-OCF(CF_3)O-$ groups [39, 40]. The attack of $AlCl_3$ on Fluid K proceeded at a lower rate than was the case with Fluid Y. At 250 °C, initial degradation (based on the ^{19}F NMR spectrum) took place at the terminal ethoxy groups, then at the propoxy and isopropoxy ends with the formation of CF_3COF and $(CF_3)_2CFO$-terminated chains. Fluid D decomposed at 250 °C, in the presence of $AlCl_3$, much more readily than Fluid K. ^{19}F NMR results indicate that chain scissions at the $-OCF_2CF_2CF_2O-$ units occur to a large extent. The lack of detection of chlorinated species is surprising since their production would be expected based on the work of Van Dyke Tiers [37]. The authors [39, 40] postulate reaction of the perfluoroalkylether oxygen with aluminum; however, we believe this to be incorrect, in agreement with the early Gumprecht work [7, 8] and the well-established aluminum–fluorine affinity.

Additives

As evident from the data discussed, anticorrosion and antioxidation additives are essential to permit the full utilization of perfluoroalkylether fluids. The early studies of Sianesi *et al.* [9] identified a series of compounds, namely phenyl-β-naphthylamine, triphenylimidazole, triphenylphosphine sulfide, tetraphenylhydrazine, tetraphenyltetrazocine, perfluorotriphenylphosphine, phenotiazine and phenyldiselenide, which were found to inhibit the degradation of Fluid Y by alumina for 30–80 min at 360 °C. Subsequently, a number of perfluoroalkylether-substituted phosphines of the general formula $(R_fOCF(CF_3)CF_2C_6X_4)_3P$ were developed, wherein X was either a proton or fluorine [41–43]. These additives were soluble in perfluoroalkylether fluids and effective at 0.5%–1.0% concentrations in preventing the decomposition of Fluid K at 316 °C in oxidizing atmospheres, both in the absence and presence of ferrous and titanium alloys for up to 24 h [17]. At 343 °C, the inhibitory action was lost [14]. The effectiveness of the additive, using hydrogen-containing Fluid

K at 316 °C in the presence of ferrous alloy M-50, was of the order of 6 d [14]. In the case of Fluid Z in oxidizing atmospheres and in the presence of Ti(4Al, 4Mn) alloy, phosphines arrested the degradation at 288 °C [17] for up to *c.* 5 d [19, 25]; however, at 316 °C the inhibiting action lasted only *c.* 24 h [21].

Mono and diphospha-s-triazines of the general arrangements **III** and **IV**



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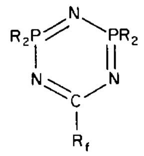

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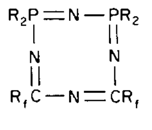

V

as well as the diphosphatetraazacyclooctatetraenes (**V**) regardless of phosphorus ($R = C_6H_5$, C_6F_5, SC_6H_5) and carbon substituents $\{R_f = n\text{-}C_7F_{15}$, $CF(CF_3)[OCF_2CF(CF_3)]_xOC_3F_7$, $C(CF_3)_2[OCF_2CF(CF_3)]_xOC_3F_7\}$ were found to exhibit anticorrosive and antioxidative action up to 316 °C when used in perfluoroalkylethers as represented by Fluids K and Z [13, 19–21, 25, 44–49]. In the case of Fluid Z, at 316 °C in the presence of ferrous alloys, the arresting action lasted 24 h; however, with titanium alloys it was extended to 72 h. Modifying Fluid Z by removing some of the weak links followed by end-capping with monophospha-s-triazine units resulted in a fluid which was stable at 316 °C in the presence of ferrous and titanium alloys for at least 24 h [21, 50].

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