

BASIC FLUID STUDIES ON HIGH-TEMPERATURE LUBRICANTS

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ABSTRACT

A short discussion on the state of the state of the art in turbo-jet lubricants and power transmission fluids is presented. Some basic fluid properties desired for a 500°F bulk oil, turbo-jet lubricant are presented and compared with the properties of available fluids. High-temperature aromatic ring type structures are discussed and the feasibility of their derivatives as high-temperature lubricants. These include derivatives of pyrazine, triazine, and hexafluorobenzene. An inorganic polymer is discussed relative to its structure, fluid properties, and possible use.

INTRODUCTION

This paper is primarily concerned with research and development effort being carried out at WADD, Materials Central, Nonmetallic Materials Laboratory, on high-temperature fluid lubricants and power transmission fluids.

A brief review of the state of the art is appropriate prior to the main discussion. A summary of the state of the art is presented in Table 1. As shown, two specifications cover presently used

TABLE 1A. TURBOJET LUBRICANTS

<u>Type (Synthetic)</u>	<u>Usable Temperature Range (Bulk Oil), °F</u>
MIL-L-7808C	-65 to 300
MIL-L-9236B	-65 to 425
Present Research	-30 to 500-600

TABLE 1B. POWER TRANSMISSION FLUIDS

<u>Type</u>	<u>Usable Temperature Range, °F</u>
Mineral Oil MIL-H-5606A	-65 to 275
Synthetic MIL-H-8446A	-65 to 400
Mineral Oil MIL-H- ?	-40 to 550-600
Present Research	-40-0 to 900

turbojet lubricants. The next year's research and development effort should yield a suitable fluid capable of 500° to 600°F bulk oil for extended time periods.

The information shown under power transmission fluids is, for the most part, self-explanatory. It is quite interesting to note that the progression is from mineral (5606A), to a

synthetic (8446A), and back to mineral oils again for a 550° to 600°F power transmission fluid. The derivation of this power transmission fluid formulation (-40 to 550° to 600°F) will be described in a future WADD report.

The research and development effort on high-temperature lubricants, carried out by the Nonmetallic Materials Laboratory, Materials Central, is not limited to propulsion system lubricants. The base fluids sought may be useful as power transmission fluids, propulsion system lubricants, and in many other areas where high-temperature lubrication or heat transfer is a problem.

Prior to discussing prototype chemical structures being studied as high-temperature lubricants, silicone fluids will be discussed as to their feasibility as high-temperature turbojet lubricants. A critical study of certain silicone fluids, as turbojet engine lubricants, resulted in a single problem, namely, carbon seal difficulty. This problem arose from the formation of sludge in the interfaces of carbon seal shaft and carbon seal-carbon seal. The sludge lifted the lightly loaded seals, causing fluid loss across the seals and high breather pressures in the engine.

Some thought that several inherent properties of silicone fluids contributed to this problem. These were: poor sliding lubricity, excess heat evolution due to shearing and oxidative gelation. Also, some thought that noncompatibility with carbon seals contributed to the problem. This was thought to be due to the binder or specifically to chemical antioxidants used in the binder resins. A program was carried out during latter 1959 and through 1960, to determine the exact cause of the problem. A small-scale seal tester was built which included coefficient of friction measurements. Figure 1 shows the test specimens. The part shown housing the carbon seal is stationary and the other specimen is rotated against the seal at some given load and rpm. Lubricant is fed to the

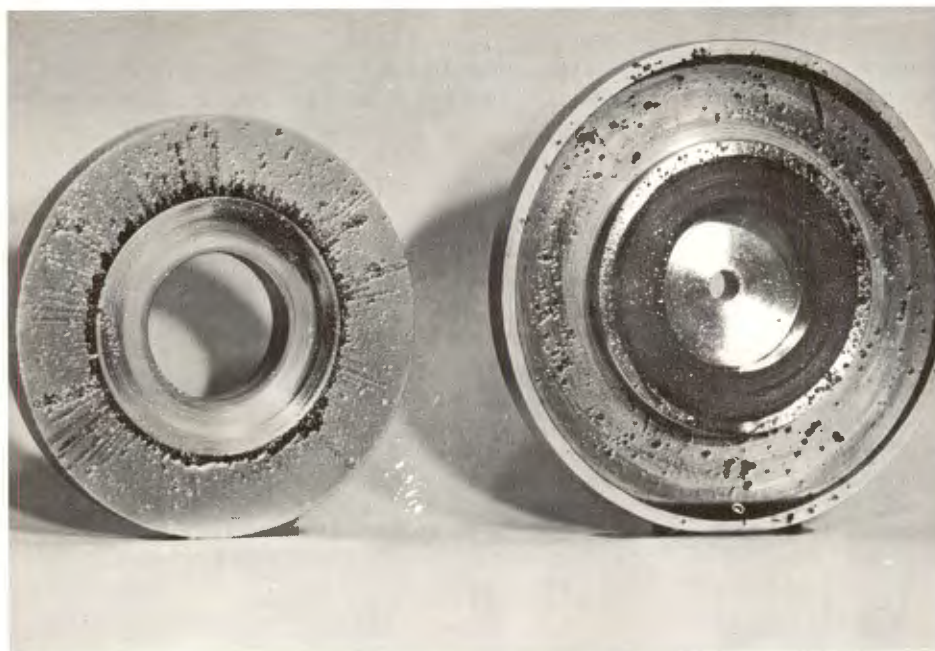


FIGURE 1. SEAL TEST SPECIMENS

seal area via the center of the specimen. Coefficient of friction measurements are taken on a continuous basis. Many tests were conducted on base silicone fluids, silicones with antioxidants present, silicone fluids exhibiting different viscometric properties, blends of silicones with ester fluids which resulted in superior sliding frictional character, as determined by Shell 4-Ball Wear studies, and finally on standard turbojet lubricants like MIL-L-7808 and MIL-L-9236B as comparisons. Tests were conducted with air and with inert atmospheres. The program concluded with the hypothesis that the one and only inherent property contributing to the sludge formation is that silicones gell when oxidized. All other operating conditions, when compared to standard turbojet lubricants, yielded comparable results. When an inert gas was used rather than air, no sludge was noted. To condense the overall problem, silicone fluids could be used as turbojet lubricants provided the seal areas are redesigned as all air seals to prevent the lubricant from contacting the seal-shaft or seal-seal interfaces.

In parting from the silicones, I would like to say that the silicone fluids represent an extremely versatile lubricant class and in certain areas are unsurpassed. Their high thermal stability, good viscometric properties, and wide liquid range make them excellent lubricants for high-temperature gears and bearings where an inert atmosphere predominates. Also, formulations of silicones show excellent performance in oxidizing environments to 500°F but the ultimate result of oxidation being sudden gellation is certainly a formidable problem. I do not wish to impart an impression that the silicones are inferior to other lubricants in an oxidizing environment because, in general, they show less physical change versus time than the commonly used lubricants such as esters, mineral oils, etc.

Table 2 shows requirements in a tentative high-temperature specification to cover a turbojet oil for use over a temperature range of -30 to 500°F bulk oil. Typical property data on MIL-L-9236B (a -65 to 425°F bulk oil turbojet engine lubricant) are shown. The MIL-L-9236B formulation endured 100 hours at a bulk oil temperature of 425°F in a turbojet engine with very little degradation. However, the same formulation lasted only 20 hours at 450°F bulk oil prior to excessive physical and chemical changes. Data shown on a complex ester derived from trimethylol propane basically meet the requirements of a 500°F turbojet lubricant except for the desired low-temperature viscosity. However, the oxidation stability of this ester at 500°F is certainly the formidable problem.

TABLE 2. TENTATIVE HIGH-TEMPERATURE SPECIFICATION

	Nitrile	Complex Ester	MIL-L-9236B -65 to 425°F Bulk Oil	MIL-L-? -30 to 500°F Bulk Oil
Pour Point, °F	-35	-50	-90	-40 max
S.I. T., °F	735	890	840	-
Flash Point, °F	550	505	475	500 min
Fire Point, °F	615	540	515	-
Viscosity, cs, at				
-65°F	-	-	14,200	-
-30°F	at 0°F 17,000	30,000	1,200	13,000 max
100°F	120	85.2	13.8	Report
210°F	12.18	12.1	3.6	Report
400°F	2.2	2.7	.98	Report
500°F	1.5 (ext)	1.4	.61	1.0 min
Evaporation Loss, %				
6.5 hrs at 500°F	-	6.7	39.0	10.0 max

The data on the nitrile type fluid is very interesting. This fluid was supplied by General Mills and is one of a series. The oxidation stability of these type compounds is quite striking, thus showing some promise as high-temperature turbojet lubricants. Basically, nitrogen-containing molecular species attracted attention because experience showed that such possessed anti-oxidation activity and oxidation stability.

It appears possible to derive a lubricant formulation which will meet the properties desired in the 500°F bulk oil specification; however, it is anticipated that considerable effort will be necessary to derive a suitable anti-oxidation package.

The following discussion is concerned with the synthesis effort presently being carried out in the search for high-temperature fluids.

Figure 2 shows the basic "pyrazine" structure where R = alkyl, alkylaryl, or aryl. Compounds of this type are highly resonating and offer considerable promise as high-temperature materials. An analogy, of sorts, can be drawn relative to the oxidation stability of "pyrazine" by subjecting "benzpyrazine" to permanganate oxidation. This yields 2,3-pyrazine dicarboxylic acid. The analogy that the pyrazine ring is more oxidatively stable than benzene could be drawn from this. However, one should state that this is only an indication that pyrazine is oxidatively stable with no reference to benzene and save much argument.

As with most aromatic type ring structures, alkyl substitution usually lowers the melting point drastically. This is also shown in Figure 2; the substitution of a methyl group upon the ring lowered the melting point from +52 to -25°C. As can be seen, the "pyrazine" ring is rather versatile, offering four sites for substitution. It can also be seen that the opportunity exists for making unsymmetrical molecules which tends to produce low melting compounds. Figure 3 shows possible structures based on pyrazine. Siloxane substitution is a rather classical method used to derive low melting compounds (II) and even polymer type materials with good low-temperature properties

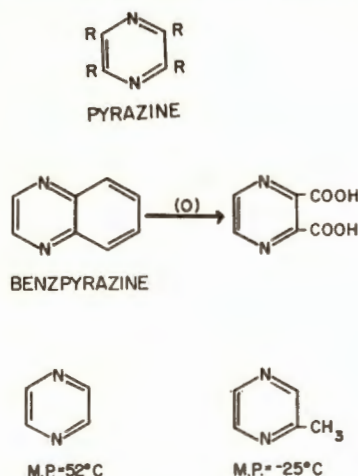


FIGURE 2. BASIC PYRAZINE STRUCTURE

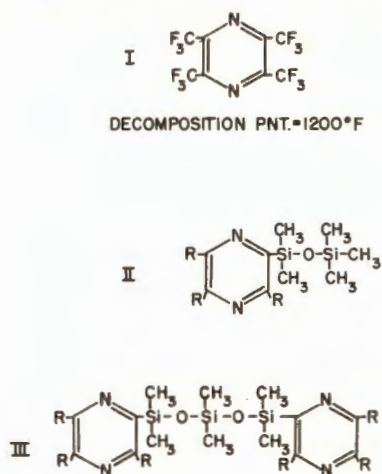


FIGURE 3. POSSIBLE STRUCTURES BASED ON PYRAZINE

(III). The number and types of compounds which are possible, based on the pyrazine ring, are practically unlimited in number since substitution can be accomplished in any combination of the four available sites. Figure 4 shows some of the possible structures and the general train of thought in the synthesis of pyrazine compounds. The pyrazine class is expected to yield compounds oxidatively stable up to 600°F with thermal stability in the 800 to 950°F range. The low-temperature fluidity of these compounds may be manipulated to fulfill specific needs.

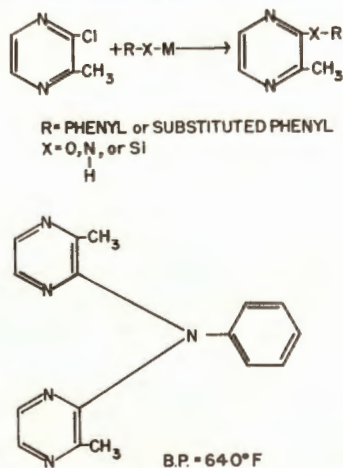


FIGURE 4. SYNTHESIS OF PYRAZINE COMPOUNDS

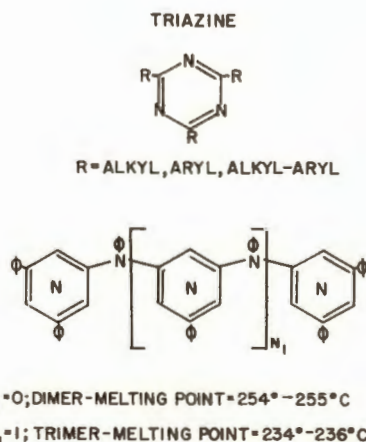


FIGURE 5. TRIAZINE COMPOUNDS

Figure 5 shows the basic triazine structure. The pros and cons of this structure are similar to those for pyrazines. The polymer structure shown is somewhat analogous to the poly-phenyl ethers, the idea here being to make compounds up to where $N_1 = 3$ thus giving a pentamer. This, then, could be compared to the 5-phenyl ether (m-linked). The 5-phenyl ether has a pour point of -5°F . The decreased melting point of the trimer as compared to the dimer indicates that the longer chain materials (pentamer) may have better melting points. The possibility of converting such a polymer to a liquid at room temperature exists by replacing the rather bulky phenyl groups on the triazine ring with appropriate alkyl groups. This will probably hinder the high-temperature stability of the resulting compound. The triazines represent possible high-temperature compounds with usefulness in many areas.

Figure 6 shows some model perfluoro-aromatics which are of interest in the high-temperature lubricants area as well as in many others. The thermal stability of benzene has paved the way for the synthesis of more resonant compounds as hexafluorobenzene (I). Methods for making C_6F_6 more efficiently are being sought. C_6F_6 would be converted to $\text{C}_6\text{F}_5\text{Br}$ (p-bromopentafluoro) benzene. The di-bromo derivative would also be made. These intermediates would be used to synthesize compounds in II and III of Figure 6. Hexafluorobenzene is one of the most thermally stable organic compounds known; therefore, the analogues should be thermally stable and certainly this type structure is extremely oxidatively stable. The perfluoro-aromatics are another chemical class which has considerable potential in the high-temperature lubricant category.

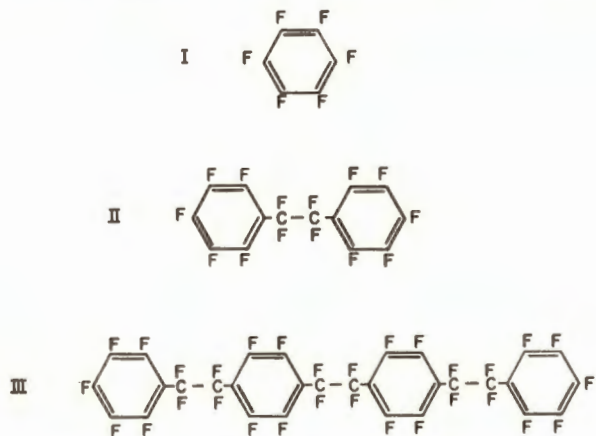


FIGURE 6. PERFLUORO-AROMATICS

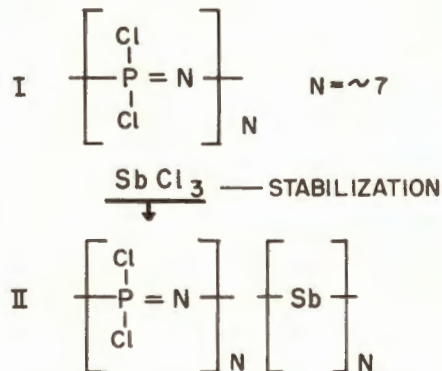


FIGURE 7. INORGANIC POLYMER

Figure 7 shows a prototype inorganic polymer. Theoretically, the inorganics represent the ultimate in thermally stable fluids, with reasonable liquid ranges, which could be used as lubricants and power transmission fluids. A polymer of the approximate structure as shown in I has been made. However, the structure has not been confirmed. The structure as in I appeared to cross-link to form an elastomeric type material at approximately 240°C . This compound appears to be hydrolytically unstable as could be expected. It appears that inclusion of SbCl_3 in the basic reaction stabilizes the resulting compound (structure unknown) which has a liquid range of 0°F to approximately 1000°F . This area shows considerable promise but is in the fetal stage and much work is yet required to yield usable materials.

LIST OF REFERENCES

1. Klaus, E. E., and Fenske, M. R., WADD TR 55-30, Part VIII, Pennsylvania State University, Contract AF 33(616)-5460.
2. Olin Mathieson Chemical Company, Contract AF 33(616)-6342.
3. Monsanto Chemical Company, Contract AF 33(616)-6851.
4. Dupont de Nemours and Company, Contract AF 33(616)-7158.
5. Wyandotte Chemical Company, Contract AF 33(616)-6749.