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AEROSPACE LUBRICANTS

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The purpose of this paper is to review the past and current technological status and future plans for liquid lubricants, greases, and solid films. This endeavor is specifically concerned with the efficient and reliable lubrication of power systems, control systems, and their associated subsystem components. Research and development effort, devoted to the advancement of the state of the art, may well deal with techniques and methods of accomplishing efficient lubrication as well as strictly material investigations. The answer to certain lubrication problems may lie in the knowledge of conditions and change thereof, rather than the necessity of using a new lubricant material.

Liquid Lubricants

Turbojet Lubes - Work has been in progress, for the past several years, to derive a satisfactory turbojet lubricant for use in the 500°F bulk oil temperature range. It is necessary to place emphasis upon the oxidation stability of the base fluids when considering their severe operational environments. Figure 1 illustrates the state of the art in turbojet lubricants relative to military specifications.

It is virtually impossible to synthesize a base fluid possessing all the performance capability required in the lubrication of a turbojet engine. Severe oxidizing conditions and high mechanical loads dictate the use of chemical additives to improve the performance characteristics of the base fluids. Research and development programs on both base fluids and additives are carried out concurrently. Two specific approaches are being followed for the derivation of high temperature turbojet base fluid lubricants. Figure 2 shows the general chemical structures concerned with the first of these approaches, "pyrazine" derivatives. Figure 2 shows the basic pyrazine nucleus which can be tetra substituted, if necessary. As shown, three different chemical bond types were investigated relative to thermal stability. Of the three types, the anilino substituted proved to be the most thermally stable. The anilino pyrazines showed good thermal stabilities at 600°F, good oxidation stability at 500°F and good viscometric properties. Most all the property data obtained on these three type pyrazine derivatives indicate the anilino or amino substituted pyrazines were thermally unstable. Cleavage generally occurred between the R group and the sulfur atom at relatively low temperatures, such as 450° to 500°F. The phenoxy substituted pyrazines showed good thermal and oxidation stability at 500°F. However, at 600°F, the phenyl group appeared to migrate to the 1 position nitrogen. Because of this thermal rearrangement at 600°F, the phenoxy pyrazines do not show exceptional promise. The rearrangement appears to be of a free radical nature; therefore, chemical blocking the other phenyl positions would not aid the situation.

Figure 3 shows two pyrazine isomers, a 2,3 and a 2,6 substituted pyrazine. The 2,6 substituted has slightly better low temperature properties than the 2,3 substituted. The 2,6 isomer has a pour point of approximately -40°F. These isomers both possess good oxidation stability at 500°F, better than the MIL-L-9236B fluids. Additional substitution is planned for the 2,6 substituted fluid to increase the molecular weight. This may be accomplished in several ways and silyl substitution at the 2 or 5 positions will be tried.

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Figure 4 shows a 2-anilino, 3-silyl pyrazine which has the best liquid range properties of any prototype fluid prepared to date. This fluid has a pour point of approximately -90°F. However, in high temperature tests, infrared spectra showed the presence of an olefin. This was attributed to cleavage between the carbon and pyrazine ring at the 3-position, forming a vinyl silane. Means have now been devised to methylene link the silyl group to the pyrazine ring. This will eliminate the possibility of olefin formation.

Another practical approach to suitable liquid range pyrazine fluids for 500°F turbojet lubricants are all alkyl substituted pyrazines or possibly halo-alkyl pyrazines (Halo = fluorine). A 2-nonyl, 5-heptyl pyrazine fluid was made and showed surprising oxidation stability at 500°F relative to other pyrazine fluids. It appears possible to synthesize a higher molecular weight all-alkyl pyrazine fluid which will be suitable as a high temperature lubricant for oxidizing environments. Comparative data on an alkyl pyrazine versus other fluids is shown in figure 5. In summary on pyrazine fluids, much work is needed and unlimited possibilities (as to chemical structures) exist to synthesize suitable high temperature fluids.

The second approach to base fluids for high temperature turbojet lubricants is narrower in scope but appears quite promising. This approach involves the synthesis and evaluation of aromatic ester fluids. Figure 6 shows a prototype aromatic ester, (Resorcinol dineoheptanoate) representative of the type materials being investigated. It appears to possess the necessary properties for a high temperature turbojet lubricant. This fluid was made from 1,3-resorcinol esterfied with neoheptanoic acid. This fluid has a pour point of approximately -50°F. The oxidation stability appears comparable to the polyphenyl ethers but is more volatile. At any rate, the aromatic esters show considerable promise and higher molecular weight fluids will be synthesized to reduce volatility.

Other promising approaches will undoubtedly evolve from current basic research programs on fluid synthesis. For example, figure 7 shows a new fluid material which has some interesting properties. This fluid is less attractive than the polyphenyl ethers relative to fluid range, thermal and oxidation stability.

Still other possibilities lie in the areas of perfluoroalkyl and perfluoroakyl-aromatic compounds. No structures are shown here since the synthesis of these is in the fetal stages. However, as oxidizing environments become more intense, the perfluorinated compounds become more attractive.

Instrument Oils - The lubrication of minute bearings of instruments has received too little attention over the past several years and problems arising with such have indicated a need for research and development in instrument bearing lubrication. Even though the operating conditions, in terms of temperature and oxidizing environments, are not as severe as other lubricant applications, other control needs require considerable attention. Indicating instrument and guidance instrument bearings, for example, gyroscope gimbal bearings are required to be as frictionless as possible. This means that only enough lubricant should be used not to flood the system, otherwise the lubricant will form varnish or oil insolubles which are capable of interfering with the bearing operation. The smaller the instrument ball bearings are that operate at thousands of revolutions per minute, the greater the lubricant problem. Extreme caution must be taken relative to the condition of the oil and the environments in which the oil is used. Considerable bearing failure has been experienced because of varnishing, and the overheating of bearings.

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In applications where long term reliability is desired from antifriction bearings operating at high rpm's and where a liquid lubricant is necessary, it is essential to deoxygenate the lubricant, and use a completely oxygen free atmosphere in the bearing area. Considerable effort has shown that varnishing is induced by minute quantities of absorbed air in the oil or in the surrounding environment, causing oxidation of the lubricating thin film.

During 1960, a high temperature instrument oil formulation was derived. This oil covers a temperature range of -65°F to 400°F and is composed of a methyl chlorophenyl silicone oil with dibutyl tin sulfide as an additive. A military specification is being prepared for the temperature range of -65°F to 400°F. This instrument oil will not solve all instrument lubrication problems but it will aid instrument bearing lubrication at some higher temperature than those presently qualified under MIL-L-6085A which covers a temperature range of -65°F to 250°F.

We shall now consider the semi-solid lubricant materials commonly referred to as greases. High temperature greases (up to 600°F) are now available. Organic thickeners and synthetic organic fluids are utilized in formulating greases operable from -100°F to +600°F, however, no individual grease is capable of operation over the entire temperature range without considerable limitations being placed upon its performance life. Considerable research and development work is needed to advance the state of the art to provide for greases and grease-like materials usable in various aerospace environments and operating conditions expected in advanced Air Force weapon systems. These lubricating greases will provide a highly reliable capability for long term operation (500 hours minimum) under conditions such as is shown in figure 8. The new and improved materials resulting from this research are intended as general and special purpose greases for lubricating control systems, gear boxes, gimbal rings, rocket control devices, generators, inverters, actuators, advanced electric motors, and other subsystems. The knowledge gained from previous efforts concerning the basic factors involving the formation and stability of grease-like colloidal gels are being applied to the development of new and improved grease structures and formulations. In order to provide for special purpose greases for use in advanced weapon systems several approaches are being followed.

Thickener Materials - A complete and comprehensive investigation is being made of organic, semi-organic, and inorganic materials, which melt above 700°F, for use as high temperature grease thickeners. Figure 9 shows the more promising organic materials which are under investigation, namely, the hydantoins, ammelines and the imides. The aluminum complex of phthalimido benzoic acid is one of the more promising imides, and will undergo further investigation, under high temperature-heavy load conditions. This thickener system has a melting point above 1200°F.

A study is being made of special surface modification techniques as shown in figure 10. Greatly improved greases with high temperature shear stability will result from the use of thickeners prepared by these special techniques. Carbon blacks, silicas, glass fibers, and metallic oxides are being investigated for suitability as grease thickeners.

Fluids - New base fluids and fluid blends with 700°F to 1000°F potential based on organic, metal-organic, and inorganic structures are being investigated in various thickener systems. The more promising base fluids are the polyphenyl ethers, silphenylenes, and high phenyl content silicones. Currently available fluids and those which will be available for grease synthesis in the future are listed in figure 11.

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Additives - The potential performance of new and improved additives are being studied for their impartation of oxidation stability, wear resistance, corrosion resistance, and heavy load carrying capacity to grease formulations.

Summary - Figure 12 shows the current and future high temperature grease capability.

The currently available greases are either commercial or experimental.

The future requirements for high temperature greases will be for high speed applications primarily (1 X 10^6 DN Value). Apparently there will be a requirement for heavy load carrying grease capable of lubricating at high temperatures (600°F).

Figure 13 shows the heavy-load carrying grease capability.

Figure 14 shows the present and future high pressure (pneumatic) grease capability.

The lubricating grease requirements for the numerous present and future applications have been outlined. Much progress is being made in research and development, nevertheless, future aerospace requirements demand that a higher rate of progress be maintained. Those future requirements for high speed, high temperature, heavy load, radiation resistant, high vacuum, high pressure, and wide temperature range greases will be met through even more intense research and development programs.

Solid Film Lubricants

The aircraft industry is making wide use of the commercially available solid film lubricants. These films are being used in slow sliding bearings operating under loads of 2000 to 80,000 psi in the temperature range of ambient to 450-500°F. A typical application is the lubrication of outer control surfaces on aircraft which are practically impossible to lubricate with the conventional grease or oil lubricants. These films are particularly useful in inaccessible compartments since the parts can be coated prior to assembly and provide adequate lubrication for very long periods.

These films are generally composed of molybdenum disulphide and/or graphite as the lubricating pigment, and are bonded to the bearing surface with an organic resin binder. The mixture of pigment and binder carried in a solvent can be applied to the bearing surface by dipping, brushing, or spraying.

The resin binders are primarily of the phenolic or epoxy type with the epoxy resin generally preferred over the phenolic. These organic resins are the limiting factors for operation of these films above 450°F. At this temperature thermal degradation begins and wear life falls off rapidly when temperatures increase. The operating temperature of these films can be extended with the use of an inorganic binder such as a ceramic, to the oxidation temperature of the pigment. Molybdenum disulphide is stable to 750°F at which time severe oxidation begins. Figure 15 illustrates that ceramic bonded MoS_2 films show a considerable decrease in wear life at the lower or ambient temperature range compared to the resin bonded films.

The age of missiles and liquid gases as fuels have also generated the need for lubrication at the other end of the temperature scale, i.e., under cryogenic environments. At temperatures below -100°F most fluids turn to solids and like greases lose their lubricating capability. The use of solid film lubricants to lubricate moving parts under these conditions seemed natural. A recent program completed at the Directorate of Materials

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and Processes was a study of commercial solid films under cryogenic conditions. As shown in figure 16, an 85 to 95 percent decrease in wear life could be expected in changing the environment from 70°F to the temperature of liquid nitrogen. No particular lubricant showed favorable wear life under these conditions. The postulated mechanism of failure was mechanical rupture of the bond between metal and film due to the initial thermal shock. It must be stressed that these films were not developed for cryogenic use but conceivably could be modified or developed further to operate satisfactorily for these environments.

Current R&D Efforts

The need for lubricants to operate above the temperature range of the grease and oil systems as well as the commercial films, has spurred the effort to develop a solid film lubricant for use at 1000°F. These efforts by the Air Force and other organizations have brought about lubricating pigments which are thermally and oxidatively stable to temperatures in excess of 1000°F. The Air Force has developed a ceramic bonded solid film which appears to meet the requirements of high temperatures and high loads, with low friction wear. The film is composed of lead sulphide as the lubricating pigment in combination with boric oxide, as the ceramic binder. This film exhibits both low friction and wear under loads to 60,000 psi and sliding speeds over 200 ft/min at 1000°F; wear life has exceeded all other films to date. This film suffers a serious drawback which has prevented it from being used in an operational capacity. This deficiency is the drastic decrease in wear life noted in tests conducted at temperatures below 700°F. Figure 17 points out the contrast with other film formulations with a decrease in wear life at higher temperatures. This phenomena is not readily explainable but much effort is being expended since the film has potential at temperatures of 1000°F.

One method to combat this deficiency has been an attempt to find an optimum mixture of MoS_2 and PbS which will provide adequate lubrication over the temperature range 80° to 1000°F. While this has improved the picture to a degree it still falls short of the necessary wear life for a successful film.

The work conducted by NASA on solid film lubrication has been similar to that of the Air Force. They have developed a ceramic bonded film composed of lead oxide and sodium silicate, which has shown good friction and wear values at 1000°F. However, this film follows the lead sulphide film in that an increase in friction and decrease in wear life is noted for lower temperatures. Recently, NASA, has turned to the use of solid films for lubrication of ball bearings as opposed to the use in plain journal or spherical bearings by the Air Force. The film used in these tests was the lead oxide with a mixture of various powdered oxides such as silicon dioxide, boric oxide, etc. Tests have indicated this film formulation shows great promise for temperatures up to 1250°F and sliding speeds to 10,000 fpm.

The Navy has also been conducting work on lubrication of ball bearings with a solid film lubricant. The work conducted at the Naval Air Material Center has been with a mixture of MoS_2 and graphite, bonded with sodium silicate. The primary interest here has been to design a bearing configuration suitable for use with a solid film lubricant. This has resulted in the reservoir theory whereas the bearing retainer contains reservoirs which provide the lubricant to the balls and races. The tests have been conducted at lower temperature, 350° to 700°F, but at high speeds of 10,000 rpm. The preliminary results indicate the bearings will operate for 20 to 30 hours under these conditions and may have the potential for successful operation at higher temperatures.

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Recently, the scope of the Air Force research and development programs for solid films has been extended to cover new approaches and temperature ranges up to 1500°F, including operation in a vacuum at these temperatures. Special equipment has been constructed to provide testing at pressures of 10^{-6} mm Hg and temperatures of 1500°F, under various speeds and loads. This equipment is in operation now and some data have been taken at 1000°F in vacuum to 10^{-6} mm Hg. Figure 18 shows that mixtures of PbS and MoS_2 have given exceptionally better wear life under these conditions than either the PbS or MoS_2 films, or the mixture when run in air. The wear life for these films is short of the life needed in an operational system and work is necessary to develop a film with both the high temperature and vacuum capability. The data gathered under these conditions will be used as guides to screen materials for higher temperatures under vacuum environments.

The problem of finding pigments and binders which are stable under these high temperature conditions have necessitated looking at other types of coatings as possible friction and wear reducing compounds. A program is underway to find lubricating techniques which are usable to temperatures of 2000°F. The use of a porous substrate impregnated with precious metal alloys, glasses, or metals which form soft oxides have shown some promise. Another method tried under these conditions has been to run metal against metal without a lubricating medium, which has been promising.

As shown in figure 19, certain alloys such as the Haynes Alloy, Lt-1B, have shown essentially constant friction values for tests conducted in air over the temperature range of 1400 to 2000°F. Tests conducted in vacuum give higher friction values over this temperature range. These are only preliminary results but indicate the possibilities of successful operation with bearings containing types of materials for high temperature environments.

Fundamental research programs have been initiated to provide basic information concerning friction and wear. They will provide data to establish a foundation on which development programs can be conducted with a greater degree of success. More information is necessary for a better understanding of the mechanisms involved in friction and wear, and how to take advantage of the mechanisms to develop better solid film lubricants for unusual environments. Some of these programs involve studies at high sliding speeds between hard and soft metals, between soluble metals, and insoluble metals, and reactive and non-reactive metals to determine their effects on various properties of friction and wear. Why some solid film formulations exhibit poor wear life while others have excellent wear over a given temperature range is being studied from a phase or composition viewpoint. The effect of ceramic type binders and their role in affecting the lubricating pigment will be pinpointed.

When the data from these programs is funneled into the development programs for solid films, it is hoped that sufficient basic data will be available to enable a formulation of a solid film lubricant for a specific application which will have a good chance for successful operation. These problem areas cannot be covered with a few programs in a short period of time but will take the combined effort of many organizations working closely to meet this challenge.

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SPECIFICATION DESIGNATION	AMBIENT APPLICABLE TEMPERATURE RANGE
Mil-L-7808 D	–65° To 300°F
Mil-L-9236 B	–65° To 400°F
(Target) Mil-L-27502	–35° To 500°F

Figure 1.

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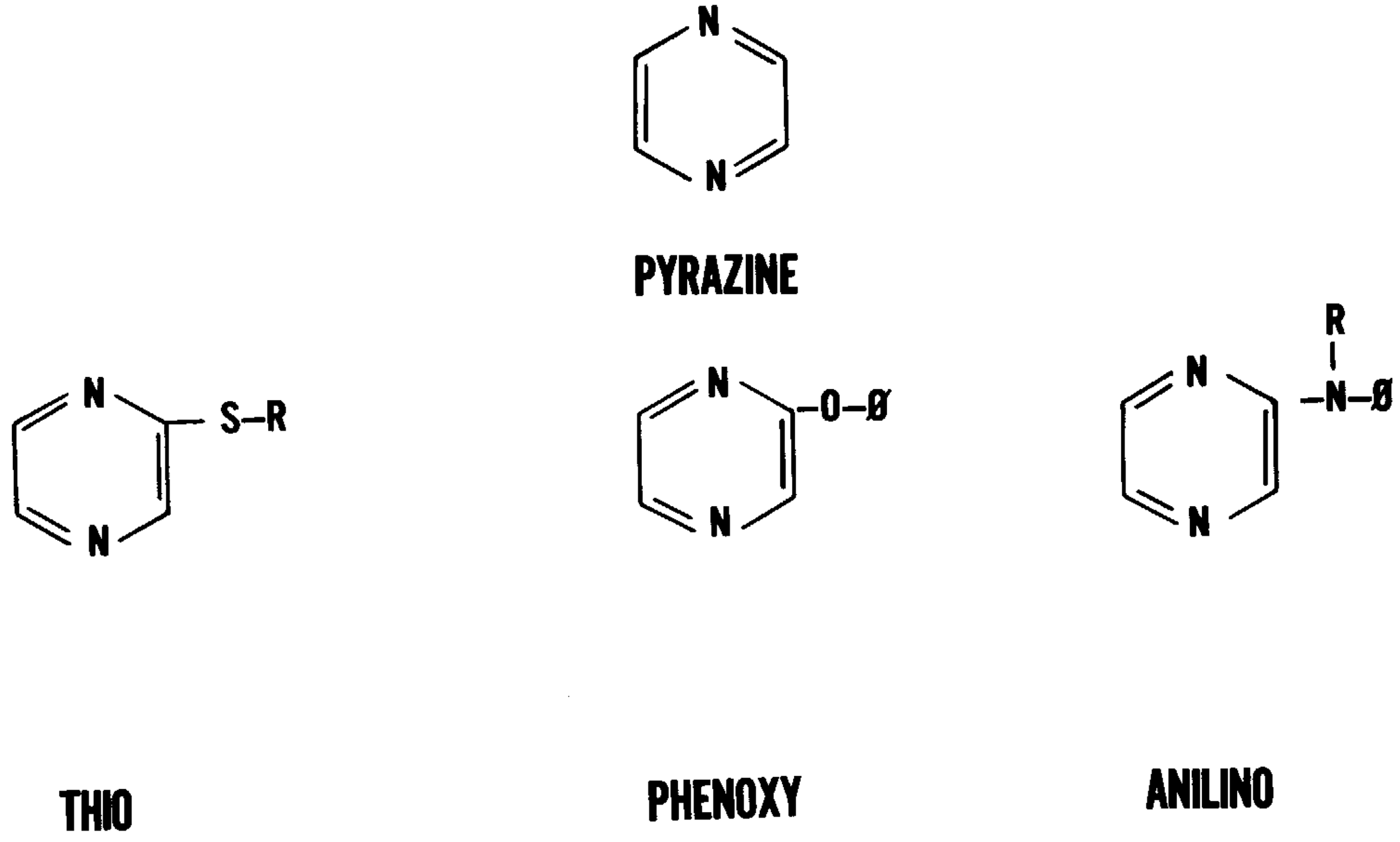

Figure 2.

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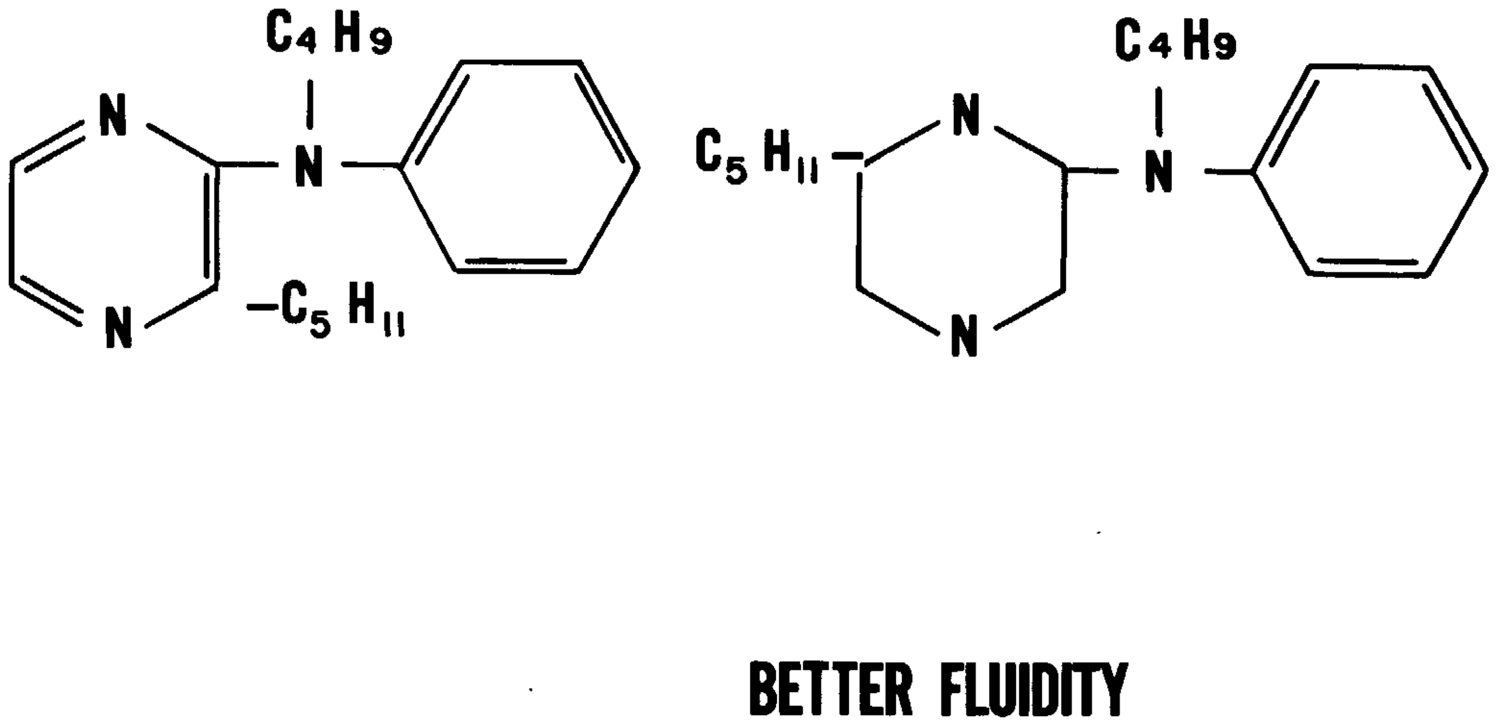

Figure 3.

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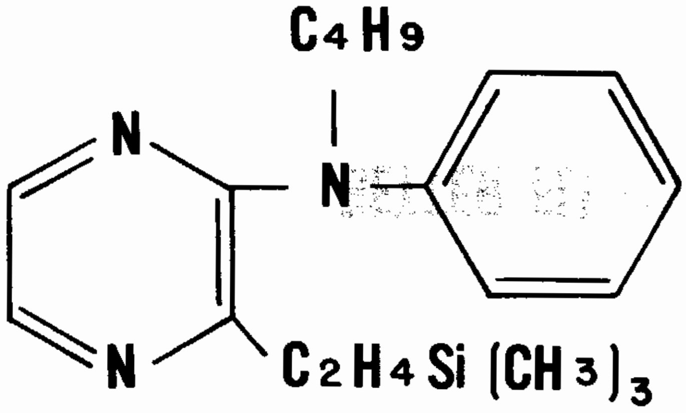

2,N-BUTYL ANILINO 3,ETHYL TRIMETHYLSILYL PYRAZINE

Figure 4.

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THERMAL STABILITY (9 HOURS)

COMPOUND	Micro B. P. °F	Test Temp. °F	Wt. Loss %	Color Change	Viscosity @100°F(Centistokes) Before	After	% Incr.	I R Change
2-n-Heptyl-5-n-nonyl-pyrazine	685	700	10.2	Very Slight	8.40	8.65	2.9	No
MIL-L-9236 Base Stock	720	700	15.2	Slight	15.35	18.94	23	No
MIL-L-9236 Formulation	720	700	15.1	Blackened	16.17	19.72	22	No
2-(Di-n-hexylamino)-3-(5-nonyl) pyrazine	695	700	23.5	Darkened	20.14	72.39	164	Yes
2-(N-Methylanilino)-3-(6-heptyldecyl) pyrazine	706	700	22.1	Darkened				

OXIDATION STABILITY (6 HOURS)

COMPOUND	Test Temp °F	Color Change	Viscosity Before	After	% Incr.	Odor After	I R Change
2-n-Heptyl-5-n-nonyl pyrazine	500	Darkened	8.65	18.31	118	Slight	Slight
MIL-L-9236 Base Stock	500	Darkened	15.35	55.06	258	Acrid	Yes
MIL-L-9236 Formulation	500	Darkened	16.17	28.02	73	Acrid	Yes
2-(Di-n-hexylamino)-3-(5-nonyl) pyrazine	500	Blackened	20.14	33.19	65	Slight	Slight

Figure 5.

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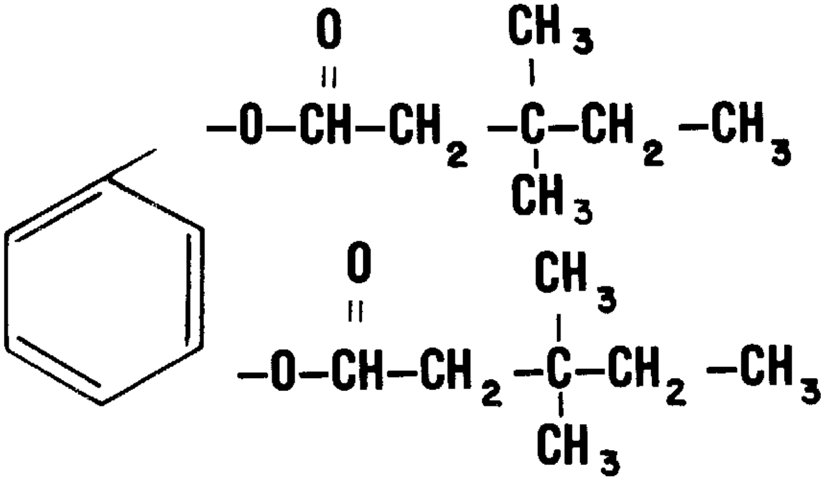
POUR POINT -50°F



1,3,Recorcinyl,Diheptanoate

Figure 6.

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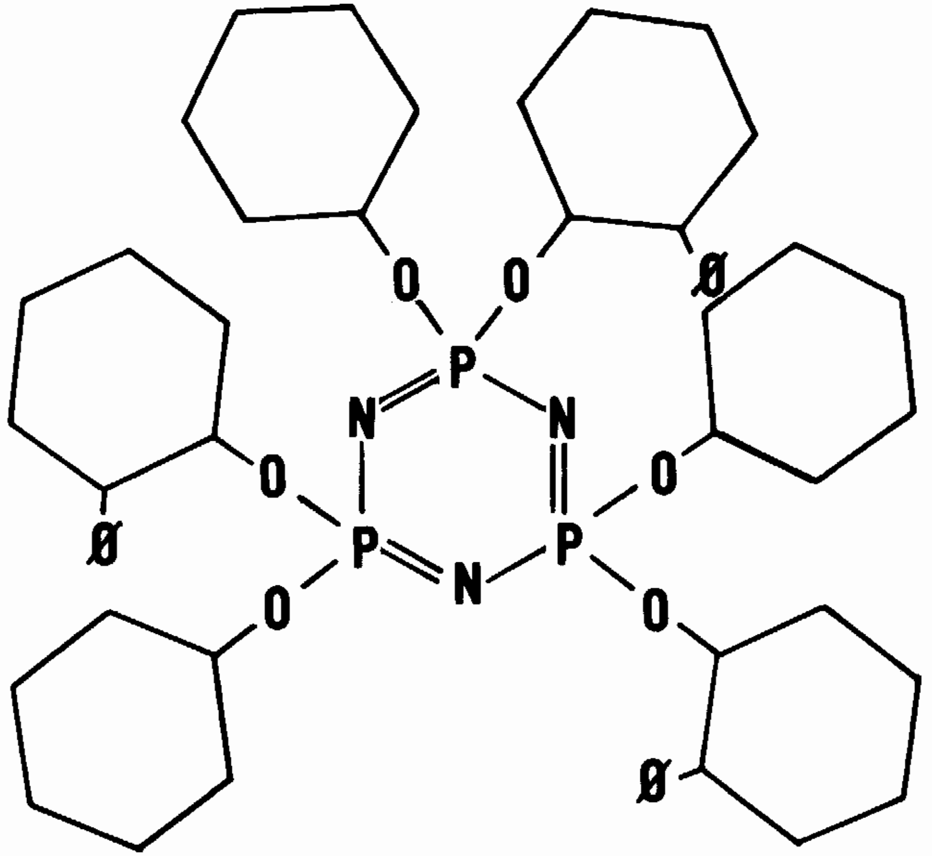

TRIS [(Q-BIPHENYLOXY),(PHENOXY)] TRIPHOSPHONITRILE

Figure 7.

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FUTURE GREASE REQUIREMENTS

- High Temperature Capability (600°F To 900°F)
- Wide Temperature Range (–100°F To +600°F)
- High Speed Capability (Up To 1×10^6 DN)
- Heavy Load Carry Capability (Mean Hertz Load Values Up To 75)
- Nuclear Radiation Resistance (Up To 1×10^{10} ergs/g Carbon)
- High Vacuum Capacity (To 10^{-7}mm Hg)
- High Pressures (Pneumatic Systems, Up To 4000 psi)

Figure 8.

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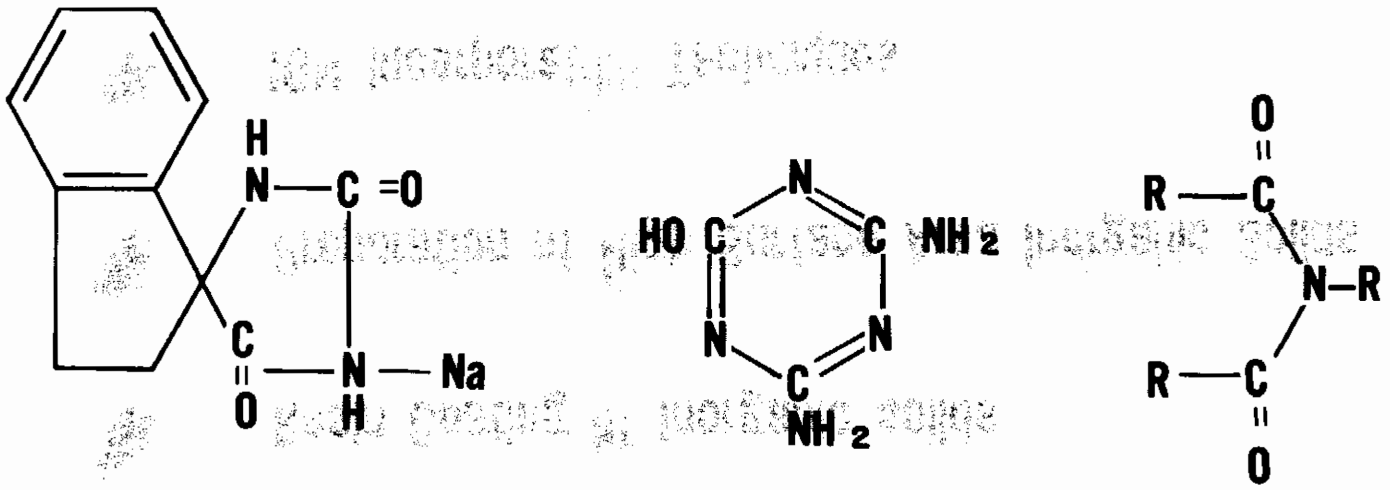
TYPICAL ORGANIC THICKENERS



Hydantoin Ammeline Imide

Figure 9.

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SPECIAL SURFACE MODIFICATION TECHNIQUES

- Resin Coating of Inorganic solids
- Preparation of High Surface Area Inorganic Solids
- ION Incorporation Techniques

Figure 10.

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BASE FLUIDS

Current	Future
Silphenylenes	Polyphenyls
Silicones	Pyrazine Derivatives
Polyphenyl Ethers	Perfluoroaromatics
Silanes	Inorganics

Figure 11.

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HIGH TEMPERATURE GREASE CAPABILITY PRESENT and FUTURE

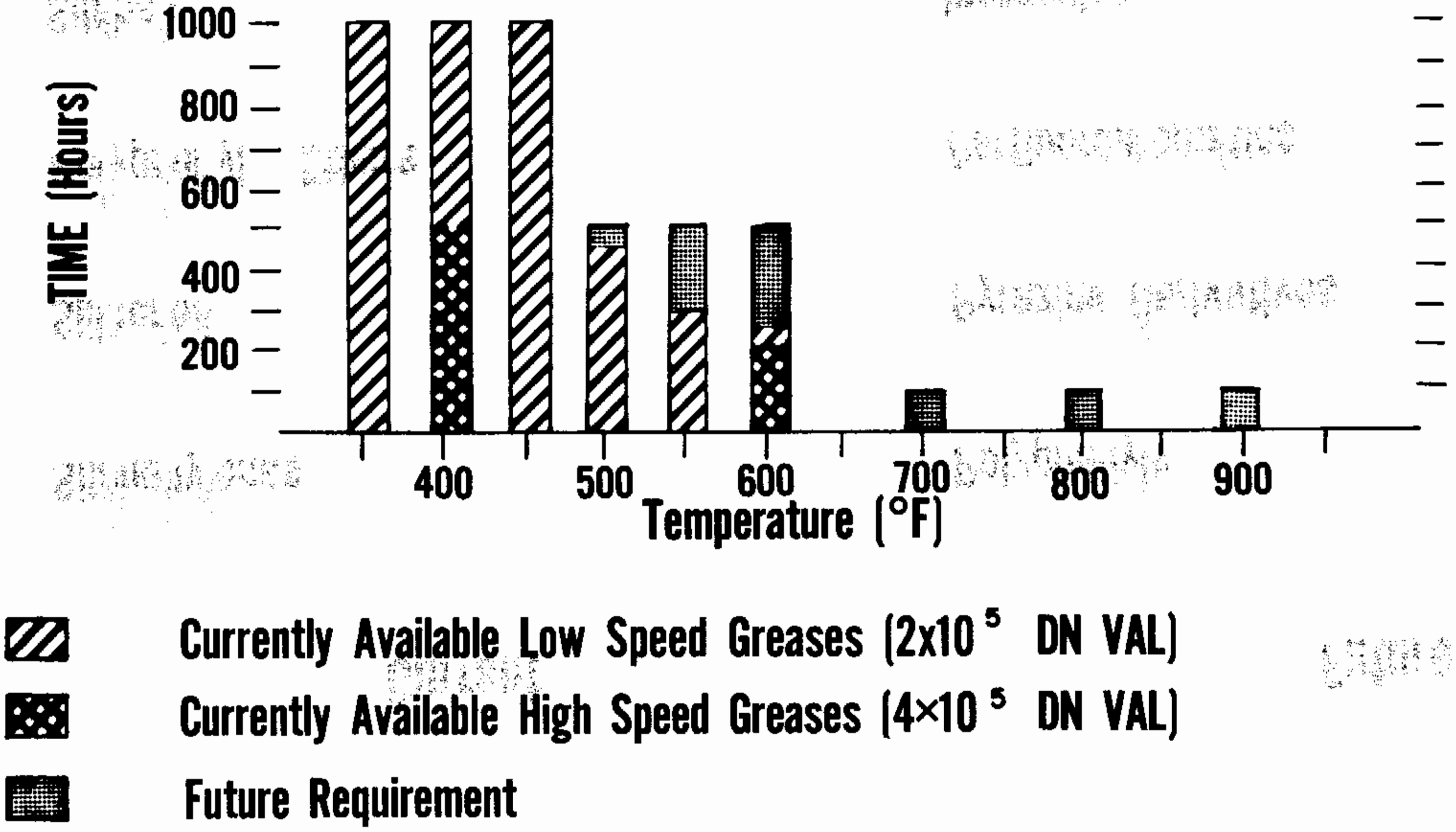

Figure 12.

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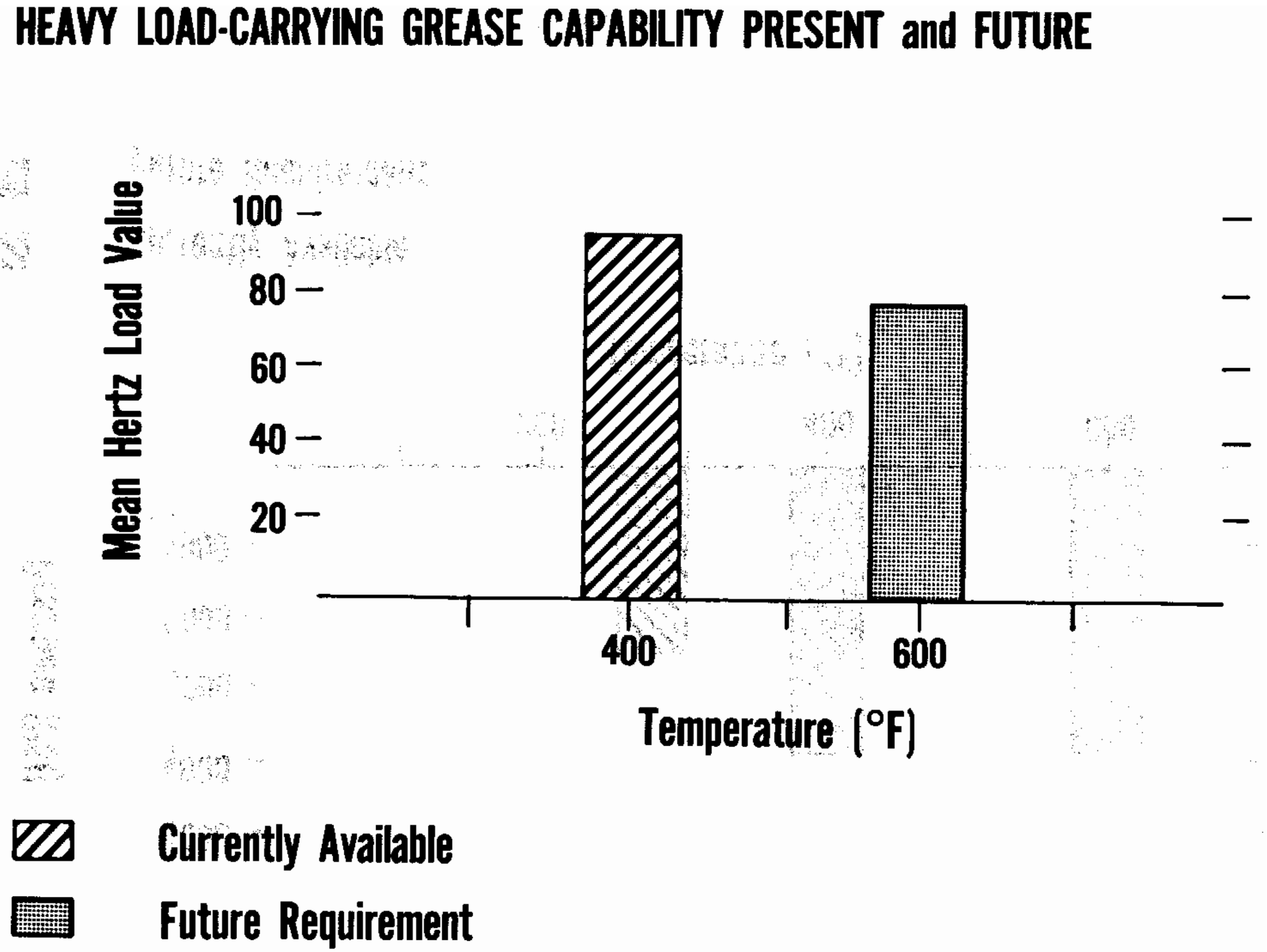

HEAVY LOAD-CARRYING GREASE CAPABILITY PRESENT and FUTURE

Figure 13.

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PNEUMATIC GREASE CAPABILITY PRESENT AND FUTURE

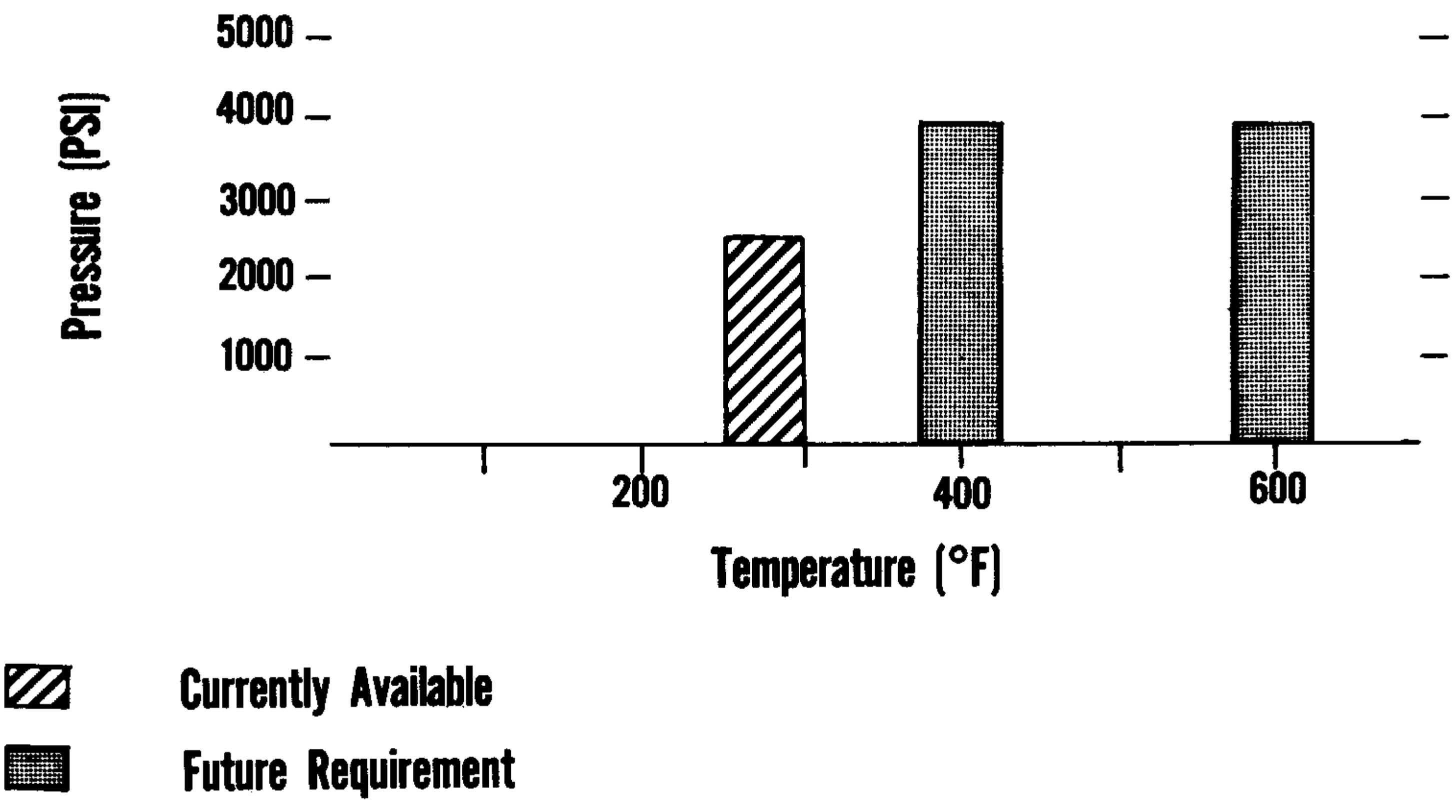

Figure 14.

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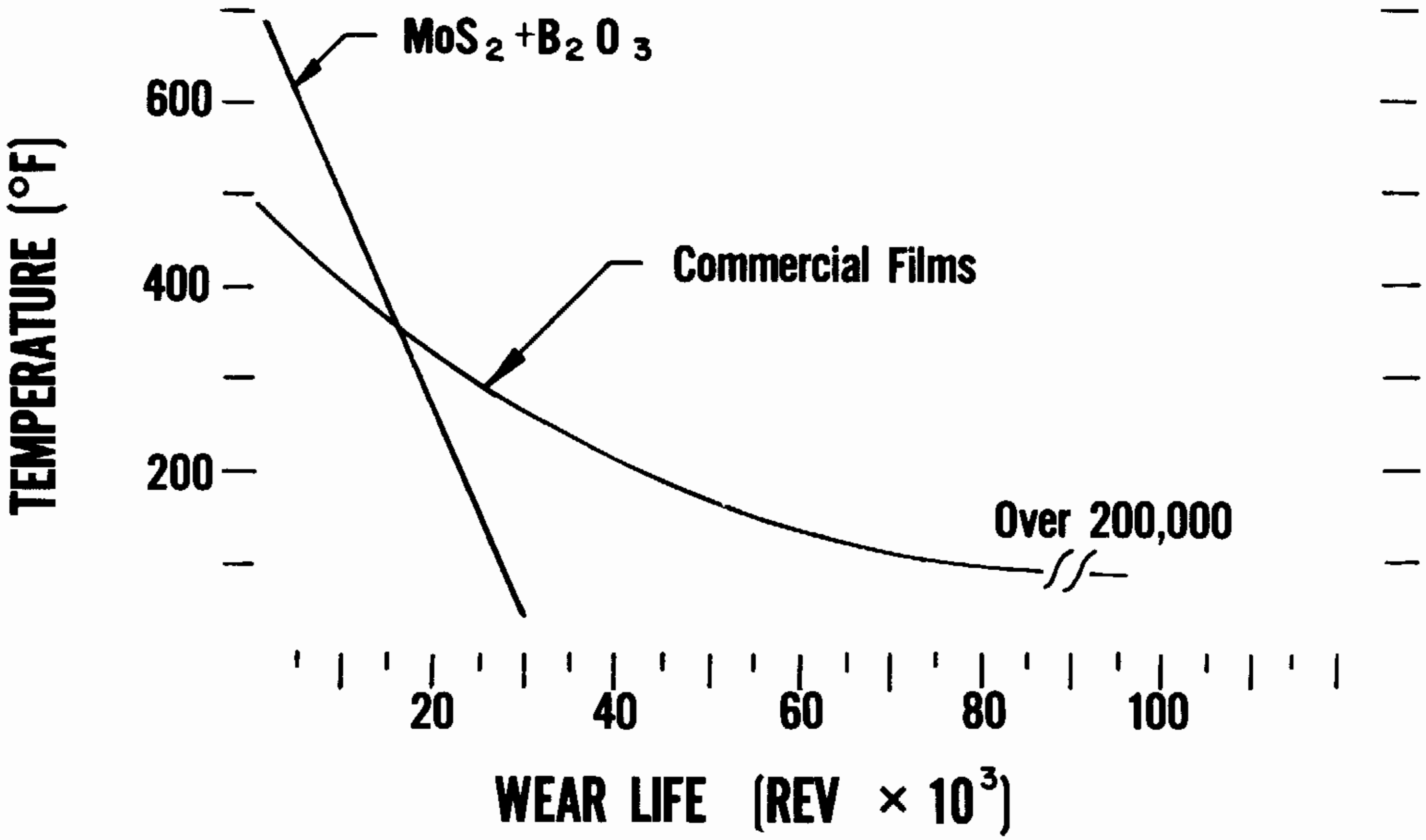

Figure 15.

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WEAR LIFE IN MINUTES FALEX TESTER, 1000 Lb. LOAD

	AVERAGE, FOUR TESTS	AVERAGE LOSS in LIFE (%)
FILM A		
Room Temperature	206	88
Liquid N_2	24	
FILM B		
Room Temperature	421	96
Liquid N_2	17	
FILM C		
Room Temperature	296	97
Liquid N_2	10	
FILM D		
Room Temperature	437	96
Liquid N_2	20	

Performance Of Solid Film Lubricants In Liquid N_2

Figure 16.

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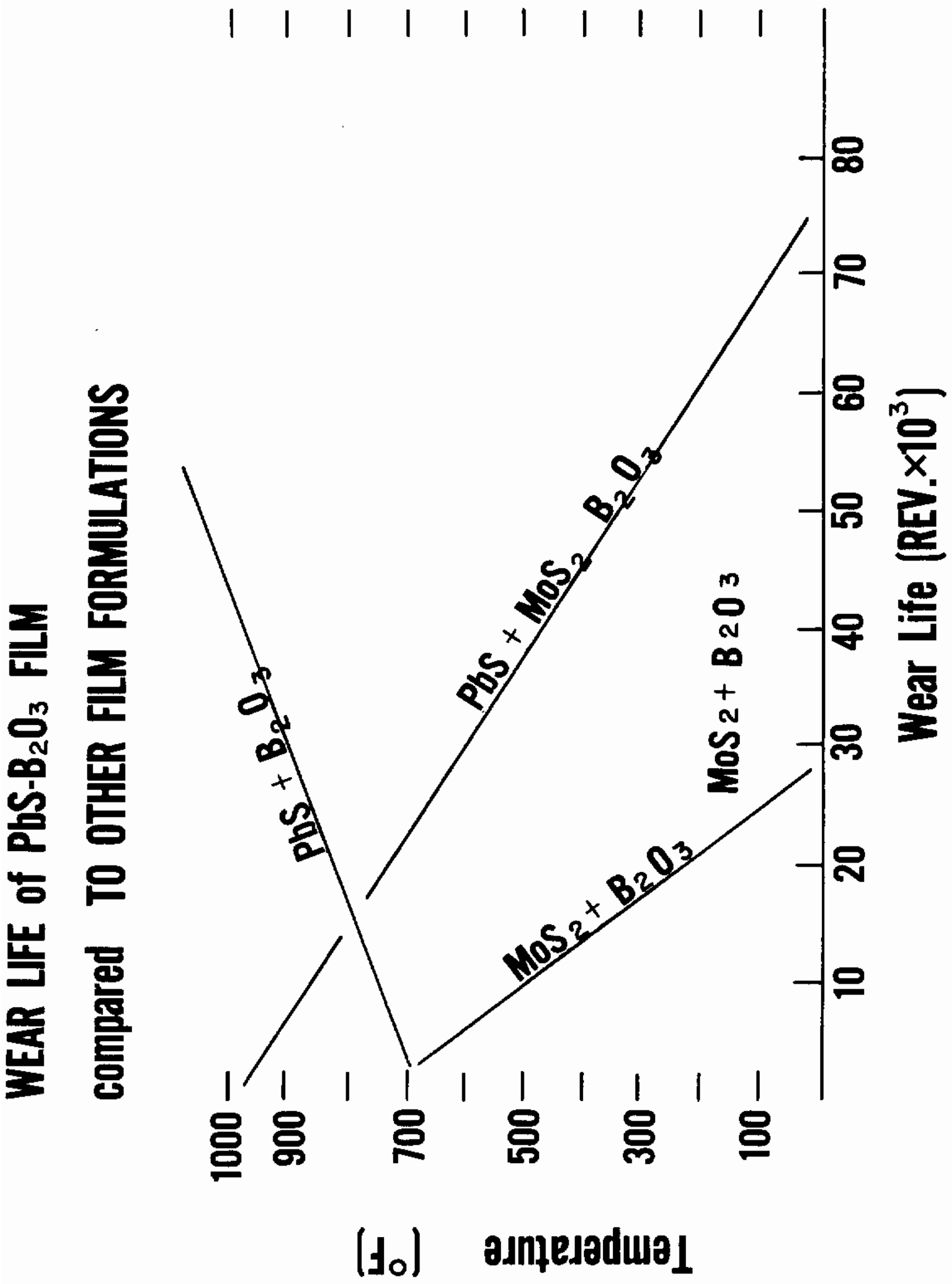

Figure 17.

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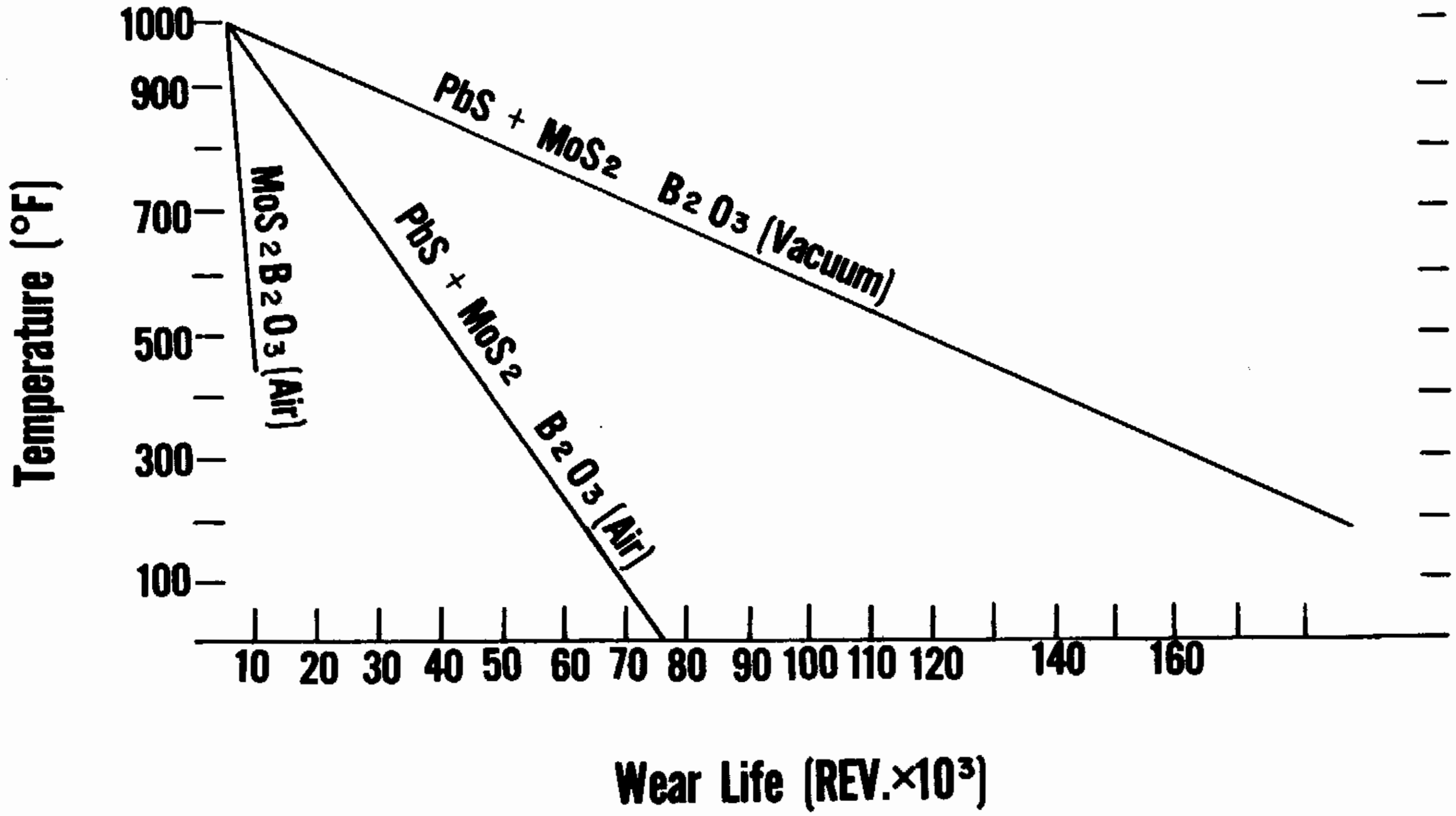
WEAR LIFE of MoS_2+PbS–B_2O_3 IN AIR and IN VACUUM (10^{-6} mm Hg)



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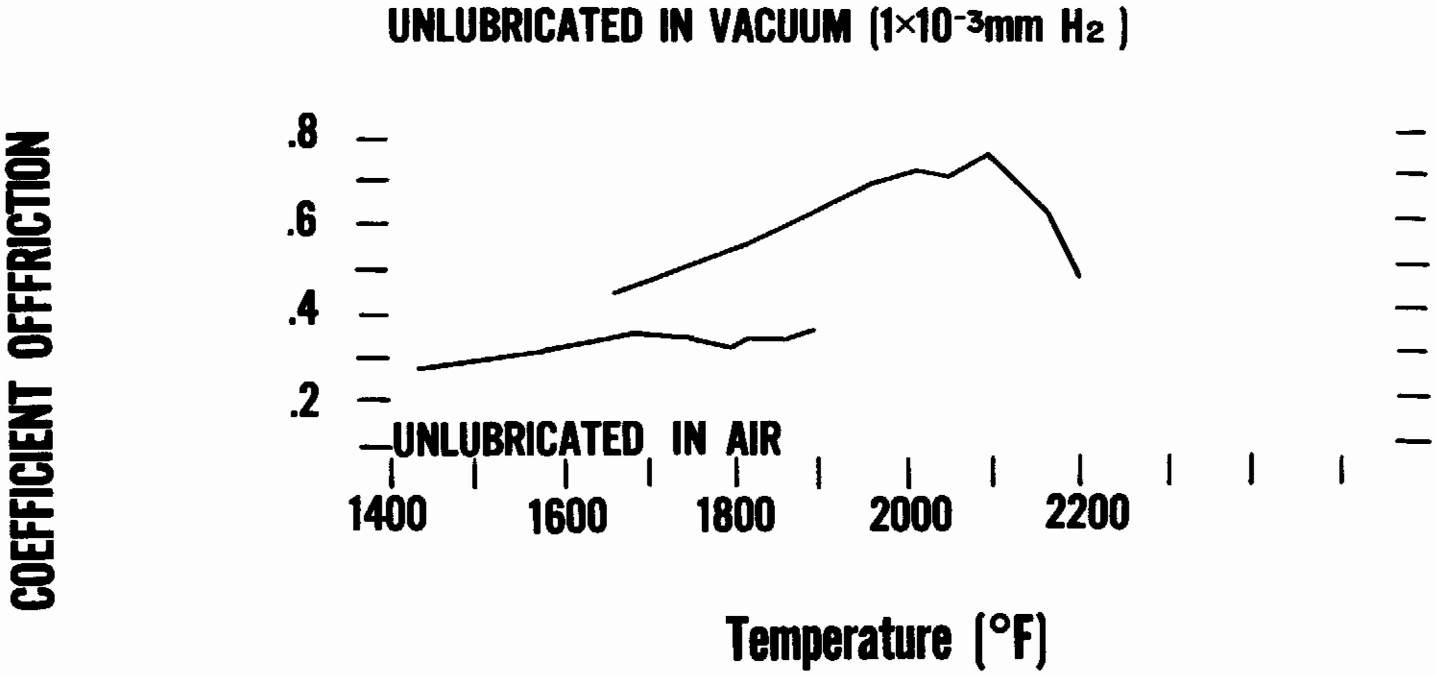

Variation of Friction With Temperature, LT-IB Against LT-IB Unlubricated, In Air And In Vacuum

Figure 19.

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