FLUIDS AND LUBRICANTS

Chairman	Dr. R. L. Adamczak
Speakers	Mr. D. A. Kirk
	Mr. H. W. Adams
	Mr. G. A. Beane
Panel Members	Mr. R. J. Benzing
	Dr. C. Tamborski
	Mr. H. Schwenker
	Mr. R. C. Sheard

AEROSPACE WORKING FLUIDS

David A. Kirk

Lt. John Roth

Harold Adams

Directorate of Materials and Processes, ASD

The requirements for fluids are becoming increasingly critical for the successful achievement of aerospace travel. Under intensive investigation are such materials as hydraulic fluids, flotation fluids, and heat transfer fluids. It should be pointed out that often the same class of material or fluid base stock can be utilized in more than one area. For example, organo-silicones have been put to important uses as hydraulic and heat transfer fluids. Liquid metals offer advantages for the rapid dissipation of large quantities of heat; and are also under investigation for use as hydraulic fluids under extreme conditions. Therefore, while specific fluid classes will be discussed the overall state of the art is a summation of all the effort in each area. Results from any one program area may greatly advance a second or third study.

High temperature stability is the area of greatest concern in most of the fluid programs. Organic fluids still offer promise at temperatures to 1000°F while above this region the liquid metals, liquid salts, and liquid nonmetals are undergoing intensive investigations. One of the major jobs for fluids in future applications is the removal of heat from other materials and systems so that they may function normally.

Heat Transfer and Working Fluids

Heat transfer and working fluids are of increasing importance as modern equipment, and power plants require fluids which must withstand the extreme conditions encountered in advanced aerospace applications. Working fluid temperature ranges required for some of the modern design concepts reach temperatures of 2500°F. Heat transfer fluids for modern use must cover temperatures from -80°F to +2500° and are in three general categories.

1. Organic compounds, 2. Liquid metals and 3. Liquid non-metals.

Working fluids are fluids which take heat energy and through a given working cycle convert that energy into mechanical or electrical energy. An example would be the conversion of energy in a nuclear reactor to rotary motion through a cycle or loop in which the fluid is converted into a gas which in turn energizes a turbine after releasing its energy cycled through a heat exchanger and the reactor. The simple Rankine cycle using nuclear power as the heat source would be one possible system.

Heat transfer fluids, on the other hand, have as their main function the removal of heat or control of temperature in a system. This is of particular concern in space where reliability will depend on proper temperature levels. Liquid metals are important because they can operate at the extremely high temperatures dictated by space where radiation is the only means of heat dissipation. In radiant heat transfer the T^4 function becomes the controlling parameter. Organic fluids find use in electronic systems where the actual components are temperature limited and where nonconducting properties are required.

With regard to electronic equipment design for modern aerospace systems, liquid phase coolants are the most reliable means of controlling temperature under adverse conditions. As more sophisticated vehicles are designed with space and mass conservation, increased equipment reliability of the critical electronic components demands more exacting temperature control. This can best be done by using an all liquid coolant. Temperature control of approximately one degree can be attained, which cannot be done with condensing vapor type cooling.

Figure 1 shows the operating temperature ranges of commercially available, experimental, and future desired fluids. Table 1 shows the desired physical properties for coolants and gives the properties of MLO-60-125 and MLO-60-107, two polysiloxanes which have been recently developed and are satisfactory for operation from -80° to 400°F. A large number of fluids have been examined including silanes, esters, ferrocenes, hydrogenated paraffins, ethers silphenylenes, siloxanes and silicate esters. They each possess potential for various applications.

Liquid Metals and Liquid Inorganics

Figure 2 shows some of the available liquid metals and their temperature range as working and heat transfer media. Inherent problems are introduced when liquid metals are used as fluids. They are extremely corrosive at higher temperature ranges. For example stainless steel is satisfactory at temperatures to approximately 1600°F., but would be unsatisfactory for service to 2500°F. Physical properties of the liquid metals are not well established at the higher temperature ranges because many experimental difficulties are involved in determining them. These liquids, as could be anticipated from their position on the periodic chart, are extremely strong reducing agents. Development of the liquid metals as working fluids requires information on heat transfer coefficients, optimum operating conditions from the viewpoint of containment materials, and instrumentation compatibility. Also needed is more information on the behavior of reduced gravity fields. Table 2 gives information on some of the current research and development efforts in this field. In general, the liquid non-metals such as sulphur and aluminum bromide offer similar advantages and present difficulties similar to those of the liquid metals.

The various heat transfer working fluids offer advantages for utilization in particular applications. Present technology alone limits the upper temperature regions. As the technological changes are met, power plants and other equipment will evolve that will operate at higher and higher temperatures.

Flotation Fluids

Flotation fluids are used in inertial gyroscopes. The space which the fluid occupies is illustrated in figure 3. The inertial-gyro-wheel-carrying gimbal is precisely floated in a dense, viscous fluid. The flotation fluid reduces the torque about the gimbal rotational axis so that minute torques, corresponding to very small input angular rates, can be detected and resolved. The fluid has the dual function of providing the required buoyancy (a function of its density) and damping (a function of its viscosity). The damping function of the fluid is necessary to provide a smoothing or integrating effect on incoming rate information and to reduce the hazard of shock or vibration damage to the instrument.

General Flotation Requirements (Table 3)

1. The fluid should be radiation resistant, but otherwise exhibit similar properties to the polychlorotrifluorethylene oil or polybromotrifluoroethylene blend.

2. After a radiation dose of 3.0×10^{10} ergs/gm C, the flotation media (2.1 cs at 160°F) may double in viscosity to 4.2 or decrease to 0.5 cs at 160°F. Density shall not change more than that which can be compensated for by 1°F change in gyro operating temperature.

3. -65°F fluidity is desired but not critical if the other requirements are met.

Two flotation fluids represent the state of the art in rate gyros using flotation fluids.

1. Polychlorotrifluorethylene
2. Polybromotrifluoroethylene

These fluids cannot be designated as high temperature fluids. However, this is of little consequence since the temperature of the gyro is generally controlled in the range of +65° to +85°F. A wider temperature range reliability becomes important only when a gyro might not be operating as when the containing vehicle is in shipment or storage and outside temperature becomes a factor.

Many fluids have the required viscosity but few possess simultaneously high density to support the gyro wheel assembly in a reasonable floated gimbal volume. The fluids used throughout the gyroscope industry are not stable to nuclear radiation and in our present effort this is the main problem. The general requirements are shown on previous page.

A literature survey was made relative to feasible chemical structures having a high density (1.8 and above) and showing potential as radiation resistant fluids stable to a dosage of 3.0×10^{10} ergs/ gm C. Hexafluorobenzene was chosen as a starting material from which to synthesize suitable flotation fluids. The aromatic nature of the molecule indicates possibilities as a radiation resistant material and the abundance of fluorine contributes to the desired high density. The fluid must have a low vapor pressure at the gyro fill temperature so that it can be properly degassed. Calculations show that a fluid having a molecular weight of approximately 650 should satisfy this requirement. Figure 4 shows typical structures whose synthesis will be attempted.

Some gyro manufacturers appear to believe that gyros of the near future will be required to operate for long periods of time at high temperature, and under the influence of high nuclear fluxes. Typical conditions expected are shown in table 4.

The manufacturers appear to believe that rate gyros can be designed and constructed to operate without liquid bearing lubricants and entirely without a flotation fluid media. The gimbal assembly might be electrically floated and dampened by a magnetic field. This type gyro would eliminate the use of flotation fluids, resulting in a weight reduction, fluid-component compatibility, and fluid gassing.

Hydraulic Fluids

The state of the art in hydraulic fluids is shown in table 5. Hydraulic fluids qualified under MIL-H-5606A are in general use throughout the Air Force, Navy and Army. MIL-H-5606B, is a tentative specification covering a super clean fluid with a better shear stable viscosity improver than that used in MIL-H-5606A. It is hoped that fluids qualified under this specification (MIL-H-5606B) will service both aircraft and missiles. MIL-H-5606A fluids are petroleum based and generally contain TCP (anti-wear additive), acryloid (viscosity index improver), and phenothiazine or PANA (antioxidant). The only fluids qualified under MIL-H-8446B are disiloxane based, with appropriate additives. Approximately 14 percent diester fluid is added to the disiloxane to produce the necessary neoprene rubber swell characteristics.

Research and Development Effort

The major research and development effort is for a type 4 system hydraulic fluid. It is anticipated that this fluid will be under specification by 1 July 1961; it is petroleum based and is usable as a hydraulic fluid up to +550°F. It is a super-refined, deep dewaxed, paraffinic mineral oil and has been designated MLO 60-294. The research effort responsible for the development of this fluid was carried out by the Petroleum Refining Laboratory, Pennsylvania State University, under contract with the Air Force. Figure 5 illustrates the general refining schematic for the origin of the base stock.

The main problem was to remove, by hydrogenation, all polar impurities, double bonds and open terminal bonds without excessive hydrocracking.

Although fractions 1 and 2, as described, exhibited excellent thermal stability at the expected operating temperatures, the low temperature properties were a problem. Low temperature dewaxing studies were carried out to improve the low temperature fluidity. The Laboratory method, using a mixture of methylethyl ketone and methylisobutyl ketone as the solvent proved to be very efficient at -65°F to -80°F. This treatment yielded 85 percent oil (-75°F pour point) and 15 percent wax (+40°F pour point). The deep or low temperature dewaxing was followed by vacuum stripping to remove the dewaxing solvent and any hydrocracked materials from the refining steps. This was followed by acid treatment to remove trace impurities and unsaturation caused by steps following hydrogenation.

Tables 6, 7 & 8 show data obtained on the formulated dewaxed oil (MLO 60-294).

The data in table 8 shows that excellent wear properties can be expected from this high temperature mineral oil. This is a very important property relative to hydraulic pump life and reliability.

A synthesis and evaluation program is being carried out on fire resistant hydraulic fluids for use over the temperature range of -65°F to 450°F and +40°F to 800°F. The program initially concentrated upon a means of molecular evaluation which could classify specific chemical bond types, relative to their fire resistance. The general type classes involved were: halocarbons, phosphine oxides, aromatic and heterocyclic compounds. Using flame velocity coefficient measurements, it was intended to correlate chemical structure with flammability. The following questions were to be answered during these initial studies:

1. What are the fire retardant atoms and groups and what are their efficiencies?

2. Are there any synergistic effects shown by two or more fire retardant atoms or groups?

3. What are the optimum linkages for incorporating a fire retardant atom or group in a molecule?

4. What are the major synthetic problems to be anticipated in the design of a fire resistant fluid?

The general observation (April 1961) appeared to be that the Phosphine oxides held promise as yielding a fire resistant -65°F to 450°F hydraulic fluid and the heterocyclic class, such as derivatives of pyridine, to yield a +40° to 800°F fluid.

Table 9 illustrates autogenous ignition temperature comparisons of halides with their hydorcarbon analogs. This table shows that the position and halogen type as well as halogen combinations have a marked influence on the AIT also, the ratio of halogen to carbon-hydrogen.

It is felt that mineral oils can be reliably used as hydraulic fluids up to 700°F. Above 700°F, the polyphenyl ether fluids may become useful but will probably not be usable over 850°F for any appreciable time. For hydraulic systems requiring fluids 1000°F or higher, it appears that considerable promise lies in the inorganic fluids. Phosphorus-nitrogen polymers have been made by DuPont, under contract to the Air Force, which have liquid ranges from 0°F to 1000°F and higher. Considerable effort is needed to derive suitable prototype fluids. However, within the next year, some inorganic fluids, with thermal stability in the 1000°F range should be available. Figure 6 shows a typical structure as of April 1961. Other possible approaches are in the area of liquid metals and salts.

General Electric Company under contract with the Air Force has been studying this area for several years. Current emphasis is in feasibility of system operation and design of servo valves for use in liquid metal systems.

In summary it should be pointed out that fluid synthesis in the case of nonmetallic materials and property studies in the case of liquid metals and salts are the areas requiring research and development for all fluid classes. Initially, high temperature stability and operation will be required prior to study of other characteristics such as radiation tolerance.

REFERENCES

1. Barsness, D.A., WADD Technical Report 60-795 Part 1 (December 1960).

2. Weatherford, W.D. Jr., Tyler, J.C. and Ku, P.M., WADC Technical Report 59-598 (December 1959).

3. NASA-AEC Liquid-Metals Corrosion Meeting, NASA TN 0-769 February 1961.

TABLE I

SILICONE FLUIDS

PHYSICAL AND CHEMICAL PROPERTIES	UNITS	DESIRED PROPERTIES	MLO-60-125	MLO-60-107
CHEMICAL COMPOSITION		N / A	METHYL POLYSILOXANE	METHYL POLYSILOXANE
COLOR		N/A	CLEAR	CLEAR
POUR POINT	°F	< -80	BELOW -134	BELOW -90
FLASH POINT	°F	> 400	480	515
FIRE POINT	°F	> 400	600	640
SURFACE TENSION	dynes/cm	> 30	21.7	23.
VISCOSITY AT 400°F	CENTISTOKES	1	2.	2.2
210°F			6	6.3
100°F			13	16.
-65°F			164	232.
-80°F		100-300	251	371
VAPOR PRESSURE AT 600°F mm Hg			35	46
500°F			8	22
400°F		< 100	2.4	12.5
300°F			.6	6.2
200°F			.1	2.4
100°F			.1	1.3
DENSITY-TEMP.	gm/cc			
400°F			0.797	0.810
210°F			0.885	0.892
100°F			0.939	0.946
77°F			0.950	0.960
40°F			0.970	0.979
0°F			0.985	0.998

TABLE 2

SUMMARY OF SELECTED CURRENT HIGH TEMPERATURE LIQUID METAL PROGRAMS (3)

LIQUID METAL	TYPE OF PROGRAM	CONTAINMENT METAL	MAX. TEMP.	STATUS
Rb	BOILING CONDENSING LOOP	316S.S	1900°F	ALMOST READY FOR OPERATION
Rb	BOILING CONDENSING LOOP	SAME AS ABOVE, EXCEPT MATERIAL IS Nb-1Zr		LOOP NOT BUILT YET
Na	TWO PHASE LOOP	304 S.S.	1832°F	———
NaK	PUMPING LOOP, CORROSION	316 S S.	1500°F	TERMINATED
Na	REFLUX CAPSULES	Nb-1 Zr	2200-2300°F	PLANNED
Na	BOILING PUMPED LOOP	— —	2400°F	DESIGN STAGE
Na, K	TWO BOILING & CONDENSING HEAT TRANSFER LOOPS	HS-25, Nb-1Zr	2200°F	PRELIMINARY EVALUATIONS
Na, K	TWO PHASE THERMAL CONVECTION LOOPS	INCONEL, Nb-1Zr	2500°F	INCONEL LOOPS RUNNING
Li	HEAT TRANSFER Li TO Ta	— —	2400°F	IN PROGRESS

Note: for explanation of table 3 (see page 340)

Table 4

FUTURE TYPICAL CONDITIONS FOR FLOTATION

OPERATING TEMPERATURE RANGE	−65° To 700°F
Time (Hrs.)	25,000
Nuclear Flux	1.0×10^{12} To ^{15} Ergs/gm/C

Table 5

HYDRAULIC FLUID STATE-OF-THE-ART

BASE CHEMICAL TYPE	SPECIFICATION NO.	TEMPERATURE RANGE
Petroleum	MIL-H-5606B	–65°F To 275°F
Synthetic	MIL-H-8446A	–65°F To 400°F
Petroleum	Proposed MIL-H-27601 USAF	–40°F To 550°F
Petroleum Or Synthetic	MIL-H-(?)	0°F To 700°F
Synthetic (Inorganic)	MIL-H-(?)	0°F To 1000°F

Table 6

SUPER REFINED, DEEP DEWAXED, PARAFFINIC MINERAL OIL

Viscosity (Centistokes)	At −65°F	22,859
	−40°F	2,820
	0°F	306
	100°F	14.08
	210°F	3.18
	400°F	1.12
	550°F	0.74
ASTM Slope (210°F To 100°F)		0.784
Pour Point, °F		−80
Flash Point, °F		385
Fire Point, °F		430
Initial Decomposition Point, °F (Isoteniscope Method)		678

Table 7

PHYSICAL PROPERTIES (DENSITY, $d_4^{20} = 0.840$)

	0°F	200°F	400°F	500°F
Coefficient Of Expansion cc/cc/°F x 10^4	4.4	5.4	6.4	
Thermal Conductivity BTU/ft^2/hr/ °F/ft	0.0813	0.0749	0.0700	0.0676
Specific Heat (BTU/lb/°F)	0.440	0.537	0.635	0.684
Bulk Modulus, psi x 10^{-5} Av. Value For 0 To 10,000psi	3.2	2.2	1.2	0.7
Vapor Pressure (mmHg)		2.0	21.0	84.0
Density ; (gm/ml)	0.866	0.796	0.726	0.691

TABLE 8

WEAR DATA

	Load (Kg)	Scar (mm, diam)
Shell 4-Ball Wear at 75°C, 1200 rpm, 2 hours	40	0.21
	10	0.26
	40	0.53
at 400°C, 600 rpm, 2 hours	4	0.19
	10	0.25
	40	0.48

TABLE 9

STRUCTURE	AIT, °F (Halide)	AIT, °F (Hydrocarbon)	AIT (Halide) — AIT (Hydrocarbon)
$F(CH_2)_4$	525	761	- 236
$Br(CH_2)_4Br$	765	761	+ 4
$Cl(CH_2)_2Cl$	825	959	- 134
$Br(CH_2)_2Br$	960	959	+ 1
$Cl(CH_2)_4Cl$	445	761	- 316
$Cl(CH_2)_2Cl$	825	959	- 134
$CH_3(CH_2)_2Cl$	790	871	-81
$CH_3(CH_2)_2Br$	1000	871	+ 129
$CH_3(CH_2)_3Br$	500	761	- 261
$CH_3(CH_2)_2Br$	1000	871	+ 129

TABLE 10

BASE CHEMICAL TYPE	SPECIFICATION NO.	TEMPERATURE RANGE
PETROLEUM	MIL-H-5606B	-65°F TO 275°F
SYNTHETIC	MIL-H-8446A	-65°F TO 400°F
PETROLEUM	PROPOSED MIL-H-27601 USAF	-40°F TO 550°F
PETROLEUM OR SYNTHETIC	MIL-H-(?)	0°F TO 700°F
SYNTHETIC (INORGANIC)	MIL-H-(?)	0°F TO 1000°F

LIQUID COOLANTS OPERATING TEMPERATURE RANGE

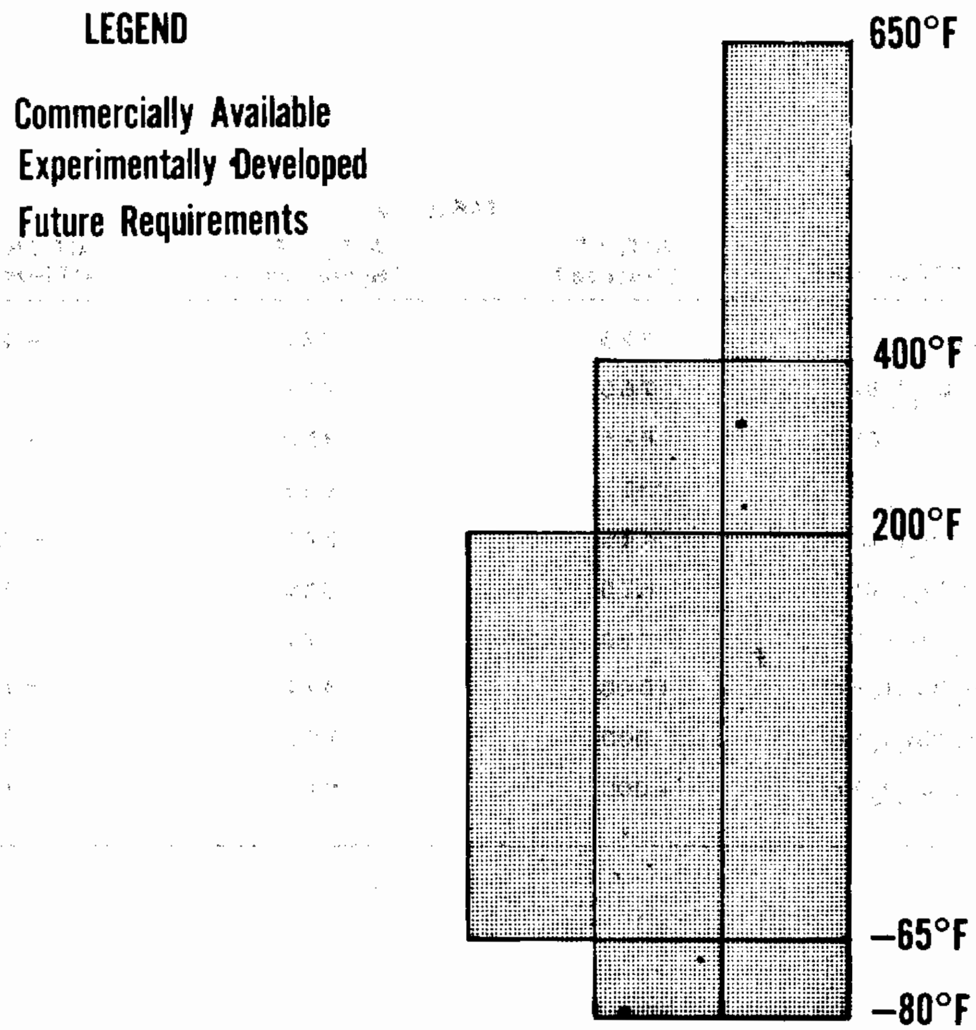


Figure 1.

LIQUID METAL WORKING FLUIDS °F

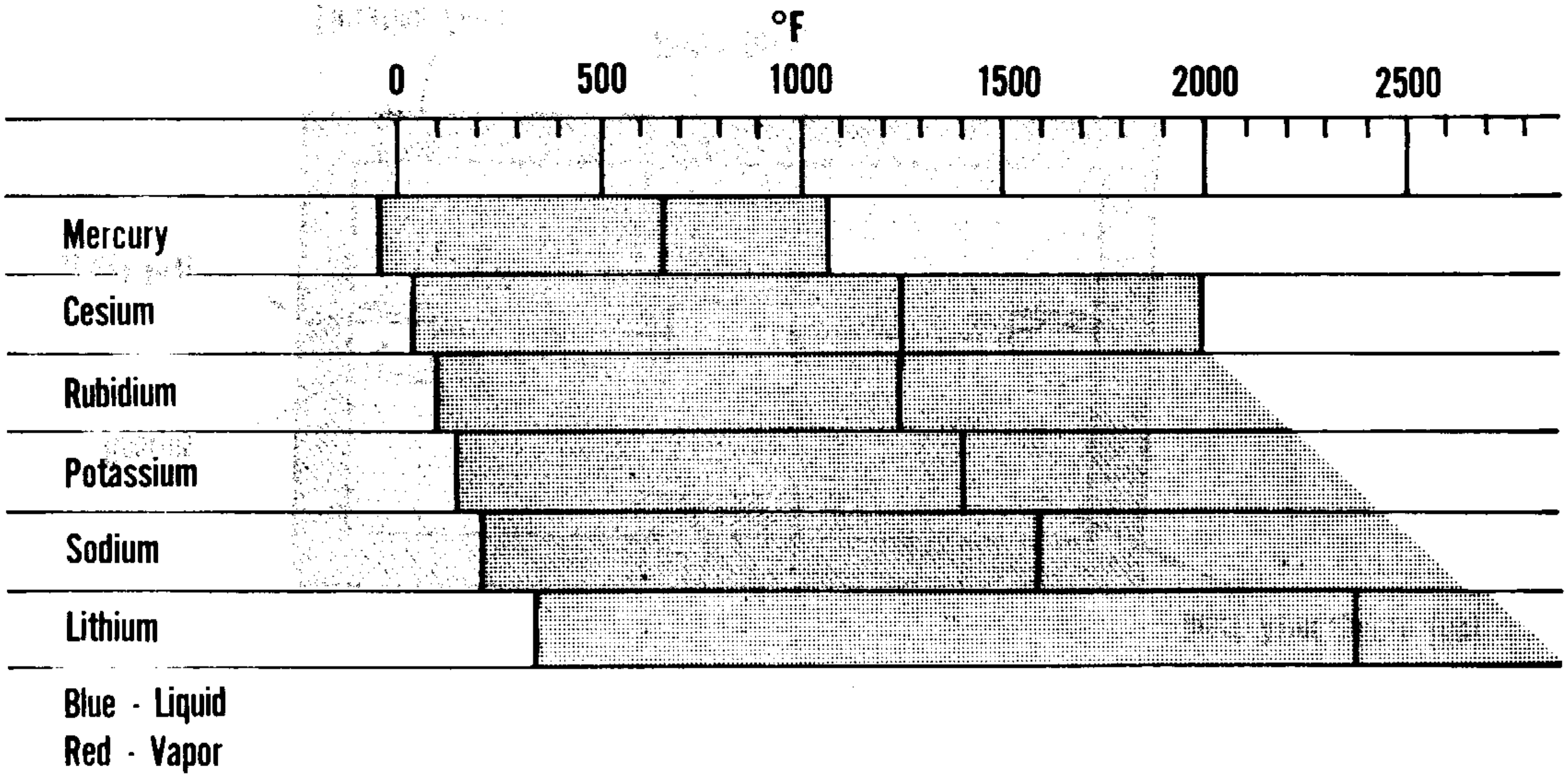


Figure 2.

DIAGRAM OF FLOTATION FLUID AREA

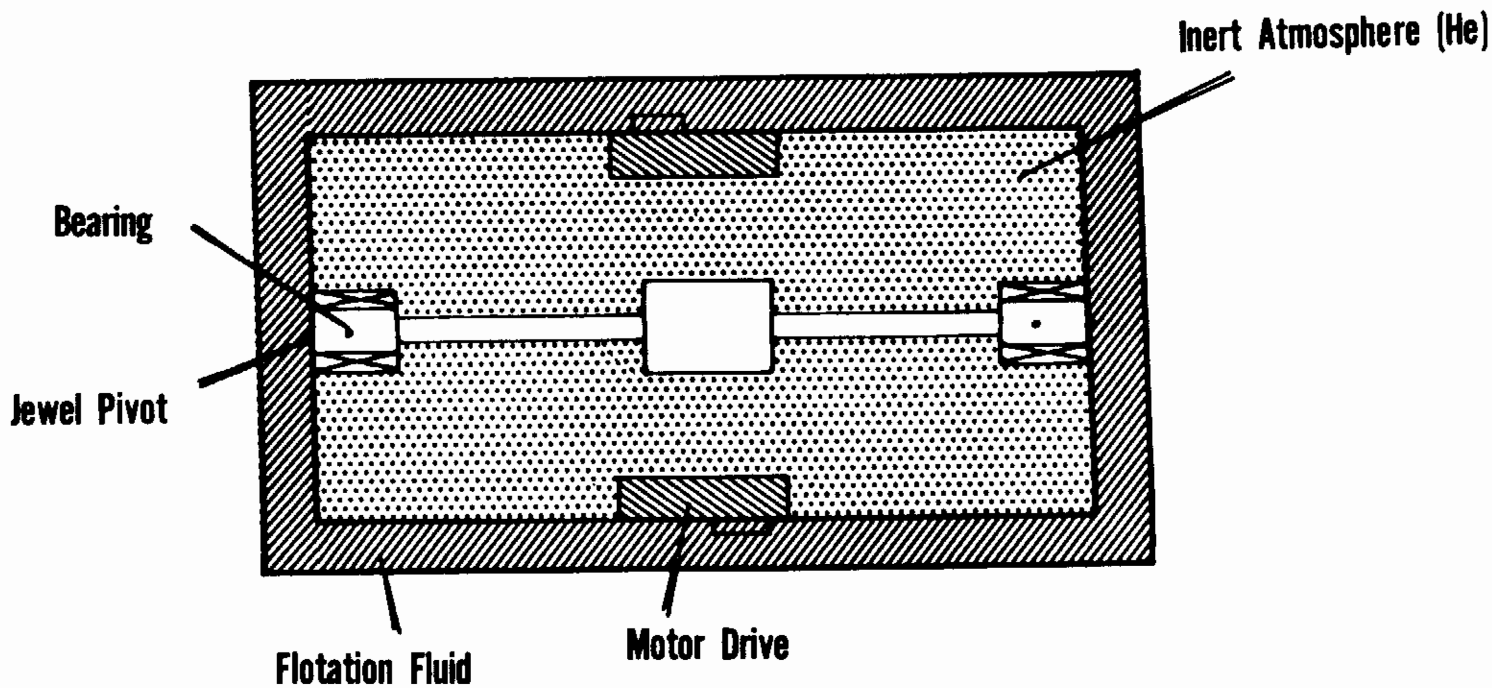


Figure 3.

POSSIBLE SUITABLE STRUCTURES

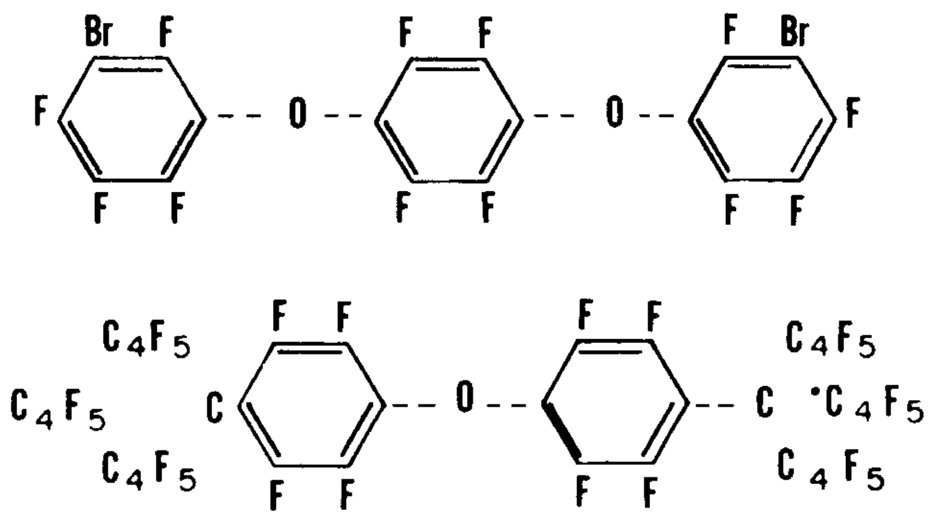


Figure 4.

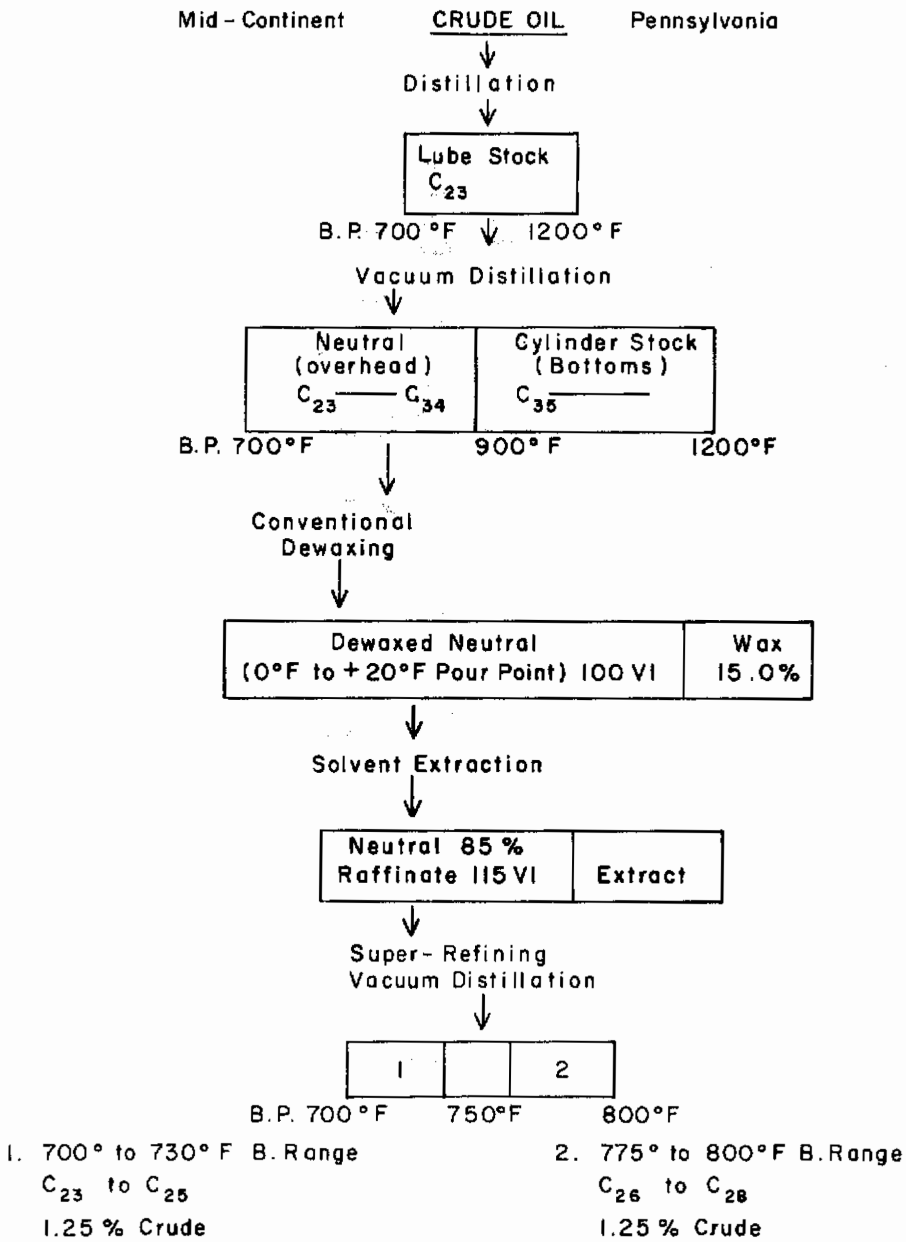
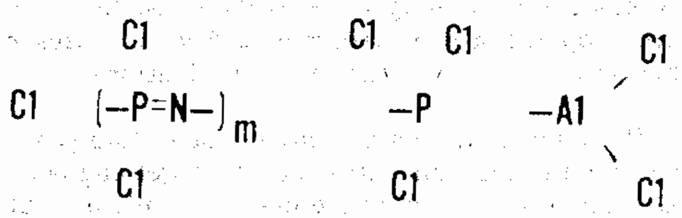

Mid - Continent
CRUDE OIL
Pennsylvania
Distillation
Lube Stock
C_{23}
B. P. 700 °F
1200° F
Vacuum Distillation
Neutral
(overhead)
C_{23} — C_{34}
Cylinder Stock
(Bottoms)
C_{35} —
B. P. 700°F
900° F
1200°F
Conventional
Dewaxing
Dewaxed Neutral
(0°F to +20°F Pour Point) 100 VI
Wax
15.0%
Solvent Extraction
Neutral 85 %
Raffinate 115 VI
Extract
Super - Refining
Vacuum Distillation
1
2
B. P. 700 °F
750°F
800°F
1. 700° to 730° F B. Range
C_{23} to C_{25}
1.25 % Crude
2. 775° to 800°F B. Range
C_{26} to C_{28}
1.25 % Crude

Figure 5.

TYPICAL INORGANIC FLUID



Lewis Acid Stabilized Phosphonitrilic Chlorides

Does Not Polymerize Up To 550°C

Hydrolytically Unstable

Figure 6.