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FLUOROCARBON OILS

INTRODUCTION

The purpose of this report is to indicate the principal available sources of fluorocarbon oils and to summarize their general properties.

No pure fluorocarbons (i.e. single compounds) are available within the oil range in appreciable quantity. However, mixtures of fluorocarbons of various boiling point ranges are available from thin oils to greases and waxes. In addition to these oils intended to contain only carbon and fluorine, chlorofluoro oils and greases are available.

The fluorocarbon oils which do not contain chlorine are being produced by two principal procedures which are indicated as the liquid phase and vapor phase methods (SAM, Hopkins, DuPont). In each case a petroleum fraction is fluorinated to very near completion. Since cracking and rearrangement reactions occur, particularly in the vapor phase method with high boiling materials, the carbon structures of the fluorocarbons obtained are not identical with those of the feed oils.

The Army code for the above oils is C-2144.

Fluorocarbon oils entirely free of hydrogen have been prepared experimentally by the polymerization of perfluoro olefins (SAM). These materials are not being manufactured at present but processes for their production are available.

Chlorofluoro oils with the general composition (C_2F_3Cl) are being produced by polymerization of C_2F_3Cl (SAM, Hooker). These polymer oils presumably have straight chain structures and are available in a wider range of viscosities and vapor pressures than the fluorocarbon oils without chlorine. There are now available by-product light oil and grease fractions. The Army code for specification polymer vacuum pump oil is MFL.

A chlorofluoro oil has also been produced experimentally by fluorinating a chlorinated aromatic hydrocarbon in the liquid phase (DuPont).

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PROPERTIES OF FLUOROCARBON OILS

C-2144 (Fluorinated hydrocarbon oils)

Hydrogen Content

Liquid phase C-2144 - about 1 H to 10 F

Vapor phase C-2144 - about 1 H to 75 F

The above values are approximate and subject to unknown experimental error, but probably are of the right order of magnitude. As may be expected from the methods of manufacture different samples may vary widely in hydrogen content.

In general it is easier to completely fluorinate the lower molecular weight oil fractions. Purification is also possible for low molecular weight fluorocarbons.

Vapor Pressure

Specification oil as manufactured has a vapor pressure of $\geq 8 \times 10^{-3}$ mm. Hg at 60°C. Most samples run close to the maximum value. The boiling point range of vapor phase oil was initially 147-201°C at 10mm. No data is available at SAM on liquid phase oil but it is probably a somewhat wider boiling range product. Most C-2144 is being produced by the liquid phase method at present.

Viscosity

Specification oil has a viscosity of ≥ 25 c.p. at 210°F. It is a stiff liquid containing some crystalline phase at room temperature with a very high viscosity index. Vacuum pumps using this oil have to be warmed for starting.

P.G. Stability

All specification oils must not reduce P.G. at 100°C sufficiently to give a 0.3% weight residue in 3 hrs. as determined by titrating the reduced T and calculating as TF_4. Oils containing considerable hydrogen may pass this test. There has been no indication that pure (all C-F) saturated fluorocarbons react at a measurable rate with P.G. at 60°C. Unfortunately the observed chemical stabilities of fluorocarbon oils have varied because of the use of incompletely fluorinated materials.

Index of Refraction

Values from 1.32 to 1.35 at 25° are usual for specification oil

Density

Approximately 2.0 at 25°C for specification oil.

Molecular Weight

Specification oil has an average molecular weight of approximately 950. Material with a molecular weight of above 1200 is not fluid at room temperature. It should be borne in mind that the physical properties of various average molecular weight products will vary with structure and molecular weight distribution.

MFL (Polymer chlorofluoro oil)

Hydrogen Content

Probably about 1H to 100 F maximum for oils prepared at Columbia. There is little direct evidence for the above value but the method of preparation, the high order of stability of MFL to aqueous alcoholic hydrolysis and to oxidizing agents supports such a conclusion. The chlorine content of these oils is approximately 30%.

Vapor Pressure

Specification oil same as C-2144. A better viscosity relationship as compared with C-2144 permits the preparation of low vapor pressure oils. An oil fairly fluid at room temperature with a vapor pressure of one micron at 60°C is regarded as near the limit.

Viscosity

MFL as manufactured has a viscosity from about 15 to 20 c.p. at 210°F, and is considerably more fluid at room temperature than C-2144 of comparable viscosity at 210°F. Low viscosity oils boiling above 200°C are available now as by-products.

Stability to TF_6

Usual order of 0.1% to 0.05% for 3 hr. test at 100°C. Oils may be prepared which do not react measurably.

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Capt. E. Hill

Index of Refraction

Values of 1.39 to 1.42 at 25° are usual for specification oil.

Density

Approxiamtely 1.95 at 25°C for specification oil.

Molecular Weight

Methods are available for the preparation of practically any desired molecular weight material. Specification oil probably averages about 850 to 900 in molecular weight.

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