EFFECT OF INHIBITORS ON FLAMMABILITY OF HEPTANE-AIR MIXTURES

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A large scale investigation of the effect of inhibitors on flammabilities of heptane-air mixtures has been reported by workers at Purdue University (2)(3). The technique involves measuring upward flame propagation at various n-heptane inhibitor-air percentages in a standard 4 ft. long, 2 in. diameter tube and plotting the percentages of extinguishant versus heptane percentages where mixtures are nonflammable. A curve such as shown in Fig. 1 is obtained.

With better inhibitors than that shown in Fig. 1, a peak in the flammability curve will be obtained at a lower percentage of inhibitor than the 6 mol. percent of Fig. 1. This peak percentage may be translated to weight percentages of inhibitor producing nonflammability of heptane-air mixtures and comparisons on a weight basis also can be obtained. These data have been found to follow fairly closely the extinguishment capability of the materials on actual test heptane or gasoline fires (3), though there is controversy over the extrapolation of data to potential fire extinguishing performance (4).

It was necessary to obtain a pre-fire test screening of extinguishants for hydrocarbon fires which would be stable at 550°F and have low vapor pressures at that temperature. This screening was accomplished by means of the combustion tube apparatus mentioned before. Since high concentrations of low vapor pressure inhibitors could not be maintained in the vapor phase with heptane-air mixtures in a conventional ambient temperature flammability limit combustion tube (5), it was necessary to design a heated combustion tube in which the flame propagation could still be observed. Visibility was necessary for evaluation of the inhibitory effects of the candidate extinguishant.

Experiments were carried out at sub-atmospheric pressures to prevent explosions or excessive pressures in the tube. Relative inhibitory effects have been found to be essentially independent of pressures down to about 200 mm (2).

The system is diagrammed in Fig. 2 and photographs are shown in Figs. 3 and 4. The gas containing sections of the apparatus are heated to 200°C to prevent condensation of the inhibitor. The glass combustion tube is heated by a baked on transparent conductive coating, while the metal inlet system and the pressure gauge are heated by electrical tapes.

The lower end of the combustion tube is closed by a metal flange, which is joined to the tube by a kovar-glass seal. The removable half of the flange has a glass feed-through insulator for the tungsten ignition wire (Fig. 4). This entire flange assembly and lower end of the tube is submerged in the 200°C silicone oil bath to insure the gases reaching a uniform temperature.

Partial pressures of the inhibitor and the heptane are measured directly with a Kern-Springham glass spiral manometer with attached mirror. Rotation of the spiral deflects the mirror and the deflection is measured on the scale.

The spiral deflection was calibrated to read pressures up to 50 mm against an external mercury manometer which was read with a cathetometer. Total pressure of the combined inhibitor-heptane-air mixtures was 300 mm.

For the larger air pressures, the manometer is used as a null indicator. The desired air pressure is introduced to the outside of the glass spiral, then balanced with pre-heated air on the system side. The gases are mixed by a sliding perforated disc, which is driven by an external magnet. After twenty minutes of mixing, the disc was brought to the top of the tube and the mixture sparked. If ignition, as evidenced by flame propagation to the top of the tube, did not occur, mixing was continued another five minutes and the mixture sparked again. It was found that the rich limit for heptane-air increased to 8.75 percent heptane at 203°C and 300 mm total pressure compared to 6.9 percent at approximately ambient temperature and 300 mm pressure (2). The lean limit did not change. A few comparison points were made in this work at 203°C with the same inhibitors used in the Purdue work at ambient temperatures. It was found that peak percentages for sym-dibromotetrafluoroethane and for trifluorobromomethane increased about 10 - 12 percent with the temperature increase. However, since experimental conditions, including mixing times and methods of mixing, are considerably different, the comparison has little meaning. It was found during this work that changes in these variables led to large differences in observed flammability.

In Figs. 5, 6, 7 and 8 are shown flammability plots for the inhibitors evaluated. The curves exhibit a variety of shapes and peaks occurring at various heptane-air-inhibitor ratios. The significance of this is not known. The peaks of the curves are of interest since these represent a comparison of the individual molecules' effectiveness as flame inhibitors. In Table I are presented data obtained on peak inhibition percentages and the weight this volume percentage represents in 100 liters of a heptane-inhibitor-air mixture. These data are taken from peaks of the curves previously shown.

The Purdue University work previously referenced contained a study of the effectiveness of 56 compounds as flame inhibitors, in a combustion tube at room temperature. This study includes many halogenated hydrocarbons, however, since their tube was not heated, they were unable to test the less volatile materials. Two major correlations emerge from their work, the first is a confirmation of work of earlier investigators who found that hydrocarbons containing iodine are better extinguishants than those containing bromine, which in turn, are better than the aliphatic chlorides. The Purdue group also found that hydrocarbon compounds containing only fluorine were very poor extinguishants. The second major correlation was the observation that as the molecular weight increases the extinguishing ability also increases, i.e., the peak percentage decreases. This relation, however, is not invariable and it is not possible to determine the extinguishing ability of a molecule from its molecular weight alone.

This study was carried out at a temperature of 203°C, thus, it was possible to determine the peak percentages of some higher molecular weight halogenated hydrocarbons. Figure No. 9 is a plot of the peak percentages from all the Purdue data plus those determined in this work as a function of molecular weight. The situation is quite complex, however, the chlorine containing compounds appear to form a rough series.

The general curvature of this line suggests that a straight line might occur if peak percentage were plotted against the inverse molecular weight. As can be seen from Figs. 10 - 14, this is the case. For a given series of halogenated hydrocarbons, the general trend is quite well marked, despite the wide variation in structures. There are two possible explanations that might clarify this relationship between peak percentage and inverse molecular weight. The first would be a purely physical process in which the extinguishant molecule acts as a "third body" to promote free radical recombinations. The alternate possibility would be to reason that the inverse molecular weight was related to some chemical property, such as bond energy, which was the actual cause of the effectiveness of the extinguishant. At the moment, we are investigating various parameters in an attempt to discover a rational correlation and explanation of the relation of extinguishant ability to the physical properties and chemical structures of the halogenated hydrocarbons.

References

1. This work was supported by the Federal Aviation Agency under U.S. Air Force Aeronautical Systems Division Administration on Contract AF33(657)-8937.

2. McBee, E. T., et al, ATI114, 903 Report on USA Contract W-44-009. ENG-507.

3. Malcolm, James E., National Fire Protection Quarterly, October 1954.

4. Engibous, E. L. and Torkelson, T. R., WADC-TR-59-463, p. 9.

5. Coward, H. F. and Jones, G. W., Bureau of Mines, Bulletin 503.

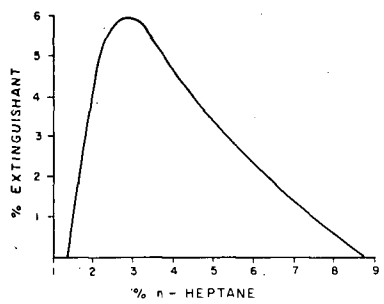

FIGURE 1

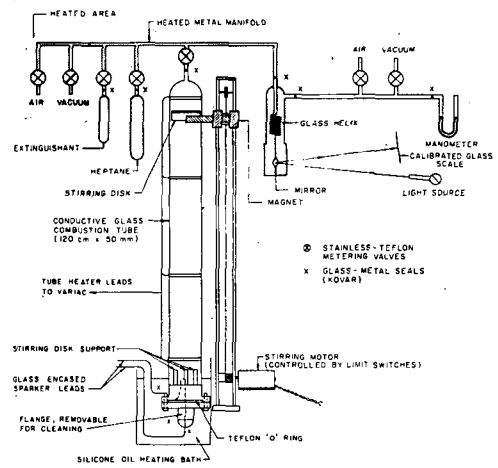

FIGURE 2

COMBUSTION TUBE FOR FLAMMABILITY LIMIT STUDIES (DIAGRAM)

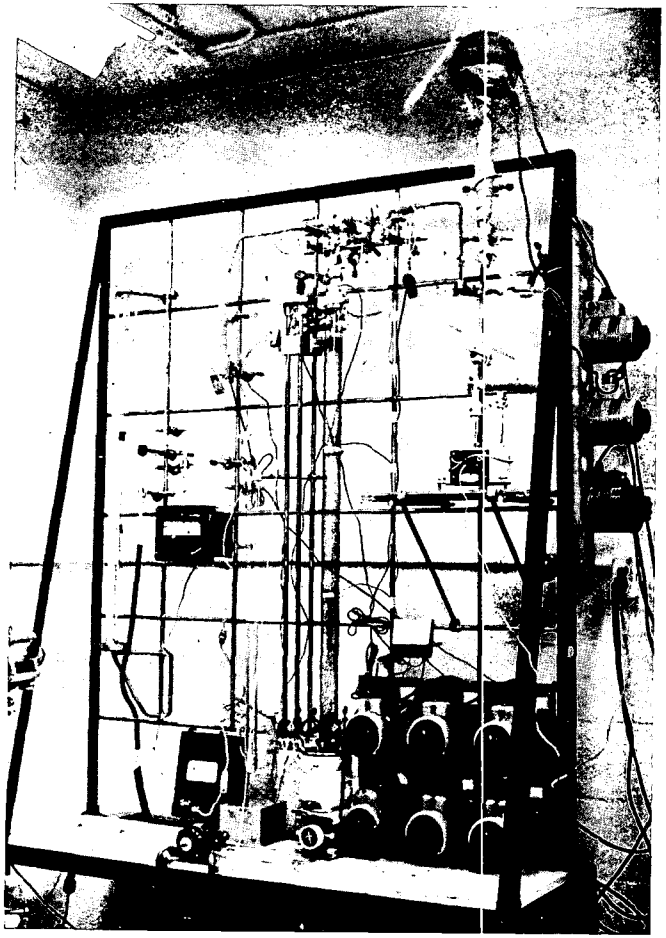

FIGURE 3 COMBUSTION TUBE

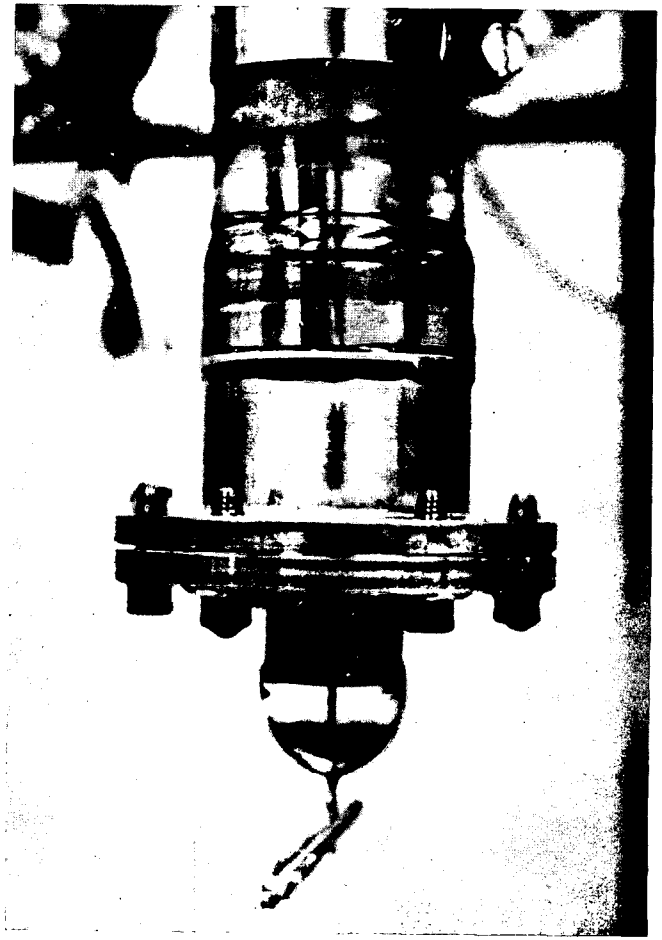

FIGURE 4 FLANGE DETAIL

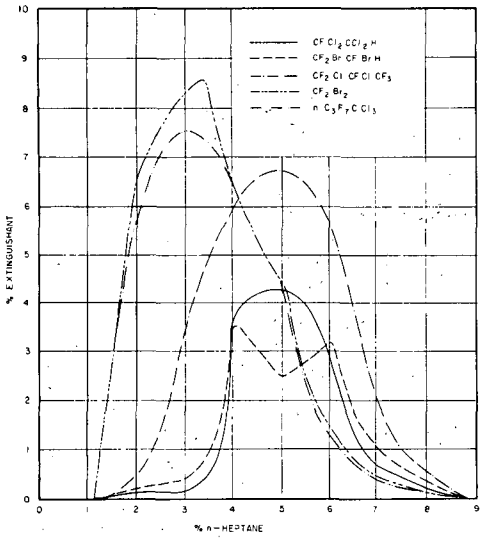

FIGURE 5
EFFECT OF CANDIDATE EXTINGUISHANTS ON FLAMMABILITY OF n - HEPTANE - AIR MIXTURES

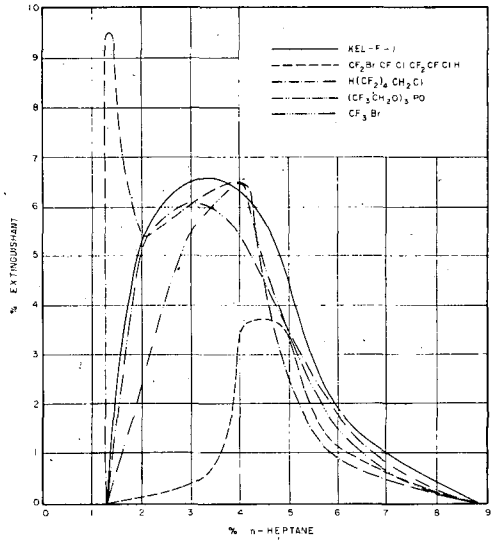

FIGURE 6
EFFECT OF CANDIDATE EXTINGUISHANTS ON FLAMMABILITY OF n - HEPTANE - AIR MIXTURES

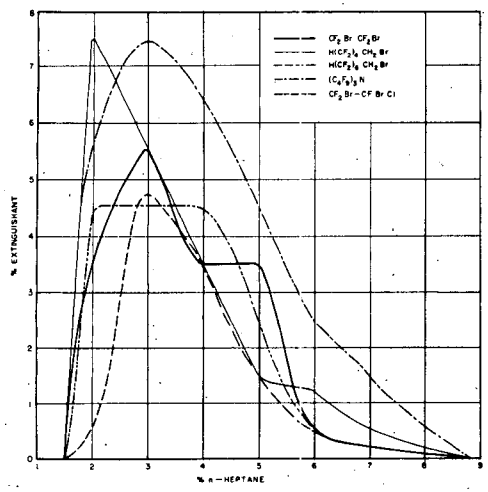

FIGURE 7
EFFECT OF CANDIDATE EXTINGUISHANTS ON FLAMMABILITY OF n - HEPTANE - AIR MIXTURES

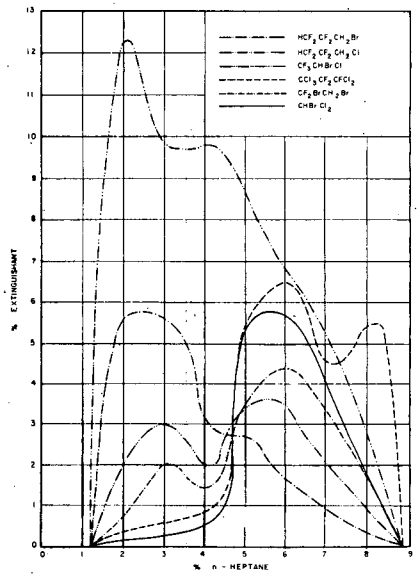

FIGURE 8
EFFECT OF CANDIDATE EXTINGUISHANTS ON FLAMMABILITY OF n - HEPTANE - AIR MIXTURES

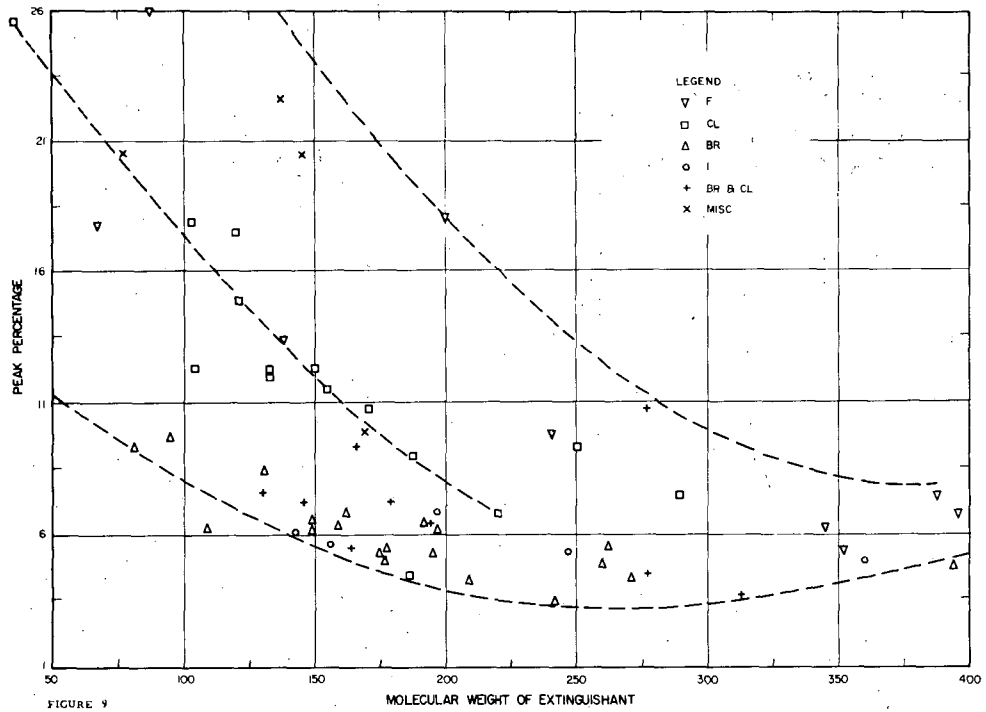

FIGURE 9

PEAK PERCENTAGE OF EXTINGUISHANT TO RENDER HEPTANE-AIR MIXTURE NON-FLAMMABLE AS A FUNCTION OF EXTINGUISHANT MOLECULAR WEIGHT

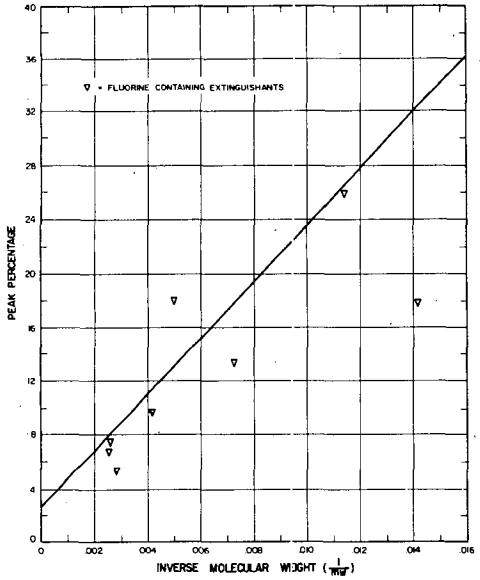

FIGURE 10
PEAK PERCENTAGE OF FLUORINE CONTAINING COMPOUNDS AS A FUNCTION OF INVERSE MOLECULAR WEIGHT

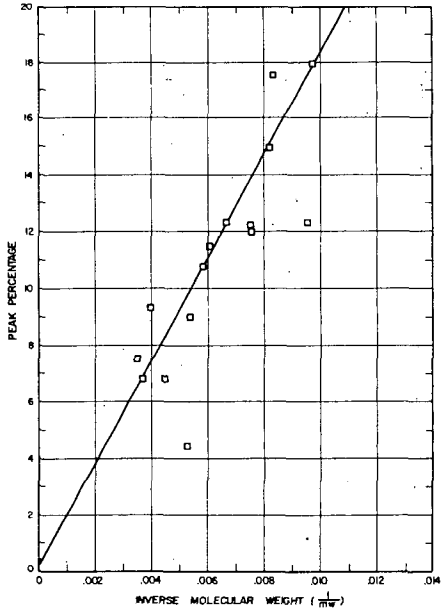

FIGURE 11
PEAK PERCENTAGE OF CHLORINE CONTAINING EXTINGUISHANTS AS A FUNCTION OF 1 / mw

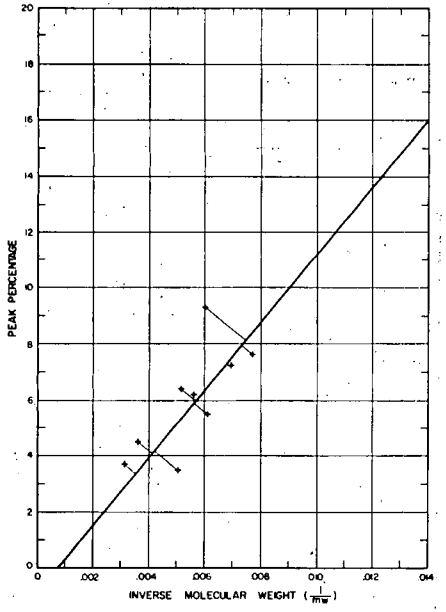

FIGURE 12
PEAK PERCENTAGES OF COMPOUNDS CONTAINING BOTH CHLORINE AND BROMINE AS A FUNCTION OF INVERSE MOLECULAR WEIGHT

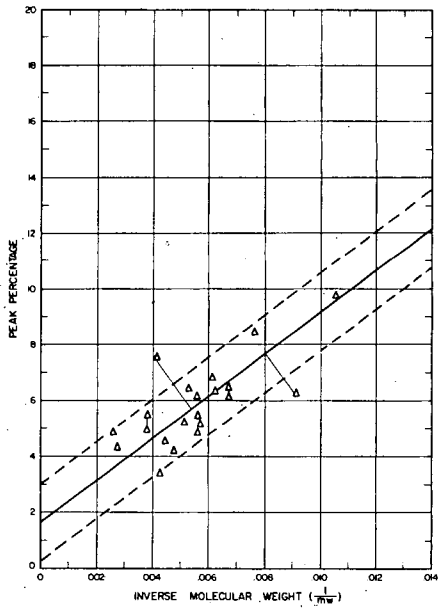

FIGURE 13
PEAK PERCENTAGE OF BROMINE CONTAINING EXTINGUISHANTS AS A FUNCTION OF 1/mw

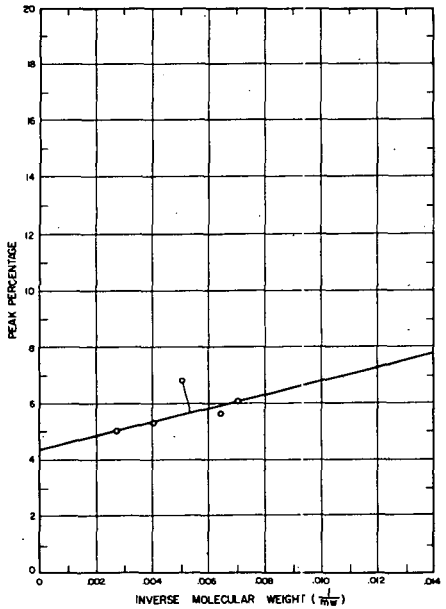

FIGURE 14

PEAK PERCENTAGE OF IODINE CONTAINING EXTINGUISHANTS AS A FUNCTION OF 1 / mw

TABLE I

EFFECT OF INHIBITORS ON HEPTANE-AIR FLAMMABILITY

Total Pressure 300 mm, Temperature 398°F

	MW	Peak %	Wgt. at Peak %	Rank Wgt. Basis	Rank Vol. Basis
$CF_3CHBrCl$	197.5	3.5	30.7	1	2
$CFCl_2CHCl_2$	186	4.4	36.6	2	4
$CF_3BrCHBrF$	242	3.4	36.8	3	1
$CHBrCl_2$	164	5.5	40.3	4	9
$CBrF_3$	149	6.5	43.2	5	13
$CH_3BrCBrF_2$	224	4.5	45.0	6	5
$CHF_2CF_2CH_2Br$	195	5.2	45.3	7	8
$CBrF_2CClFCF_2CHClF$	314	3.7	51.8	8	3
$CBrF_2CBrClF$	276.5	4.5	55.5	9	6
$CBrF_2CBrF_2$	260	5.5	65.8	10	10
$CClF_2CClFCF_3$	221	6.8	67	11	14
$CCl_3CF_2CCl_2F$	270.5	6.8	78.5	12	15
$CHF_2CF_2CH_2Cl$	150.5	12.3	82.6	13	20
$CHF_2(CF_2)_5CH_2Br$	395	4.75	83.6	14	7
$CF_3CF_2CF_2CCl_3$	287.5	7.5	96.5	15	16
$(CF_3CH_2O)_3PO$	344	6.3	96.7	16	11
$CHF_2(CF_2)CH_2Br$	295	7.5	99.0	17	17
$CHF_2(CF_2)_3CH_2Cl$	250.5	9.3	104.2	18	19
KEL-F-1 chloro-fluoroolefin polymer	500 av.	6.5	145.0	19	12
$(CF_3(CF_2)_3)_3N$	671	7.5	219.0	20	18