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NEW CHEMICAL EXTINGUISHING AGENTS FOR ROCKET PROPELLANT AND METALLIC FIRES

TECHNICAL DOCUMENTARY REPORT RTD-TDR-63-4208

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FOREWORD

This report was prepared by the National Engineering Science Company, Pasadena, California on Air Force Contract AF 33(657)-8015, "New Chemical Fire Extinguishants for Rocket Propellant and Metallic Fires". The contract was initiated under Project No. 8119, 'Checkout and Hazard Control Techniques', Task No. 811932, 'Fire and Explosion Suppression Techniques'. The work was administered by the AF Aero Propulsion Laboratory with Mr. Robert E. Cretcher as Project Engineer.

The study began in February 1962 and concluded in October 1963. Work was directed by Herbert Landesman, Program Manager. Experimental work was performed by the former and by Eugene B. Klusmann.

ABSTRACT

Fluoroalkyl esters of boric, phosphoric, silicic and sulfurous acids, boroxines and alkoxydifluoroborane trimers have been prepared as possible extinguishants for metallic and/or exotic propellant fires. Their mode of action is to form an inorganic oxide coating on metals. For propellants, they dissolve the fuel and produce nonflammable dilute solutions. The fluoroalkyl groups utilized have been $H(CF_2CF_2)_xCH_2$ - where x = 1, 2, 3 and in the borate case, 4. Attempts to prepare fluoroalkyl esters of aluminic acid gave products which could not be purified. Fluoroalkoxydifluoroborane trimers and fluoroalkyl sulfate esters could not be prepared. Physical properties, stabilities and compatibilities with materials of construction and with metals and propellants are reported for all materials synthesized. It was found that nonflammable solutions containing esters with pentaborane and with hydrazines could be prepared.

This report has been reviewed and is approved.

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LIST OF ABBREVIATIONS & SYMBOLS

b. p.	Boiling Point
BF_3	Boron Trifluoride
B_5H_9	Pentaborane
B^{11} NMR	Boron Nuclear Magnetic Resonance Spectrum
H^1 NMR	Proton Nuclear Magnetic Resonance Spectrum
HEF	High Energy Fuels (Alkylated Boron Hydride Base-Type)
N_2H_4	Hydrazine
N_2O_4	Nitrogen Tetroxide
UDMH	Unsymmetrical Dimethylhydrazine
δ	Chemical Shift (for boron-containing compounds this is referred to boron trifluoride etherate taken as $\delta = 0$)
ψ'	The group $H(CF_2CF_2)_x CH_2$-. Where $x = 1$ this is the ψ' -propyl group.
μl	Micro liter

I. INTRODUCTION

The purpose of this research was to prepare a series of fluoroalkyl esters of inorganic acids which were postulated to be suppressants for metallic and exotic fuel fires. Properties pertinent to their future development were also to be investigated and samples supplied to AF Aero Propulsion Laboratory for testing. The mode of extinguishant action of these materials is to form a coating of inorganic oxide on hot or burning metals which will prevent the diffusion of oxygen or other oxidizer to the metal. The inert materials will also act as nonflammable coolants and prevent secondary fires. For fuels such as boranes or hydrazines, and for liquid oxidizers, the materials will dissolve in and dilute the fuel or oxidizer. Since the esters are nonflammable, this will produce in limit, a fuel-ester solution which will not burn or a less dangerous oxidizer-ester solution. Thus, these fluoroalkyl esters would be useful as scavenging agents where spills of fuel or oxidizer occurred. The usefulness of these agents is inferred from previous work on magnesium fires (Refs. 1, 2, 3) and on some exotic fuel fires (Refs. 4, 5, 6).

These studies conclude that for magnesium fires and probably for other metal fires, the cooling effect of the extinguishant is most important. For this reason solid agents are not as desirable as liquid agents; the heat absorbed in vaporizing the liquid gives more cooling than that absorbed in the sensible heating of nonvolatile solids. Thus, in the absence of rapid cooling of the metallic object, the mass coated with a solid can reignite if the slag protective cover were broken (Ref. 1). Several liquid coolants have been used (Ref. 2) but they have the disadvantage that they give secondary fires. For example, tricresyl phosphate; triethylene glycolorthoboric acid; di-iso-decylphthalate and chlorobromoethane or difluorodibromomethane; and trimethoxyboroxine all are flammable or have a flammable component. Though secondary flammability is not a great disadvantage in metal fires, it is in rocket fuel or jet fuel fires (Ref. 1) where the cooling effect is not as necessary as exclusion of oxidant and oxidizable material from the fire.

The excellent survey cited in Ref. 1 gives other characteristics desirable in a metal fire extinguishant. One of these is that a halogen, preferably fluorine, be present to give the burning metal a coating of metal fluoride, which prevents further oxidation. (Chlorine is not desirable in a halocarbon since phosgene may form in use, though this is perhaps an overrated danger. The original agent toxicity probably is more significant). The presence of boron is desirable since this gives a liquid B_2O_3 coating to the burning metal, thus excluding oxidant. Boric oxide melts at 450°C and boils about 2200°C. The glassy B_2O_3

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coating would also be useful in fighting fires of nuclear origin since the skin would prevent the dispersal of finely divided fission products and thus confine radioactive materials to a smaller area.

Both boron trifluoride and boron trichloride have been used to extinguish magnesium fires (Ref. 3) but neither is a good coolant, and the fact that both are gases under normal conditions makes them less desirable than liquid agents.

There has been a recent study on pentaborane fires (Ref. 4) aimed mainly at delineating inhibitors for borane combustion and scavengers for pentaborane spills. The dilution technique suggested here with such fuels has not been well investigated. A previous work (Ref. 5) on fuels related to pentaborane (the HEF compositions) indicated that complexing materials and foams made with inert gases were effective. This report also noted that hydrogen liberation on hydrolysis of boranes could lead to explosions and fires if oxygen were not excluded from the borane.

The extinguishment of hydrazine fires was well investigated by Markels et al (Ref. 6) and water was found to be acting as an extinguishant by dilution. As has been noted, it is to be expected that the extinguishants of this work would have the same action as water, with the added effect of complexing with the hydrazines to form compounds with lower vapor pressures than the hydrazine. It is possible that this might reduce flammability.

The fluoroalkyl esters of boric, phosphoric, silicic and sulfurous acids prepared during this work contained the fluoroalkyl groups $H(CF_2CF_2)_xCH_2$ - where x = 1, 2, 3 and in the borate case, 4. This group, where x = 1 is known as the "ψ'-propyl" group; where x = 2, it is the "ψ'-amyl" group, etc. This abbreviation, used throughout this report, was coined by P. D. Faurote, et al [Ind. Eng. Chem. 48, 445 (1956).].

II. EXPERIMENTAL PROCEDURES

A. Thermal Stability

A 130-150 cc pyrex tube previously baked out at 300°C was used. Three cc of the material was sealed in the evacuated tube and heated two hours at 400°C (750°F). In the test of ψ'-amyl borate a 200 cc high pressure stainless steel cylinder previously baked out at 150°C was used for 5 cc of ester under an atmosphere of argon. The results of this test were in agreement with those with ψ'-propyl borate in pyrex. After cooling, the volatile material was sampled for mass spectral analysis. The remaining liquid, if any, was analyzed by gas chromatographyfor comparison with the original material. All compounds were highly stable except for the ethoxy difluoroborane trimer, the ψ'-propyl polyphosphate, and the ψ'-alkyl sulfites. Results of this and most other physical property testing are collected in Table I.

B. Hydrolytic Stability

Air, saturated with water vapor was bubbled through 10 cc of the material at ambient, 100°C and approximately the boiling point of the ester. The rate of air delivery was 75 cc/min. The partial pressure of water is 17.5 mm at 20°C. After one hour, the alcohol and ester were distilled away from the inorganic acid, or oxide produced in hydrolysis. The percent of hydrolysis was calculated from the weight of alcohol, acid, or oxide. As might be expected, the esters of inorganic acids are not extremely stable to hydrolysis.

C. Film Formation on Metals, Fire Tests with Metals

Molten aluminum at red heat (approximately 660°C) was poured into the ester, the metal was examined for coating formation and compared with molten aluminum poured onto transite.

MSA Research Company reported that samples of ψ'-amyl borate, ψ'-amyl phosphate and ψ'-amyl silicate gave violent reactions and in some cases, explosions when used on sodium metal fires (Ref. 7).

Eight to ten pound samples of ψ'-propyl and amyl borates, ψ'-propyl boroxine - ψ'-propyl borate solution, ψ'-propyl and amyl phosphates, ψ'-propyl polyphosphate, ψ'-amyl silicate and ψ'-amyl sulfite were supplied to AF Aero Propulsion Laboratory.

The ψ'-esters were used as coolants for approximately one pound magnesium blocks heated near the ignition temperature at AF Aero Propulsion Laboratory (Ref. 8). All esters acted as coolants and gave secondary fires which varied in time to self ignition. The ψ'-amyl sulfite appeared to give the least significant secondary fire and shortest time to self-extinguishment.

D. Corrosivity to Metals

Metal samples weighing from 0.7 to 2.3 gms. were kept in contact with the ester for 30 days at ambient temperatures and at the boiling point of the ester after which weight changes were determined. Two tests were run at room temperature, one with a dry sample; the other with a metal sample previously wet with water. After 30 days, changes in appearance of metals or esters were noted, samples were washed with methanol and decomposition products removed before drying and weighing. At the elevated temperature, a control was run in which no metal was present. Stainless steel alloys, as would be expected, are least affected by any of the extinguishants.

E. Compatibility with Nonmetallic Materials

Measured samples of polyethylene, polytetrafluoroethylene, rubber, neoprene, and silicone rubber were kept in contact with the extinguishant at ambient temperatures for 30 days, then remeasured and any change in length or properties of sample or extinguishant noted. Results are given in Table II. Polytetrafluoroethylene is not affected by the esters and neoprene is the most resistant elastomer. The generally poor chemical resistance of silicone rubber is evident in these results.

F. Propellant Solubilities

To determine pentaborane solubilities, tubes containing various amounts of the esters were attached to a vacuum line and quantities of pentaborane condensed in to give a series of B_5H_9-ester ratios. Tubes were shaken and observed for solution formation. This same procedure was used for N_2O_4 solubilities. Tubes were 5 mm pyrex.

To determine solubilities with N_2H_4, UDMH and JP-4, the propellants were added dropwise from a buret to a weighed amount of ester with stirring until two phases were obtained.

G. Viscosity

Viscosities were determined utilizing Ostwald Viscometers calibrated against standard glycerol-water solutions. Viscosities are generally high for fluorine containing compounds because of resistance to free rotation within the molecule caused by interfering fluorine atoms on adjacent carbons. In addition, the low intermolecular attractive forces of fluorine atoms lend stiffness to the perfluoroalkyl chain and increase viscosity. It is possible that additives such as used for improving viscosities of lubricating oils might be effective in lowering viscosities of the agents here reported.

H. Vapor Pressure, Heat of Vaporization

The compound was sealed into a bulb attached to a Stock Valve U tube which could be filled from a mercury reservoir. The material was cooled and the system evacuated. The mercury closed the valve's ground glass seats to prevent vapor loss. The U tube was connected to a mercury manometer. The bulb and the U tube containing mercury were totally immersed in a silicone oil bath which was heated. For high vapor pressures, air was admitted to the external manometer to approximately balance the vapor pressure of the liquid. The air pressure read on the manometer was added to the pressure difference in the Stock Valve U tube. Pressure readings were made with a cathetometer.

The heat of vaporization was calculated from points on the vapor pressure curve using the Clausius-Clapeyron equation.

The vapor pressure is unusually high for the ethoxydifluoroborane trimer, probably because of the high symmetry of the molecule or because dissociation to the monomer occurs on heating. The boroxine unaccountably has low stability and cannot be distilled. The vapor pressure is quite close to that of the borate. It is possible that ring formation in the boroxine is accomplished in this case only with steric strain though this should be minor.

I. Specific Heat

A Dewar cylinder, 2-1/2 inches by 9 inches, was equipped with a cork, a thermometer calibrated in tenths of a degree centigrade, and a glass stirrer. The heat capacity of the system was then determined by the following method. An aluminum rod heated in boiling water was added to a weighed amount of water in the system. The time in seconds, and the temperature were observed as many times as possible during the period of increasing temperature. Thus the time at which the maximum temperature occurred was observed. The rate of cooling was determined and a correction, equal to the cooling rate multiplied by the time to the maximum temperature, was added to the maximum temperature. Since the heat capacities of aluminum and water are known, and the heat lost by the aluminum must equal the heat gain by the system, the heat capacity of the calorimeter was calculated.

The calorimeter was then emptied and dried and the procedure was repeated for each of the samples. Since the heat capacity of the calorimeter was known, it was possible to calculate the heat capacities of the various samples. In the latter cases, the aluminum rod was heated in an oven for over one hour. The long heating period was necessary to obtain consistent results.

J. NMR Spectra, Infrared Spectra, Mass Spectra, Gas Chromatographic Retention Times

The proton NMR spectra were measured on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. The B^{11} NMR spectra were obtained on a Varian V-4300 spectrometer operating at 12.83 Mc for boron. Infrared spectra were obtained with a PE model 21 spectrometer. Mass spectra were obtained on a CEC model 21-620 and gas chromatographs on a F and M model 720 with temperature programming, or a Perkin-Elmer model 154. It was noted that with the latter, utilizing Apiezon L on firebrick, it was often necessary to condition the column first with the ester before reproducible spectra were obtained. With the ψ'-propyl and ψ'-heptyl sulfite esters it was necessary to utilize samples of less than 0.2 μl in order to prevent flooding the column.

K. Small Scale Testing

Several nozzles (Spraying Systems Company) were tested for use on small scale fires. The first nozzles tried were pneumatic, using varying atomizing pressures to regulate delivery. This system was used on hydrazine fires and gave inconsistent results, attributed to varying rates of application due to differences in viscosity. It was found that the application rates were vastly different. Different sizes of nozzles were tried but again with viscous materials the flow rates were not appreciably increased with a larger nozzle.

Two types of liquid nozzles, a full cone and a flat spray, were tried since the delivery rate can be determined from the pressure on the liquid. A full cone spray nozzle was satisfactory for the less viscous materials but with the viscous materials, the liquid was not atomized; only a stream was obtained. With the flat spray similar results were observed, and it was very difficult to get even coverage of the fire area.

An effectiveness study should give a series of application rates and quantities delivered, so that comparisons of agents can be made. The difficulties in obtaining a comparison application system with agents of widely varying viscosities led to abandonment of the small scale test program. System development was beyond the scope of the contract. Testing of these agents on small scale magnesium fires has already been accomplished by AF Aero Propulsion Laboratory.

III. RESULTS

A. Fluoroalkyl Borate Esters and Boroxines

Three materials, ψ'-propyl borate, ψ'-amyl borate, and a solution of ψ'-propyl boroxine in ψ'-propyl borate, were synthesized in test size quantity for fire testing. In addition, the following compounds of the ester series were prepared in small quantity; 2, 2, 2-triethyl borate, ψ'-heptyl borate, and ψ'-nonyl borate. Complete physical properties (Table I) and compatibility characteristics, (Table II) were determined for the materials prepared for testing.

The fluoroalkyl borate esters were synthesized by the reaction of boron trichloride with the appropriate fluoroalkanol.

$$3RCH_2OH + BCl_3 \longrightarrow (RCH_2O)_3B + 3HCl$$

$$R = CF_3 \text{ or } H(CF_2CF_2)_x, \text{ where } x = 1,\ 2,\ 3, \text{ or } 4.$$

In the reaction, yields of 85-95 percent were obtained.

The reactions were run without a diluent using nitrogen gas as a carrier to remove hydrogen chloride. In the preparations of ψ'-nonyl borate it was necessary to use benzene as a diluent since the alcohol is a solid. It was necessary to carefully meter the boron trichloride to prevent an excess being added to the alcohols since the borate ester reacts further to yield dialkoxychloro or alkoxydichloro boranes. The gas flow meters were calibrated by absorbing timed flows of boron trichloride in weighed amounts of pyridine.

The ψ'-amyl borate was also prepared, though in poorer yield, from transesterification of ethyl borate with the alcohol. Attempts were also made to prepare the ester from ψ'-amyl alcohol and boron trichloride in the presence of pyridine as an acid acceptor. The pyridine appeared to react preferentially with the boron trichloride and no ψ'-amyl borate was obtained by this method.

The ψ'-alkoxy boroxines were of interest since TMB (trimethoxyboroxine) is used as a magnesium fire extinguishant. It was considered that fluorine substitution would lower intensity of the secondary fire. The viscosity of the ψ'-propoxy boroxine was high (Fig. 31) and it was necessary to dilute the material with ψ'-propyl borate to produce more fluid compositions. As with alkoxyboroxines, the ψ'-propoxyboroxine decomposed to B_2O_3 and the borate on heating. The solution prepared was more viscous than commercial TMB but was not flammable.

The hydrolytic stabilities measured for the borates are suspect though repetition of the hydrolysis of ψ'-propyl borate gave duplicate results. It does not appear reasonable that the lower molecular weight ψ'-propyl ester should be more hydrolytically stable than the ψ'-amyl ester. Flammability of these materials is low; they burn weakly at the boiling point and below the boiling point will ignite in a flame but will not support combustion.

It is noteworthy that methyl borate will only coordinate weakly with UDMH and not at all with allyl borate. Both methyl and allyl borates coordinate with hydrazine, a weaker base than UDMH, though less sterically hindered than UDMH. The fact that ψ'-amyl borate coordinates with UDMH is evidence that the inductive effect of the fluorines, making the boron more electron deficient, is sufficient to overcome great steric hindrance to coordination.

ψ'-Heptyl borate was too viscous for detailed characterization. It was of interest, however, that this borate formed coordination complexes with hydrazine, a weak base, and piperidine and pyrollidine, which are strong bases. Mixtures with UDMH and pyridine were too viscous to give an NMR signal and it was not possible to determine by NMR whether reaction occurred. Here coordination compounds form even though the boron is surrounded by three ψ'-alkoxy chains containing seven carbon atoms, while allyl borate, with three carbon atom chains, appeared the limit for reaction with bases in the aliphatic series. The inductive effect of the fluorines, making the boron more electron deficient than in alkyl borates, is obvious here.

ψ'-Nonyl borate was of interest for continuing the observations on acid strength of ester and coordinating power with weak amine bases as a function of ψ'-chain length (steric factor). The material was found to be a solid and contained such small boron percentages that B^{11} NMR analysis of viscous borate-amine solutions was not possible.

The mass spectrum of ψ'-propyl borate (Table III) has major peaks at m/e 31 ($C\text{-}F^+$), m/e 29 (HCO^+) and m/e 51 (HCF_2^+). The peak at m/e 82 is either a rearrangement ion species $HCFCF_2^+$ or the end group HCF_2CF^+. The other borates had vapor pressures too low for good mass spectra to be obtained.

Infrared and NMR spectra were obtained for each of the materials (Figs. 3-10). The proton NMR of these compounds show interesting secondary hydrogen-fluorine splittings. For instance, the H^1 NMR spectrum hydrogen-fluorine coupling and secondary splitting of fluorine an additional carbon atom removed. The α hydrogen to β fluorine coupling is very evident in ψ'-propanol (Fig. 30) as well as the ω-H to ω-1 F. The former coupling disappears with line broadening in all other ψ'-esters, but the ω to ω-1 coupling remains visible. The alcohol was run alone so that estimates of alcohol in the borates (from hydrolysis) could be made. It is interesting that the chemical shift of the OH proton is dependent on solvent. The shift for the pure alcohol was at higher field from that of the alcohol in chloroform.

The B^{11} spectrum of the ψ'-amyl borate gave a chemical shift value of $\delta = -20.0$ in diglyme. The viscosity of the pure material was high and only a broad resonance was obtained. The observed B^{11} chemical shift (Ref. 9) is at slightly lower field from that of other borate esters such as trimethyl, triethyl, and tripropyl borates ($\delta = -18$) but gives little indication of any different electronic character of the boron atom compared to the common borate esters. The slight shift to low field possibly indicates less oxygen to boron back coordination in the fluoroalkyl borate but the shift change is too small for assurance of this.

1. ψ'-Propyl Borate

a. Preparation

In a 5,000 ml three necked flask equipped with stirrer, reflux condenser protected with a drying tube, and a gas dispersion tube for addition of boron trichloride, was put 3,710 g (28.1 moles) of ψ'-propanol. Boron trichloride was added through the gas dispersion tube at the rate of 165 g/hr, as determined by a calibrated flow meter, for nine hours to deliver the required amount (1,480 g). The product was distilled at atmospheric pressure through a 65 cm column packed with Raschig rings. Recovered was 814 g of unreacted alcohol and 2,611 g of the borate ester boiling at 202-206°C. The yield was 88.4 percent allowing for the recovered alcohol.

The product was analyzed for boron by hydrolysis in acid solution and titration potentiometrically in the presence of mannitol. The boron was found to be 2.80 percent as compared to the formula value of 3.01 percent.

b. Gas Chromatographic Analysis

A one μl sample was introduced onto a two foot column of Apiezon L on Chromsorb P at 100°C. At a helium flow rate of 28 cc/min, the retention time was 36 sec. There were no visible impurities.

c. Coating of Hot Metal Surfaces

Molten aluminum at red heat (approximately 660°C) was poured into the borate ester. The recovered metal was only thinly coated as evidenced by a dulled metal surface.

d. Corrosivity to Metals

In all tests at the boiling point (205°C), including the control, the borate had turned amber and black solids were formed. In contact with mild steel the ester had completely decomposed to black solids. The mild steel had turned black but all other metal samples appeared unchanged.

In all tests at ambient temperatures no change in the appearance of the metal samples or the borate ester were observed.

Change in Weight of Metals

Metal	Ambient Temperatures		
	Wet	Dry	Boiling Point
Stainless 302/304	-0.3 mg	-0.3 mg	-0.1 mg
Mild Steel	-0.3 mg	-0.2 mg	+0.2 mg
Aluminum - 1100	-0.2 mg	none	none
Magnesium-Dow AZ31B	-0.1 mg	none	-0.1 mg

2. ψ'-Amyl Borate

a. Preparation

(1) From the Alcohol and Boron Trichloride

In a 5 liter round bottom flask with gas inlet tube, stirrer and reflux condenser connected to a roof vent was put 5,380 grams (23.2 mols) of ψ'-amyl alcohol (du Pont). With a dry nitrogen flow of approximately 100 cc/min, boron trichloride was passed through at a meter reading calculated to add the required amount in five hours. Hydrogen chloride was evolved and the flask was heated to 125°C for three hours with nitrogen sweeping to remove hydrogen chloride. The excess alcohol was removed at atmospheric pressure by distillation in a 25 cm column packed with Raschig rings. Recovered alcohol was 249 g. The borate was distilled under vacuum in the same column. Yield was 4,965 g. This is 95.7 percent of theoretical after allowing for unreacted alcohol. The boiling point was 114°C at 1 mm.

The compound was analyzed for boron by hydrolysis and titration of the boric acid in the presence of mannitol. Calculated for $C_{15}H_9F_{24}O_3B$, B = 1.54 percent. Found B = 1.49 percent.

(2) Trans-esterification of Ethyl Borate with ψ'-Amyl Alcohol

In a 500 cc three necked flask with condenser, stirrer and drying tube were placed 73 g (0.5 mole) of ethyl borate, 348 g (1.5 moles) of the ψ'-amyl alcohol and 5 g of anhydrous aluminum chloride. The mixture was stirred under reflux one hour and allowed to stand overnight then distilled. A small amount of unidentified forerun boiling at 64°C was obtained, possibly methanol from the denatured ethanol used in preparing the ethyl borate. Ethanol and unreacted ethyl borate were also obtained. Vacuum distillation of the residue gave 136.5 g (40 percent) of ψ'-amyl borate, b.p. 117-120°C at 1.2 - 2.0 mm. The index of refraction and infrared spectrum were identical with those of the ester from boron trichloride and the ψ'-amyl alcohol.

b. Gas Chromatographic Analysis

A ten μl sample of the borate ester was injected into a two meter column of Apiezon L Grease on firebrick kept at 200°C. Helium elution was at 70 cc/min. It was necessary to first condition the column by running three consecutive samples of the ester to obtain reproducibility. The elution time was 6 min and 15 sec. The instrument was a Perkin-Elmer gas chromatograph, Model 154. There was indication of a trace of alcohol, probably from hydrolysis, being present in the material.

c. Coating of Hot Metal Surfaces

Molten aluminum at red heat (approximately 660°C) was poured into ψ'-amyl borate. The recovered metal showed formation of a coating of dark grey not evident on a sample of molten aluminum poured onto transite.

d. Corrosivity to Metals

In all tests at the boiling point (260°C), including the control, the ester became amber and a black decomposition product was deposited on the flasks and on the metal samples. The deposit could not be entirely removed without scraping away unchanged metal. Consequently, weight increases are recorded for these samples.

In tests at ambient temperatures the only change observed was the formation of a small quantity of boric acid where the ester was in contact with wet metal.

Change in Weight of Metals

	Ambient Temperatures		
Metal	Wet	Dry	260°C
Stainless 302/304	none	-0.8 mg	+0.2 mg
Mild Steel	none	-0.4 mg	+3.4 mg
Aluminum - 1100	none	-0.5 mg	+1.8 mg
Magnesium-Dow AZ31B	none	+0.4 mg	+0.7 mg

e. Propellant Solubilities

These data are given in Table I.

Hydrazine was soluble in the borate ester to the extent of 130g hydrazine per 100g of the borate ester. A B^{11} NMR spectrographic analysis of the solution indicated that reaction had occurred (Ref. 10) to form an addition compound $[HCF_2(CF_2)_3CH_2O]_3B{:}N_2H_4$.

UDMH was infinitely soluble in the borate and again B^{11} analysis showed a chemical shift value of $\delta = -2.4$ for the solution compared to $\delta = -20$ for the ester alone. This is evidence that the UDMH and the borate form an addition compound similar to that formed from hydrazine and the borate (Ref. 10). B^{11} NMR analysis of the tube contents showed absorption due to both pentaborane and the ester, i.e., no reaction had occurred.

3. ψ'-Heptyl Borate

a. Preparation

The procedure described under 1.a. above was used with 99.6g (0.3 mole) of ψ'-heptyl alcohol reacting with 11.7g of boron trichloride. Distillation yielded 10g of unreacted alcohol and 81.0g (88.9 percent) of the borate boiling at 180-5°C/3 mm. Other properties are shown in Table I.

4. ψ'-Nonyl Borate

a. Preparation

In a 500 cc three necked flask with stirrer, gas inlet tube, condenser and drying tube were placed 65g (0.15 mole) of ψ'-nonyl alcohol (du Pont) and 300 cc of purified benzene. The alcohol was not completely soluble at room temperature but dissolved at the boiling point of the benzene. Boron trichloride (0.05 mole) was passed into the solution through a calibrated flow meter. The benzene was distilled and last traces removed under vacuum. The solid residue was distilled through a Claisen head at 235-240°C at 2 mm. It melted at 37-40°C.

5. 2,2,2-Trifluoroethyl Borate

a. Preparation

The procedure of 1.a. above was used with 30g (0.3 mole) of trifluoroethanol (Pennsalt Chemicals) reacting with 11.7g (0.1 mole) of boron trichloride. The yield was 8.0g (26 percent) of material boiling at 116-119°C/748 mm.

A B^{11} NMR spectrum showed this contained some $(CF_3CH_2O)_2BCl$, $\delta = 22.0$, in addition to the borate ester $\delta = 17.0$. A lower boiling fraction b.p. 70-96°C/748 showed via B^{11} NMR that both $(CF_3CH_2O)_2BCl$ and $CF_3CH_2OBCl_2$, $\delta = -32$, were present. (Ref. 9).

6. Boroxine-Borate Solution

a. Preparation

The entire preparation of the boroxine was carried out in a nitrogen filled dry box. In a 2,000 ml round bottom flask was put 1,700g (4.21 moles) of ψ'-propyl borate and 330g (4.72 moles) of boric oxide. The mixture was heated to boiling for one hour, allowed to cool and filtered through a coarse sintered disk. A small amount of unreacted boric oxide passed through the filter to leave the product slightly cloudy. A medium porosity sintered disk was used but the liquid was too viscous to pass through. Paper filters were tried but none were found satisfactory.

The slightly cloudy amber product obtained weighed 3 lbs. 7 oz. (1,560 g), a yield of 78.2 percent. The yield would have been much higher if not for the mechanical loss from the many attempts at filtration. Analysis: Calculated for $C_9H_9F_{12}O_6B_3$; B = 6.97 percent. Found: B = 7.32 percent. High boron content is due to boric oxide which passed through the filter. The analysis was made on a sample hydrolyzed in acid solution and titrated potentiometrically in the presence of mannitol.

This product was added to approximately 3 lbs. and 11 oz. (1,673 g) of ψ'-propyl borate to give the solution shipped to AF Aero Propulsion Laboratory for evaluation and also used for characterization. The borate solution was also analyzed and found to contain 4.9 percent boron. From this value the actual composition of the solution was calculated to be 47.4 percent boroxine and 52.6 percent borate ester.

b. Coating of Hot Metal Surfaces

Aluminum at red heat was poured into the boroxine-borate solution. The aluminum was only slightly coated as evidenced by a slight dulling of the metal surface.

c. Corrosivity to Metals

In all tests at 205°C the solution had decomposed noticeably with the formation of large quantities of black solid. The stainless and mild steels had turned black while the aluminum and magnesium were only slightly darkened.

At ambient temperatures no change was observed in the metals or the solutions except for some boric acid which was formed immediately when the wet metals were added to the solution.

Change in Weight of Metals

Metal	Ambient Temperatures		205°C
	Wet	Dry	
Stainless 302/304	-0.5 mg	-0.3 mg	+0.3 mg
Mild Steel	-0.6 mg	-0.9 mg	-0.5 mg
Aluminum - 1100	-0.5 mg	-0.4 mg	-0.3 mg
Magnesium-Dow AZ31B	-0.5 mg	-0.5 mg	-0.2 mg

d. Coating of Hot Metal Surfaces

Molten aluminum at red heat was dropped into the borate trimer. The aluminum showed no signs of having a coating.

e. Propellant Solubilities

The addition of the trimer to both UDMH and hydrazine gave exothermic reactions and complete miscibility. Analysis of both solutions by NMR spectroscopy showed two peaks with chemical shifts at $\delta = -2.25$ and $\delta = -12.7$ compared with $\delta = 0$ for the trimer. From these data it is inferred that reaction occurred to give ethyl borate which complexes slightly with the hydrazine. The peak of the equilibrium complex would be $\delta = -12.7$ according to previous work (Ref. 10). The other peak would then be attributed to either BF_3-hydrazine complexes or to alkoxy difluoroborane monomer complexes with hydrazine. Such species cannot be differentiated by use of B^{11} NMR.

The material and pentaborane are infinitely soluble. B^{11} NMR indicates no interaction. The trimer and JP-4 are insoluble.

f. Flammability

The trimer is flammable at the boiling point. Below the boiling point, it burns in a flame but does not support combustion.

g. Thermal Stability

Three ml of borane trimer was heated for two hours at 400°C (750°F) in a 130 cc pyrex tube which had previously been baked out at 300°C. The trimer was almost completely decomposed to a yellow-brown material. A very small quantity of liquid remained which was found by B^{11} to contain no boron. Ethylene was found to be the volatile pyrolysis product by mass spectral analysis of the vapors.

It is presumed that the liquid product is a low molecular weight polyethylene.

B. Alkoxydifluoroborane Trimers

Ethoxydifluoroborane trimer was synthesized in quantity for fire testing by AF Aero Propulsion Laboratory. It would have been desirable to have prepared a fluoroalkoxydifluoroborane trimer, but attempts to synthesize 2, 2, 2-trifluoroethoxydifluoroborane trimer and ψ'-propoxydifluoroborane trimer were unsuccessful.

Alkylborates such as methyl, ethyl, etc., react with boron trifluoride to give alkoxydifluoroborane trimers (Ref. 10). These dissociate to the borate and boron trifluoride on heating though they are stable at ambient temperatures. It was postulated that when the alkoxy

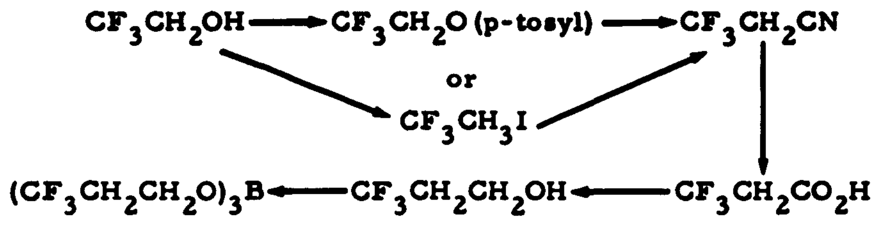
$$(RO)_3B + 2BF_3 \underset{\Delta}{\rightleftharpoons} (ROBF_2)_3$$

group was fluorinated the borane trimer would give boric oxide films on hot or burning metals; be soluble in hydrazines and pentaborane; be nonflammable and also be a coolant by reason of absorbing heat in dissociating. The reaction of boron trifluoride with borate esters has been known for about 70 years (Ref. 11 and Ref. 12) but the nature of the products was not known until recently (Ref. 10).

Boron trifluoride was allowed to react with ψ'-amyl borate but was not absorbed. B^{11} NMR analysis of the reaction mixture showed that the borate ester was unchanged. On the chance that steric effects of the bulky perfluoroamyl group prevented reaction, ψ'-propyl borate and tris-(2, 2, 2-trifluoroethyl) borate were reacted with boron trifluoride. In neither case did reaction occur. It was concluded that the inductive effects of fluorine on carbon, even one carbon removed from the oxygen of the borate ester, lowered the electron availability on the borate oxygen and prevented intermediate reaction of the ester with boron trifluoride.

This inductive effect of fluorine would also be transmitted to the boron and would lower the electron density of the boron of the borate ester. That this happens is indicated by the fact that ψ'-amyl borate forms addition complexes with hydrazine and UDMH. It was found previously (Ref. 10) that only lower borate esters such as methyl, ethyl, and allyl borates complex with hydrazine and none complex with UDMH. The longer chain fluorinated alkyl borate esters used in this work must be considerably stronger Lewis acids than the alkyl borates to coordinate with the hydrazine bases since sterically the reaction is not favored.

In the hope that two methylene groups between the borate oxygen and the carbon carrying fluorines would lower the fluorine inductive effect, attempts were made to prepare tris-(3, 3, 3-trifluoropropyl) borate for reaction with boron trifluoride. The sequence of reactions to be tried was:



The p-tosyl ester of trifluoroethanol was prepared (Ref. 13) and direct reaction of this with copper cyanide and potassium cyanide in diethylene glycol at 200°C gave no nitrile. The p-tosyl ester was used to prepare 2, 2, 2-trifluoroethyl iodide but the reaction of this with potassium cyanide in refluxing ethanol gave no nitrile. Reaction of the iodide with copper cyanide in a sealed Carius tube at 150-200°C gave explosions which demolished the tube. Since the avenue chosen for the synthetic approach was not fruitful, this work was discontinued and the reaction products of ethyl borate and boron trifluoride investigated. Properties of this product are shown in Table I. The material fumes in air but does not hydrolyze rapidly. The material has a high melting point but a solution with another of the trimers such as the methoxy or propoxy would have a lower freezing point. It could also be used in solution with one of the ψ'-esters as a freezing point lowering agent. Thermal stability of this material is poor.

1. Preparation of 1-iodo-2, 2, 2-trifluoroethane

The method of Tiers, et al (Ref. 10) was used where trifluoroethanol (Pennsalt) was reacted with p-toluene sulfonyl chloride. The resultant p-tosyl ester was heated with potassium iodide in ethylene glycol to 180°C and the distillate dried and rectified, b.p. 55°C/745 mm.

2. Ethoxydifluoroborane Trimer

a. Preparation

Ethoxydifluoroborane trimer was prepared by bubbling boron trifluoride through 543 g of triethylborate in a round bottom flask cooled by an ice bath and equipped with a stirrer and reflux condenser with a drying tube. Addition was continued until BF_3 was given off, indicating no further reaction. The product was distilled at atmospheric pressure to give 895 g of material boiling at 82°-84°C. The yield was 85.2 percent.

b. Gas Chromatographic Analysis

The gas chromatograph of the borane trimer has given a number of conflicting results, depending on the column used and the temperature of the column.

An eight µl sample was introduced onto a two meter column of Apiezon L on firebrick at 200°C. Helium flow rate was 75 cc/min and the retention time was 25 sec. There was a very small impurity visible just ahead of the major component.

The instrument used for this assay was a Perkin-Elmer Model 154. All the following chromatographs were obtained with an F and M Model 720 programmed chromatograph. A one µl sample was introduced onto a two foot column of silicone gum rubber on Chromsorb P at 75°C. Helium flow rate was 46 cc/min and retention time 20 sec. There was a very small impurity visible as a shoulder on the trailing side of the major peak.

When a sample was introduced onto a six foot carbowax column on Chromsorb P, the sample could only be eluted at temperatures of 150° to 200°C. Even then the peaks were very broad and at least three components were distinguishable. On a six foot column of silicone oil (550) on firebrick similar results were observed. Elution was not complete at lower temperatures (175° to 225°C); five components were visible.

When a sample was introduced onto a new silicone gum rubber column at 50°C, three components were apparent, one ahead and one trailing the major component. The separation was not sufficient to collect pure samples and identify the components.

The material was also introduced onto an Apiezon L column in the F and M instrument at 50°C and only one peak was obtained. It is concluded that Apiezon L will not separate the components or that decomposition to other materials occurred on the other columns. The latter is most likely.

The high number of components apparently at the higher temperatures are probably due to decomposition products such as boron trifluoride, ethyl borate, ethoxydifluoroborane monomer and hydrolysis products. This is evidenced by the observation that ethoxyfluoroborane trimer fumes in air and at lower temperatures the sample fumes upon exit from the chromatograph while at higher temperatures it does not.

c. Mass Spectrum

The mass spectrum of ethoxydifluoroborane trimer is tabulated in Table IV. The instrument used was a CEC Model 210 mass spectrometer. The spectrum was compared to that of Zmbov and Ribnikar (Ref. 14).

The most noticeable difference is the higher fragmentation in our spectrum, which is explained by the higher ionization potential of the Model 210 mass spectrometer. The ions at 100 to 106 cannot be attributed to $(EtOBF_2)_3$ and probably are due to an impurity.

d. Propellant Solubilities

The borane trimer reacts with N_2O_4. When allowed to react in a sealed 5 mm NMR tube, the mixture exploded on warming to room temperature. In a larger volume, with an excess of trimer, a volatile product identified as nitric oxide was formed. The oxidation product was not identified. A B^{11} NMR analysis of the solution showed a broad band at approximately $\delta = 0$. Since the spectrum of the trimer is a sharp spike, it is concluded that the boron containing product exchanges with the trimer. Probably $BF_3 \cdot N_2O_4$ is formed and the oxidation product is boron acetate.

e. Corrosivity to Metals

In all tests at the boiling point (83°C) the borane trimer decomposed to a brown solid or brown viscous material in contact with the metals. In the control and in contact with magnesium and aluminum the borate had become solid after 17 days. It was difficult to remove this solid without damaging the metal. The magnesium sample was so seriously damaged in the attempt to remove the solid deposit that it was not weighed. Areas of the metal samples where the deposit chipped off cleanly appeared to be roughened by corrosion. In contact with stainless steel and mild steel the borane was decomposed to a viscous brown material in 19 days, so the metal samples were removed while they could still be cleaned easily. Examination of the condensers after cleaning showed etching on the outside above the ground joint where some of the vapors had escaped. It appeared that there may have been slight etching inside the condenser. The possibility that HF may be a product of decomposition was investigated in the thermal stability tests, but none was found.

In tests at ambient temperatures the borane was discolored and became various shades of amber from very light to almost black. The discoloration seems to be random with respect to conditions and materials. In tests with dry stainless steel the discoloration was very light amber. The amber color became darker in contact with dry mild steel, wet magnesium, and wet aluminum. In contact with dry magnesium, dry aluminum, wet stainless, and wet mild steel the discoloration was very dark, almost black.

Change in Weight of Metals

Metal	Ambient Temperatures		$83^{\circ}C$
	Wet	Dry	
Stainless 302/304	+ 0.1 mg	+0.1 mg	+ 0.3 mg
Mild Steel	-19.5 mg	-0.1 mg	-12.6 mg
Aluminum - 1100	none	-0.3 mg	-34.9 mg
Magnesium-Dow AZ31B	- 5.9 mg	none	see text

C. Fluoroalkyl Phosphate Esters

Three materials, ψ'-propyl phosphate, ψ'-amyl phosphate and ψ'-propyl polyphosphate, were synthesized in quantity for evaluation by AF Aero Propulsion Laboratory. Complete physical properties (Table I) and compatibility characteristics (Table II) were determined for these materials. In addition, 2, 2, 2-trifluoroethyl phosphate was prepared for screening as an extinguishant for use on the Supersonic Transport, and physical property data are included in this report. Although the compound's hydrocarbon flame inhibiting capability compared to the best brominated fluorocarbons tested, the low temperature properties of the compound were not suitable.

The fluoroalkyl phosphate esters were synthesized by the reaction of phosphorus oxychloride and the appropriate fluoroalkyl alcohol. Yields up to 90 percent were obtained.

$$3RCH_2OH + POCl_3 \longrightarrow (RCH_2O)_3PO + 3HCl$$

$$R = CF_3 \text{ or } H(CF_2CF_2)_x \text{ where } x = 1 \text{ or } 2$$

Difficulty was first encountered in preparing ψ'-propyl phosphate from phosphorus oxychloride and the alcohol even with added pyridine. It was later found that longer reaction times without pyridine being present were necessary to obtain good yields of the ester. The ψ'-amyl ester was easily prepared from the alcohol and phosphorus oxychloride. Reaction times necessary were shorter than with ψ'-propyl phosphate.

As might be expected, the ψ'-propyl phosphate ester was less hydrolytically stable than the higher molecular weight and presumably less soluble ψ'-amyl ester. This is more reasonable than the data on hydrolysis of the borates.

The ψ'-amyl phosphate was of high viscosity but was also the least flammable material prepared. Though the trifluoroethyl and ψ'-propyl esters were flammable at their boiling points, the ψ'-amyl ester did not ignite in a flame at $300^{\circ}C$ ($572^{\circ}F$). The thermal stabilities of the phosphates tested here are quite good. Pentaborane solutions in the ψ'-amyl ester did not ignite in air. Since the viscosity of the ψ'-amyl phosphate is high, it is suggested that the less viscous trifluoroethyl or ψ'-propyl phosphate be added to decrease the viscosity without destroying the desirable properties of the ψ'-amyl phosphate.

The polyphosphate ester was prepared because of the additional phosphorus content above that of the phosphate. This was considered advantageous in metallic fires because of phosphorus oxide coatings which could be formed. Unfortunately because of the problem of analyzing for phosphorus in the presence of fluorine, the composition of the material is not known. Because of ψ'-propyl phosphate losses in polyphosphate preparation a material balance which would give composition was not obtained. The analysis obtained showed the material contained a smaller percentage of phosphorus than the phosphate ester used in its preparation; the analytical results are thence unreasonable.

1. 2, 2, 2-Trifluoroethyl Phosphate

a. Preparation

In a 500 cc round bottom flask with dropping funnel, stirrer and condenser with drying tube was put 316 g (3.16 moles) of trifluoroethanol. Phosphorus oxychloride (150 g, 0.98 mole) was added and the mixture refluxed twenty hours until hydrogen chloride evolution ceased. The product boiled at 45° - 60°C at 9 mm. Yield, 179.5 g (55 percent).

b. Gas Chromatographic Analysis

A two µl sample was introduced onto a two foot column of Apiezon L on Chromsorb P at 150°C. At a helium flow rate of 15.6 cc/min the retention time was 48 sec. An impurity of slightly longer retention time was found by comparison with the chromatogram of a mixture of phosphates to be the di-substituted phosphorus oxychloride $(CF_3CH_2O)_2POCl$.

c. Corrosivity to Metals

In tests run at the boiling point, magnesium in contact with the compound, formed large amounts of a white solid. In the tests with stainless and mild steels the phosphate became dark amber. In the test with aluminum the phosphate was only a light amber after 30 days contact, while the control was unchanged.

In tests at ambient temperatures no difference was observed in the action of wet or dry metal samples. There was no change in the ester in contact with aluminum, while in contact with stainless and mild steels the ester turned light amber. The magnesium in contact with the ester again formed a white solid only in smaller quantity than at the boiling point.

Change in Weight of Metals

Metal	Ambient Temperatures Wet	Ambient Temperatures Dry	Boiling Point
Stainless 302/304	-62.0 mg	- 15.6 mg	- 5.9 mg
Mild Steel	-17.8 mg	- 17.7 mg	- 56.7 mg
Aluminum - 1100	-33.8 mg	-482.7 mg	- 0.8 mg
Magnesium-Dow AZ31B	-54.6 mg	-165.4 mg	-165.9 mg

d. Coating of Hot Metal Surfaces

Molten aluminum at red heat was dropped into the phosphate ester. The aluminum became coated with a light gray material.

e. Effect on Flammability Limits of Heptane-Air Mixtures

The phosphate ester was tested for inhibitory effect on the flammability limits of heptane-air mixtures at 398°F. The peak in the flammability curve was at 5 percent extinguishant. This corresponds to 76.7 g per 100 liters of heptane-air-extinguishant (Ref. 15). This is not quite as good an inhibiting effect as with the materials $CF_2BrCFBrCl$ or $CBrF_2CBrF_2$. At 398°F, these are among the best inhibitors (Ref. 16).

2. ψ'-Propyl Phosphate

a. Preparation

(1) In the Presence of Pyridine

In a 2,000 ml three necked flask equipped with a stirrer, additional funnel and reflux condenser protected with a drying tube, was placed 333.4 g (2.5 moles) of ψ'-propanol, 221 g of pyridine and 221 g of benzene. The mixture was cooled to 0°C and 130 g (0.85 moles) of phosphorus oxychloride added at such a rate that the temperature did not exceed 10°C. Then the reaction mixture was heated at reflux for two hours. After cooling to room temperature, 416.5 ml of water was added. The benzene layer was separated, washed with water, and then dried and completely neutralized with solid sodium carbonate. This mixture was filtered and the benzene removed by distillation. The product was distilled through a 65 cm column packed with Raschig rings at 10 mm. The ester, 122.6 g, boiled at 143°C. The yield was 32.9 percent.

(2) Without Acid Acceptor

In a 5,000 ml three necked flask, equipped with stirrer and reflux condenser protected with a drying tube, was put 3,565 g (27 moles) of ψ'-propanol and 1,005 g (6.56 moles) of phosphorus oxychloride. The mixture was heated at reflux for 64 hours. The system was vented through a water trap to remove the evolved HCl. The excess alcohol (1,083 g) was distilled at one atmosphere and 2,350 g of phosphate ester was collected at 88°C at 4 mm. The yield was 85 percent.

b. Gas Chromatographic Analysis

A two µl sample was introduced onto a two foot column of silicone gum rubber on Chromsorb P at 200°C. At a helium flow rate of 20.6 cc/min the retention time was 55 sec. There were no visible impurities.

c. Coating of Hot Metal Surfaces

Molten aluminum at red heat (approximately 660°C) was poured into the phosphate ester. The recovered metal showed no evidence of a coating.

d. Propellant Solubilities

Pentaborane and the phosphate ester were found to form conjugate solutions. Samples of the materials were prepared in various ratios (1:4, 1:2, 1:1, 2:1 and 4:1) in pyrex tubes, containing measured amounts of the phosphate, by attaching the tubes to a vacuum line and condensing measured amounts of pentaborane in each. The solubility of the materials were calculated from the relative volumes of the conjugate phases at 22°C. Solubility of pentaborane in the phosphate ester is 31 g/100 cc at 22°C. Solubility of the phosphate ester in pentaborane is 18.6 g/100 cc at 22°C. Upon standing, the samples turned yellow, but B^{11} NMR analysis indicated that no interaction occurs. The ester and UDMH were infinitely soluble but with JP-4 no solubility was noted. It is initially immiscible with N_2H_4 but dissolves on standing.

e. H^1 NMR Spectrum (Fig. 16)

The spectrum shows the interaction of fluorine and hydrogen and secondary splitting by coupling of the ω-hydrogen and the ω-1 fluorines. There is also evident coupling of phosphorus with the α-hydrogens through the oxygen of the ester.

f. Corrosivity to Metals

In all tests at the boiling point (205°C) noticeable changes occurred except with the control which was unchanged. In contact with mild steel for 30 days, a large quantity of white solid was precipitated and the metal was etched. In contact with stainless steel the ester turned amber and a black solid was deposited, but the metal appeared unchanged. In the presence of magnesium the flask became heavily coated with a black solid while the metal was only darkened. In contact with aluminum the ester turned amber and a small amount of black solid was precipitated.

In all tests at ambient temperature there were no changes observed in the appearance of the ester or the metals.

Change in Weight of Metals

Metal	Ambient Temperatures		Boiling Point
	Wet	Dry	
Stainless 302/304	+0.3 mg	+0.5 mg	- 1.9 mg
Mild Steel	+1.4 mg	+0.6 mg	-37.2 mg
Aluminum - 1100	+1.2 mg	+4.6 mg	+ 0.3 mg
Magnesium-Dow AZ31B	-1.2 mg	-0.9 mg	- 2.2 mg

3. ψ'-Amyl Phosphate

a. Preparation

In a five liter three necked flask with stirrer, addition funnel and condenser vented to the roof was placed 3,180 gms (13.7 moles) of the ψ'-amyl alcohol. Phosphorus oxychloride (709g, 4.62 moles) was added over 30 minutes. The addition funnel was replaced with a gas dispersion tube and dry nitrogen swept through the mixture, while refluxing, until no further hydrogen chloride was evolved. This was approximately ten hours. The reaction mixture was distilled through a 25 cm column packed with Raschig rings. Small quantities of unreacted phosphorus oxychloride and the fluoroalcohol were recovered but not weighed. Small foreruns of material boiling at 110°C/7 mm and a sublimable white solid were obtained. The phosphate ester, 3,050 grams (90 percent yield), was collected at 169-171°C/7 mm.

b. Gas Chromatographic Analysis

A seven μl sample was introduced onto a two meter column of Apiezon L on firebrick at 200°C. Helium flow rate 75 cc/min, retention time, 2 min 32 sec. There were no visible impurities.

c. Corrosivity to Metals

In all tests at the boiling point (300°C), the ester formed black tars including the control. In contact with mild steel approximately one-half of the ester decomposed while the others gave minor amounts of decomposition.

At room temperature only mild steel and magnesium were visibly changed. Under both wet and dry conditions the mild steel became dull and the magnesium appeared slightly corroded.

Change in Weight of Metals

Metal	Ambient Temperatures		Boiling Point
	Wet	Dry	
Stainless 302/304	-0.2 mg	none	- 0.1 mg
Mild Steel	-0.5 mg	-1.2 mg	-91.3 mg
Aluminum - 1100	none	none	+ 0.5 mg
Magnesium-Dow AZ31B	+0.2 mg	-0.2 mg	+ 0.8 mg

d. Propellant Solubilities

The phosphate ester was added by buret to measured quantities of JP-4, Hydrazine and UDMH. No solubility was observed in JP-4 while there was infinite solubility in UDMH. The ester appeared initially insoluble in hydrazine but in standing two hours, the two layer mixture could be shaken and an apparently homogeneous mixture obtained. Additional ester was now soluble in all proportions in this mixture. When propellant was added to the ester the results were identical except that hydrazine was immediately soluble. To determine solubility of the ester in pentaborane, measured amounts of ester were placed in pyrex tubes attached to a vacuum line and measured amounts of pentaborane condensed in each tube. The tubes, containing various ratios of ester to pentaborane were sealed off, allowed to warm and then shaken. In each case the decrease in the pentaborane phase volume was attributed to solubility in the ester and this was calculated to be approximately 15 grams per 100 cc. On standing for several days the tubes containing pentaborane and the ester became yellow. B^{11} NMR analysis of the solutions did not show evidence for any boron containing species other than the unchanged pentaborane dissolved in the ester. The yellow material is either too small in quantity or too insoluble to be analyzed by nuclear magnetic resonance spectrometry.

4. ψ'-Propyl Polyphosphate

a. Preparation

ψ'-Propyl phosphate was prepared as previously described. To eight pounds of this product was added one pound of phosphorus pentoxide. All materials were handled in a dry box. The mixture was shaken on a shaker for 30 hours. Three times during the shaking the mixture was removed from the shaker and heated to 130°C in an oven and returned to the shaker. A part of the phosphorus pentoxide did not go into solution, so the product was filtered in a dry box and eight pounds, nine ounces of dark brown liquid was obtained.

b. Gas Chromatographic Analysis

A two μl sample was introduced onto a two foot column of silicone rubber on Chromsorb W. This gave a peak of retention time equal to ψ'-propyl phosphate. This would indicate that the polyphosphate had decomposed on the column.

c. Coating of Hot Metal Surfaces

Aluminum heated to red heat was poured into the polyphosphate. The recovered aluminum was coated with a heavy coating of black material.

d. Flammability

The polyphosphate burns very weakly in a flame at the boiling point, but does not support combustion.

e. Corrosivity to Metals

In all tests at the boiling point (240°C), the ester was more than 50 percent decomposed to black tars including the control. The metal samples were heavily coated with this material which could not be completely removed without damage to the metal.

At ambient temperatures only wet magnesium was visibly changed. The metal sample was noticeably corroded and a white solid had precipitated which clouded the liquid.

Changes in Weight of Metals

	Ambient Temperatures		
Metal	Wet	Dry	240°C
Stainless 302/304	+ 1.2 mg	+1.4 mg	+ 0.5 mg
Mild Steel	+ 0.6 mg	+1.6 mg	- 8.4 mg
Aluminum - 1100	+ 1.0 mg	+0.9 mg	+ 1.7 mg
Magnesium-Dow AZ31B	-44.9 mg	+1.0 mg	-59.6 mg

f. Propellant Solubilities

Pentaborane and the polyphosphate were found to react with the precipitation of a white solid. Samples of the materials were prepared in various ratios (1:4, 1:2, 1:1, 2:1 and 4:1). In the samples which were 4:1 and 2:1 (pentaborane/polyphosphate) there were two liquid phases while in all other samples there was only one phase. Because of the solid precipitate it was not possible to calculate solubilities. B^{11} NMR analysis indicated that no interaction occurs.

The polyphosphate also reacted slightly with N_2O_4 with the precipitation of a small quantity of white solid. The remaining liquids were completely miscible. The polyphosphate was infinitely soluble with UDMH and N_2H_4 but insoluble in JP-4.

D. ψ'-Amyl Silicate

Complete physical properties (Table I) and compatibility characteristics (Table II) were determined for this material.

The method of synthesis was reaction of silicon tetrachloride with ψ'-amyl alcohol

$$4H(CF_2)_4CH_2OH + SiCl_4 \longrightarrow [H(CF_2)_4CH_2O]_4Si + 4HCl$$

Conversions of silicon tetrachloride to the silicate ester were poor though yields were fair. It appeared that the silicon tetrachloride must have been swept out with the evolved hydrogen chloride. In addition, there are reactions in which presumably the partially esterified mono, di-and tri-silicon halides are produced, and these apparently do not react further since alcohol is recovered unchanged. Even with long reflux of the mixture, complete reaction is not obtained, the ester was more viscous than the corresponding ψ'-amyl borate and offered no advantages over the latter in either physical properties, or presumably, as an extinguishant (AF Aero Propulsion Laboratory data). It ignites in a flame at the boiling point but does not support combustion.

1. Preparation

a. From the Alcohol and Silicon Tetrachloride (Ref. 17)

The ψ'-amyl alcohol, (duPont) 1,997 g (8.61 moles), was placed in a two liter round bottom flask with addition funnel, stirrer, and condenser connected to a roof vent through a calcium chloride drying tube. Silicon tetrachloride (Matheson, Coleman, Bell) 365 g, (2.74 moles) was added over two hours with stirring. No heat effect was noted.

Dry nitrogen at approximately 100 cc/min was swept through the flask while heating to 125°C with stirring for three hours. Unreacted alcohol, 432 g, was recovered by distillation through a 25 cm column packed with Raschig rings. The ψ'-amyl silicate was distilled under vacuum, boiling point 137-139°C/1 mm. The amount obtained was 1,326 g, which is an 82.6 percent yield, allowing for recovered alcohol. Higher boiling materials (b.p. 182°C/1 mm) were noted but not further investigated. Analysis: Calculated for $C_{20}H_{12}F_{32}O_4Si$; Si = 2.94 percent. Found: Si = 2.37 percent.

A weighed sample of the ester prepared from silicon tetrachloride and the alcohol was hydrolyzed by heating under reflux for twenty-four hours. The silica was filtered, ignited and weighed. The low value here is presumably due to formation of some volatile silicon tetrafluoride during hydrolysis or to incomplete hydrolysis.

b. From the Alcohol and Silicon Tetrachloride in the Presence of Pyridine

In a one liter three necked flask with stirrer, condenser, drying tube and dropping funnel were placed 693 g (3 moles) of the ψ'-amyl alcohol and 236 g (3 moles) of pyridine. Silicon tetrachloride (127 g, 0.75 mole) was added slowly (one and one-half hours) while cooling the flask with an ice bath. The ice bath was removed and the mixture stirred an additional hour, then allowed to stand overnight. It solidified on standing and the solid was extracted with benzene and filtered. The benzene was removed and the residue distilled. A white solid found to be pyridinium hydrochloride sublimed into the condenser and it was necessary to stop the distillation several times to remove this material. The amine salt is somewhat soluble in the ester and the product still contained traces of the amine salt even after adding ether to precipitate it. The yield of silicate ester was 310 g (43.5 percent).

c. Trans-esterification of Tetraethylsilicate with ψ'-Amyl Alcohol

In a 300 cc flask with condenser and drying tube was placed 43.7 g (0.21 mole) of ethyl silicate, 234 g (1.01 moles) of the ψ'-amyl alcohol and 1.1 g of titanium isopropoxide (Ref. 18). The latter was prepared from titanium chloride and isopropyl alcohol. The mixture was refluxed eight hours, then ethanol and excess fluoroalcohol removed by distillation. The residue was vacuum distilled to yield 105.7 g of the silicate ester. After accounting for 76.5 g of recovered ψ'-amyl alcohol, the yield was 64.8 percent.

2. Gas Chromatograph Retention Time

On a two meter column (Apiezon L on firebrick), it was necessary to condition the column with one injection of sample before reproducibility was obtained. The elution time was four minutes at 235°C; 60 cc/min helium flow rate. The instrument was a Perkin-Elmer Model 154. The chromatographic analysis did not show the presence of any impurities.

3. Coating of Hot Metal Surfaces

Aluminum heated to redness was poured into the silicate ester. The recovered metal had a dark gray coating not visible on a control sample.

4. Corrosivity to Metals

In all tests at the boiling point (305°C) including the control, the ester became amber and black decomposition products were formed which could not be completely removed from the metal. Thus weight increases are recorded at this temperature. In tests at ambient temperature only the wet magnesium and wet mild steel appeared slightly corroded. The wet samples caused silica formation and the ester became cloudy. The ester also became cloudy with dry mild steel and stainless steel.

Change in Weight of Metals

	Ambient Temperatures		
Metal	Wet	Dry	305°C
Stainless 302/304	+0.3 mg	none	+0.6 mg
Mild Steel	+0.5 mg	-0.2 mg	+1.5 mg
Aluminum - 1100	+0.3 mg	none	+0.3 mg
Magnesium-Dow AZ31B	-1.8 mg	+0.3 mg	-3.0 mg

E. ψ'-Alkyl Sulfite Esters

One compound, ψ'-amyl sulfite, was prepared in quantity for evaluation by AF Aero Propulsion Laboratory. This compound was completely characterized; see Tables I and II. Also synthesized were small quantities of ψ'-propyl sulfite and ψ'-heptyl sulfite. These compounds were prepared by the reaction of thionyl chloride and the appropriate ψ'-alcohol. Yields of 90-95 percent were obtained. Considerable difficulty was encountered in purifying ψ'-propyl sulfite. It was necessary to carefully distill the product through a packed column. In light of the meager amount of information on sulfite esters in the literature it was of interest to investigate several reactions of these esters. Reactions attempted were the alkylation of thiourea and the alkylation of phenol. Both reactions occur with sulfate esters, however, neither occurs with sulfite esters. In the attempted phenol alkylations, the

$$2RCH_2OH + SOCl_2 \longrightarrow (RCH_2O)_2SO + 2HCl$$

$$R = H(CF_2CF_2)_x \text{ where } x = 1, 2 \text{ or } 3$$

stringent heat and hydrolytic conditions actually caused total hydrolysis of the sulfite ester.

The ψ'-amyl sulfite burns in a flame at the boiling point but does not support combustion. The ψ'-amyl sulfite gave the secondary fire of shortest duration in the tests with magnesium at AF Aero Propulsion Laboratory. The material is comparable in hydrolysis resistance to the other ψ'-inorganic esters but is less thermally stable. The liberation of sulfur dioxide in decomposition of the sulfite esters in a fire could be dangerous unless personnel used masks.

The ψ'-heptyl ester was prepared in excellent yield and of fine purity as shown by gas chromatographic analysis yet the analyses were poor even though analyses for the ψ'-propyl and ψ'-amyl sulfites (for sulfur and fluorine at least) were excellent. The identity of the compound should not be questioned since the analysis obtained does not fit a sulfite or a ψ'-sulfurous acid, and it is pure, as indicated by gas chromatography.

1. ψ'-Propyl Sulfite

a. Preparation (Ref. 19)

To 264 g (2.0 moles) of ψ'-propyl alcohol in a one liter three necked flask with stirrer, condenser and ice cooling bath was added 110 g (0.92 mole) of thionyl chloride over one-half hour. Heating was noted during the first ten minutes but then the reaction became endothermic. The mixture was heated to reflux for two hours, cooled and distilled. Ten cuts were taken. The range of boiling points of the first five were from 105-180°C and contained unreacted alcohol and several unidentified compounds. Cuts No. 6 - 10 boiled from 180-195°C. The last two were essentially pure sulfite ester from gas chromatographic analysis but Nos. 6, 7 and 8 still contained a more volatile unidentified material. These were combined and redistilled through a 60 cm Raschig ring packed column. The pure sulfite boils at 195°C. The material saturates gas chromatographic columns and must be injected in less than 0.2 μl quantities. Analysis: Calculated for $C_6H_6F_8O_3S$, C = 23.2, H = 1.93, S = 10.3. Found: C = 23.7, H = 2.11, S = 10.54.

2. ψ'-Amyl Sulfite

a. Preparation

In a 5,000 ml flask 4,000 g (17.24 moles) of ψ'-amyl alcohol and 860 g (7.23 moles) of thionyl chloride were refluxed for eight hours. The product was distilled through a 30 cm Vigereux column. Recovered was 1,585 g of alcohol and 2,427 g of product. This is a yield of 91.4 percent. Analysis: Calculated for $C_{10}H_6F_{16}O_3S$, C = 23.55, H = 1.17, S = 6.27, F = 59.6. Found: C = 16.48, H = 1.74, S = 6.23, F = 60.5.

It is common with fluorocarbons and their derivatives to obtain low carbon analyses. Decomposition on pyrolysis will often occur to yield CF_4 rather than oxidation to CO_2.

b. Gas Chromatographic Analysis

A two µl sample was introduced onto a two foot column of Apiezon L on Chromsorb P at 200°C. With a helium flow rate of 19.7 cc/min, retention time was 57 sec. There were two very small impurities of lower retention time.

c. Coating of Hot Metal Surfaces

Molten aluminum at red heat (approximately 600°C) was poured into the sulfite ester. The recovered metal was coated with a layer of black material.

d. Propellant Solubilities

The sulfite ester and UDMH were observed to be infinitely soluble, but a slow reaction occurred which precipitated a white solid.

The sulfite and hydrazine were found to be insoluble, but reacted exothermically with gas evolution having a strong hydrogen sulfide odor. The reaction started very slowly but the rate increased as the temperature increased, giving two immiscible liquids. Analysis by gas chromatography has shown that each phase contains at least two compounds. These were not identified.

e. Corrosivity to Metals

In all tests at the boiling point (236°C), as well as the control, the sulfite ester turned amber. The metal samples all appeared very clean although the metal surface was dulled as if etched.

In all tests at ambient temperatures the ester was unchanged in appearance. All metal samples appeared corroded and were covered with corrosion products, particularly the wet samples.

Change in Weight of Metals

Metal	Ambient Temperatures Wet	Ambient Temperatures Dry	Boiling Point
Stainless 302/304	-2.2 mg	-0.8 mg	-0.5 mg
Mild Steel	-8.7 mg	-0.8 mg	-0.3 mg
Aluminum - 1100	none	+1.7 mg	-0.2 mg
Magnesium-Dow AZ31B	+3.6 mg	-0.3 mg	+0.2 mg

f. Thermal Stability

Three ml of the sulfite ester was heated for two hours at 400°C (750°F) in a 130 cc pyrex tube which had previously been baked out at 300°C. The ester was completely decomposed to a gas, a colorless liquid, and a black solid coating the walls. After cooling the gas was identified by mass spectral analysis as a mixture of sulfur dioxide, carbon monoxide and a trace of carbon dioxide. Gas chromatographic analysis of the liquid showed it to be a pure compound of retention time less than the sulfite. The elemental analysis of the liquid indicated the compound was ψ'-amyl ether, after accounting for the small amount of sulfur present as the dioxide. The major decomposition products of the sulfite ester are ψ'-amyl ether and sulfur dioxide.

	Analysis	After Removal of SO_2	Calculated For Ether
C	24.18 %	25.0 %	26.9 %
H	1.67 %	1.73 %	1.3 %
F	67.2 %	69.4 %	68.2 %
S	1.66 %	-----	----
O	5.59 %	4.07 %	3.6 %

g. Attempted Alkylation of Thiourea (Ref. 19)

In a 500 cc flask was placed 15 g (0.25 mole) of thiourea and 63.8 g (0.125 mole) of ψ'-amyl sulfite. The mixture was heated at 150°C overnight. The thiourea melted and darkened but was not dissolved in the ester which turned yellow. The mixture was allowed to cool and the solid which deposited was recrystallized from alcohol twice. The melting point and mixed melting point identified it as thiourea. Fifty-two grams of the recovered liquid was identified as the starting Y'-amyl sulfite by infrared and gas chromatographic analysis.

h. Attempted Alkylation of Phenol (Ref. 20)

To 7.5 g of phenol was added 40.7 g of ψ'-amyl sulfite and 3.2 g of sodium hydroxide in 50 cc of water. The mixture was stirred and refluxed for twelve hours. The organic layer was extracted with benzene and dried with Drierite. The benzene was evaporated and the residue distilled to give a wide boiling material (117-160°C) with a strong odor of phenol. The distillates were combined and washed with base, dried and redistilled. The material boiled at 135-140°C and was identified as ψ'-amyl alcohol by gas chromatographic retention time and infrared red spectrum.

3. ψ'-Heptyl Sulfite

a. Preparation

To 296 g (0.89 mole) of heptyl alcohol in a one liter three necked flask with stirrer and condenser was added 53.1 g (0.45 mole) of thionyl chloride. No heat effect was noted. The mixture was heated at 60°C for two hours, cooled and vacuum distilled. There was recovered 135 g of unreacted alcohol containing a small quantity of the sulfite ester and 163 g (approximately 94 percent) of the yellow sulfite ester, boiling at 105°C at 0.5 mm. The material was redistilled through a 60 cm Raschig ring packed column and gave a water white liquid boiling at 154°C/9 mm. Gas Chromatographic analysis of 0.2 µl on activated charcoal at 300°C indicated the material to be pure. Saturation of the column occurred on injection of larger quantities. Analysis: Calculated for $C_{14}H_6F_{24}O_3S$, C = 23.7, H = 0.85, S = 4.5, F = 64.2. Found: C = 19.7, H = 1.0, S = 5.3, F = 62.3.

F. Attempted Preparation of ψ'-Amyl Sulfate

There were no reports in the literature on trans-esterification of sulfate esters so this method was first explored. Even in the presence of titanium isopropoxide, a catalyst in silicate trans-esterification (Ref. 14), no reaction occurred. Other oxidative procedures with sulfite esters which yield sulfates in the aliphatic series (Refs. 21, 22) did not succeed with fluoroaliphatic sulfites. Apparently hydrolysis occurred with oxidation in all cases. Since usual synthetic methods failed, attempts to prepare sulfate esters were dropped.

1. Attempted Trans-esterification of Dimethylsulfate

In a 300 cc flask with reflux condenser were placed 31.5 g (0.25 mole) methyl sulfate and 72 g (0.3 mole) of ψ'-amyl alcohol. The material was heated to reflux for two hours then distilled. A small amount of material was obtained at 60-90°C and the bulk of material distilled over a range of 90-140°C. The low boiling material was not the expected methyl alcohol and was not further separated. Gas Chromatography indicated the presence of at least four components.

2. Attempted Trans-esterification in the Presence of Titanium Isopropylate

In a 250 cc flask equipped with a reflux condenser and drying tube, were placed 73 g (0.31 mole) of ψ'-amyl alcohol, 32 g (0.25 mole) of dimethylsulfate, and 9.5 g of titanium isopropylate. The mixture was heated to reflux for two hours and then distilled. The bulk of the product distilled at 110-115°C and is believed to be ψ'-amyl ether. There was a small cut boiling at higher temperatures but none lower, as would be expected, if the trans-esterification had occurred yielding methyl alcohol (b.p. 65°C).

The procedure was repeated except that the flask was equipped with a distillation head in place of the reflux condenser. After heating for one hour the first distillation product was obtained at 90°C. Again, no methanol was detected.

3. Attempted Oxidation of ψ'-Amyl Sulfite with Sulfuryl Chloride

In a three necked 500 ml flask equipped with stirrer, addition funnel, and reflux condenser protected with a drying tube was placed 268.5 g (0.53 mole) of ψ'-amyl sulfite. To this, 35.5 g (0.26 mole) of sulfuryl chloride was added slowly with stirring (Ref. 22). The mixture was heated slowly to 180°C and maintained at that temperature for two hours. The condenser was replaced with a Vigreux column and the mixture heated to 200°C, yielding only a trace of product distilling at 120°C. The product was distilled at 120-122.5°C/9 mm, and found to be the unreacted fluoroamyl sulfite. Gas chromatographic analysis of the residue showed a small higher boiling component.

4. Attempted Oxidation of ψ'-Amyl Sulfite with Potassium Permanganate (Ref. 21)

In a 500 ml erlenmeyer flask was put 100 g (0.065 mole) of ψ'-amyl sulfite and 145 cc of acetic acid. Potassium permanganate (22 g, 0.65 mole) dissolved in hot water was added in small portions. The mixture was cooled under tap water after each addition. The mixture was then poured into 300 cc of ice water which contained 95 g of sodium bicarbonate. The resulting solution was extracted three times with ether and the etheral extract distilled. After removal of the ether the residue was distilled at 9 mm yielding only acetic acid.

The preparation was repeated in a 500 ml round bottom flask, cooled in an ice bath and equipped with a stirrer. Sodium bicarbonate was added to the aqueous solution until it became neutral to litmus. Upon distillation the only product obtained was a small quantity of ψ'-amyl alcohol.

5. Attempted Oxidation of ψ'-Amyl Sulfite with ψ'-Amyl Chlorosulfonate (Ref. 22)

The chlorosulfonate was prepared by the reaction of ψ'-amyl alcohol and sulfuryl chloride. The alcohol was added

$$H(CF_2)_4CH_2OH + SO_2Cl_2 \longrightarrow H(CF_2)_4CH_2OSO_2Cl + HCl$$

slowly to the sulfuryl chloride in a 500 ml three necked flask, cooled with an ice bath and equipped with addition funnel, stirrer and reflux condenser protected with a drying tube. After addition was completed the addition funnel was replaced with a gas dispersion tube and nitrogen bubbled through the mixture to remove HCl. Very little HCl was evolved so the mixture was heated for twenty hours and HCl was slowly evolved.

The crude chlorosulfonate was added slowly from an addition funnel to ψ'-amyl sulfite in a 500 ml three necked flask equipped with a stirrer and reflux condenser protected with a drying tube. There was no visible reaction during the addition, so the mixture was heated to reflux for thirty hours. HCl was slowly evolved and the mixture darkened. A portion of the mixture was distilled at 9 mm and three major products were apparent from gas chromatographic analysis. Two of these were identified as ψ'-amyl alcohol and ψ'-amyl sulfite. The third, of intermediate retention time, was not definitely identified but could possibly be the chlorosulfonate. A fourth component was observed in small quantity. This had a retention time longer than the sulfite but it disappeared after the mixture stood for two weeks. It is seen from the postulated reaction course that ψ'-amyl chloride should be a

$$H(CF_2)_4CH_2OSO_2Cl + [H(CF_2)_4CH_2O]_2SO \longrightarrow$$

$$[H(CF_2)_4CH_2O]_2SO_2 + H(CF_2)_4CH_2Cl$$

by-product, yet none was found by gas chromatographic analysis or infrared analysis.

G. Attempted Preparations of ψ'-Alkyl Aluminates

Numerous reaction conditions were investigated as routes to these aluminate esters. The methods used to prepare aliphatic aluminates were partially successful but product purification was impossible in all cases. The most pertinent observation made was that vacuum distillation of ψ'-aluminate preparations invariably ended in decomposition of the product. This is in contrast to aliphatic aluminates which are easily vacuum distilled. It is possible that the ψ'-aluminates are thermodynamically unstable with respect to formation of carbon and aluminum fluoride.

Only in one preparation (1-f below) was a product obtained that appeared to be close to the desired compound. Since this work was not productive it was abandoned.

1. ψ'-Amyl Aluminate

a. Attempted Preparation from Amalgamated Aluminum

Aluminum turnings were kept in contact with a mercuric chloride solution for one minute then washed three times with anhydrous methanol. The fluorinated alcohol, dried over calcium hydride, was then added. Reaction occurred, with darkening of the solution, for five minutes then stopped. Heating did not cause a restart.

b. Attempted Preparation Using Stannic Chloride

To aluminum turnings washed with ether was added the fluoroalcohol and approximately 1 cc of stannic chloride. No reaction occurred at reflux.

c. Attempted Preparation Using Hydrogen Chloride

To aluminum turnings washed with ether was added a dilute ether solution of hydrogen chloride. After one minute of vigorous reaction the ether was decanted, the aluminum washed with dry ether and the fluoroalcohol added. The reaction giving a dark colored solution lasted for approximately ten minutes then stopped. It could not be restarted with heating. The solution was decanted from unreacted turnings and evaporated to give a dark viscous oil which dissolved in benzene. The benzene was removed and attempts to distill the residue under vacuum were not successful.

d. Preparation From Aluminum Chloride and the Fluoroalcohol

Fifty grams of aluminum chloride was added to 275 grams of alcohol in a 500 ml flask cooled with an ice bath. The flask was equipped with a stirrer and reflux condenser with a drying tube. Hydrogen chloride was evolved and the mixture slowly turned a very dark brown. An attempt was made to decolorize with charcoal but this was not effective. Solution chromatography as a means of separation was investigated, but was not successful.

e. Preparation by Precipitation of HCl with NH_3 (Ref. 23)

In a 250 ml three necked flask equipped with stirrer, reflux condenser protected with a drying tube, and gas dispersion tube, was placed 8 g (0.06 mole) of aluminum chloride in ether solution. Then 44 g (0.19 mole) of ψ'-amyl alcohol were added and ammonia bubbled into the mixture until ammonia was given off (about one hour). The white ammonium chloride precipitate settled leaving a yellow ether solution which turned green on standing. This was filtered with decolorizing charcoal and evaporated on a rotary evaporator. There was obtained 31.1 g of a pale yellow liquid containing a small quantity of white solid. The infrared spectrum of this product is shown in Fig. 29. It is noted that there is only a small -OH group absorption in this spectrum.

Gas chromatographic analysis of the product showed it to contain at least two components. A large component was identified from the retention time to be ψ'-amyl alcohol. This probably arose from hydrolysis since the infrared spectrum showed only small quantities of alcohol and the minor component was ether. The third component, the ψ'-amyl aluminate, was not eluted from the column: only half as much material was eluted as when an equal sample of pure ψ'-amyl alcohol was introduced. The aluminate absorption on the chromatographic column is apparently quite strong.

f. Preparation from Sodium ψ'-Amyl Alcoholate

In a 500 ml three necked flask equipped with stirrer, addition funnel, and reflux condenser protected with a drying tube, was put 30 g (0.12 mole) of sodium ψ'-amyl alcoholate, freshly prepared in 70 percent yield from the ψ'-amyl alcohol and a sodium dispersion in toluene. Aluminum chloride (5.3 g, 0.04 mole) in 50 ml of ether was added slowly while stirring, precipitating a white solid (sodium chloride). Stirring was continued for one hour, and then the product filtered through a sintered glass filter. The filtrate was evaporated in a rotary evaporator to yield a brown viscous material from which a crystalline material precipitated upon standing several days.

Dry benzene was added to the products of the reaction of sodium ψ'-amyl alcoholate and aluminum chloride. All products were soluble except for a white crystalline material. The mixture was filtered in the dry box and the crystals washed with dry benzene. The infrared spectrum of this material contained an OH band and was similar to that of ψ'-amyl alcohol.

The elemental analysis of the material was compared to the calculated analysis of ψ'-amyl aluminate. The product was

	Elemental Analysis	Calculated
Carbon	13.83 %	25.0 %
Hydrogen	2.00 %	1.25 %
Fluorine	50.00 %	63.33 %
Aluminum	7.07 %	3.75 %

obviously not the desired aluminate but would more closely approximate a mixture of partially substituted aluminum chlorides.

The preparation was repeated, except that the entire preparation was carried out in a nitrogen filled dry box. The reaction was run in a Waring Blender. In the blender was put 160 g of freshly prepared sodium fluoroamyl alcoholate and 700 ml of ether, 13.5 g of aluminum chloride in ether solution was added slowly, and the mixture blended for one hour. The product was so finely divided it could not be filtered. It was also found that the ether used was not dry but probably contained up to 1 percent water, enough to hydrolyze approximately the entire quantity of aluminate expected.

2. 2, 2, 2-Trifluoroethyl Aluminate

a. Attempted Preparation From Amalgamated Aluminum (Ref. 24)

The aluminum was prepared by washing aluminum turnings repeatedly with acid and alkali, then covering with 0.5 percent mercuric chloride for 1.5 minutes, then washing with water, alkali and water, immersing the material once more in mercuric chloride and finally, washing with dry methanol and anhydrous ether.

In a one liter flask equipped with a reflux condenser protected with a drying tube, was put 35 g (1.3 moles) of amalgamated aluminum turnings and 285.5 g (0.95 mole) of trifluoroethyl alcohol. The mixture was heated to reflux for two hours and when no reaction started 1.5 g of mercuric chloride was added. Again, no reaction was observed. Then 3 g of iodine was added and the reaction appeared to start but did not continue at a visible rate. Three hundred ml of redistilled benzene was added to the mixture but did not appear to aid reaction.

After refluxing for one week the flask was filled with benzene, heated to boiling and then the mixture was centrifuged. The residue was also washed with hot benzene and centrifuged. The benzene solutions were combined and the alcohol-benzene azeotrope distilled off in addition to most of the excess benzene. The remainder was then evaporated in a rotary evaporator, leaving a brown residue which was too small to investigate further.

b. Attempted Preparation in the Presence of Triethyl Aluminate

Triethyl aluminate was prepared by the reaction of aluminum and ethyl alcohol in the presence of mercuric chloride and iodine (Ref. 25). When this reaction was partially complete, trifluoroethyl alcohol in benzene and aluminum turnings were added. When the aluminum turnings were used up, the product was distilled. After the benzene and excess alcohol had been distilled off the product decomposed leaving a brown to black flocculent material.

3. ψ'-Propyl Aluminate

a. Attempted Preparation by the Method of Fieser (Ref. 26)

In a 500 ml round bottom flask was placed 10 g (0.37 mole) of freshly turned aluminum-6061. The flask was heated with a free flame while sweeping with dry nitrogen. Then the flask was equipped with a reflux condenser protected with a drying tube, and 250 cc of ψ'-propyl alcohol (redistilled sodium) with a few crystals of mercuric chloride were added to the aluminum turnings. The mixture was heated to reflux. When no reaction had started after one hour, a crystal of iodine was added. The reaction started as evidenced by hydrogen evolution and darkening of the solution. The mixture was allowed to reflux for sixteen hours, when all the aluminum had reacted.

The excess alcohol was distilled off at one atmosphere and distillation continued under vacuum. It was impossible to get a vacuum better than 10 mm, probably due to noncondensable decomposition products. After about one half hour, the decomposition increased leaving a black flocculent material in the flask.

b. Preparation Without Distillation

The procedure was repeated as above except for the distillation of the aluminate. The dark gray liquid residue remaining after distillation of the excess alcohol turned crystalline on standing for two days. A crystalline product precipitated out of a toluene extract, but could not be identified.

H. Pentaborane Decontamination with Solutions of ψ'-Alkanols in ψ'-Alkyl Esters

All compounds prepared were good solvents for pentaborane. The small scale tests of flammability of pentaborane-ester mixture merely suggest that ψ'-amyl phosphate may be suitable as a diluent for the borane which will achieve the goal of extinguishant by dilution. Further testing with control comparisons is necessary.

It was found that pentaborane in ψ'-ester-ψ'-alcohol solutions will evolve hydrogen at rates dependent on the alcohol, i.e., the longer the chain, the slower alcoholysis occurs. Concentration effects were not investigated. Since the alcohol-ester solution is not ordinarily flammable, and dilution should lower pentaborane flammability, it is suggested that such solutions would be useful in scavenging pentaborane spills.

The slow rate of hydrogen evolution with ψ'-amyl or ψ'-heptyl alcohol would lower the possibility of a hydrogen fire or explosion associated with normal hydrolytic scavenging of boranes.

1. Flammability of Pentaborane-Ester Mixtures

Samples of pentaborane and extinguishant which had been made up for solubility determinations were broken open to determine whether they would burn spontaneously. The samples contained the following materials:

Ethoxydifluoroborane Trimer
2, 2, 2-Trifluoroethyl Phosphate
ψ'-Amyl Phosphate
ψ'-Amyl Silicate

The ratios of the mixtures were, 1:5, 1:2, 1:1, 2:1 and 5:1. All samples ignited spontaneously except these containing pentaborane and ψ'-amyl phosphate. No mixture ratio of these burned.

2. Alcoholysis of Pentaborane in ψ'-Ester Solutions with ψ'-Alcohols

a. Procedure

Two cc of liquid pentaborane was condensed into a flask in a vacuum system, dry nitrogen added and the flask attached to a wet test meter. The mixture of alcohol and ester was added through a dropping funnel containing a nitrogen atmosphere and the volume of hydrogen measured with time. Volumes were corrected for water vapor and reduced to S. T.P.

b. ψ'-Propyl Alcohol

A 40 percent solution of the alcohol in ψ'-amyl silicate (165 g) was added to the borane. The total volume of hydrogen measured (corrected) in twelve hours was 4.04 liters (80.2 percent). In three hours, there was generated 3.0 liters (60 percent) of the theoretical amount of hydrogen. The exit gas from the wet test meter had a discernible borane odor.

c. ψ'-Amyl Alcohol

A 40 percent solution of the alcohol in the ψ'-amyl silicate was added to the borane. The total volume (corrected) generated after four days was 4.83 liters (95.8 percent). After three hours 2.0 liters (39.5 percent) of the theoretical quantity of hydrogen had been evolved.

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TABLE I

PROPERTIES OF FLUORINA

Sample No. to AFAPL	Compound	Molecular Weight	Freezing Point	Boiling Point	Density	Viscosity (Centistokes)	Index of Refraction	Heat of Vaporization (Cal./Mole)	Th Deco (400 °C
	$(CF_3CH_2O)B$	308		116-119°C 241-246°F					
VII	$(HCF_2CF_2CH_2O)_3B$	404	glass-80°C mobile-45°C	202-6°C/747.7mm 396-403°F	1.5715/23.1°C	7.97/25.0°C 1.1/100.0°C	1.3294/20°C	1.11×10^4	
I	$[H(CF_2)_4CH_2O]_3B$	704	glass-80°C mobile-45°C	260-3°C/745mm 500-5°F	1.6964/25°C	19.9/25.0°C 1.2/100.0°C	1.3210/24°C	1.25×10^4	trac
	$[H(CF_2)_6CH_2O]_3B$	1004		180-5°C/3mm	1.8156/24°C		1.3210/20°C		
	$[H(CF_2)_8CH_2O]_3B$	1304	m.p. 37-40°C	235-40°C/2mm					
VIII	Boroxine-Borate Solution *	- -	glass-45°C mobile-15°C	205°C/744mm 401°F	1.5611/25°C	46.3/25.1°C 2.54/101.1°C		1.27×10^4	
IV	$(CH_3CH_2OBF_2)_3$	282	14-18°C	82-3°C/745.6mm 180-1°F	1.2839/25.8°C	3.90/25.0°C 2.11/50.0°C	1.3497/22°C	1.42×10^4	1
II	$[H(CF_2)_4CH_2O]_4Si$	952	glass-80°C mobile-50°C	304-5°C/745.5mm 579-81°F	1.7691/23.2°C	29.7/25.0°C 2.4/100.0°C	1.3235/24°C	1.545×10^4	
	$(CF_3CH_2O)_3PO$	344		45-60°C/9mm	1.6076/24.8°C		1.3293/20°C	7.46×10^3	
V	$(HCF_2CF_2CH_2O)_3PO$	440	glass-80°C mobile-40°C	205°C/746mm 401°F	1.6749/27.4°C	34.1/25.0°C 3.4/99.0°C	1.3450/21°C	1.07×10^4	
III	$[H(CF_2)_4CH_2O]_3PO$	740	glass-50°C mobile-25°C	298-300°C/745.5mm 568-72°F	1.8038/24°C	59.8/25.1°C 3.8/100.0°C	1.3320/24°C		
IX	$(HCF_2CF_2CH_2O)$ - Polyphosphate **	- -	glass-65°C mobile-45°C	240°C/744mm 464°F	1.6681/25°C	61.7/25.0°C d./100°C		1.225×10^4	~5
	$(HCF_2CF_2CH_2O)_2SO$	310		195°C 383°F	1.6278/24°C	5.77/23.6°C 1.10/100°C	1.3610/22°C		
VI	$[H(CF_2)_4CH_2O]_2SO$	610	glass-45°C mobile-30°C	236°C/745mm 457°F	1.7844/26.3°C	11.57/25.0°C 1.74/99.7°C	1.3431/18°C	1.405×10^4	1
	$[H(CF_2)_6CH_2O]_2SO$	910	approx-20°C	154°C/9mm	1.8145/24°C	32.74/23.6°C 3.11/100°C	1.3346/24°C	1.058×10^4	

* 47.4% $(HCF_2CF_2CH_2OBO)_3$ and 52.6% $(HCF_2CF_2CH_2O)_3B$

** Composition of material unknown, see Section III-C

[redacted]

TABLE I

PERTIES OF FLUORINATED ESTERS

Index of Refraction	Heat of Vaporization (Cal./Mole)	Thermal Decomposition (400°C, 2 Hrs)	Propellant Solubilities					Hydrolytic Stability (% Hydrolysis)			Specific Heat
			B_5H_9	UDMH	N_2H_4	JP-4	N_2O_4	Ambient	100°C	b.p. of Ester	(Cal./g°C)
1.3294/20°C	1.11×10^{4}	<2%	∞	∞	∞	insoluble	∞	0.3%	0.3%	0.6%(190°C)	0.48 ± 0.03
1.3210/24°C	1.25×10^{4}	trace only	∞	∞	84.5g/100cc	insoluble	∞	10%	13%	20%(250°C)	0.44 ± 0.03
1.3210/20°C											
	1.27×10^{4}	<2%	∞	∞	∞	insoluble	∞	7.7%	9.1%	8.0%(170°C)	0.51 ± 0.03
.3497/22°C	1.42×10^{4}	100%	∞	∞	∞	insoluble	reacts, see Sec. III-B-2-d	0.88%		0.11%(84°C)	0.58 ± 0.03
.3235/24°C	1.545×10^{4}	<2%	∞	∞	∞	insoluble	∞	5%		20%(210°C)	0.47 ± 0.03
.3293/20°C	7.46×10^{3}										
.3450/21°C	1.07×10^{4}	<2%	31g/100cc 18.6gB_5/100cc Ester	∞	∞	insoluble	∞	6.4%	10.4%	7.7%(190°C)	0.44 ± 0.03
.3320/24°C		<2%	15g/100cc	∞	∞	insoluble	∞	0.15%	0.82%	5.2%(205°C)	0.47 ± 0.03
	1.225×10^{4}	~50%	reacts, see Sec. III-C-4-f	∞	∞	insoluble	reacts, see Sec. III-C-4-f	6%	17.2%	21.6%(210°C)	0.43 ± 0.03
1.3610/22°C											
1.3431/18°C	1.405×10^{4}	100%	∞	∞	reacts, see Sec. III-E-2-d	insoluble	∞	3.1%	5.6%	8.1%(210°C)	0.41 ± 0.03
.3346/24°C	1.058×10^{4}										

[redacted]

TABLE II

COMPATIBILITY WITH NONMETALLIC MATERIALS
(30 Days at Ambient Temperatures)

Compounds		Polyethylene	Polytetra-Fluoroethylene	Rubber	Neoprene	Silicone Rubber
$(HCF_2CF_2CH_2O)_3B$	(1)	N. C.	N. C.	+2. 3%	+2. 1%	N. C.
	(2)	N. C.	N. C.	light amber	light amber	N. C.
$[H(CF_2)_4CH_2O]_3B$	(1)	N. C.	N. C.	+2. 1%	+1. 6%	crumbled
	(2)	N. C.	N. C.	amber	amber	amber
Boroxine-Borate	(1)	+0. 4%	N. C.	+1. 3%	+1. 6%	N. C.
Solution *	(2)	N. C.	N. C.	N. C.	N. C.	N. C.
$(CH_3CH_2OBF_2)_3$	(1)	N. C.	N. C.	+2. 1% stiff	+5. 1%	crumbled
	(2)	light amber	light amber	dark amber	dark amber	amber
$(CF_3CH_2O)_3PO$	(1)	N. C.	N. C.	+5. 9%	+5. 8%	crumbled
	(2)	N. C.	N. C.	gray	dark amber	amber
$(HCF_2CF_2CH_2O)_3PO$	(1)	N. C.	N. C.	N. C.	N. C.	N. C.
	(2)	N. C.	N. C.	light amber	light amber	N. C.
$[H(CF_2)_4CH_2O]_3PO$	(1)	N. C.	N. C.	+2. 0%	+0. 8%	crumbled
	(2)	N. C.	N. C.	black	amber	amber
$[H(CF_2)_4CH_2O]_2SO$	(1)	+3. 1%	N. C.	+1. 6% darkened	+0. 8%	N. C.
	(2)	N. C.	N. C.	N. C.	N. C.	light amber
$[H(CF_2)_4CH_2O]_4Si$	(1)	-0. 74%	N. C.	+1. 45%	+0. 36%	+3. 8%
	(2)	cloudy	N. C.	amber	amber	amber
$HCF_2CF_2CH_2O$ -	(1)					
polyphosphate	(2)					

*47. 4% $(HCF_2CF_2CH_2OBO)_3$ and 52. 6% $(HCF_2CF_2CH_2O)_3B$

(1) change in length or other physical characteristic of material

(2) change in appearance of ester

N. C. = No Change

TABLE III

MASS SPECTRUM OF ψ'-PROPYL BORATE

m/e	ion intensity
13	0.2
14	1.5
15	5.2
26	0.7
27	0.8
28	4.9
29	22.5
30	1.5
31	100.0
32	5.3
33	7.1
41	0.3
42	0.7
43	4.5
44	0.8
45	2.7
46	0.2
47	0.3
49	4.8
50	0.3
51	15.3
55	0.3
56	0.3
57	1.1
58	1.1
59	0.3
60	0.6
61	3.7
62	0.5
63	0.8
64	1.5
65	6.0
69	0.6
70	0.2
79	0.5
80	0.5
81	1.7
82	14.7
83	1.1
112	4.3
113	0.6

TABLE IV

MASS SPECTRUM OF ETHOXYDIFLUOROBORANE TRIMER

m/e	ion intensity
11	1.0
12	1.2
13	2.6
14	7.9
15	17.7
24	.3
25	2.0
26	14.7
27	51.9
28	19.7
29	83.5
30	5.9
31	60.8
41	2.0
42	2.4
43	13.1
44	3.0
45	42.4
46	14.5
47	34.8
48	6.0
49	23.7
55	2.0
56	1.3
57	3.7
58	.7
59	4.6
60	2.4
61	7.0
62	1.3
63	3.8
64	1.6
65	1.7
66	1.1
72	2.0
73	8.7
74	2.8
75	7.6
76	2.8
77	12.1
78	26.6
79	100.0
80	4.5
81	6.6
82	2.9
89	1.1
90	3.7
91	17.1
92	10.5
93	21.9
94	1.3
100	1.3
104	9.2
105	37.1
106	2.0

TABLE V

MASS SPECTRUM OF
ψ' - PROPYL PHOSPHATE

m/e	ion intensity
13	0.2
14	0.9
15	1.1
26	0.5
27	0.3
28	4.4
29	15.5
30	1.1
31	100.0
32	3.7
33	6.0
42	0.4
43	0.9
44	0.8
45	1.7
49	4.0
50	0.5
51	12.3
61	2.0
62	0.4
63	0.6
64	1.1
65	3.2
82	8.1
83	0.8
112	3.7

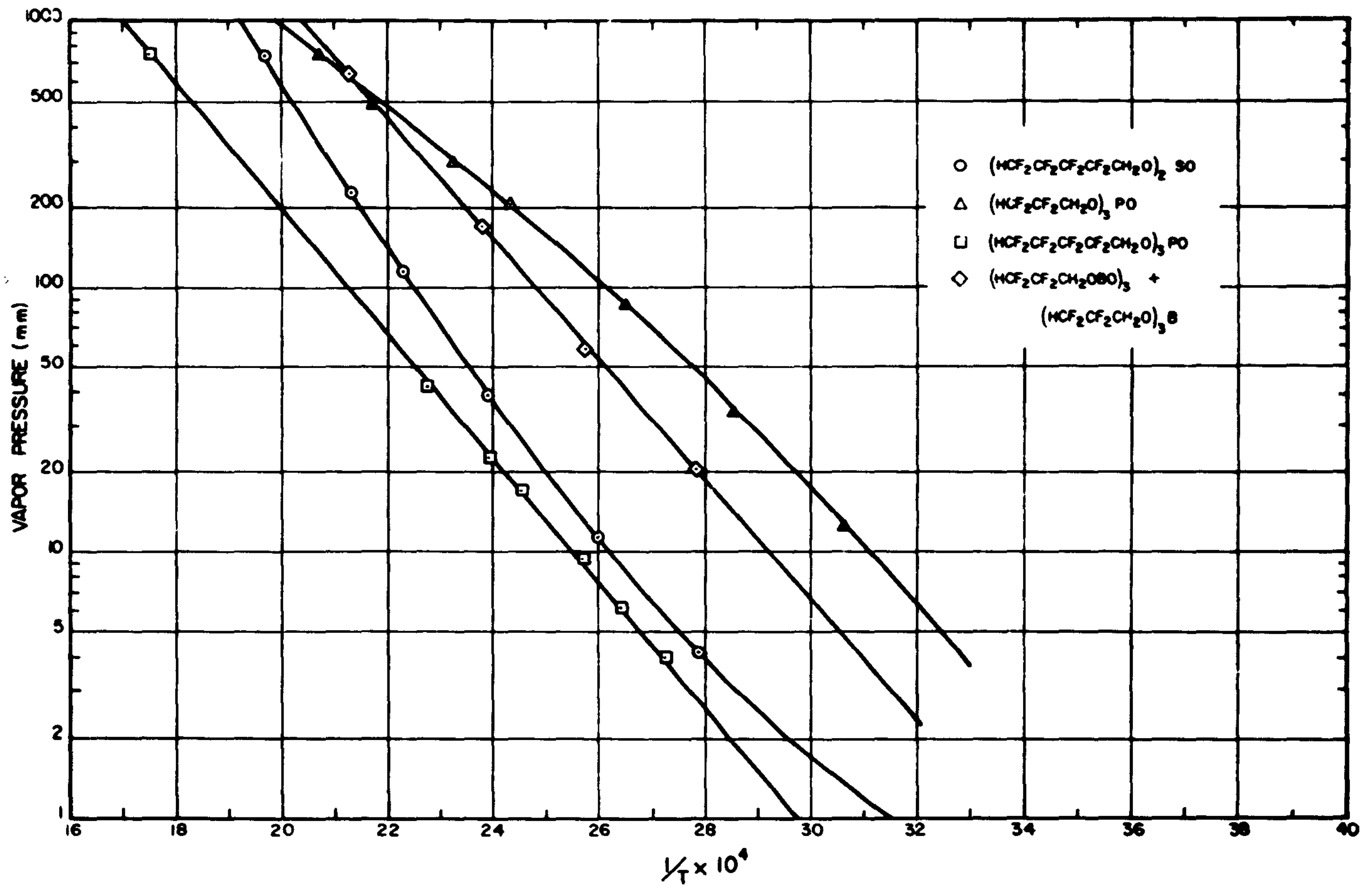

FIGURE 1

VAPOR PRESSURE CURVES OF EXTINGUISHANTS

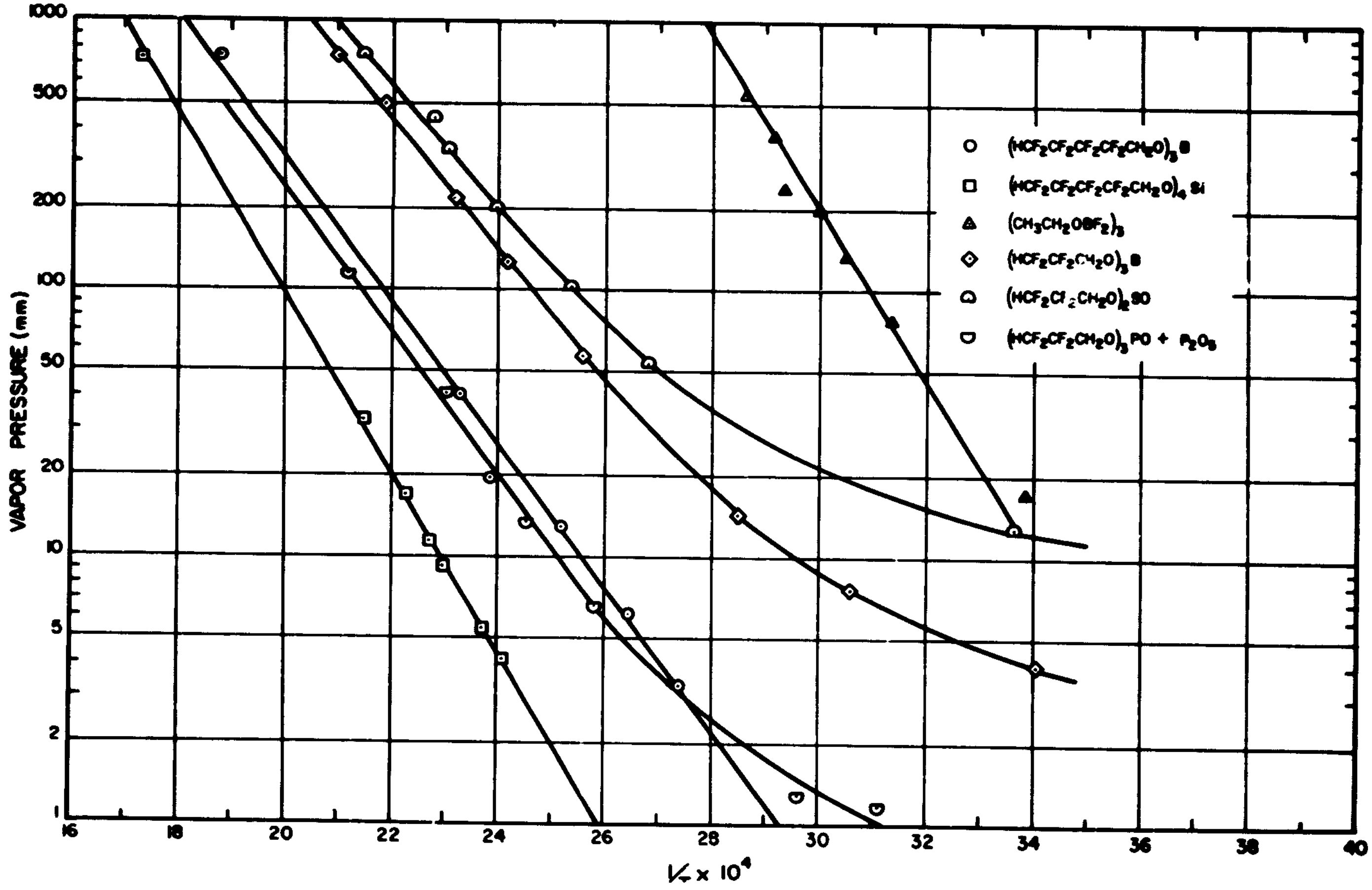

FIGURE 2

VAPOR PRESSURE CURVES OF EXTINGUISHANTS

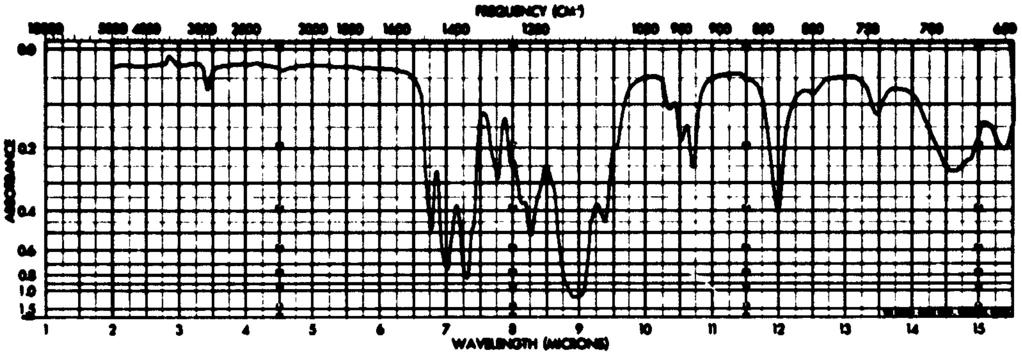

FIGURE 3
INFRARED SPECTRUM OF ψ'-PROPYL BORATE

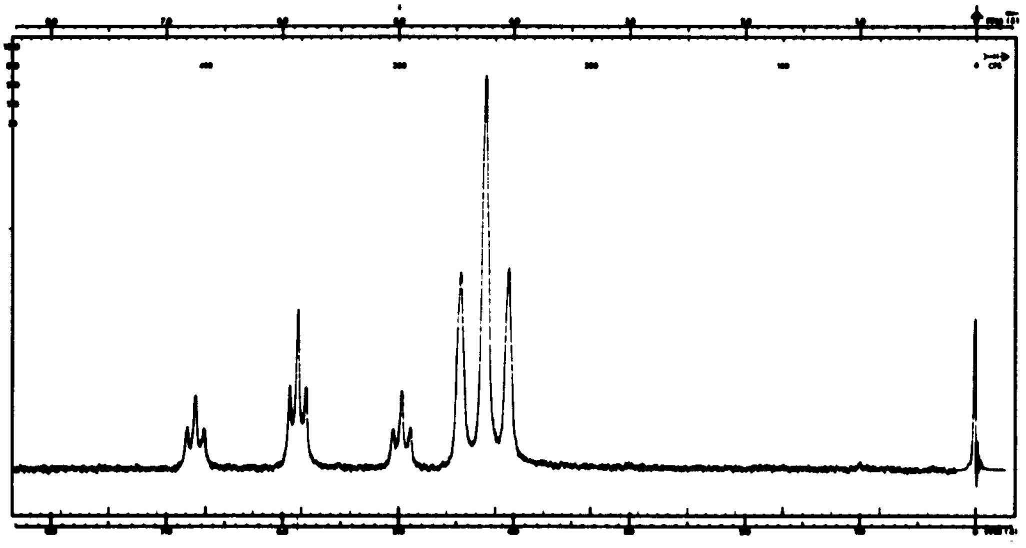

FIGURE 4
H^1 NMR SPECTRUM OF ψ'-PROPYL BORATE

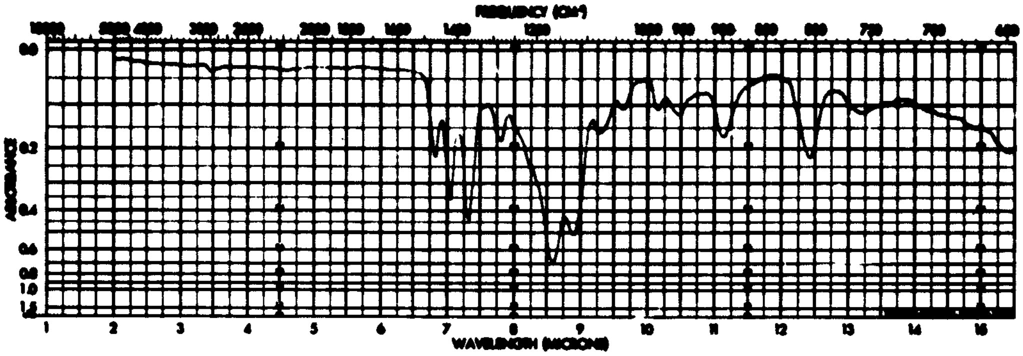

FIGURE 5
INFRARED SPECTRUM OF ψ'-AMYL BORATE

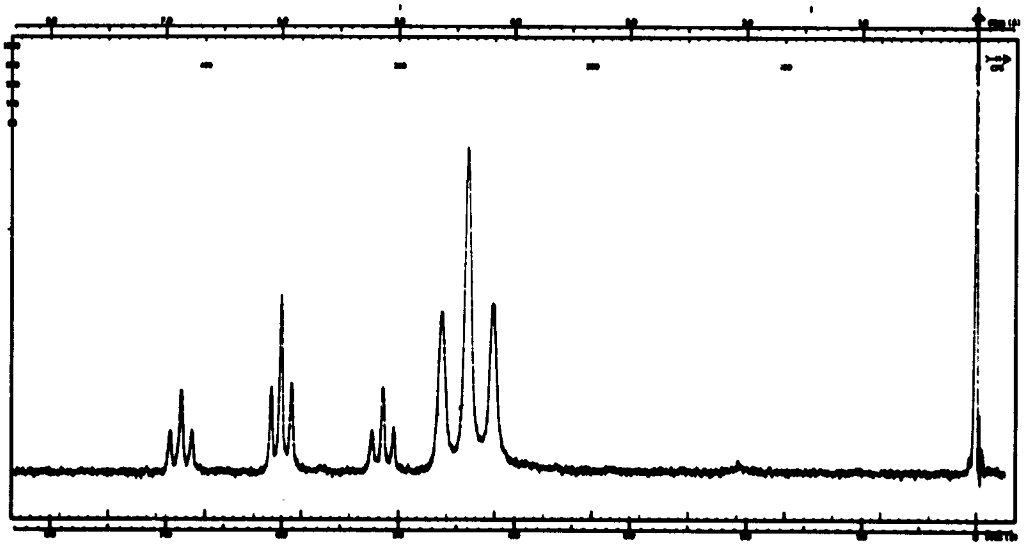

FIGURE 6
H^1 NMR SPECTRUM OF ψ'-AMYL BORATE

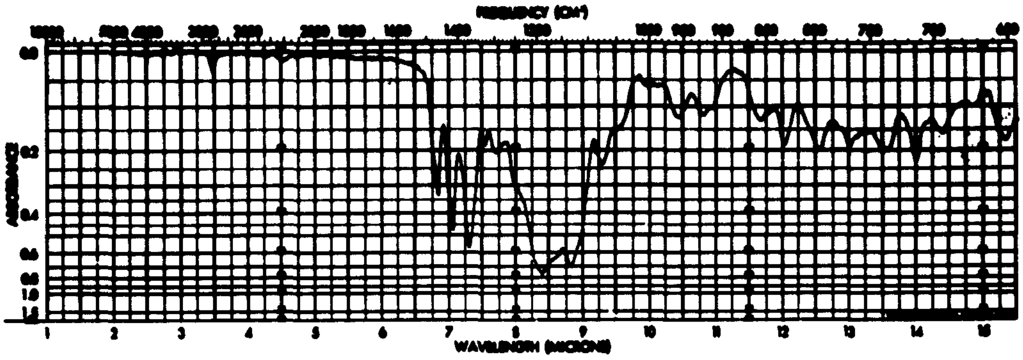

FIGURE 7
INFRARED SPECTRUM OF ψ'-HEPTYL BORATE

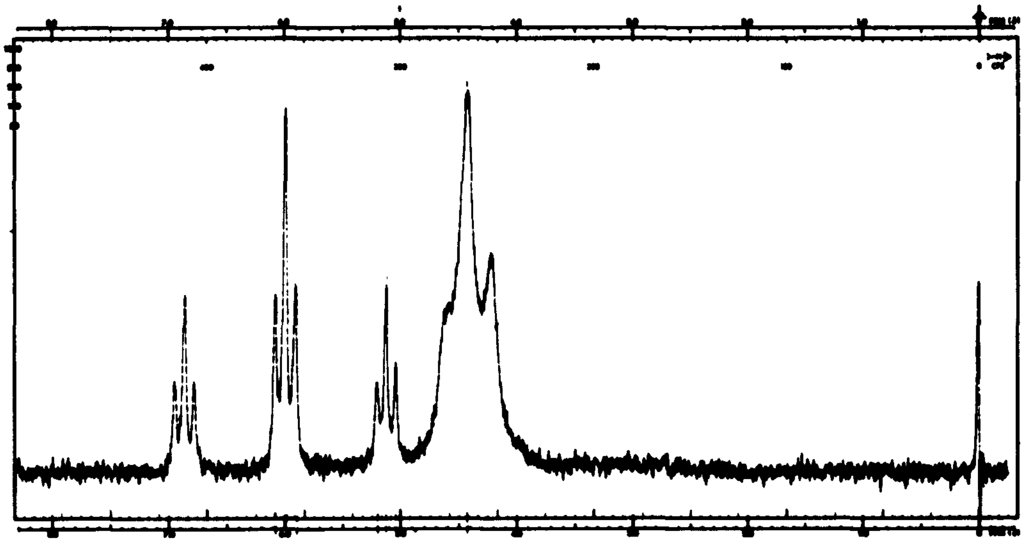

FIGURE 8
H^1 NMR SPECTRUM OF ψ'-HEPTYL BORATE

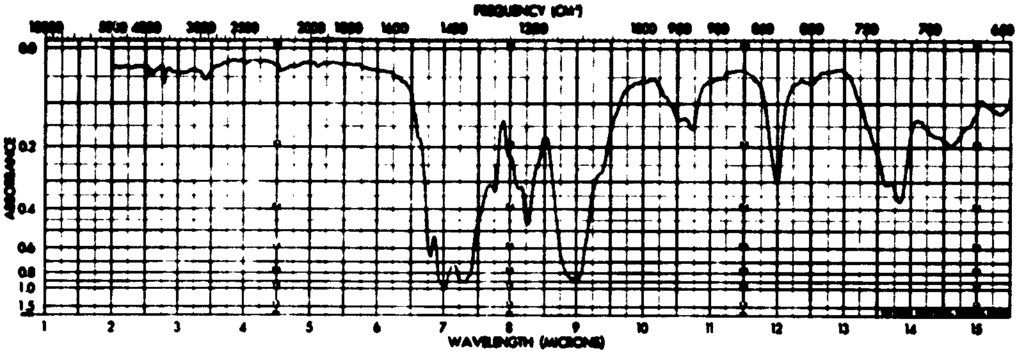

FIGURE 9
INFRARED SPECTRUM OF ψ'-PROPYL BOROXINE

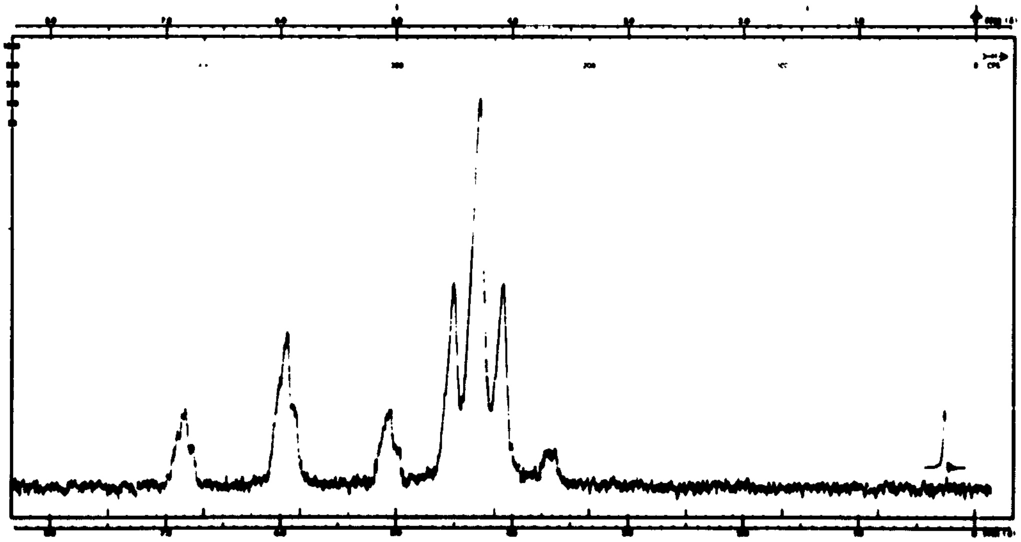

FIGURE 10
H^1 NMR SPECTRUM OF BOROXINE-BORATE SOLUTION

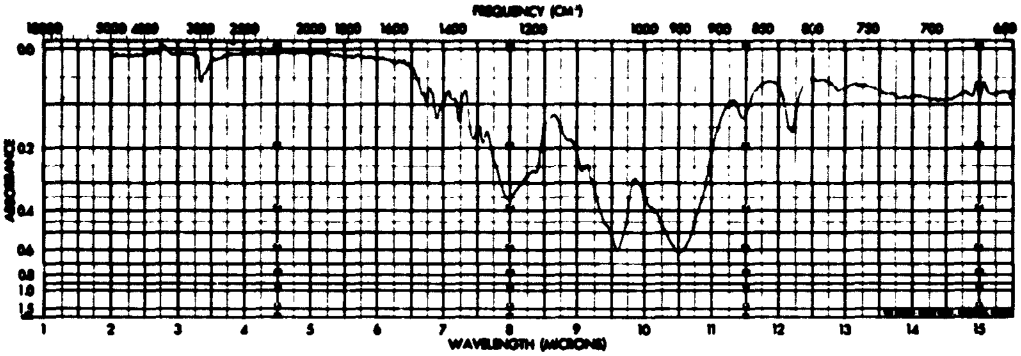

FIGURE 11

INFRARED SPECTRUM OF ETHOXYDIFLUOROBORANE TRIMER

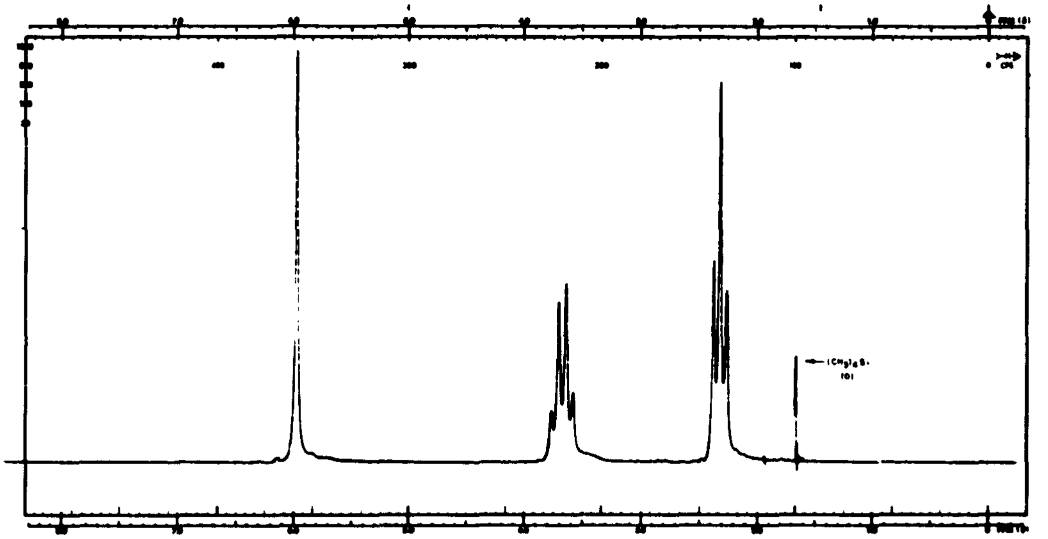

FIGURE 12

H^1 NMR SPECTRUM OF ETHOXYDIFLUOROBORANE TRIMER

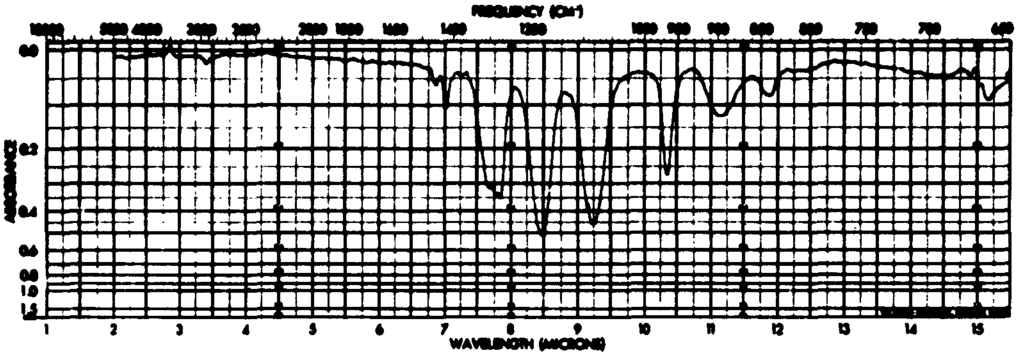

FIGURE 13
INFRARED SPECTRUM OF 2, 2, 2-TRIFLUOROETHYL PHOSPHATE

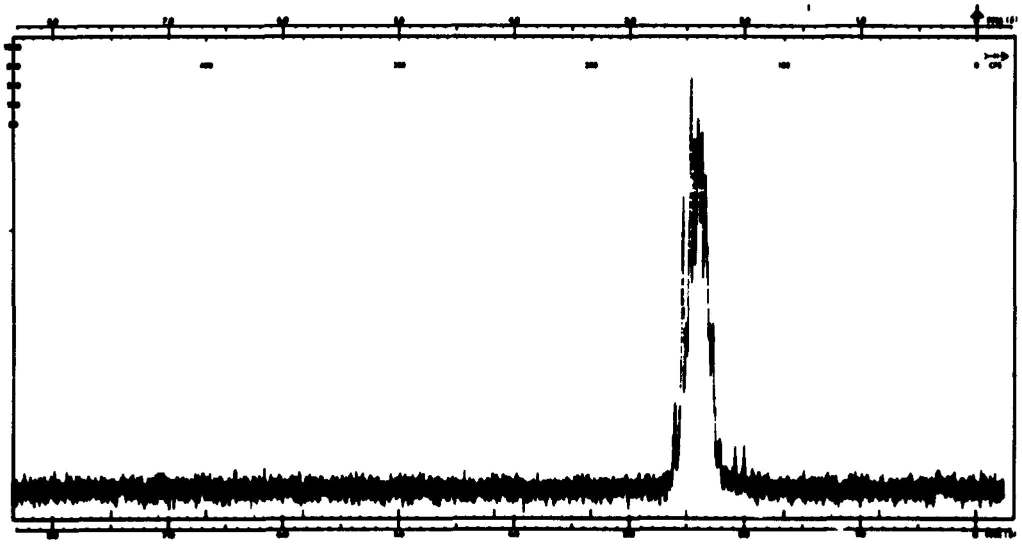

FIGURE 14
H^1 NMR SPECTRUM OF 2, 2, 2-TRIFLUOROETHYL PHOSPHATE

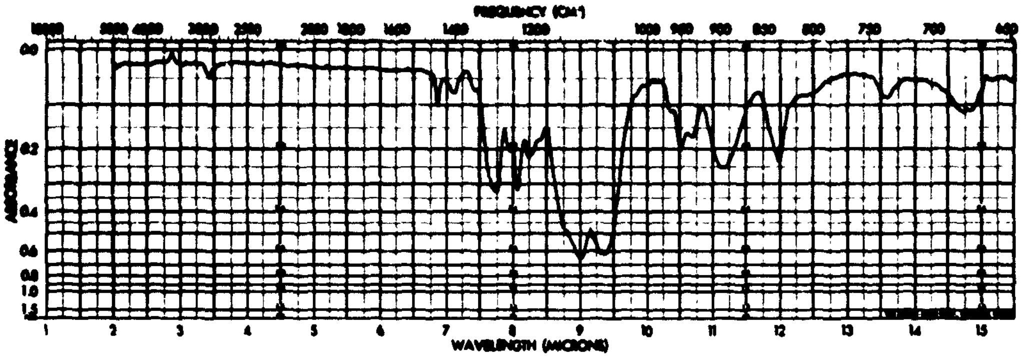

FIGURE 15
INFRARED SPECTRUM OF ψ'-PROPYL PHOSPHATE

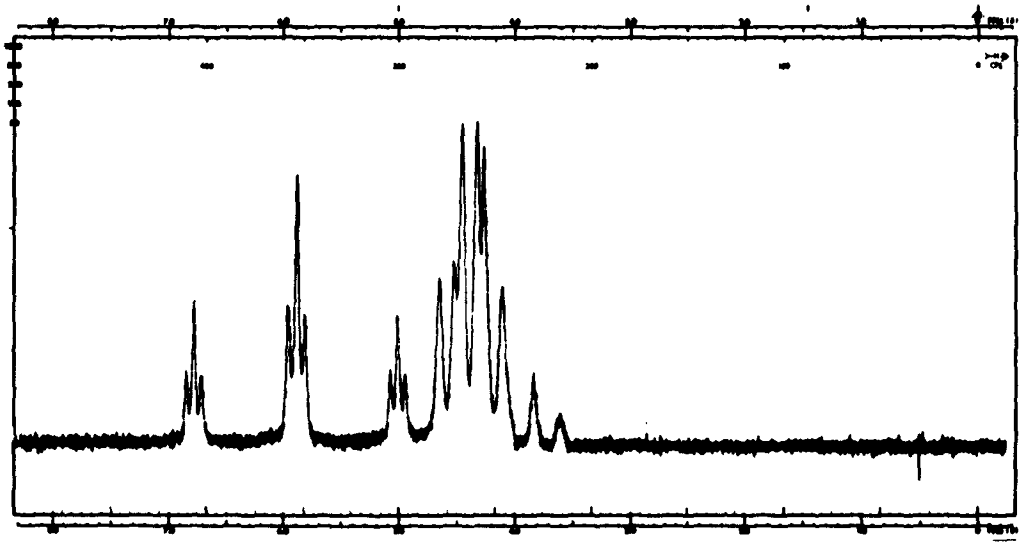

FIGURE 16
H^1 NMR SPECTRUM OF ψ'-PROPYL PHOSPHATE

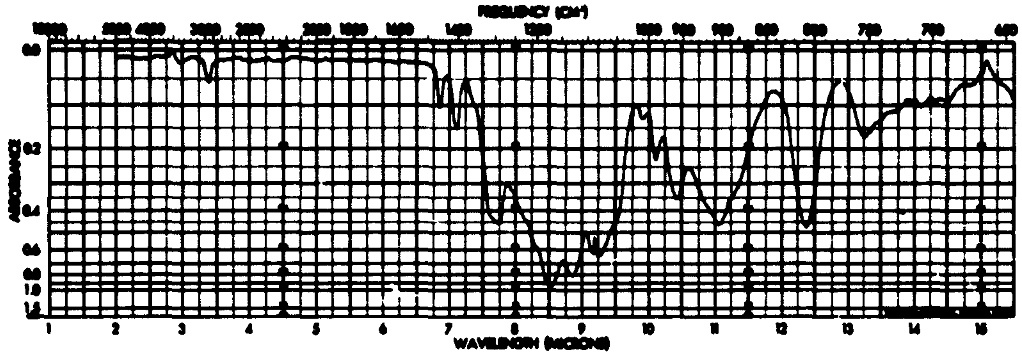

FIGURE 17
INFRARED SPECTRUM OF ψ'-AMYL PHOSPHATE

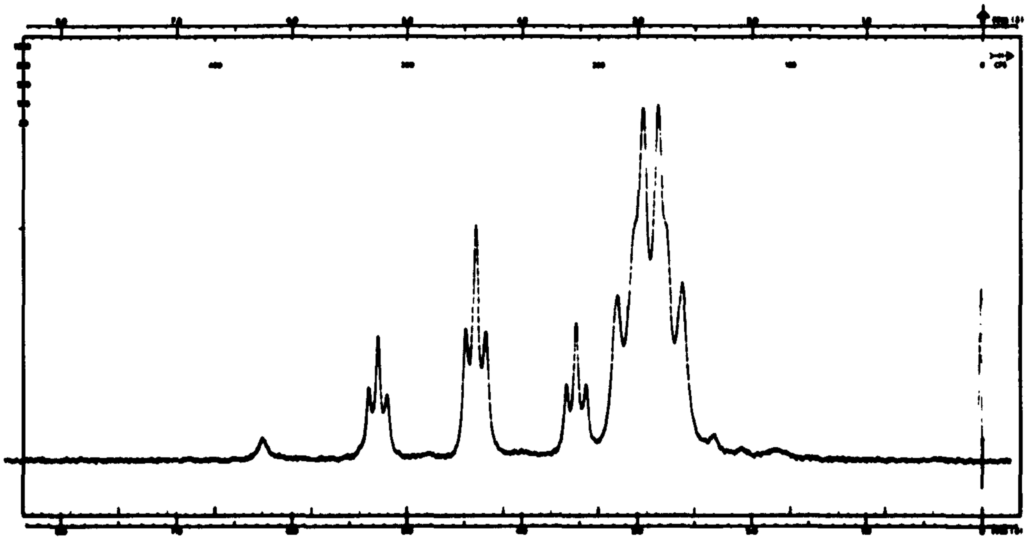

FIGURE 18
H^1 NMR SPECTRUM OF ψ'-AMYL PHOSPHATE

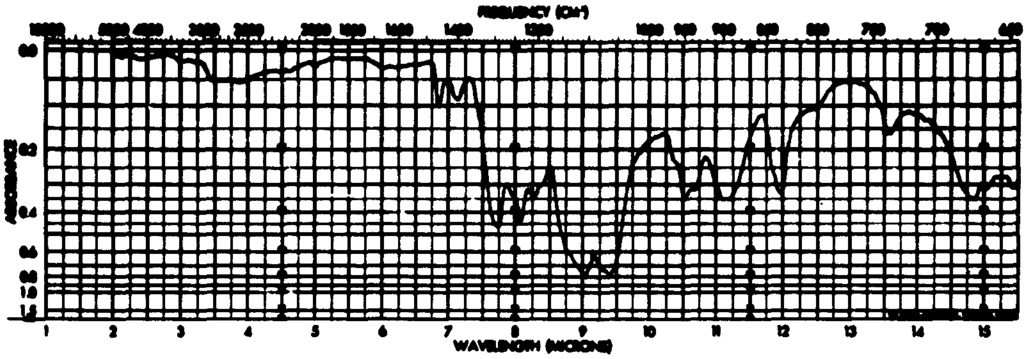

FIGURE 19

INFRARED SPECTRUM OF ψ'-PROPYL POLYPHOSPHATE

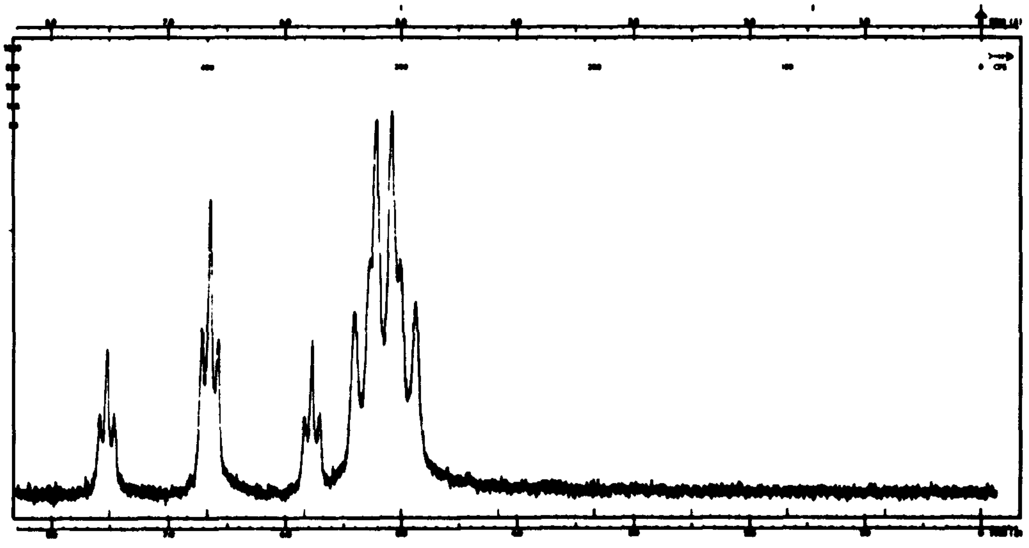

FIGURE 20

H^1 NMR SPECTRUM OF ψ'-PROPYL POLYPHOSPHATE

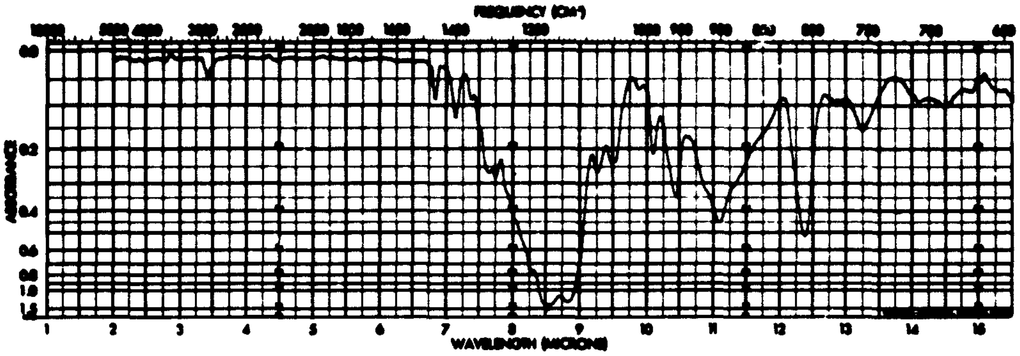

FIGURE 21
INFRARED SPECTRUM OF ψ'-AMYL SILICATE

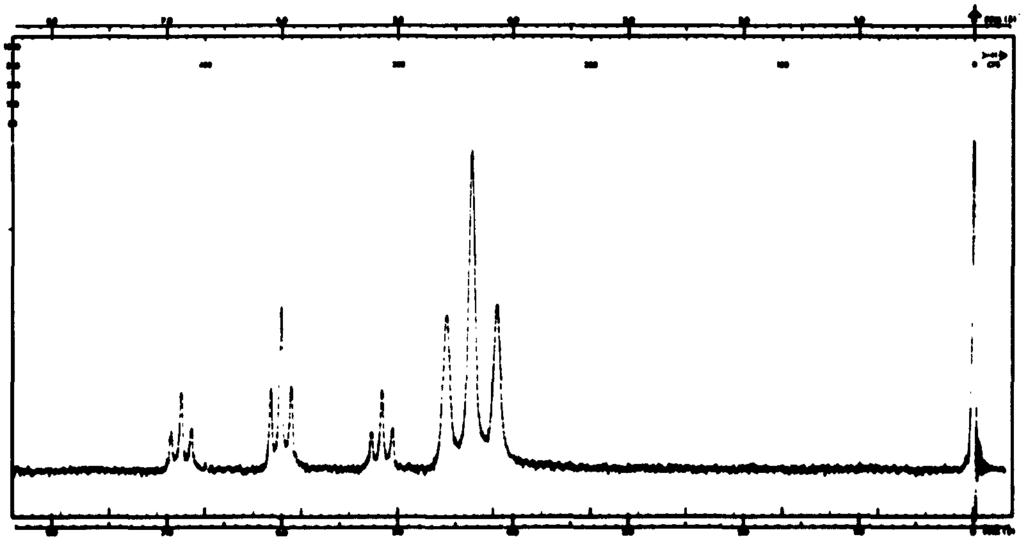

FIGURE 22
H^1 NMR SPECTRUM OF ψ'-AMYL SILICATE

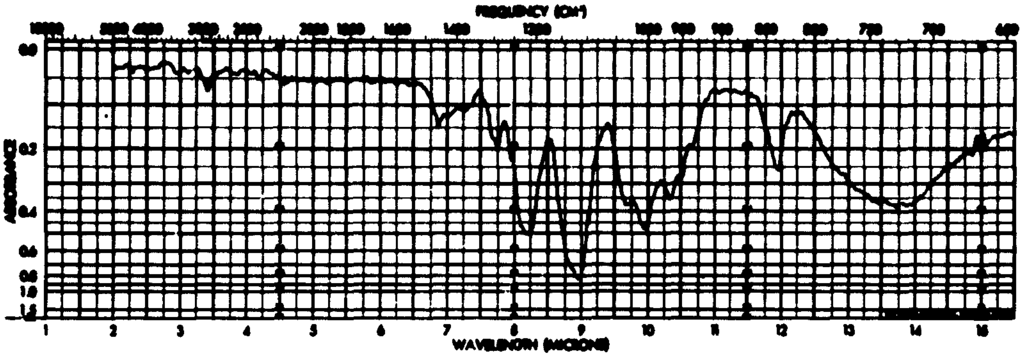

FIGURE 23
INFRARED SPECTRUM OF ψ'-PROPYL SULFITE

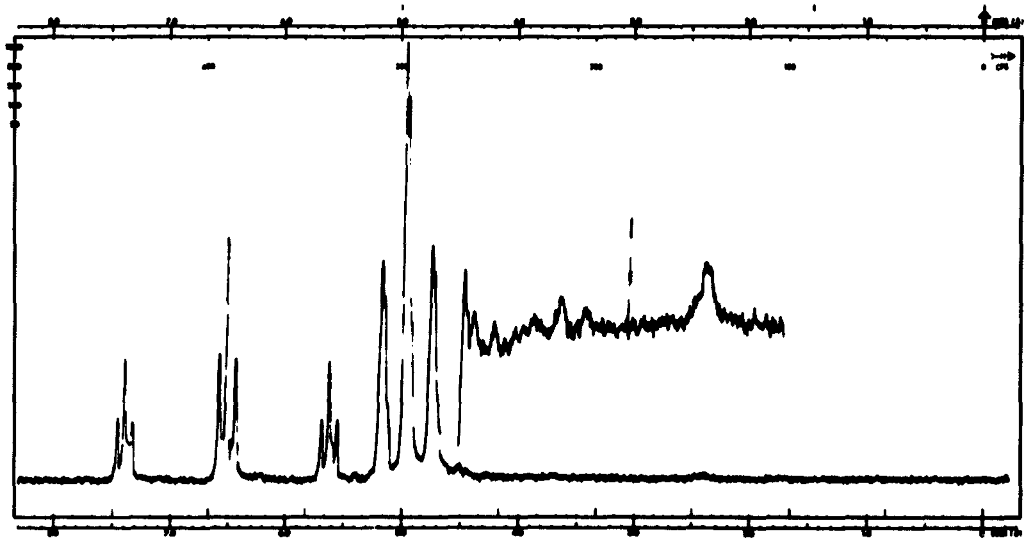

FIGURE 24
H^1 NMR SPECTRUM OF ψ'-PROPYL SULFITE

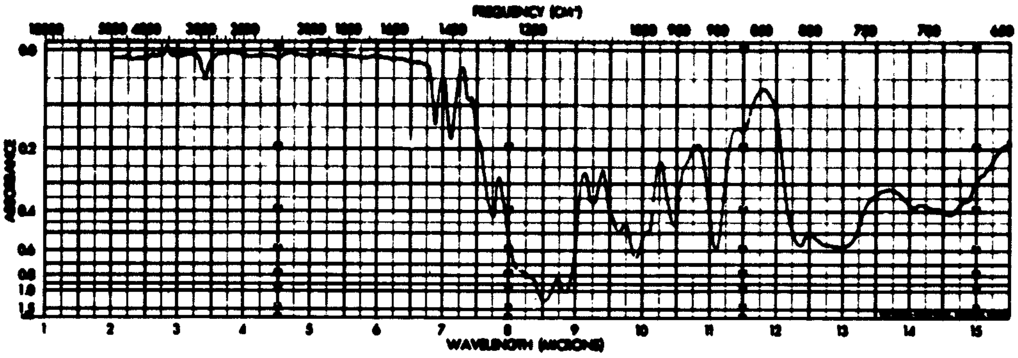

FIGURE 25
INFRARED SPECTRUM OF ψ'-AMYL SULFITE

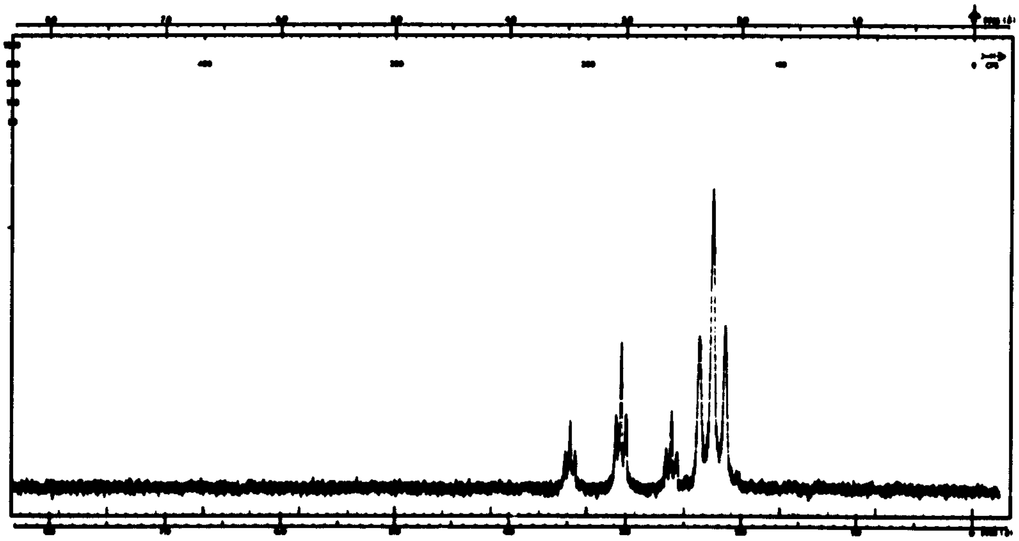

FIGURE 26
H^1 NMR SPECTRUM OF ψ'-AMYL SULFITE

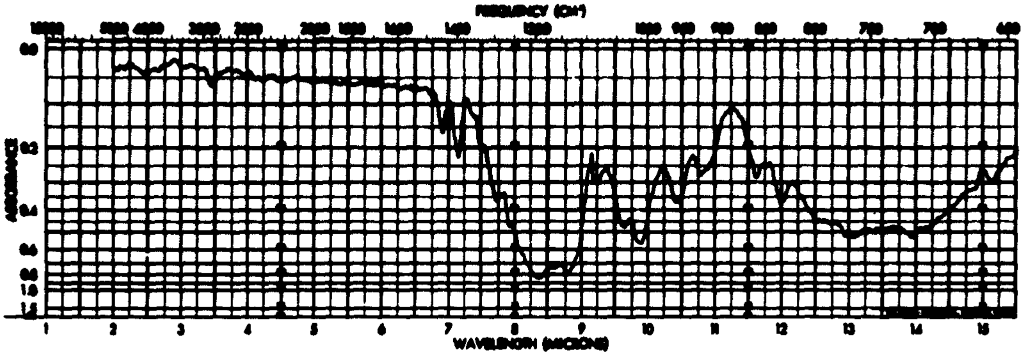

FIGURE 27
INFRARED SPECTRUM OF ψ'-HEPTYL SULFITE

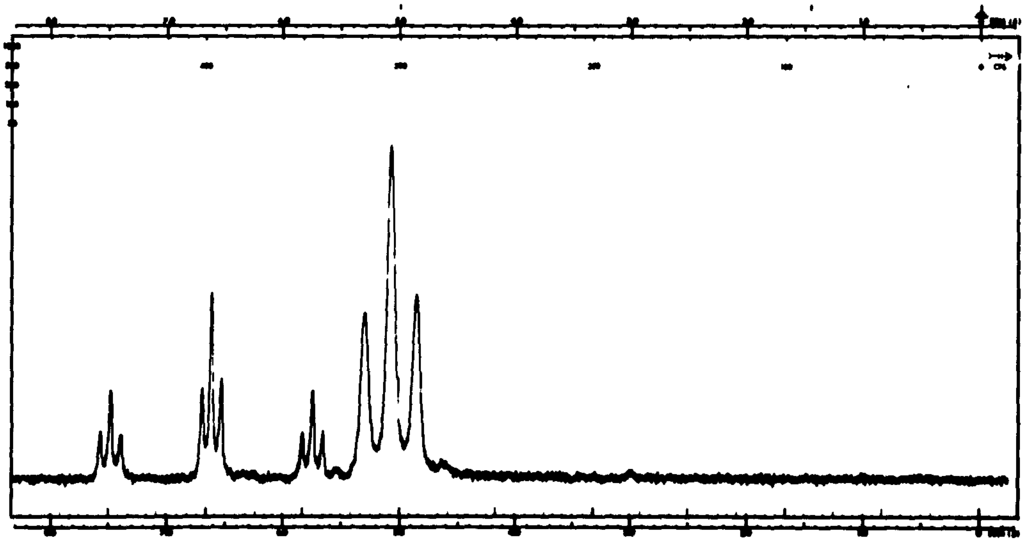

FIGURE 28
H^1 NMR SPECTRUM OF ψ'-HEPTYL SULFITE

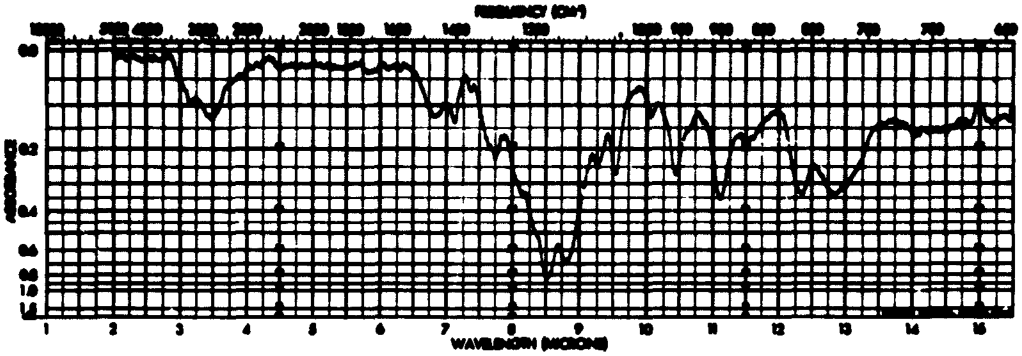

FIGURE 29
INFRARED SPECTRUM OF ψ'-AMYL ALUMINATE

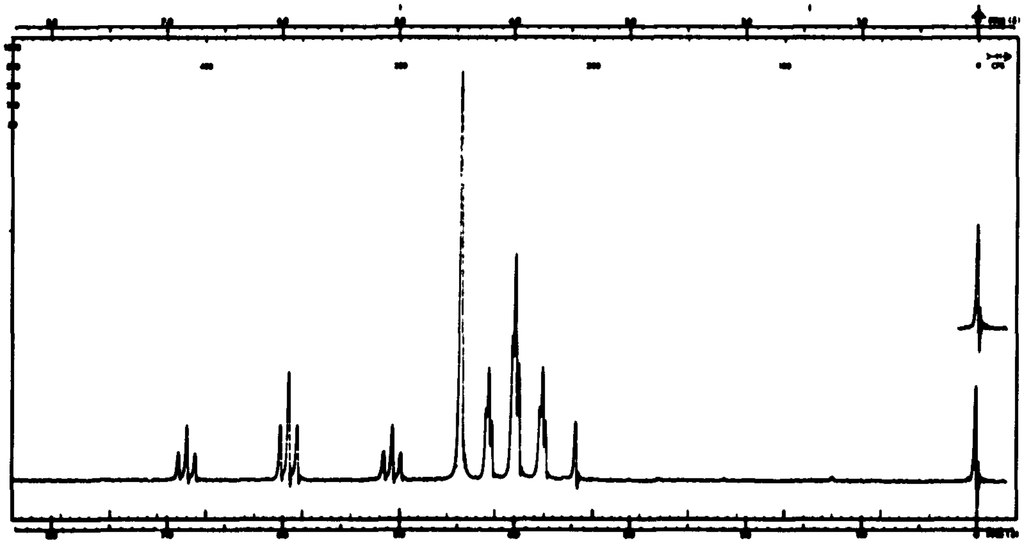

FIGURE 30
H^1 NMR SPECTRUM OF ψ'-PROPYL ALCOHOL

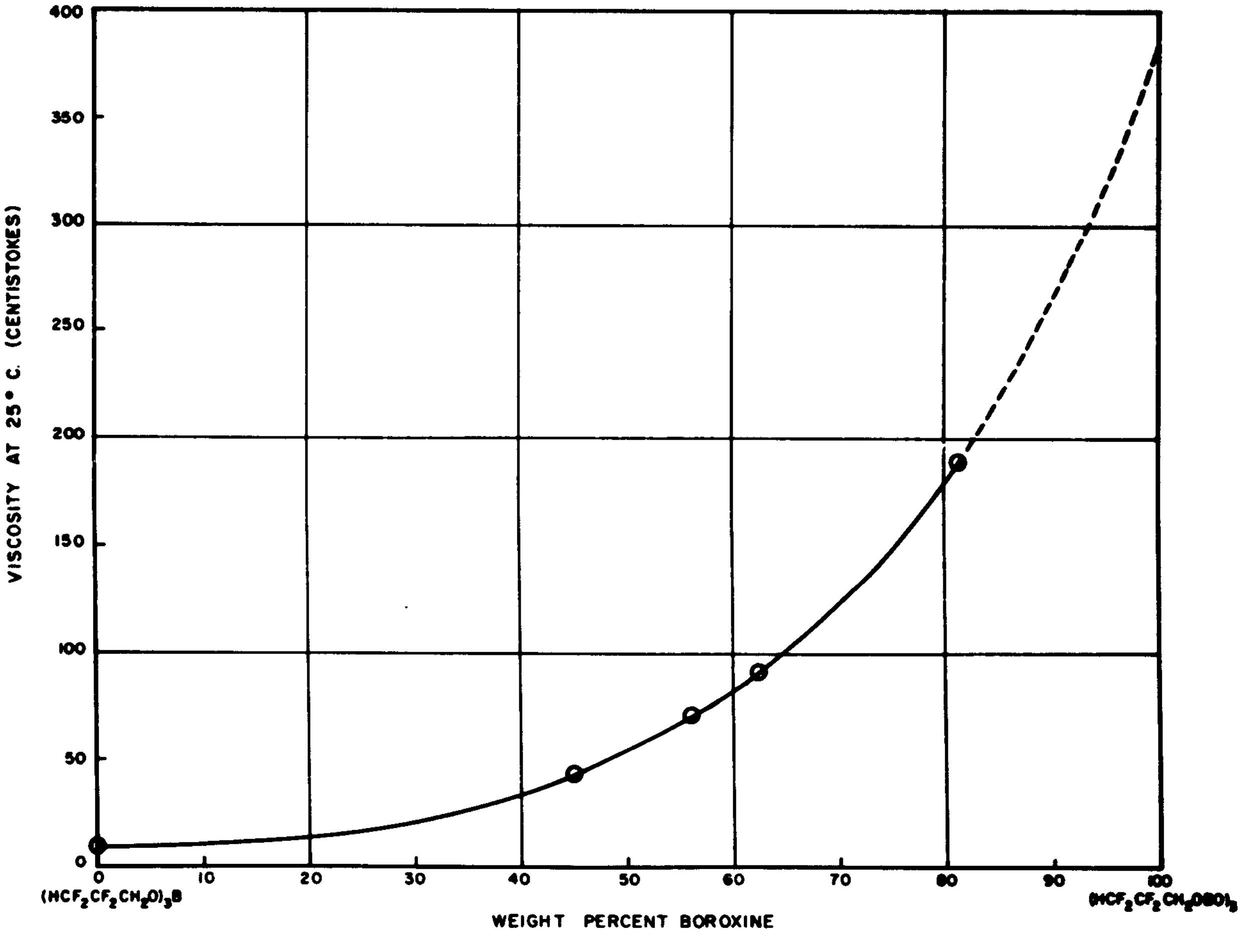

FIGURE 31

VISCOSITIES OF ψ'-PROPYL BORATE SOLUTIONS OF ψ'-PROPYL BOROXINE