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GELLING OF LIQUID OXYGEN DIFLUORIDE

By

A. J. Beardell

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract NAS 3-4180

Thiokol CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

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FINAL REPORT

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Cleveland, Ohio
Liquid Rocket Technology Branch
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Reaction Motors Division
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FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, under Contract NAS 3-4180. This work is administered under the technical direction of the Liquid Rocket Technology Branch, NASA Lewis Research Center.

The research effort reported here was conducted during the period 18 November 1963 to 17 November 1964 on RMD Project 5039. Principal contributors to the research described are: Dr. A. J. Beardell (Project Supervisor), T. Hirata (Research Chemist), E. Avrutik (Research Chemist) and R. Mahar (Chemist).

GELLING OF LIQUID OXYGEN DIFLUORIDE

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Thiokol Chemical Corporation

ABSTRACT

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A study was performed to gel liquid oxygen difluoride, to characterize the candidate system, and to determine its mechanical and chemical stability. Inorganic fluorides and oxides were screened as possible OF_2 gellants and Cab-O-Sil, a pyrogenic silica, was chosen as the candidate gellant. OF_2 was also gelled with Alon C and TiO_2 although the gels did not appear to be of comparable quality.

The OF_2-Cab-O-Sil gel was evaluated for thermal stability, mechanical stability, evaporation rate relative to liquid OF_2 and shock sensitivity, and was shown to have satisfactory characteristics. Quantitative rheological data were not obtained.

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GELLING OF LIQUID OXYGEN DIFLUORIDE

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I. SUMMARY

The object of this program was to gel liquid OF_2 and to evaluate the gel in terms of its chemical and structural stability. Because of the high reactivity of the OF_2 with most organic and inorganic material, it was only possible to consider those substances which are in the oxidized state. The two classes of compounds that were screened were inorganic oxides and fluorides. The inorganic oxides SiO_2(Cab-O-Sil), Al_2O_3(Alon C) and TiO_2 were found to successfully gel OF_2, while none of the fluorides tested were found suitable.

The OF_2-Cab-O-Sil gel was subjected to a number of tests in order to determine its chemical and mechanical stability. The gel was stored for 9 weeks at -78°C without undergoing any reaction. It gave a low brisance as determined in a modified Trauzl test, was stable to centrifugation, and did not exude liquid when stored in an inverted position. Evaporation data on the OF_2-Cab-O-Sil gel indicate that the gel has a somewhat slower rate of evaporation than OF_2 alone. The recommended concentration of Cab-O-Sil in OF_2 is 4 to 5% bw (3.3 to 4.3 volume percent).

Limited attempts were made to obtain rheological data on the OF_2-Cab-O-Sil gel using both rotational and capillary viscometer techniques, but were not successful. OF_2 gelled with Alon C and TiO_2 were chemically stable at -196°C after four days storage and are possible alternates to the OF_2-Cab-O-Sil system.

II. INTRODUCTION

In recent years, there has been an increasing interest in the gelation of liquid propellants for rocket applications. This interest has been generally attributed to several reasons, minimizing the safety hazards associated with the handling of propellants, reducing sloshing in propellant tankage, lowering evaporation rates of volatile liquids, and suspending energetic solid powders in the gelled material.

The interest in oxygen difluoride as a space storable oxidizer has led to corresponding interest in using it in the gelled form. The primary purpose for gelling OF_2 is to reduce sloshing that may occur even in low ullage tankage. Gelling OF_2 might also reduce the hazards associated with its handling and decrease the evaporation rate relative to that of the liquid.

Oxygen difluoride is a liquid between -224°C (mp) and -145°C (bp) and is considered to be a cryogenic material. Studies of cryogenic gels are very meager although a limited effort has been made to gel liquid N_2 (Ref 1) and liquid H_2 (Ref 2). Colloidal silica gel and carbon were used to gel liquid N_2; liquid H_2 could also be gelled but large amounts of gellant (30 to 50% bw) were required. For this reason efforts have been made to use fuel type gellants ($LiBH_4$) that can contribute to the energetics of the fuel.

The approach that was taken to gel liquid OF_2 was to disperse fine particles of solid in the liquid. These fine particles should remain in suspension and should be linked in a three dimensional network which imparts some rigidity to the total mass. Two types of gellants are generally considered, long chain polymers that might dissolve (or disperse as colloidal particles) in the liquid and form a gel through entanglement and crosslinking and particulate gelling agents. Unfortunately the substances of the first type are organic in nature and their use is limited because of the strong oxidizing power of OF_2. The only organic polymers that may be useful are perfluorinated materials such as Teflon or Viton. Recent work at Thiokol-RMD had made use of Viton as an oxidizer gellant (Ref 3). The mixture proved to be a hazard and it was concluded that any substance containing the C-C bond is susceptible to attack by the oxidizer.

The particulate type of gellants offer the best possibility of gelling OF_2. They consist of finely divided substances, less than 1μ in size which will easily disperse in OF_2 and are compatible with it. The only substances of this nature which are available are inorganic oxides such as SiO_2 and Al_2O_3 as well as various carbon black preparations. The utilization of carbon is not recommended because of the potential monopropellant character of such a mixture. However, the inorganic oxides offer good possibilities as OF_2 gellants.

Oxygen difluoride reacts spontaneously with many oxides but frequently the reaction can only be initiated by the use of heat or other source of initiation. Thus, CaO reacts with OF_2 only on heating (Ref 4). SiO_2 may react with OF_2, but the literature does not appear to be clear as to whether SiO_2 reacts with OF_2 or with impurities in the oxidizer. It has been reported, for example, that OF_2 is compatible with glass if it is sufficiently pure (Ref 4).

Another possible source of OF_2 gellants are inorganic fluorides, fluorosilicates and fluoroborates. These substances most likely are compatible with OF_2. However, they are not always available in sufficiently fine particle size to make them useful as gellants. At Thiokol-RMD a study had been performed previously in which attempts were made to prepare simple fluorides in fine particle size by vapor sublimation, chemical precipitation and mechanical grinding (Ref 3). The vapor sublimation method was tedious and very low yields were obtained. Colloidal size particles were obtained by chemical precipitation but upon separating them from the mother liquor, the particles tended to grow. Mechanical grinding failed to produce particles below 1μ in size. However, Monsanto has prepared complex fluoride salts which were reported to be useful gellants (Ref 5). In view of this it was considered worth while to investigate simple and complex inorganic fluorides as OF_2 gellants.

The OF_2 gel study includes the preparation of a candidate system and the determination of its mechanical and chemical stability for extended periods of time. The results indicate that it is possible to gel OF_2 using small amounts of gellant (3 to 5% bw) and that the gelled system is stable under storage conditions.

III. EXPERIMENTAL

A. APPARATUS AND PROCEDURES

1. OF_2 Handling

To transfer OF_2 from commercial cylinders with safety, it was necessary to construct a remote handling transfer line. The cylinder of OF_2 is tapped remotely into a metal vacuum line from which it is condensed into a 25 cc Hoke cylinder and small quantities are then removed from this cylinder, as required.

2. Gel Preparation

In the initial phases of this work the method of mixing OF_2 with a candidate gelling agent was as follows: a weighed amount of gellant and a glass enclosed magnetic bar were placed in a flask fitted with a ball joint. The assembly was then attached to a vacuum manifold and evacuated. A measured amount of OF_2 was then condensed into the flask at -196°C, the dewar of liquid N_2 was removed, and the contents were mixed with a magnetic stirrer for a few seconds. Before the liquid OF_2 attained an appreciable pressure, the flask was recooled, OF_2 recondensed, and the cycle was then repeated.

This was obviously a tedious and inefficient procedure. Stirring could only be maintained for a few seconds since the OF_2 pressure rapidly increased. Condensation of water on the flask made visual observation difficult. In addition, the manual procedures involved made the operation hazardous.

As a consequence of these difficulties, the following mixing apparatus was fabricated and used in all the gelation experiments reported herein. The apparatus, shown in Figure 1, consists essentially of three parts: (1) mixing tube, (2) stirrer and (3) housing. The mixing tube (1) is a ball jointed tube into which the gellant is placed and weighed. The stirrer is a glass rod with a broad flattened end with or without spirals and attached to its upper end is a glass encased bar magnet (4). The stirrer passes through guide sleeve tubing (5) which is ring sealed to the housing. The stirrer is positioned by a pair of split Teflon washers (6) which are friction fitted into the guide sleeve tubing at the bottom and top of the housing. A ball type T/S outer joint with a Teflon

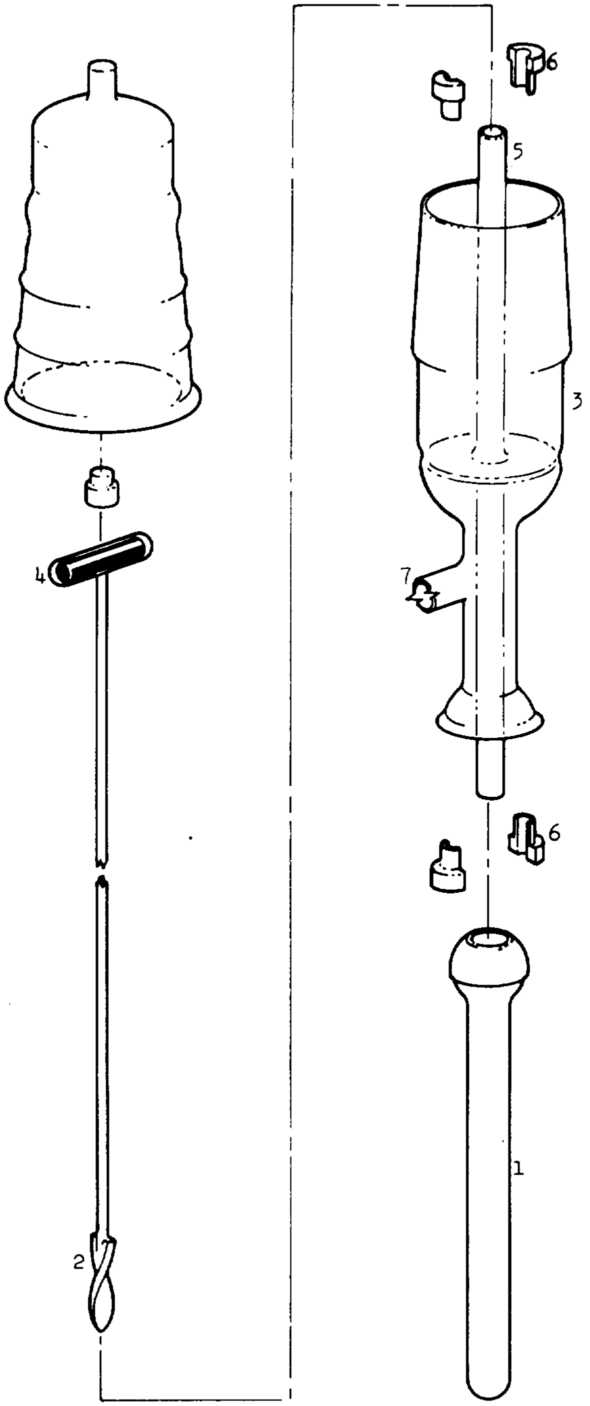

Figure 1. OF_2 Gel Mixing Apparatus

shock absorber is fitted into the top slot and placed on the housing. The shock absorber prevents severe damage if the bar magnet is suddenly pulled upwards. The stirrer is activated by use of a stirring magnet positioned above the outer joint cover. Evacuation of the apparatus and admission of OF_2 to the mixing tube is accomplished through the side arm (7).

Using a partially silvered dewar, the stirring of the gellant and OF_2 mixture could be observed easily, continuously, and with relative safety.

3. Gellant Characterization

Sedimentation Volume - For the determination of sedimentation volume, standard 50 cc graduated cylinders were used. A weighed amount of the solid was transferred to the graduated cylinder and diluted to volume with toluene. The settling tube was then inverted end over end eight to ten times to disperse the solid particles throughout the volume. The solid was then permitted to settle to a constant volume. The settled volume of the solid is the sedimentation volume. Knowing the quantity of solid, the specific sedimentation volume (volume in cc/g of solid powder) can be determined.

Surface Area Measurement - The surface area measurements on selected materials were performed using an adsorption flow apparatus (Nuclear Materials and Equipment Corporation). The method, developed by Innes, is a single point measurement consisting of the approximation of equilibrium adsorption conditions by maintaining a small constant flowrate of gas over the sample (Ref 6).

Thermal Analysis - Differential Thermal Analysis of the gellants was performed using a commercial instrument, Model 14AC-2 obtained from Robert L. Stone Co., Austin, Texas.

4. Storage Stability Tests

The chemical interaction between OF_2 and candidate gellants was investigated at $-196^{\circ}C$ and at $-78^{\circ}C$.

The procedure used to perform the runs at $-196^{\circ}C$ was as follows: The gelling agent was first weighed into a glass tube fitted with a stopcock and a known amount of OF_2, measured as a gas, was condensed over it. The tube was then stored in a large dewar of liquid N_2. It was desirable to maintain the tubes at $-196^{\circ}C$ for several days and an automatic liquid N_2 leveling device was used for the purpose (Cryogenics, Inc., Alexandria, Va).

At the termination of the storage period the sample tube was connected to the vacuum line, held at -196°C and the stopcock was opened. Any non-condensable gases present at this temperature could be measured on a mercury manometer. The liquid N_2 was then removed, the gases expanded into the manifold, measured, and sampled for mass spectral analysis. The solid residue was retained for fluoride analysis.

In the storage tests at -78°C the gelling agents were weighed into Kel-F tubes which were attached to metal valves by means of Swagelock connectors. After evacuation, sufficient liquid OF_2 to cover the solids was condensed in the tube at -196°C. The mixtures were then stored at -78°C where liquid OF_2 has a vapor pressure of approximately 500 psi. The first samples were stored in short Kel-F tubes (3 in.) so that the entire system including the metal valves were buried in Dry Ice. These samples leaked, possibly because of the difference in thermal expansion of the metal and Kel-F and the high pressure of OF_2 at -78°C. This was rectified by increasing the length (6 in.) and only immersing the Kel-F tube portion. At the termination of the test, gases were sampled and analyzed with a mass spectrometer, particularly for the presence of excess oxygen, or, in the case of Cab-O-Sil gellant,for oxygen and SiF_4. The residual solids were heated under vacuum and then analyzed for the presence of fluoride.

5. Rheology

Attempts were made to obtain flow property measurements on OF_2-Cab-O-Sil gels with a modified rotational viscometer (Epprecht Rheomat RM 15) The modification consists in using a glass bob which can be attached to the metal coupling of the rheomat and a glass cup, both of which have approximately the same dimensions as a bob-cup pair used under ordinary conditions. A slow helium flow over the gel was used to prevent condensation of water vapor or O_2 into the system. A calibration was obtained using the above apparatus with a water-Carbopol gel whose flow curve was also obtained on the unmodified apparatus.

For a given run, the gel was mixed in the cup in the usual manner and the cup, with a helium atmosphere over the gel, was transferred to the rheomat which was provided with a liquid N_2 bath to maintain the gel at -196°C. The glass bob, previously cooled, was then carefully inserted into the gel and attached to the chuck of the rheomat. The chuck was provided with a shoulder attachment to prevent it from touching the wall of the cup.

A Brookfield Model LVF rotating viscometer and a capillary flow apparatus were also employed in an attempt to measure the flow properties of cryogenic gels. The capillary apparatus consists of a glass mixing tube to which a capillary tube is attached. The apparatus was constructed in such a way that one side of the tube containing the gel was pressurized (at 1 to 100 mm Hg) to force the gel through the capillary, the other side being under vacuum. The assembly was sufficiently compact so that it could be immersed in liquid N_2 in a 300 ml dewar.

6. Mechanical Stability Tests

Inverted Tube Test - The gellant-OF_2 mixture was sealed in a thick walled glass tube one end of which was a length of calibrated capillary tubing. Gelation was attained by vigorous manual shaking of the sealed ampoule. The gel was then stored under liquid N_2 in an inverted position. The liquid OF_2 exuded from the gel was derived from measuring its volume in the calibrated capillary section.

Centrifuge Tests - The gels for this test were prepared in the low temperature mixing apparatus described previously. After vigorous stirring, the ball jointed tube was removed from the apparatus under a helium atmosphere, reattached to the vacuum system, evacuated and flame sealed. The samples were then centrifuged under liquid N_2 by placing them in centrifuge tubes attached to a shaft turned by a heavy duty drill. The rotational speed of the drill shaft was measured by use of a tachometer. Knowing the rotational speed (1/T) (where T is the time in seconds needed for 1 revolution) and the distance from the axis to the perimeter of the tube (r), the g force was calculated by use of the formula $g = 4\pi^2 r/T^2 32$. In our studies, the gel was exposed to a g force of 30-40 g for 1/2 hour.

7. Shock Sensitivity Tests

The shock sensitivity of the OF_2 gels was examined by use of a modified Trauzl block test. The test apparatus consists of a lead cylinder 2 in. OD, 2.4 in. high with a 1 in. ID hole in the center, and a No. 8 blasting cap. A known amount of OF_2 was condensed at $-196^\circ C$ over the gellant in a glass or Kel-F vial and the lead block with the blasting cap in place was positioned around the test vial. This operation required approximately 20 sec, so that the OF_2 was still in the liquid state. Immediately, the blasting cap was exploded and the expansion of the block, with a consideration of the effect of the blasting cap, was taken as a measure of the brisance of the material.

8. Evaporation Rates

The vaporization rates of neat and gelled OF_2 were determined at -160°C where the liquid has a vapor pressure of approximately 200 mm Hg. The samples were maintained at -160°C with an isopentane slush bath and allowed to distill into a calibrated tube at -196°C. The volume of distillate was read from the calibration marks and the time was marked on a stop watch. One OF_2 gel was prepared in the mixing apparatus, and another was made by mixing OF_2 and gellant with a Kel-F coated stirring bar. Mixing was accomplished by vertically agitating the stirring bar with a magnet.

B. MATERIALS

The oxygen difluoride employed on this program was obtained from Allied Chemical Corporation. The material as received is 97% pure, the major impurities being CO_2 and CF_4. Prior to use the OF_2 was further purified to approximately 99% + by vacuum distillation.

The principal gellants used on this program were obtained from Cabot Laboratories. Some of their characteristics are shown below:

Material	Trade Name	Particle Size (millimicrons)	Surface Area (m^2/g)
SiO_2	Cab-O-Sil	8-15	175-225
TiO_2	P-25	33	45
Fe_2O_3	E-7	20	35
Al_2O_3	Alon C	10-40	50-100

The complex fluoride salts used on this program were prepared using procedures presented in a classified report (Ref 5).

IV. RESULTS AND DISCUSSION

A. GELLANT CHARACTERIZATION

The inorganic fluorides and oxides offer good possibilities as OF_2 gellants. However, the factors which may influence the ability of a particular substance to gel OF_2, while qualitatively predictable, are uncertain. The particle size and surface area of the gellant certainly are important factors but interparticle attractions must be sufficiently strong in the dispersing medium to result in true gelation.

A means of indirectly measuring relative particle size and adhesion between particles is through a knowledge of the sedimentation volume of a powder. The sedimentation volume is defined as the volume occupied by unit weight of particulate matter in a liquid medium when allowed to settle under gravity at some specified standard condition. Generally, the finer the particle size and the higher the adhesion forces the larger is the sedimentation volume (Ref 7).

The sedimentation volume and to a lesser extent the surface area were used as a means of screening the candidate gellants. It was assumed that those substances which have large sedimentation volumes and large surface areas possess characteristics which will make them useful as OF_2 gellants.

1. Sedimentation Volume Studies

a. Inorganic Fluorides

Shown in Table I are the equilibrium sedimentation volumes for 11 inorganic fluorides in toluene. The substance which has the largest value (10 cc/g) is lithium fluoride which has an average particle size of approximately 1 μ. The remainder of substances screened have values close to that of the undispersed material. This essentially means that the particle size is quite large, that they undergo minimum solvation and the particles pack in a manner similar to that in the dry state. For these reasons, the fluorides tested were considered not to be suitable as OF_2 gellants, with the possible exception of LiF.

TABLE I

SEDIMENTATION VOLUMES OF INORGANIC FLUORIDES

Component	Source	Sedimentation Volume (cc/g)
LiF	Baker	10.0
CaF_2	Mallincrodt	2.9
CoF_2	Harshaw	2.4
MgF_2	Matheson, Coleman and Bell	1.9
KBF_4	Harshaw	1.6
NiF_2	Baker	1.5
BaF_2	Harshaw	1.5
Aluminum Sodium Fluosilicate	Amend Drug	1.2
$MgSiF_6$	Amend Drug	1.1
$CaF_2 \cdot 2H_2O$	Baker	1.1
K_3CrF_6	Harshaw	1.0

b. Inorganic Oxides

The sedimentation volume measurement of twenty candidate oxide gellants was also carried out. The results of this investigation are shown in Table II. Of the oxides investigated, the Monsanto Al_2O_3, Alon C, Fe_2O_3 and TiO_2 have reasonably high sedimentation volumes. Attempts to obtain data on Cab-O-Sil, a pyrogenic silica gel were not successful, probably because the particles are of colloidal dimension and will not settle under gravity.

The Monsanto Al_2O_3, while it has a reasonably high sedimentation volume (40 cc/g), is of doubtful utility as an OF_2 gellant because it contains acetic acid, which is reactive with the oxidizer.

The iron oxide is an extremely fine powder that did not wet toluene. For this reason, it was necessary to use water as the dispersing medium. The comparison of the value on iron oxide (26 cc/g) and other oxides appears to be valid since others have found that the sedimentation volume is only slightly affected by the liquid (Ref 7). As long as the liquid medium does not permit flocculation of the particle, the value should be independent of the liquid used.

Attempts were made to obtain sedimentation data for Cab-O-Sil using different liquid medium (toluene, CCl_4, H_2O), however, in no case was a value obtained.

TABLE II

SEDIMENTATION VOLUMES OF INORGANIC OXIDES

Material	Vendor	Sedimentation Volume (cc/g.)
Micra Al (Al_2O_3)	Monsanto	40.0
Alon C	Cabot Laboratories	30.0
Fe_2O_3 (Pyrogenic)	Cabot	26.0$^+$
TiO_2	Cabot	25.0
Cr_2O_3	Baker	3.6
Zinc Borate	Amend Drug	2.8
P_2O_5	Baker	2.5
Fe_2O_3	Fisher	2.3
MgO	Merck and Co.	2.2
CaO	Matheson, Coleman and Bell	2.1
Talcum	Fisher	1.9
B_2O_3	------	1.7
B_2O_3	Baker	1.7
NiO	------	1.6
Aluminum Borate	Amend Drug	1.5
SnO_2	Baker	1.5
PbO	Baker	1.3
Co_2O_3	Baker	0.8
BaO_2	Baker	0.78
Cab-O-Sil	Cabot	++

$^+$ In water

$^{++}$ No value could be obtained (see text).

In view of the above results, the Cab-O-Sil, Fe_2O_3, Alon C and TiO_2 were considered for evaluation as OF_2 gellants.

2. DTA and Surface Area Measurements of Candidate Gellants

The ability of a particular substance to gel OF_2 may be affected by adsorbed impurities and the OF_2 may react with impurities such as water which is most likely present on fine powder surfaces. For these reasons it was considered desirable to perform differential thermal analysis on the candidate gellants. The region where thermal changes occur may be attributed to such factors as dehydration, phase changes or reactivity.

The candidate gellants, Cab-O-Sil, Alon C, TiO_2, Fe_2O_3, Micra Al (Monsanto Al_2O_3), were studied as well as MgO which was investigated as a standard. Alon C had a peak at 110°C which is attributed to water desorption and some smaller peaks up to 400°C. These peaks are either intermolecular conversions or evolution of other adsorbed materials. Cab-O-Sil, TiO_2, Fe_2O_3 and Monsanto Al_2O_3 had no thermal change up to 400°C. MgO had only one peak at 330°C which is no doubt due to a phase change.

Using the NUMEC Adsorption Flow apparatus the surface area of Cab-O-Sil was measured and a value of 196 m^2/g was obtained. This high value is not surprising in view of the fine particle size of the material. The value reported by the manufacturer, Cabot Laboratories, Inc. is 175-225 m^2/g.

B. OF_2 GEL SCREENING STUDY

The results of the sedimentation volume study indicate that the 4 oxides, Cab-O-Sil, Alon C, TiO_2 and Fe_2O_3 are potential OF_2 gellants and they were screened. The study on the inorganic fluorides indicated that LiF may also be a useful OF_2 gellant. Among the other fluorides investigated were arsenic pentafluoride (AsF_5) which is a gas at room temperature and selected complex fluoride salts which were prepared in our laboratory.

In those cases where a gel was formed, the candidate gellant was investigated for its short term compatibility with OF_2. The compatibility was investigated by analyzing the gas phase and the solid powder for possible reaction products after the mixture was stored for several hours.

With emphasis on safety, the amount of OF_2 utilized in this study in any one experiment was limited to approximately 2 g. This was a sufficient quantity for visual observation and adequate stirring of the mixture could be accomplished.

1. Inorganic Oxides

a. Silica Gel

Prior to the initiation of this program a suspension of Cab-O-Sil (6% bw) in liquid OF_2 was prepared and was found to form a thick gel. No evidence of reaction of the Cab-O-Sil was observed over a period of several hours and the gel appeared to retain its rigidity.

During this program the OF_2-SiO_2 system was reinvestigated. Initially the compatibility of gaseous OF_2 with Cab-O-Sil was examined. Approximately 100 mm Hg pressure of OF_2 was placed in contact with Cab-O-Sil at ambient temperature for 2 days in a quartz container. After this period the gas was sampled and was found to contain SiF_4 by IR analysis. However, there was a possibility that reaction with the quartz vessel occurred. Consequently, liquid OF_2 was mixed with Cab-O-Sil in the Teflon tube and a gel was formed; the mixture was allowed to stand for 4 days at $-196^{\circ}C$ after which the gas phase was analyzed and was found to contain only a trace of SiF_4. In a subsequent experiment, a carefully dried Pyrex glass tube was found to be sufficiently compatible with OF_2 to be of use and therefore was used throughout the remainder of this study.

Shown in Figure 2 is an OF_2-5% Cab-O-Sil gel which indicates its gel nature. The gel will support a magnetic stirring bar which shows that a gel structure was formed.

In one experiment, an OF_2-3.8% Cab-O-Sil gel was maintained at $-196^{\circ}C$ for 18 hours at which time an attempt was made to restir it. At this point the gel began to glow and then it exploded. The liquid nitrogen dewar shattered but the vacuum rack and the upper portion of the mixing vessel were untouched. This reaction is not considered to have been due to any reaction between OF_2 and the Cab-O-Sil. It is more likely that Kel-F grease which was used in the glass system or trace amounts of water, may have reacted with the OF_2. The matter was investigated further in storage stability and shock sensitivity testing which will be discussed later.

b. Aluminum Oxide Gels

The gelation of Alon C, in liquid N_2 and OF_2 was carried out. The Alon C formed a gel with liquid N_2 at a concentration of approximately 7%. The gel had the characteristics of wet sand and after approximately a half hour, settling

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Figure 2. OF_2 Gel Supporting a Metal Rod

of the solid particles was observed. Alumagel, another aluminum oxide gellant, began to settle immediately after mixing. It appears that the forces which are responsible for the gelation characteristics of these substances in liquid N_2 are so weak that the structure does not hold together.

The case is somewhat different when the Alon C is dispersed in OF_2. A 5.5% bw mixture of Alon C and OF_2 forms a thick gel which appeared to remain intact for approximately 5 hours. The gel was not mobile by visual observation and there was no observable liquid layer. An 8.3% Alon C-OF_2 mixture was also prepared which appeared to be stable after 6 hours storage at -196°C. Analysis of the solids indicated 3-4% fluoride.

c. Titanium Dioxide

An OF_2 gel with 5.6% pyrogenic TiO_2 was prepared. The mixture was similar in appearance to a 5.5% Alon C in OF_2 gel. No separation occurred after 4 hours storage; the mixture was relatively thick and appeared to be homogeneous. Wet analysis indicated that there was approximately 1% fluoride in the solid residue after the OF_2 was pumped off.

d. Iron Oxide

Pyrogenic Fe_2O_3 (Cabot 6112) at approximately 6.8% was used to gel OF_2. A thick gel was formed and the mixture was maintained for 50 hours at -196°C. Wet chemical analysis of the residue indicated the presence of 11% fluoride. Thus the iron oxide appears to become fluorinated in the presence of OF_2. In this respect, the work of Clark and Sadana on fluorination is of some interest (Ref 8). They found that the ease of fluorination of metal oxides with BrF_3 differed markedly, such that MgO, ZnO, MnO_2, and Fe_2O_3 did not react or did so slowly, but TiO_2, As_2O_3, SeO_2 were completely fluorinated. Nevertheless from the OF_2 gels, more fluoride was found in the Fe_2O_3 than in the TiO_2 residues.

2. Inorganic Fluorides

a. Simple Fluorides

A mixture of 5% LiF in liquid OF_2 was prepared. Initially the mixture was a slurry which did not appear to thicken and after 5 minutes the LiF began to settle without any apparent effect.

An attempt was also made to utilize arsenic pentafluoride (AsF_5) as a gellant. This compound is a gas at room temperature and has a melting point of -80°C. Therefore, if the AsF_5 is quickly condensed into the liquid OF_2, it may form ultrafine particles which will set up into a gel structure. Furthermore, the As in AsF_5 is highly electropositive and may attract a fluorine from the OF_2 in a H bonding type structure. The coordination shell of As is sufficiently large to accommodate the fluorine as indicated by the existence of the AsF_6 ion (Ref 5).

The gaseous AsF_5 was quickly condensed into stirred liquid OF_2. The AsF_5 solidified but settled to the bottom of the container without gel formation. In this experiment the particles formed were probably too large. It may be necessary to introduce the fluoride into the OF_2 in the form of a jet at low temperatures to effect the formation of the fine particles necessary for gelation. This approach should be pursued further.

b. Complex Fluoride Salts

It is believed that the utilization of simple inorganic fluorides as OF_2 gellants requires that these substances be prepared in colloidal dimensions. As stated previously the only reference to this type of investigation is the work performed at Monsanto in which complex fluorides were used to gel a propellant oxidizer (Ref 5). As a result, a study was undertaken to prepare some of these compounds.

One compound, a barium salt, was prepared in an oxidizer medium, as reported in Ref 5. The oxidizer was then removed from the mixture and OF_2 was added. The mixture was stirred using a Teflon coated stirring bar but no gel appeared to form.

Three additional complex inorganic fluorides were prepared and were tested as OF_2 gellants. In each case gelation of the OF_2 could not be achieved. Factors such as particle size, stirring, and polarity of the liquid may have prevented gel formation. This approach is also worthy of further study.

C. OF_2 GEL CHARACTERIZATION STUDIES

1. Storage Studies

An obvious requirement for a gellant-oxidant system is that the solid and liquid phases should be compatible for a reasonable period of time, perhaps 2 weeks, at temperatures below -145°C, the boiling point of liquid OF_2. A chemical interaction would consume the liquid and destroy the gel. To determine this factor, storage tests were conducted with the 4 candidate gellants (Cab-O-Sil, Alon C, TiO_2 and Fe_2O_3) in OF_2. The tests were performed at 2 temperatures, -196°C, the boiling point of liquid N_2 and at the Dry Ice temperature of -78°C.

a. Storage Tests at -196°C

Samples of each mixture were stored at -196°C for 4 days after which the system was checked for non-condensables. Following this, the OF_2 was separated from the solid and examined on the mass spectrometer. The results of the storage tests are tabulated in Table III.

TABLE III

RESULTS OF FOUR DAY STORAGE TESTS ON OF_2 GELS AT -196°C

Sample No.	Gellant (% bw)	Gaseous Products (mole %) OF_2	Air	CO_2	Fluoride (% bw)
A	Fe_2O_3 (4)	99.5	0.3	0.2	0.25
B	TiO_2 (2)	99.3	---	0.7	0.54
C	Alon C (5)	99.5	---	0.5	0.47
D	Cab-O-Sil (5)	98.5	1.3	0.2	0.21

As can be seen, no oxygen was detected in any of the samples and the gas phase was essentially pure OF_2 indicating no reaction had occurred. These results were confirmed by fluoride analysis on the solid phase where the fluoride analysis was between 0.21 and 0.54% by weight. The CO_2 is an impurity found in the commercial cylinder of OF_2.

In the case of Cab-O-Sil, it was expected that fluorination would lead to the formation of SiF_4. Therefore after obtaining a sample of gas from the storage tube, a simple fractionation was performed to concentrate any SiF_4 present. Mass spectral analysis of this mixture failed to detect any SiF_4.

b. Storage Tests at -78°C

An arbitrary maximum temperature of -145°C where the pressure of OF_2 is one atmosphere was thought to be a reasonable temperature to conduct long term tests. However, because of convenience, these tests were conducted at -78°C using Dry Ice slush baths. The vapor pressure of OF_2 at this temperature is approximately 500 psi. Reactivity was determined by the mass spectroscopic analysis of the gas phase as well as an analysis of the solid phase for the presence of fluorides.

Table IV summarizes the results of the storage tests performed on OF_2 gelled with Alon C, TiO_2, and SiO_2. In each case the systems leaked, probably because of the high pressure in the container and the difference in the coefficient of thermal expansion of the metal and the Kel-F. The runs were discontinued while the systems were still under positive OF_2 pressures and analysis of the gas phase and solid residue was performed. Only minimal reactivity was observed, as shown by analysis of the OF_2 and the solid phase. The condensables contained only OF_2 while the non-condensable fraction contained excess air O_2.

Since OF_2 has a vapor pressure of 1 mm Hg at -196°C, it was also present in the partially fractionated sample. The solid phase from both the Alon C and TiO_2 systems contained 0.1 and 0.07% fluoride, respectively.

Following this experiment a number of OF_2-Cab-O-Sil gels were prepared using various concentrations of gellant. The mixtures were stored in 6 in. Kel-F tubes for periods up to 9 weeks and were analyzed in the usual manner. The results of this analysis are shown in Table V.

Only minimal reactivity was observed even after 9 weeks storage. The detailed analysis of the OF_2-5.8% Cab-O-Sil gel which was stored for 9 weeks is given below:

(1) The gel was cooled to -196°C, the pressure of non-condensables was measured and a sample of the gas was removed for analysis. At -196°C the pressure in the tube was 1 mm Hg. The gases were analyzed using the mass spectrometer and were found to contain 27% OF_2, 32% O_2, and 41% air.

(2) The OF_2 was recovered from the gel and the quantity obtained compared favorably to the amount originally present. The amount of OF_2 recovered was 1.78 g (as measured by PV relations, and 1.96 g, as determined by direct volume measurements). The original quantity introduced was 1.89 g.

TABLE IV

OF_2 - GELLANT STORAGE TESTS AT $-78^{o}C$

Gellant	Storage Time	Condensables	Non-condensables moles/ mole OF_2	Non-condensables Composition (mole %)	Fluoride (% bw)	Comment
Alon C	24 hr	OF_2 only	$1.5x6^{-4}$	O_2 - 36.5% N_2 - 5.5% OF_2 - 58.0%	0.10	Excess leakage
TiO_2	18 hr	OF_2 only	$1.0x10^{-4}$	O_2 - 60% Air - 40% Trace OF_2	0.07	Excess leakage
Cab-O-Sil	18 hr	OF_2 only	$1.0x10^{-4}$	O_2 - 30% OF_2 - 70%		Excess leakage

TABLE V

OF_2-CAB-O-SIL STORAGE TESTS AT -78°C

Cab-O-Sil (% bw)	Storage Time (days)	Analysis		
		Condensables	Non-condensables	Fluoride (% bw)
2.0	9	OF_2 only	Air	0.32
2.0	14	OF_2 only	Air	0.15
2.0	21	OF_2 only	---	0.10
5.8	9 weeks	SiF_4, CO_2 (Trace)	O_2 + Air	0.9

(3) The condensables obtained at -196°C other than OF_2 were CO_2, SiF_4 and air and represented about 0.1% of the OF_2 present.

(4) The solid residue was recovered and analyzed for fluorine and approximately 0.9% fluoride was observed.

The above results indicate that OF_2 and Cab-O-Sil react only to a very minor extent after 9 weeks storage at -78°C.

2. Mechanical Stability Studies

An obvious requirement for a gellant-oxidant system is that the gel should be mechanically stable under various stress conditions. A rapid liquid-solid separation under minor stresses would defeat the purpose of gelling liquid OF_2; therefore, two simple tests were conducted at -196°C on gelled OF_2. In one test, the gel was placed in an inverted position and liquid exudation was measured. Extensive separation under this condition would indicate that the liquid is only weakly held in the gel structure. In a second test the gel was exposed to high g forces to determine if liquid separation occurs under these conditions.

a. Inverted Tube Test

A visual determination of liquid exudation from a gel can be made by placing a gel at the bottom of a glass tube and then inverting it. Liquid-solid separation is easily observed and the approximate amount of liquid exuded can be monitored volumetrically. In Table VI are shown the results from studies on the OF_2-Cab-O-Sil system and the OF_2 - Alon C system.

Two sets of experiments were performed on the OF_2-Cab-O-Sil gel. In the first set, the gel concentration was varied between 3.2 and 4.5% and the samples were stored for 2 days in the inverted position. Some liquid exuded from the 3.2 and 4.2% gel samples and the sample containing 4.5% gellant remained intact. In the second set of experiments, the gellant concentration was varied between 1.4 and 4.5% and the samples were stored for 11 days. In this case, the 1.4% mixture was very fluid and could not be stored in the inverted position. The gel containing 2.5% Cab-O-Sil exuded 28% liquid while only a trace of liquid exuded from the 3.3% gel; the 4.5% gel showed no liquid exudation.

The OF_2-Alon C gel, at concentration of gellant varying from 4.1 to 6.3% were stored for 9 days and in no case was liquid exudation observed.

b. Centrifuge Test

The second test used to observe the structural stability was the centrifuge test to simulate sudden accelerations as in vehicle launch or manuever. Two OF_2-Cab-O-Sil gel samples were centrifuged for 30 minutes at approximately 30-40 g while two samples were centrifuged for 2 minutes and then stored in an inverted position. Neither set showed any adverse effects. The results are summarized in Table VII.

3. Shock Sensivitity Studies

As part of the program objectives, the shock sensitivity of OF_2 gels was examined. A modified Trauzl block test was used for this purpose because the method lends itself readily to the handling of highly volatile materials.

The systems investigated were neat OF_2 and the gel mixtures of OF_2-Cab-O-Sil, OF_2-Alon C, OF_2-TiO_2 and OF_2-Fe_2O_3. The effect of water, container material, and the cryogenic nature of the liquid were examined. The results are shown in Table VIII.

TABLE VI

INVERTED TUBE TESTS ON OF_2 GELS AT -196°C

Gellant	Gellant Concentration (%)	OF_2 (g.)	Storage Time (days)	Comments
Cab-O-Sil	3.2	1.12	2	Some liquid exuded
Cab-O-Sil	4.1	1.44	2	Some liquid exuded
Cab-O-Sil	4.5	0.607	2	No liquid exuded
Cab-O-Sil	1.4	1.57	11	Very fluid mixture
Cab-O-Sil	2.5	1.58	11	Approximately 28% OF_2 exuded
Cab-O-Sil	3.1	1.19	11	Approximately 8% OF_2 exuded
Cab-O-Sil	3.3	0.83	11	Trace OF_2 exuded
Cab-O-Sil	4.5	1.37	11	Not thoroughly mixed but no liquid exuded
Alon C	4.1	1.125	9	Very thick sand-like gel with no OF_2 exuded
Alon C	5.0	1.2	9	Very thick sand-like gel with no OF_2 exuded
Alon C	6.3	1.47	9	Very thick sand-like gel with no OF_2 exuded

TABLE VII

CENTRIFUGE TESTS ON OF_2 GELS AT -196°C

Cab-O-Sil (% bw)	OF_2 (g)	Comments
3.7	1.29	Centrifugation for 30 minutes, gel remained rigid.
5.3	1.07	Centrifugation for 30 minutes, gel remained rigid.
4.1	1.80	Centrifuged for 2 minutes, then inverted for 5 days. No liquid was exuded
4.1	1.80	Centrifuged for 2 minutes, then inverted for 5 days. No liquid was exuded

The expansion of the lead cylinder produced by OF_2 alone in 1 and 2 g samples were 7 and 11 cc/g, respectively, which indicates a negative result when compared to the value for a standard explosive such as RDX (30 cc/g). The OF_2 gels gave values ranging from 8 cc/g for the OF_2-Cab-O-Sil and OF_2-TiO_2 systems to 16 cc/g for the OF_2-Alon C system. In none of these tests are the results considered positive. Thus, as shown in Runs No. 11 and 12, the expansion of 5 cc/g obtained for liquid N_2 alone was attributed to the extremely rapid volatilization of the liquid N_2 on initiation of the blasting cap. Also, the gas formed when the blasting cap explodes is essentially a fuel which can then react with the OF_2 causing a further contribution to the expansion of the lead block. Therefore, it is expected that OF_2 and its gels will show some expansion in the Trauzl test.

In Runs No. 14 and 15 Kel-F grease and H_2O, respectively, were added to the lead cylinder in addition to the OF_2 in the vials. This was done to determine if impurities might sensitize the mixture. The expansions of 10 cc/g and 3 cc/g indicate that these impurities do not contribute to the detonability of OF_2. Cab-O-Sil and OF_2 have been mixed many times on this program and in a number of these experiments the mixture was stirred at -196°C in an open tube. In none of these later experiments was there any sign of a reaction. Thus, the question of the cause of the single explosion, previously mentioned, remains unanswered.

TABLE VIII

RESULTS OF TRAUZL TESTS ON OF_2 GELS

No.	Container	OF_2 (g)	Gellant	Gellant (% bw)	Total Expansion (cc)	Expansion per g OF_2 (cc/g)
1	Glass	1.00	---	---	7	7
2	Glass	2.0	---	---	22	11
3	Glass	1.00	Cab-O-Sil	3.1	14	14
4	Glass	1.30	Cab-O-Sil	2.6	10	8
5	Glass	1.44	Alon C	4.0	17	12
6	Glass	1.00	Alon C	4.8	16	16
7	Glass	1.00	TiO_2	3.4	11	11
8	Glass	0.92	TiO_2	2.7	6	7
9	Glass	1.44	Fe_2O_3	3.0	13	9
10	Glass	1.20	Fe_2O_3	4.2	9	8
11	Glass	---	Liq N_2[+]	---	5	---
12	Glass	---	Liq N_2	---	5	---
13	Kel-F	1.30	---	---	11	9
14	Glass	1.00	Kel-F No. 90 Grease	1.3	10	10
15	Glass	1.00	1 cc of H_2O[++]	---	8	8
16	Control (RDX)			---	---	30

[+] Liquid nitrogen was run as a blank in place of liquid OF_2.

[++] 1 cc of H_2O was placed outside of OF_2 tube in the Trauzl block.

4. Evaporation Rates

The problem of boiloff is always a consideration in evaluating cyrogenic liquids. One effect of gelation which is of value in this respect is the possible decrease in vaporization rates. This was determined by comparing the rates of neat OF_2 and OF_2 gelled with 3.8 and 5.4 percent Cab-O-Sil. The data are presented in Figure 3. Although the initial rates were nearly identical at the higher concentration of gellant the rate gradually diminished. This is probably due to heat transfer effects since, as the liquid OF_2 evaporates, the OF_2 in the central portion of a gel-clump remains cool and/or must escape from the confining "cage" of the gelling agent.

5. Rheological Characterization of Cryogenic Gels

One of the objectives of this program was to obtain measurements of the flow characteristics of OF_2 gels at various concentrations of gelling agents.

The flow properties that serve to characterize a gel are the yield value and the flow curve. The yield value is defined as the minimum stress that must be applied to a gel to start laminar flow (Ref 9). The flow curve shows the relation between the applied shear stress and shear rate. For a Newtonian liquid the relation is given by

$$T = \eta \frac{dv}{dx} \qquad (1)$$

where T is the shear stress in dynes/cm^2, dv/dx is the shearing rate in reciprocal seconds and η is the viscosity. For a non-Newtonian material Equation (1) is not applicable and, depending on the shape of the shear stress-shear rate curve, different types of flow behavior are obtained. The type of flow behavior on gels is well documented and will not be further discussed here (Ref 9).

The two most practical methods for measuring flow characteristics of gelled systems are by use of the concentric rotational viscometer and the capillary viscometer. In the former method the liquid is placed in the annular space between 2 cylinders and 1 of the cylinders is rotated. The rate of rotation of the cylinder is proportional to the shear stress. This method is especially useful because its use makes possible the identification of flow characteristics of the gel.

In a capillary viscometer the pressure required to force the fluid through a capillary is proportional to the shearing stress and the mass rate of flow of the fluid through the capillary at a given pressure head is a measure of the shear rate.

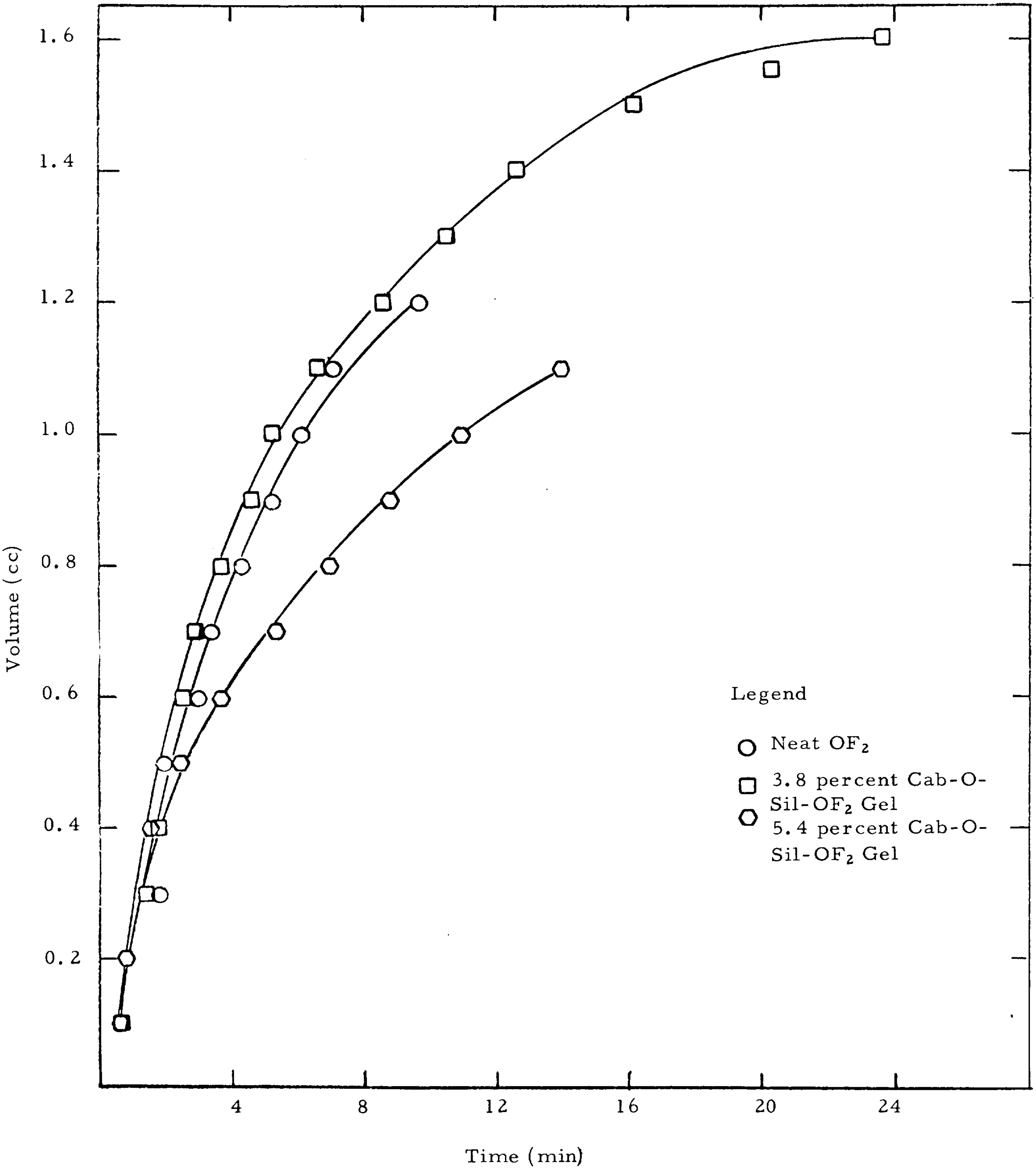

Figure 3. Distillation Rate of OF_2 and OF_2 Gels

Both of the above techniques were used on this program in an attempt to obtain flow data on OF_2 gels. Because of the necessity of working with small quantities of material (2-3 grams) at liquid nitrogen temperatures, it was not possible to obtain flow data by either of these methods.

a. Rotational Viscometer

A Brookfield Model LVF rotational viscometer was employed in an attempt to obtain viscosity measurements of liquid nitrogen gelled with carbon or Cab-O-Sil. However, it was not possible to obtain a shear stress measurement. The rotating bob slipped over the gel intermittently causing a random oscillation of the torsion needle. If it is possible to wet the surface of the bob by the liquid medium, this method may prove useful in the future. OF_2 gels were not investigated with the Brookfield instrument because of the necessity of using relatively large quantities of gel.

There is available in the Thiokol-RMD laboratory a precision rheometer (Epprecht Rheomat Model RM15) which was modified, as previously mentioned, to accommodate small amounts of gel at -196°C.

OF_2 gelled with Cab-O-Sil ranging in concentration from 2 to 8% was investigated. Generally, the gels were too thin causing free turning of the bobs, or too thick in which case the bobs would core the gel and turn freely. In either case, no data could be recorded. The primary difficulty was the necessity of making the measurements at -196°C on small quantities of material. It is felt, that with sufficient precautions, larger quantities of gel can be made and data can be obtained either with the Epprecht or a Brookfield rheometer.

b. Capillary Viscometer

A capillary flow apparatus was constructed for the measurement of the flow characteristics of cryogenic gels. The apparatus was designed so that the gel can be prepared in the same section that the flow measurement is to be made. To check-out the system cis-butene-2 which has a boiling point of 3°C, was used as a simulant for OF_2 and Alon C was used as the gellant.

A known volume of cis-butene-2 was condensed at-78°C into a flask which contained a weighed amount of Alon C and a magnetic stirring bar. This mixture was then stirred by means of the stirring bar and was examined visually. A 12% Alon C gel appeared to be too thick while a 7% mixture formed a good gel. This gel showed no separation after a standing period of 2 hours.

An attempt was made to measure the rheological properties of the 7% Alon C gel by determining its flowrate in the capillary tube. When a small difference of pressure (1 mm Hg) was applied over the gel, the nitrogen gas, which was used as the pressurizing gas, tunneled through the gel almost immediately. At pressure differences below 1 mm Hg, the gel failed to flow. It is believed that plugging occurs at the capillary tube entrance which prevents the smooth transition to flow. As a consequence, this method was not investigated further.

V. CONCLUSIONS AND RECOMMENDATIONS

The gelation of liquid oxygen difluoride has been accomplished by use of finely divided inorganic oxides in a concentration of 3 to 8% bw. The inorganic oxides which are most useful for this purpose are Al_2O_3 (Alon C), TiO_2, and SiO_2 (Cab-O-Sil). The latter substance appears to form the most satisfactory gel with OF_2 and is currently the recommended gellant.

The OF_2-Cab-O-Sil mixture was subject to a number of tests to determine its chemical and mechanical stability. The gel was stored for periods up to 4 days at -196°C and for periods up to 9 weeks at -78°C. Analysis of the mixture indicates that it is stable. The mixture was tested for shock sensitivity by a Trauzl block method and did not detonate. It was shown to be stable to acceleration at forces of 30-40 g and a gel containing 4.5% Cab-O-Sil did not exude liquid when stored in an inverted position. The gel will support a steel weight indicating its gel nature. However,it was not possible to obtain flow data using small amounts of gel at liquid nitrogen temperatures. Evaporation data studies on OF_2-Cab-O-Sil gels indicate that the gel has a slower rate of evaporation than OF_2 alone.

OF_2 gelled with Alon C and TiO_2 were also chemically stable at -196°C after 4 days storage and are recommended as possible alternates to the OF_2-Cab-O-Sil system.

The OF_2-Cab-O-Sil system has been brought to a stage which indicates that the system is feasible for space storable applications. However, there are a number of studies which we recommend if the system is to find acceptance in future missions.

1. It will be necessary to prepare the OF_2-Cab-O-Sil gels in larger quantities than heretofore. This will make possible the measurement of its rheological properties using standard techniques and also the shock sensitivity using the card gap technique can be utilized.

2. In preparing large batches of OF_2 gels, formulation techniques using properly defined mixing conditions should be evaluated and handling requirements should be specified.

3. Laboratory data should be obtained which will make possible its extrapolation to full-scale storage conditions.

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