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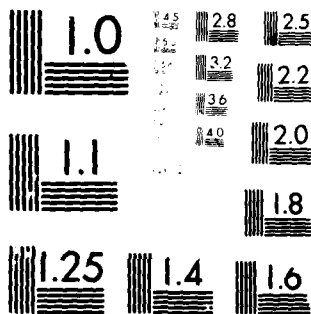
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INVESTIGATION OF A HIGH PRESSURE OXYGEN FIRE IN THE RECOMPRESSION CHAMBER SYSTEM AT THE FLEET DIVING UNIT, PACIFIC

L.K. Yee and R. Rowland

December 1979

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6 INVESTIGATION OF A HIGH PRESSURE OXYGEN FIRE
IN THE RECOMPRESSION CHAMBER SYSTEM AT THE
FLEET DIVING UNIT, PACIFIC.

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ABSTRACT

A fire in the piping system of the high pressure oxygen side of the recompression chamber at the Fleet Diving Unit, Pacific has led DREP to undertake a comprehensive look at the cleaning procedures and the materials used in an oxygen environment. As a result of this investigation, it was established that Teflon and Viton coated with Krytox, (a fluorosilicone grease) could be used in a high pressure oxygen system. A cleaning procedure for parts used in oxygen service is also included.

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INTRODUCTION

In the past few years, DREP has been involved in the investigation of fires that occurred in piping systems where high pressure oxygen was used. These fires usually resulted in a explosion of a regulator or the sudden occurrence of a foul smell around the area where valves were located. This smell was due to the rapid oxidation and degradation of organic materials used as packings and lubricants.

A recent fire in the high pressure side of the piping system of the recompression chamber at Fleet Diving Unit, Pacific caused a monitoring and cleaning system to be set up to ensure that the piping system was free of combustible materials and lubricants before the chamber was put into service.

Materials such as Teflon, Viton and Krytox were found to be acceptable for oxygen service, but they could burn or be thermally decomposed if other combustible contaminants were present to supply the necessary heat to initiate the decomposition process. Petroleum-based grease and silicon grease were found to be the chief sources of combustible contaminant found in the system.

The present investigation involved the infrared analysis of residual materials found in valves, valve seats, regulators and pipes after flushing with Freon 113. This report also discusses the characterization of materials frequently found in systems used for oxygen service.

EXPERIMENTAL PROCEDURE AND RESULTS

Since fire is related to heat energy output per unit mass, the determination of the calorific value (Table 1) gives a direct comparison of combustibility of the various materials used.

Grease, gaskets, seals, "O" rings and other packing materials were identified by gas chromatographic and infrared analysis either directly or indirectly by analysing the correspondent pyrolysis products.

Freon 113 solvent was used to extract the soluble organic material. After solvent evaporation, the residue was transferred onto a potassium bromide salt plate and an infrared spectrum was taken of the sample between the plates.

TABLE I

| | <u>Avg BTU/lb</u> | <u>Avg CAL/gm</u> |
|-------------------------------------|-------------------|-------------------|
| Dow Corning grease #44 | 14,000 | 7,778 |
| Silicone grease | 9,500 | 5,278 |
| Fluorosilicone | 7,100 | 4,278 |
| Molydisulfide powder | 3,000 | 1,667 |
| Loctite | 11,000 | 6,111 |
| Blue Goop | 9,100 | 5,056 |
| Dow Corning Silicone Sealant | 10,000 | 5,556 |
| Krytox | 1,480 | 822 |
| Nitrite Rubber "O" Rings, Buna N | 14,900 | 8,278 |
| Butadiene-Styrene "O" Rings, Buna S | 15,000 | 8,333 |
| Silastic 733 RTV | 7,500 | 4,167 |
| Viton | 6,457 | 3,587 |
| Teflon | 2,515 | 1,397 |

Details of the infrared spectra are discussed in Appendix A.

The thermal values of the identified samples were determined by the Parr oxygen bomb calorimeter. This method involved the burning of approximately 1.0 gm of material in pure oxygen under pressure. Ignition was provided by an electric fuse wire connected to the outside of the bomb. Sometimes a wick was used to provide a burning path from the wire to the sample. This was particularly true for Teflon which was a very difficult material to ignite. Once ignition was achieved, the liberated heat was absorbed by a known amount of water, the temperature rise was monitored and the caloric value then calculated.

TOXICITY CONSIDERATION

Whenever there was a fire in the oxygen system, the accompanying foul smell aroused the operating personnel to enquire into the toxic effect in the immediate environment.

Assuming that an oxygen fire was started by the rapid oxidation of oil and grease, including silicone grease, the oxidation products would be CO₂, SiO₂ and H₂O which are not considered to be toxic. While the rapid oxidation was taking place, a sufficient amount of heat was produced to

cause the "inert" fluorinated materials to thermally decompose. This thermal degradation of Teflon would result in components other than combustion products. According to R. Lefaux¹, the products of thermal decomposition of Teflon are fluorocarbon gases such as perfluoroisobutylene (a very toxic substance), hexafluoropropene, octafluorocyclobutene and a negligible amount of hydrogen fluoride. He also stated that "In man the effect of the thermal decomposition products of polytetrafluoroethylene is very characteristic. It comprises an influenzal state, with occurrence of fevers resembling those experienced by metallurgical workers suffering from foundryman's fever". Other symptoms are irritation in the throat and lungs, which usually clear up after forty-eight hours. When people are exposed to toxic fumes during a fire, the period is usually short; therefore, the toxicity of fumes and exposure time must be considered together. Table II indicates the relative toxic nature of common toxic fumes, which are usually formed at the beginning of a fire.

TABLE II

| Toxic effect | Concentration (ppm) | | | | | | | | |
|---|---------------------|-----------------|-------------|-------------------|--------|---------|-----------------|------------------|-----------------|
| | CO | Cl ₂ | HCl | COCl ₂ | HF | HCN | NH ₃ | H ₂ S | NO ₂ |
| No effect over several hours | 100 | 0.35-1 | 10 | 1 | 1.5-3 | 20 | 100 | 20 | 10-40 |
| No effect in one hour | 400-500 | 4 | 50-100 | | 10 | 50-60 | 100 | | |
| Dangerous in ½-1 hour | 1,500-2,000 | 40-60 | 1,000-2,000 | 25 | 50-250 | 100-240 | 2,500-4,500 | 200 | 100-150 |
| Fatal in ½ hour | 4,000 | | | | | 200-450 | | 600 | |
| Rapidly Fatal | | 1,000 | 1,300-2,000 | | 50 | 3,000 | 5,000-10,000 | 1,000 | 200-700 |
| Minimum Am't causing throat irritation | | 15 | 35 | | 3.1 | | 408 | 100 | 62 |
| Minimum Am't for which odour detectable | | 3.5 | | | 5.6 | | 53 | 10 | |

It is observed from the above table that most of the adverse effects on humans are not from the products of oxidation of oil and grease. If the oil and grease were absent as a source of fuel, the decomposition of fluorocarbon could be eliminated.

ACCEPTABLE MATERIALS FOR HIGH PRESSURE OXYGEN SYSTEMS

In the following section some properties of materials acceptable for use in high pressure oxygen systems are described.

Teflon

Teflon is a trademark of DuPont Co., for polytetrafluoroethylene (PTFE). The molecular structure consists of repeating units of $-CF_2 -CF_2-$. When it is exposed to flame it decomposes into lower molecular weight fluorinated compounds. The working temperature is up to $260^{\circ}C$. It is inert in high pressure oxygen.

Viton

Viton is a trademark of DuPont Co., for a co-polymer of vinylidene fluoride and hexafluoropropylene. This fluorelastomer has been formulated to operate under 100% oxygen at 6.2 psia. General purpose Viton will burn when exposed to flame but is self-extinguishing. It is less inert than Teflon. When Viton is coated with a film of Krytox, a fluorinated grease, its inertness in oxygen is similar to Teflon.

Krytox Greases

Krytox Greases (also a trademark of DuPont Co.), are fluorinated oils (perfluoroalkylpolyethers) thickened with fluorotelomer solids. These greases are very inert and do not react with oxygen at pressures up to 7,000 psi. When Viton is coated with these compounds, the gas permeability and chemical inertness is improved.

DISCUSSION

Once ignition is started, the presence of silicone grease in the valve seats is the heat source for the decomposition of the Teflon insert. The generally accepted mechanism for ignition of the silicone grease is a sudden pressure change when a regulator is either turned on or shut off causing the sudden movement of oxygen in the line. This pressure change cannot be avoided, but the presence of silicone grease can be eliminated.

After cleaning the recompression chamber, new valves and regulators obtained from suppliers for oxygen service conditions, were all found to be contaminated with silicone grease. That and other instances demonstrate convincingly that no parts should be installed in oxygen systems unless they are cleaned for oxygen service by the method described in Appendix B or by equivalent methods.

In the case of Viton, it was observed that certain amounts of organic solubles were detected in the Freon 113 extract (see IR spectrum 3 in Appendix A). It was not clear whether these solubles were formed under oxygen service conditions or by contaminants permeating the Viton matrix. However, it was felt that an improved maintenance procedure should be followed in order to eliminate any accumulation of combustible "fuel" in the oxygen service system.

Viton "O" rings, wherever they are used, should be removed and cleaned with Freon every 12 months to eliminate any oxidation or degradation products, thus avoiding the accumulation of combustion "fuel". Whenever possible and available, Krytox should be used to coat the Viton parts for oxygen service. The use of Krytox provides two advantages; one, it decreases the permeability of oxygen into the Viton matrix; and two, it increases the inertness of Viton to oxidation.

The Freon cleaning of Viton caused a little concern at the beginning because of its permeability to gases. It was found that Viton increased in volume by 2% after being immersed in Freon 113 for 24 hours at room temperature. However, the sample returned to its original volume with no trace of the Freon after vacuum treatment for 30 minutes at 150°F. Details on the cleaning procedure are listed in Appendix B.

Materials used for oxygen service should be fluorinated compounds with a heat of combustion of less than 3,600 cal/gm (6,480 BTU/lb). This restriction is based on the difficulties in achieving ignition and complete combustion of these fluorinated materials in the preceding laboratory studies.

CONCLUSIONS

It was found that to eliminate the possibility of an oxygen fire, the system must be free from petroleum-based or silicone-based oil or grease. To ensure this, a rigorous maintenance and cleaning procedure must be followed.

Only Teflon and Viton coated with Krytox should be used in the oxygen system.

Checking of factory cleaned parts has shown that they were contaminated. Consequently, all new parts must be cleaned thoroughly (as in Appendix B) before installation.

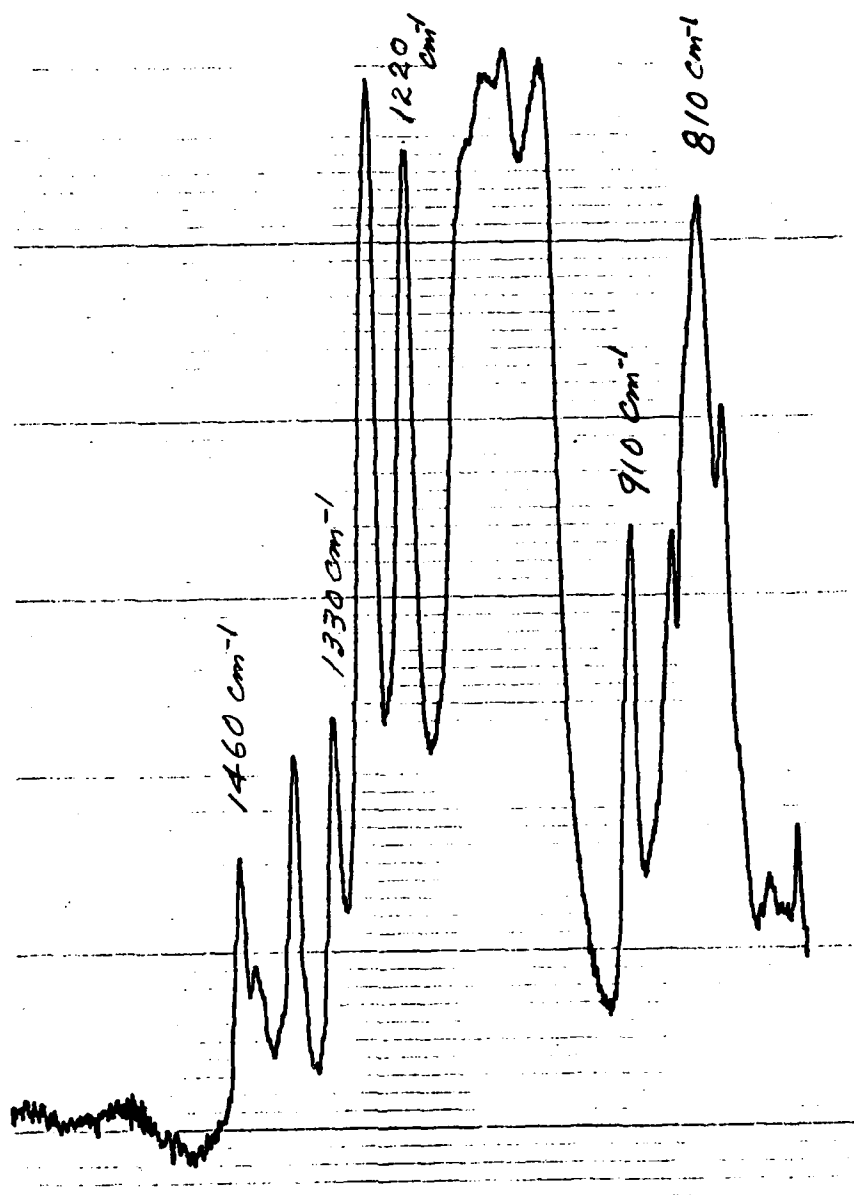
A periodical dismantling and examination of valves and regulators would reveal whether or not contamination is present.

REFERENCES

1. R. Lefaux, Practical Toxicology of Plastics, Iliffe Books Ltd., London, pp. 205-106, 1968.
2. Ibid, p. 207.

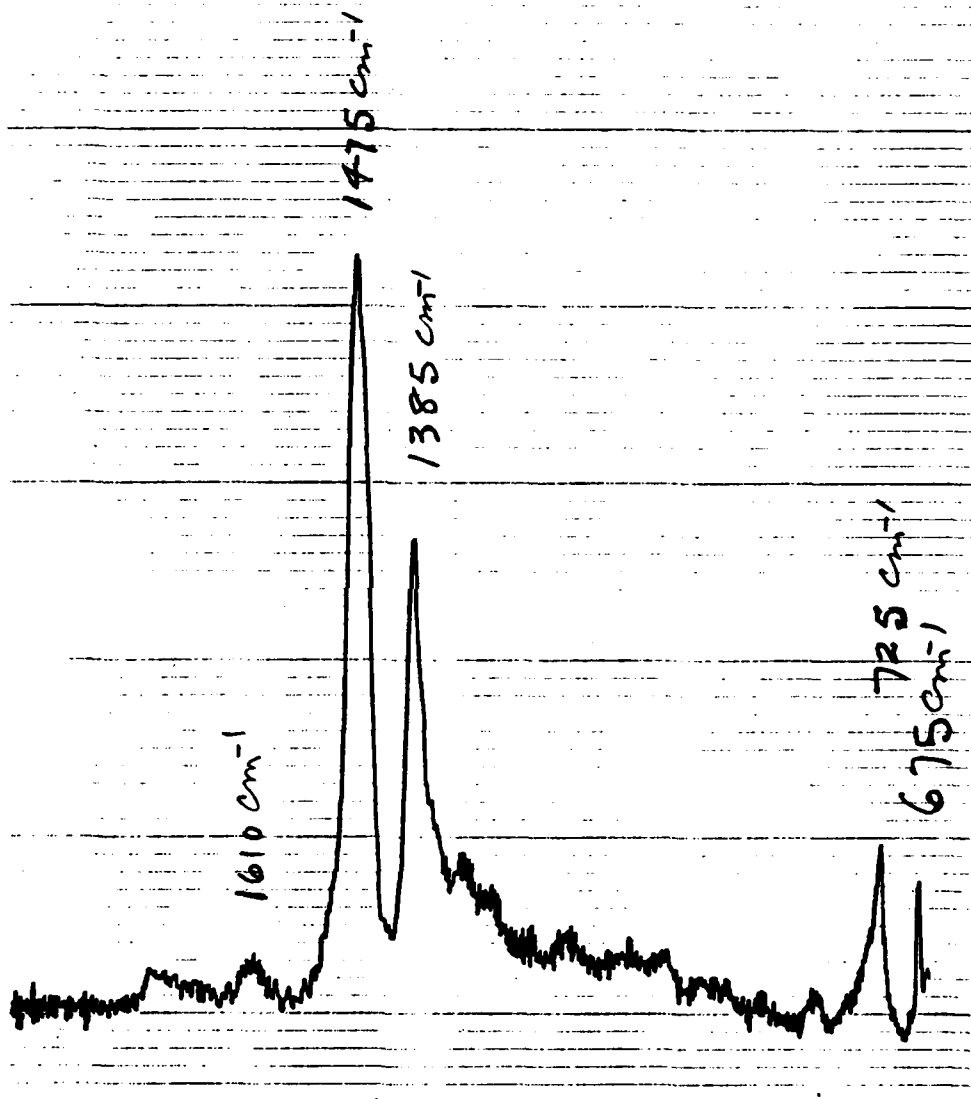
APPENDIX A
INFRARED SPECTRA

The infrared spectra of the grease, gaskets, seals, "O" rings and other packing material found in valves, valve seats, regulators and plots in the high pressure oxygen systems were taken with a double beam Unicam 100 infrared spectrophotometer. The instrument was set at maximum sensitivity and highest resolution.



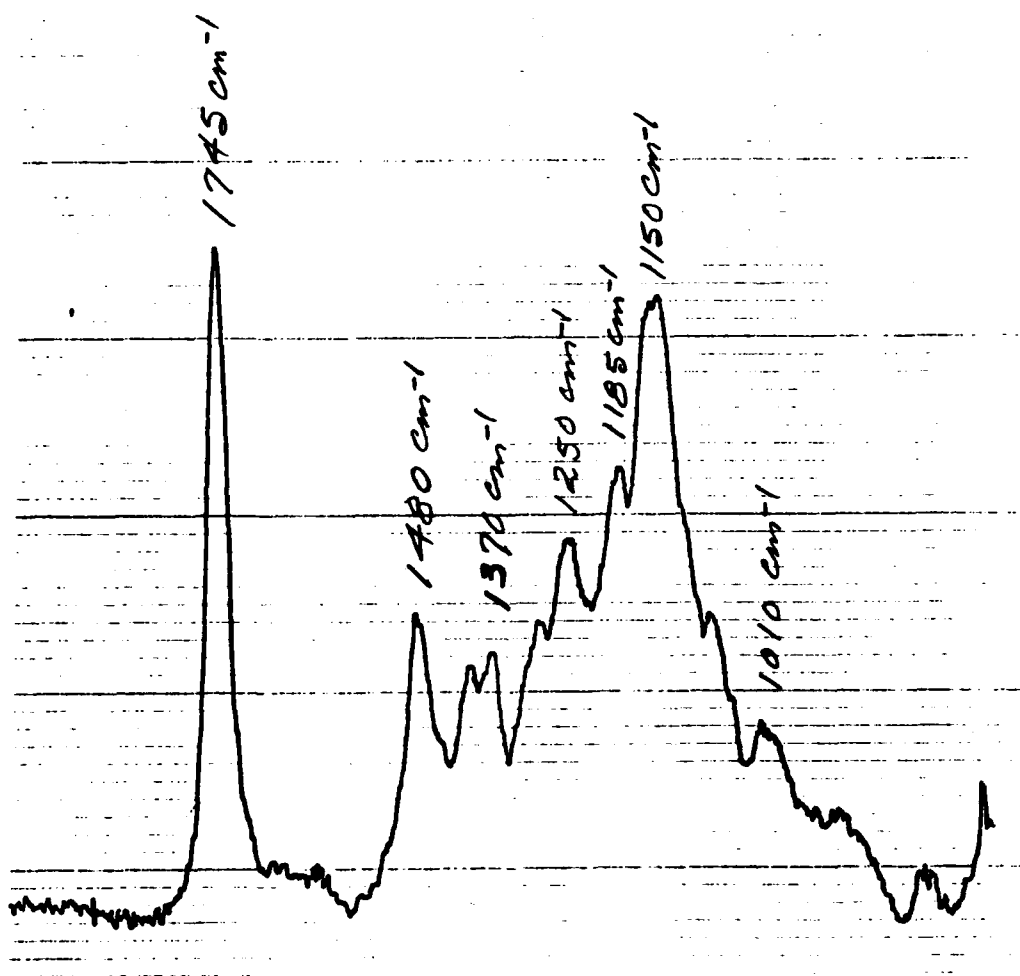
SPECTRUM #1

IR spectrum of residue found in the valve seat of a regulator in the high pressure oxygen system. An identical spectrum obtained from a sample taken from a new regulator was identified with Dow Corning silicone grease.



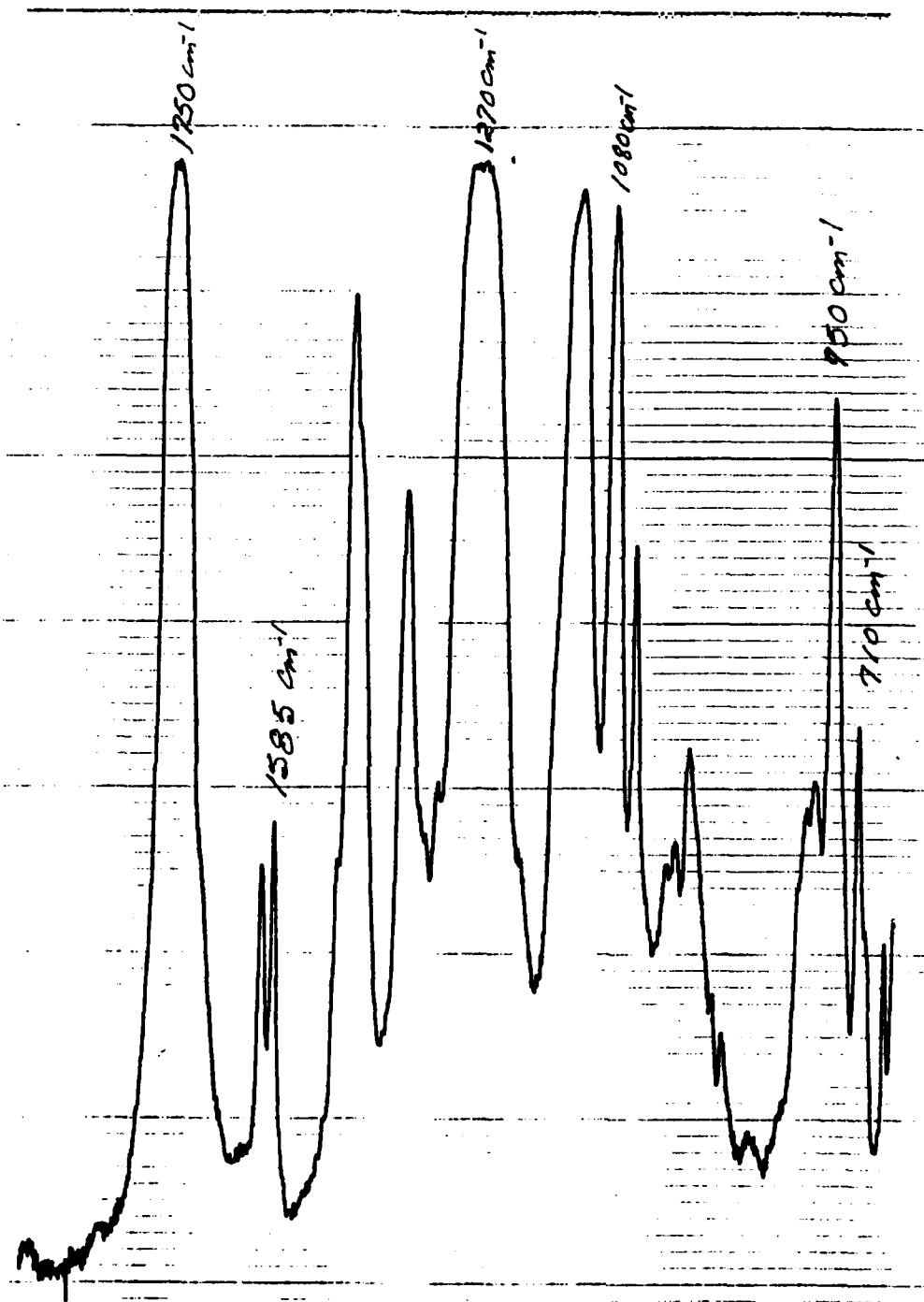
SPECTRUM #2

IR spectrum of a Freon extract of a valve stem coated with a film of graphite. It indicates that an oil-based lubricant was used.



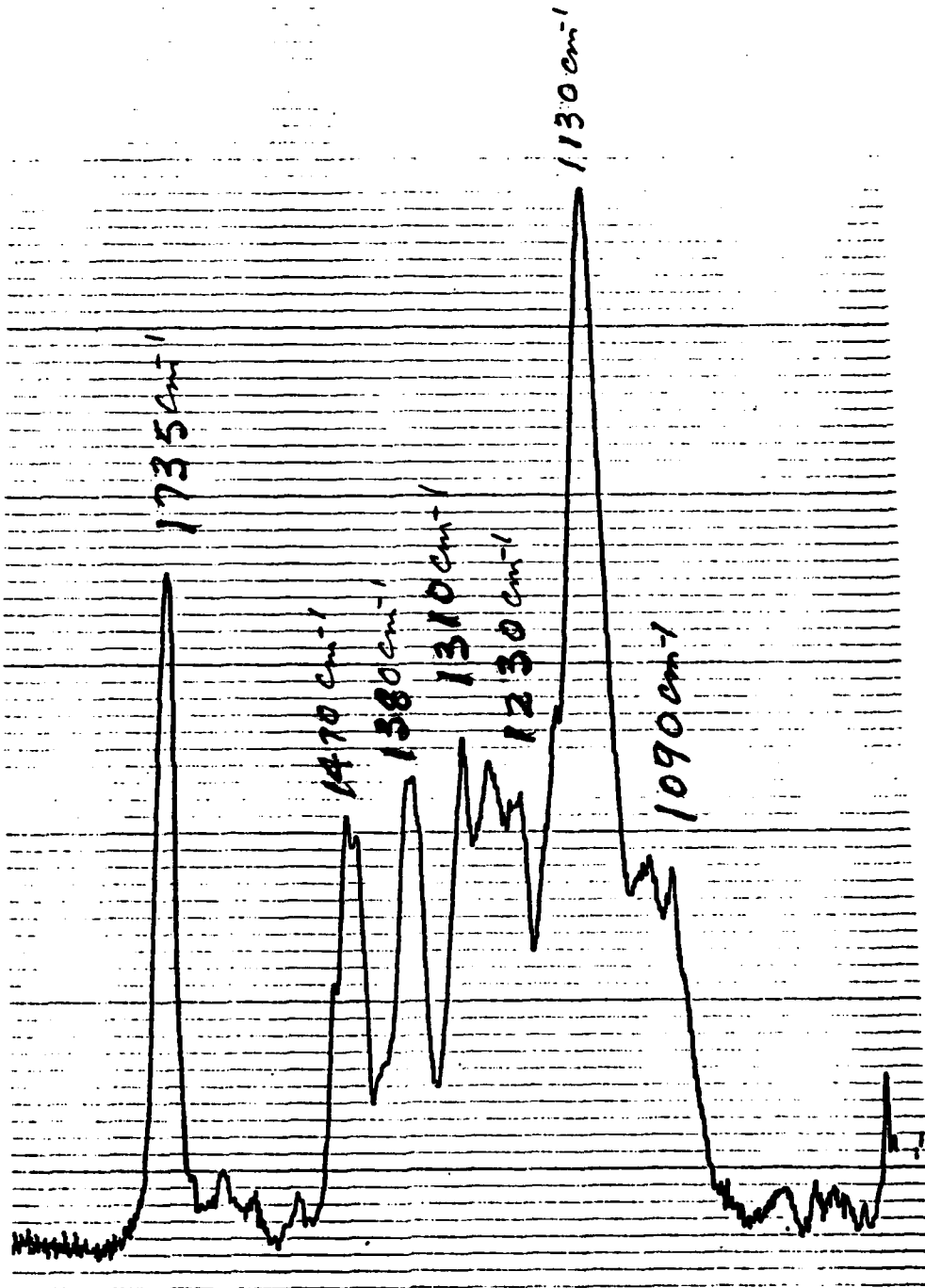
SPECTRUM #3

IR spectrum of a Freon extract of a used Viton "O" ring used in the oxygen system. It is a typical spectrum of an ester of a fatty acid. The origin of this ester was not known, but there was a strong possibility that it was an oxidation product of an oil-based lubricant contaminating the "O" ring.



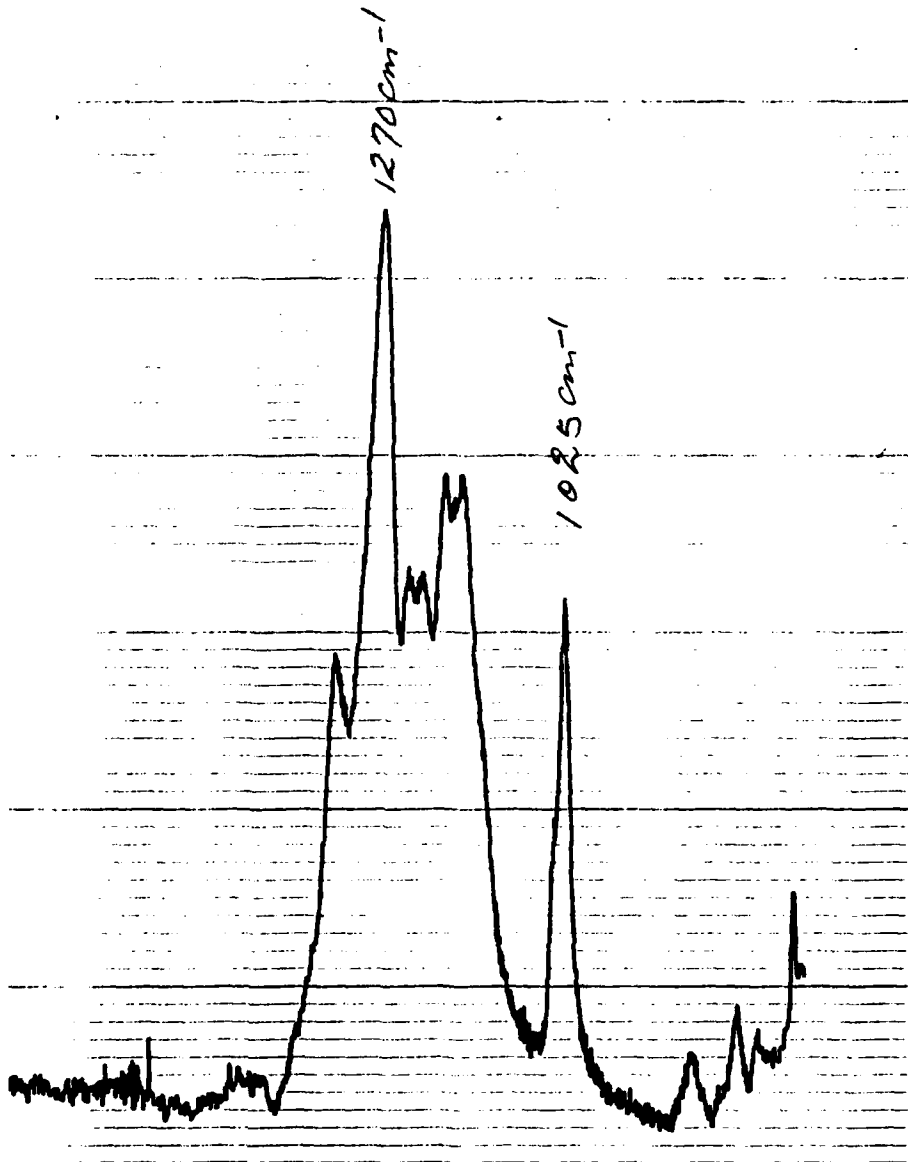
SPECTRUM #4

IR spectrum of residue recovered from the first Freon flushing of the oxygen piping system after the fire. It was identified as a dialkylphthalate, a common plasticizer. Its origin was not known because the flushing unit does not involve any plastic parts except the polyurethane diaphragm in the pump used for circulating the Freon 113.



SPECTRUM #5

IR spectrum of extract from a new polyurethane diaphragm used in the Freon pump. It confirmed that the dialkylphthalate (spectrum #4) was not coming from the diaphragm.



SPECTRUM #6

IR spectrum of a fluorinated oil thickened with fluorotelomer solids, a typical Krytox grease which should be the only grease used in the high pressure oxygen system.

APPENDIX B

PROCEDURE USED TO CLEAN VALVES AND REGULATORS

IN OXYGEN BREATHING GAS SYSTEM OF MAIN RECOMPRESSION CHAMBER

1. Strip valves and regulators.
2. Clean parts in ultrasonic cleaner using Freon TF for a minimum of 10 minutes.
3. Repeat step 2 using clean Freon TF.
4. Clean parts in ultrasonic cleaner using Alconox for a minimum of 10 minutes.
5. Rinse parts in distilled water and dry in air.
6. Reassemble valves and regulators and store in plastic bags until needed.

NOTE:

Step 4 and 5 can be omitted if a vacuum oven is available by placing parts in the vacuum oven for 30 minutes with a temperature of about 150°F (60°C) and a vacuum of about 29" (735 mm) of mercury.

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KEY WORDS

High pressure oxygen, Teflon, Viton, Krytox, recompression chamber,
Freon, Cleaning procedure.

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