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Second Quarterly Progress Report

Chemistry Section
Research Division of Rocketdyne
A Division of North American Aviation, Inc.
Canoga Park, California

TECHNICAL REPORT AFRPL-TR-66-317

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Air Force Rocket Propulsion Laboratory
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FOREWORD

The research reported herein was sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards Air Force Base, California, under Contract AF04(611)-11620.

This program is being conducted in the Chemical Research Section of the Rocketdyne Research Division; Dr. J. Silverman is the Program Manager and Dr. E. F. C. Cain is the Project Scientist. The principal areas of study and the corresponding assigned personnel are as follows:

Phase I: Compound Formation

Dr. A. E. Axworthy
(Responsible Scientist)
Dr. W. Nigh
Dr. H. Schultz

Phase II: Compound Identification

Dr. A. E. Axworthy
(Responsible Scientist)
Dr. J. D. Ray
Dr. J. Gerhauser
Mr. P. Ennis

Phase III: Compound Solubility and Phase IV: Compound Elimination

Dr. C. Fujikawa
(Responsible Scientist)
Dr. F. Gunderloy
Dr. H. Schultz

Phase V: Efficiency of Elimination

Dr. S. Rodriguez
(Responsible Scientist)

This report has been assigned the Rocketdyne report No. R-6702-2.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Second quarter progress is reviewed on a 12-month program to ascertain methods for the elimination of the corrosion products in N_2O_4 (iron-nitrate-containing species) which are responsible for the phenomenon of "flow decay."

Studies on the rate and mechanism of solution of iron in anhydrous N_2O_4 are described. Nuclear magnetic resonance and electron resonance spectroscopy studies of the solvated iron nitrate species are presented.

Compounds of the type $Fe(NO_3)_3 \cdot xN_2O_4$ have been synthesized and purified. The properties of these materials have been found to match the properties of the flow decay substance. Solubility studies of the "synthetic" flow decay material in anhydrous N_2O_4, N_2O_4 containing NO, and N_2O_4 containing small quantities of H_2O have been initiated and are discussed in detail. Preliminary experiments have indicated possible candidate coordinating agents for further investigation.

A flow bench designed to study this phenomenon is being constructed. Design considerations are discussed.

CONTENTS

ILLUSTRATIONS

PHASE I: COMPOUND FORMATION

The objective of this task is to determine the mechanism of formation of species involved in the flow-decay process. The initial effort has centered on a study of the rate and mechanism of solution of iron in anhydrous N_2O_4. Metallic iron, some of its alloys, and iron oxide have been investigated. The effect of added water or NO, and temperature variation on formation of the compounds will be investigated.

One approach to determining the mechanism of formation of the iron species in N_2O_4, probably solvated iron nitrates, is to study the kinetics of the dissolution of iron-containing metals. The initial series of experiments was designed to determine the nature of this process in anhydrous N_2O_4.

DISCUSSION AND RESULTS

Dissolution of Iron Powder

Experiments conducted at 21 C in the glass/Teflon reaction cell described in Ref. 1 have been completed. Five grams of iron powder were added to 113 grams of anhydrous iron-free N_2O_4 (<0.1 ppm Fe and <0.01 ppm water) and the mixture was stirred continually with a glass-coated magnetic stirrer. Filtered 1-milliliter aliquots of N_2O_4 were withdrawn at 0.5, 6, 96, and 240 hours and were analyzed for total iron. The results obtained are presented in Fig. 1. The concentration of total iron in the N_2O_4 reached a concentration of approximately 1.5 ppm after several hours and then remained approximately constant.

Because several experimental difficulties were encountered with the glass/Teflon apparatus, an ampoule technique, described in detail in the Experimental Procedure Section, was adopted. The difficulties with the glass/Teflon apparatus involved (1) the possibility of leakage, (2) the required

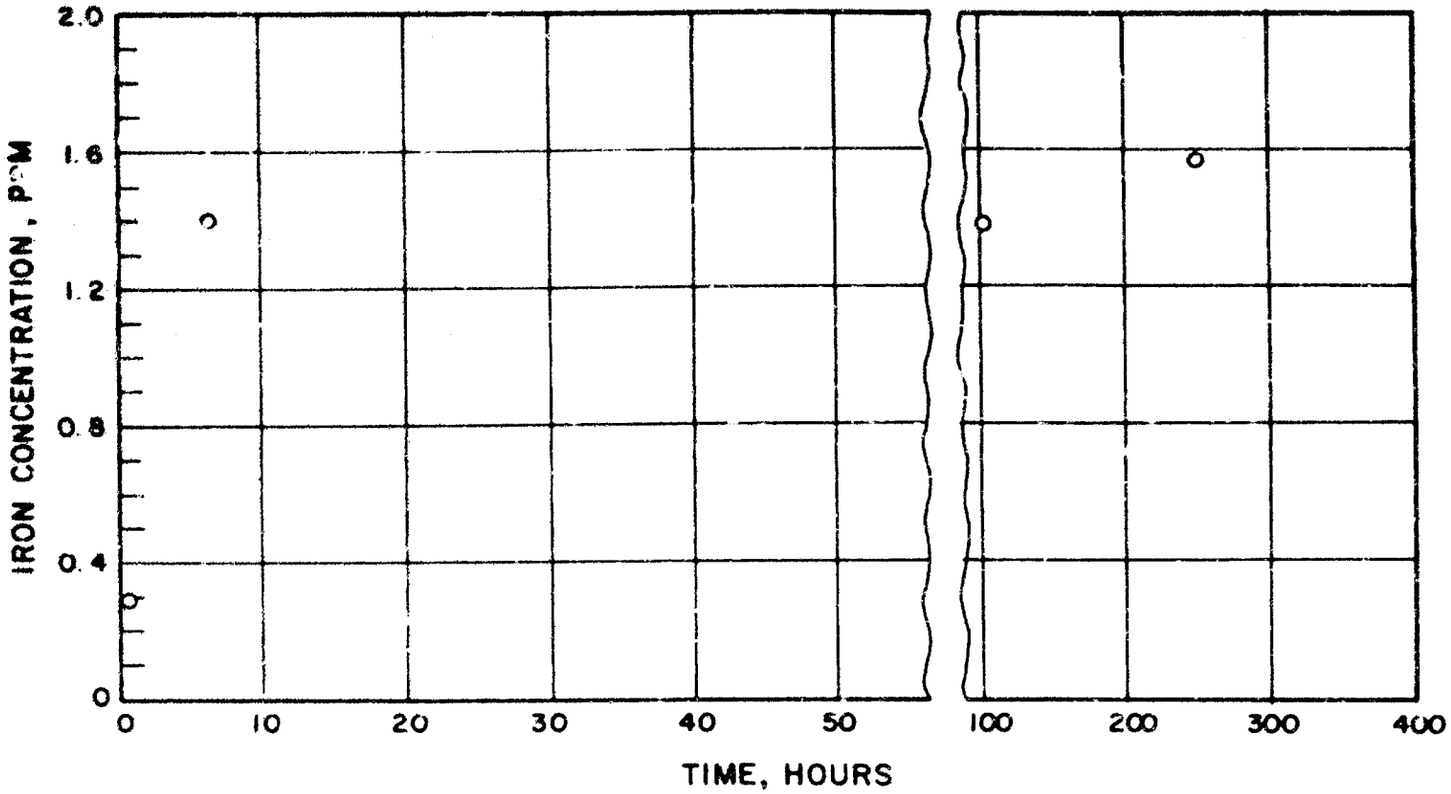

Figure 1. Dissolution of Iron Powder in N_2O_4 at 21 C. (Glass/Teflon Apparatus, 5 grams Fe/113 grams N_2O_4)

capacity of the cooling system, and (3) mechanical problems with the method of temperature control employed. There is no basis, however, for rejecting the experimental results reported in Fig. 1.

Samples of iron powder and N_2O_4 are sealed in one end of an ampoule which contains a fritted glass disk at the center. In this procedure, no agitation of the sample is provided. At the conclusion of each experiment, the N_2O_4 is filtered through the disk to separate it from the iron powder, hydrolyzed in water, and analyzed for total iron. Using this technique, each ampoule provides one datum point.

Two series of experiments were conducted at 30 C in which 0.5 gram of iron powder was placed in contact with 10 grams of anhydrous iron-free N_2O_4 in each ampoule. The results are shown in Fig. 2. The same trend appeared as in the experiments above, i.e., a rapid increase in the concentration of total soluble iron to a relatively constant value. However, the final iron concentrations were lower (about 0.5 and 1.0 ppm, respectively), and the presumably identical series of experiments shown in Fig. 2 did not yield the same final concentration. The reason for the nonreproducibility in these two series of experiments has not been established. Although the same batch of purified N_2O_4 was used in all of the experiments reported in Fig. 2 through 4, the results suggest that some parameter other than those being controlled may be important. This point will be investigated further.

The observed time dependence of the iron concentration in these initial experiments is compatible with several possible mechanisms. A coating which is readily soluble in N_2O_4 may be present initially on the surface of the metal. A more likely possibility, however, is that the metal dissolves rapidly until a passive film is formed. Another possibility is that the iron species formed reaches a solubility limit in N_2O_4. This last mechanism is supported by the results obtained in Phase III where the synthetic solvated iron nitrate was found to be soluble to an extent similar to that obtained here with iron powder (based on the concentration of total iron). If the surface of the metal became coated with an insoluble material, the observed concentration plateau could be reached without excessive precipitation or redeposition of insoluble material.

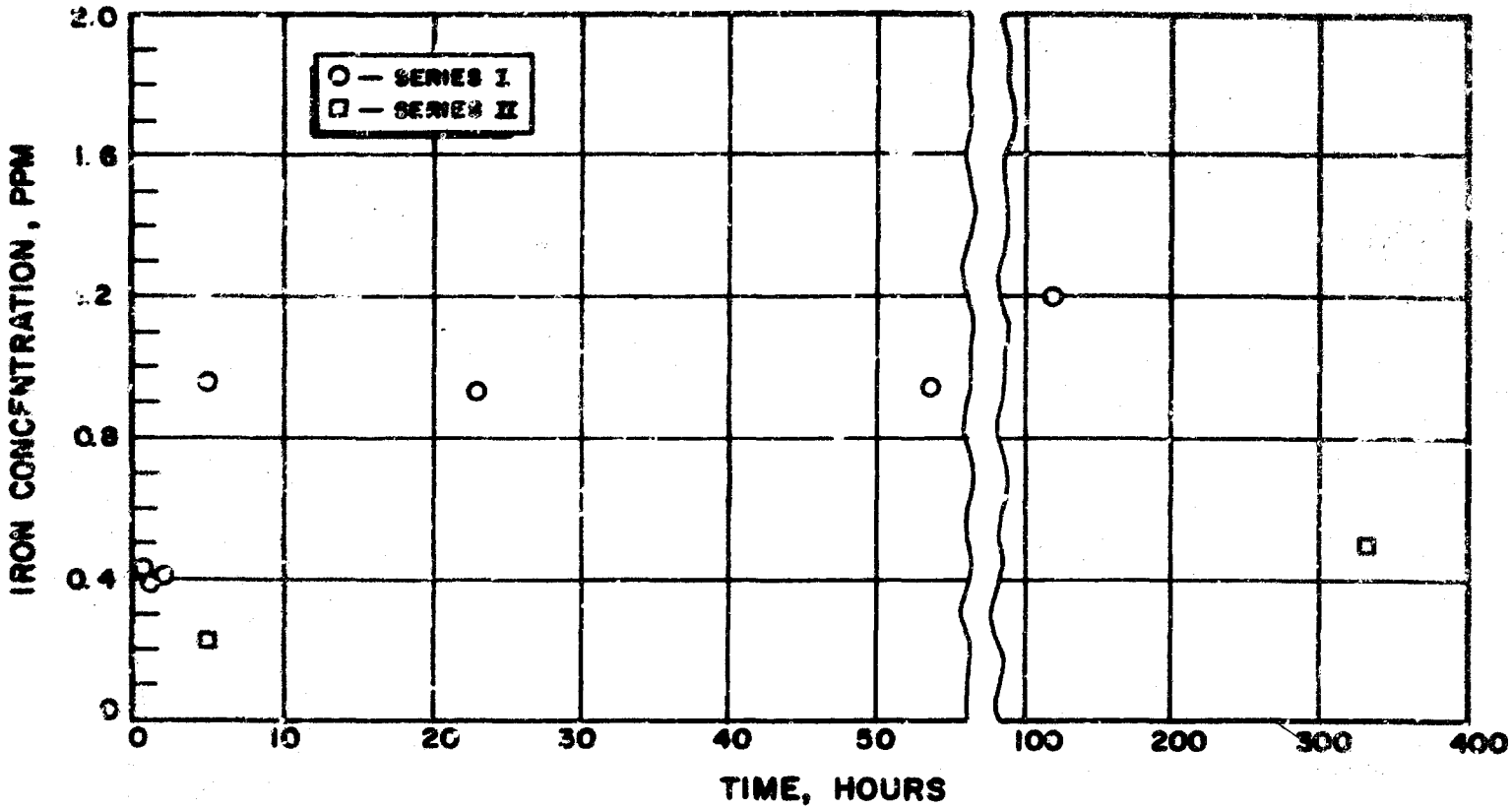

Figure 2. Dissolution of Iron Powder in N_2O_4 at 30 C.
(Ampoule Technique, 0.5 gram Fe/10 grams N_2O_4)

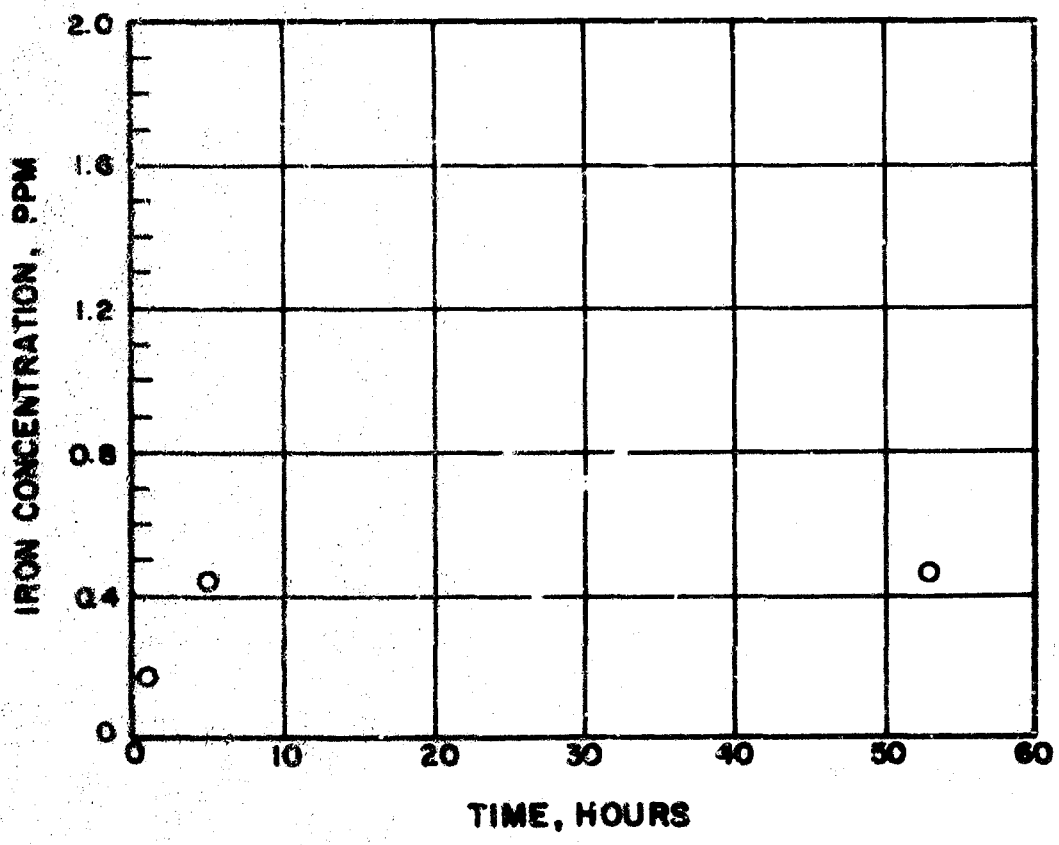

Figure 3. Dissolution of Iron Powder in N_2O_4 at 30 C
(Ampoule Technique, 0.1 gram Fe/10 grams N_2O_4)

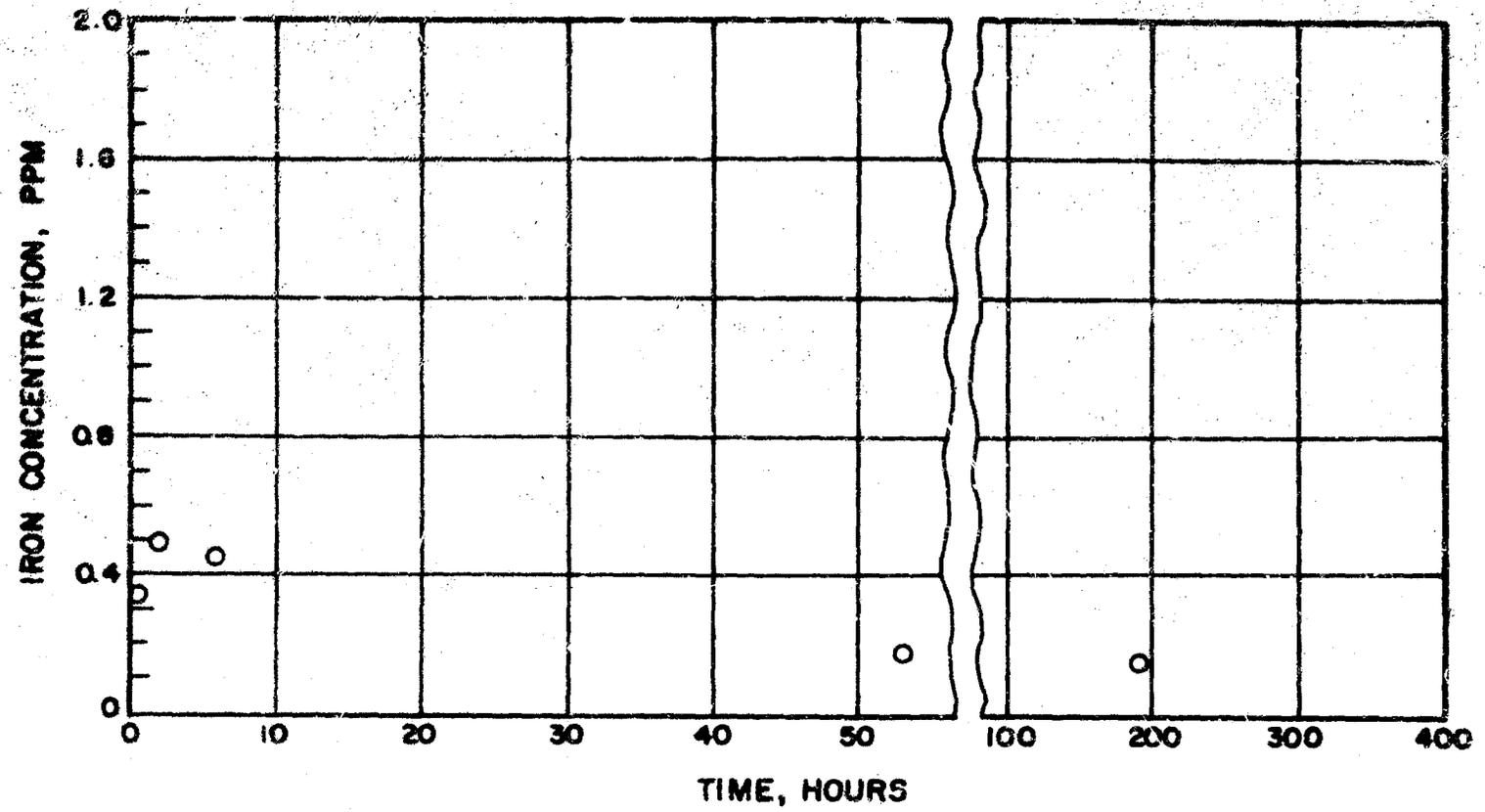

Figure 4. Dissolution of Iron Oxide Powder in N_2O_4 at 30 C.
(Ampoule Technique, 0.05 gram Fe_2O_3/10 grams N_2O_4)

If a solubility limit is involved, the final concentration under a given set of conditions would be independent of the amount of surface available. If only a passive film is formed, the iron concentration at which the rate of increase becomes slow should be proportional to the surface area. To test this point, an ampoule experiment was run at 30 C with only 0.1 gram of iron powder present in 10 grams of the anhydrous N_2O_4. The results shown in Fig. 3 indicate that the iron concentration levels off at about 0.5 ppm in this experiment. The results in Fig. 3 (0.1 gram iron) indicate that reducing the available surface area by a factor of five diminishes the iron concentration only by a factor of two, if compared to series I of the high surface area experiments (Fig. 2); if compared to series II (Fig. 2), no difference is noted. The results thus far suggest that surface area may not be the predominant factor. If this is the case, the solubility limit mechanism would be favored over the passive film mechanism.

Dissolution of Iron Oxide Powder

The solubility and rate of dissolution of iron oxide was studied because the alloys of interest may have an initial oxide coating or form such a coating during contact with N_2O_4. A series of ampoule experiments was conducted in which 0.05 gram of Fe_2O_3 powder was placed in 10 grams of anhydrous N_2O_4 and then filtered out before analysis. The results are shown in Fig. 4. The final concentration of iron was small, being only slightly greater than the detectability limit of the analytical method. With N_2O_4 samples of only 10 grams, the uncertainty of the chemical analysis for total iron is about ±0.1 ppm (about 1 microgram). No explanation is apparent for the decrease in iron concentration observed after the first few hours during the experiments with the oxide powder.

Dissolution of Iron Alloys

The rate of formation of soluble iron when steel disks are immersed in N_2O_4 was measured using a modification of the ampoule technique. The disks were 1/16 inch thick and 3/8 inch in diameter and weighed approximately

2.3 grams. Each disk was sealed in an ampoule containing 11 to 14 grams of the purified N_2O_4. A fritted glass filter was not incorporated in these ampoules. The steel disks were simply removed from the solution before analysis. The following results were obtained at 30 C:

Sample in N_2O_4	Contact Time, weeks	Iron, ppm
None	-	0.1
304 Stainless Steel	1	0.3
	2	1.2
	3	0.6
316 Stainless Steel	1	0.3
1018 Carbon Steel	1	2.7

It would appear that further experiments will have to be conducted with these alloys before any definite conclusions can be drawn. The decrease in iron concentration during the third week suggests precipitation or redeposition of the species which had formed; but it may also be the result of experimental error. Further experiments with 1018 carbon steel are indicated to determine if the high iron solubility of 2.7 ppm is real and, if so, what is the dissolution mechanism involved.

EXPERIMENTAL PROCEDURE

Aliquot Technique

The glass/Teflon apparatus used for this procedure was described in Ref. 1. Several problems (previously discussed) were encountered with this system, and it was abandoned in favor of the ampoule technique.

Ampoule Technique

The sealed ampoule technique has the advantage, particularly for long-term experiments, of eliminating the possibility of leakage and contamination. A schematic of a typical ampoule is shown in Fig. 3. The ampoules

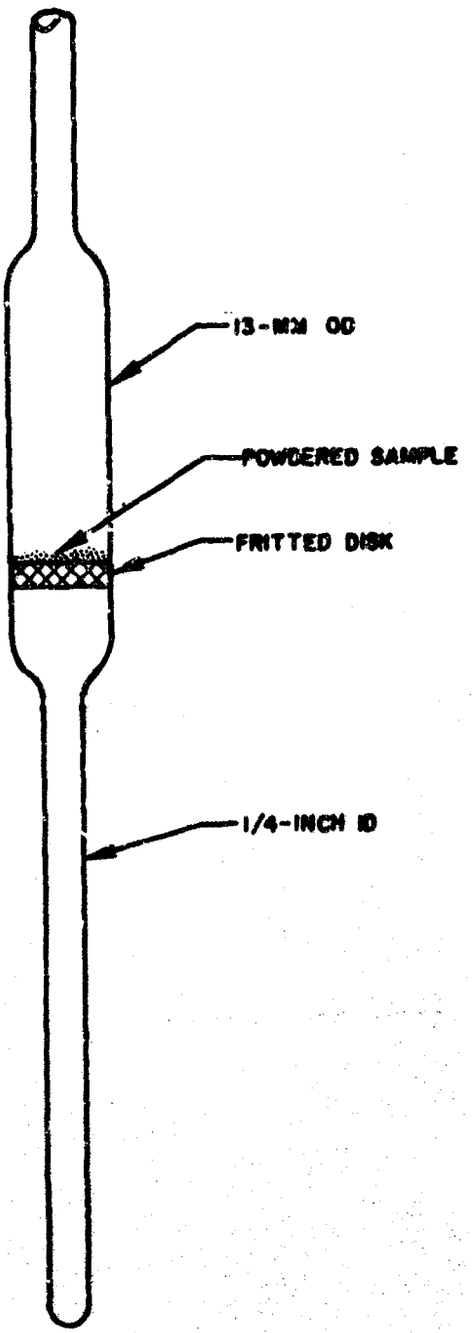

Figure 5. Pyrex Ampoule

are constructed of Pyrex, and the fritted glass disk has a pore size of about 15 microns.

All glassware is cleaned thoroughly with hot HCl, rinsed with 1:1 HCl/demineralized water, rinsed with demineralized water, and dried for 24 hours at 200 C. With the ampoules in the position shown in Fig. 5, powdered samples are weighed into the upper compartments, and a series of approximately 10 ampoules is sealed directly to a common vacuum manifold. The liter storage bulb containing the purified N_2O_4 is attached to the manifold with a Teflon-sealed joint and valve. The vacuum system is evacuated and then warmed with a heat gun to complete outgassing. Approximately 10 grams of N_2O_4 are distilled into one ampoule at a time while the lower ampoule compartment is cooled with LN_2. The coolant is then raised above the sintered disk and the system is evacuated through LN_2 traps. The ampoule is sealed shut with a torch and removed from the manifold. This procedure is repeated successively for each ampoule. The lower tube is warmed to 0 C, and the height of the liquid column is measured to determine the quantity of N_2O_4 in the ampoule, which was previously calibrated.

The ampoule is then inverted, and the larger diameter compartment is cooled in LN_2 to draw the N_2O_4 through the fritted disk into contact with the powder. The ampoules are then immersed in a constant temperature bath for the required time. At the conclusion of the heating period, they are withdrawn, inverted, and the lower tip cooled in LN_2 to draw the liquid through the sintered disk, thereby filtering out the solid powder. The tube containing the frozen N_2O_4 is broken from the ampoule, and its contents are hydrolyzed in 40 milliliters of water. The sample is then analyzed for total iron by the method described in Appendix A.

The use of a destructive method of chemical analysis makes this ampoule technique rather time consuming (one ampoule for each datum point). Preliminary e.p.r. experiments (discussed under Phase II) indicate that the soluble iron can be measured nondestructively while the sample remains sealed in the ampoule. If this procedure is successful, each sealed sample

will yield data as a function of time. The sealed sample which has been analyzed by e.p.r. can also be placed in the n.m.r. spectrometer to determine the exact water content of the N_2O_4 in the sample. The utility of this method currently is being established.

Materials

Materials used for these dissolution experiments were:

1. Iron Powder. Baker Analyzed Reagent, lot No. 26209 (98.2 percent Fe)
2. Iron Oxide Powder. Baker Analyzed Reagent Fe_2O_3, lot No. 30245 (99.3 percent Fe_2O_3).
3. Steel Alloys. The alloy disks used were originally purchased for the Inhibited Nitrogen Tetroxide Program under Contract AF04(611)-10809, and were surplus from that program. They had been carefully cleaned and degreased by the previously developed procedure (Ref. 2).

PHASE II: COMPOUND IDENTIFICATION

The objective of this task is to determine the structure of species involved in the flow-decay process. A number of approaches are being investigated.

The nuclear magnetic resonance (n.m.r.) spectrum of iron in solids was investigated first. The primary difficulty with this approach is that single crystal samples are not available. N^{14} n.m.r. requires a single crystal because of the large crystallite-angle-dependent splitting of the N^{14} resonance; in a powder this results in too broad a spectrum. Therefore the first approach was to attempt detection of resonances of N^{15} which has spin 1/2 and no quadrupole broadening, but has a natural abundance of only 0.365 percent with n.m.r. spectra having very weak signal-to-noise ratios.

The second approach was the construction of a nuclear quadrupole resonance (n.q.r.) spectrometer for detection of N^{14} quadrupole resonance frequencies. The instrument is complete, but spectra of iron nitrate samples have not yet been taken. This approach is extremely important because it will allow observation of separate resonances for NO_3^-, NO_2^+, NO^+, N_2O_4 and NO_2 groups. It might be possible, for example, that the only real difference between material that causes flow stoppage of valves and iron nitrate at equilibrium under ambient conditions is an oxidation change of NO^+ to NO_2^+, n.q.r. will show this.

The third approach was an initial study to determine the effect of water on the iron species formed in N_2O_4. Military specification N_2O_4 may contain up to 0.1 percent water, and it is important to establish whether this water could enter into the corrdination sphere of iron in the iron nitrate species. To this end, broad-line H^1 n.m.r. studies were made to determine if water is indeed incorporated into dry iron nitrate on exposure to "wet" N_2O_4 and the actual state of this water, whether it exists in the crystals as -OH, HNO_3 or H_2O.

The fourth approach was to investigate the possibilities of using e.p.r. spectrometers to determine structural parameters of both solid and dissolved iron nitrate. Preliminary e.p.r. studies are reported which confirm the results of the broad-line H^1 studies. Structural information appears to be limited, but the method does appear promising as an analytical tool for quantitative determination of iron in N_2O_4 solutions.

DISCUSSION AND RESULTS

Nitrogen 15 Resonance Studies

The large chemical shifts of N^{15} resonances (so large, that the first observation of the chemical shift phenomenon was made on the two nitrogen isotopes in NH_4NO_3) make attractive the possibility of determining the structural components of iron nitrates by running a spectrum at the N^{15} resonance frequency. Although N^{14} is the more abundant isotope, the large electric quadrupole splittings result in too broad an n.m.r. spectrum of a powder sample (thousand of gauss), whereas N^{15} ($S = 1/2$) has no quadrupole moment and does not broaden the spectral features. Thus a potentially useful spectrum can be obtained from N^{15}.

During a previous study at Rocketdyne, the C^{13} resonance was observed in compounds containing C^{13} in natural abundance. In this case, a Varian high-resolution RF unit and a Varian lock-in amplifier were used. Based on this experience, a study of N^{15} resonance was initiated. Because a high-resolution RF unit was not available for the N^{15} frequency, a variable-frequency Varian RF unit was employed, together with a Princeton Applied Research lock-in amplifier (PAR). The latter has approximately 10 times the sensitivity of the Varian lock-in amplifier. No resonances were observed even in a single crystal of $NaNO_3$ (which contained N^{15} in natural abundance). It was concluded, therefore, that the variable-frequency Varian RF unit had a much lower sensitivity than the high-resolution unit, which could not be compensated for by the very high sensitivity of the PAR. It was believed, however, that because of the expected narrow N^{15} lines the problem would not be solved entirely by changing the RF unit and

that a higher sensitivity was necessary. Conversion of the variable RF unit to a high-resolution unit was initiated and a new technique was developed to increase the sensitivity of narrow n.m.r. lines. At the same time, considerable enhancement of resolution was achieved.

It is believed that narrow N^{15} lines will result from some of the nitrogen species in iron nitrate because they are largely surrounded by oxygen atoms which have no magnetic moment, and therefore give no nuclear magnetic dipolar broadening of the adjacent N^{15}. Under these conditions, there are very long relaxation times. It is well known that long relaxation times are best controlled by lock-in amplifier techniques; however, when an n.m.r. line is sharp, existing high-frequency lock-in amplifier methods do not give high sensitivity.

The basis of the new technique is that an n.m.r. signal will have maximum intensity when the width of the modulating magnetic field used for lock-in amplifier detection is comparable to the natural n.m.r. line width. To test the sensitivity of the PAR, which can operate at as low as 1.5 Hz, and remain compatible with any conceivable N^{15} line width (whether in solution or in a solid), the following study was conducted on the H^1 spectrum of ethyl alcohol at 60 MHz.

With the Varian high-resolution RF unit operating at 60 MHz, the magnetic field homogeniety coils were adjusted by running with regular high resolution so that the adjustments could be made on the oscilloscope (such adjustment cannot be made while using the lock-in amplifier because the spectral line is not displayed on the oscilloscope). The output of the RF receiver was then connected to the PAR through the recorder outlet with the recorder level set at 1000. This connection was necessary to optimize the impedance match of the RF receiver output circuit to that of the PAR input circuit. The internal sinusoidal voltage of the PAR was connected to the Varian probe Helmholtz coils through a 600-ohm series resistor with the reference attenuator and vernier of the PAR set at maximum resistance. This was done to achieve a modulating magnetic field width slightly less than the frequency of the modulating field used for

detection (PAR set at minimum of 1.5 Hz). The sensitivity of the PAR was set at 20 millivolts, the phase at 0, the time constant 300 seconds at 12 decibels and Q=25. The RF power level was down 70 decibels from 0.25 watt. The receiver gain was set at position 5 and the RF phase detector frequency response in the 4 position.

Using the above technique, the following spectra were obtained. The entire ethyl alcohol spectrum is shown in Fig. 6. This spectrum is identical in resolution to that obtained on a Varian A-60 spectrometer. The spectrum is the second derivative of the absorption mode, which accounts for the deep wings on each side of a spectral line. These wings cause the progressive deepening of the apparent base line toward the middle of a multiplet.

The spectrum of the ethyl alcohol quartet is presented in Fig. 7, employing a slower passage than for the complete spectrum (Fig. 6). Immediately prior to running the spectrum of the quartet shown in Fig. 7, an ordinary high resolution spectrum was run (Fig. 8). It is evident that the PAR method effects considerable enhancement in splitting of the individual lines of the quartet into their fine structure components. Comparing Fig. 7 and 8, it is seen that the method yields a better resolution than the ordinary high-resolution technique. An additional advantage of the new Rocketdyne method is that line voltage surges and other instabilities caused by opening of laboratory doors (with attendent pressure change effect on electronic components) can be damped with the larger output time constants available through use of the PAR. The high resolution spectrum displayed in Fig. 8 is the best one selected from approximately 15 successively run spectra. However, the spectrum in Fig. 7 was obtained repeatedly without noise spikes and distortions.

In addition to eliminating noise-generated spectral distortions, the PAR method has another advantage. As summarized by Challice and Clark (Ref. 3), there is considerable literature dealing with the subject of resolution enhancement of spectra by means of second derivative recording. Resolution is easily doubled, while an isolated doublet which visually shows no splitting can be mathematically resolved into two spectral lines by

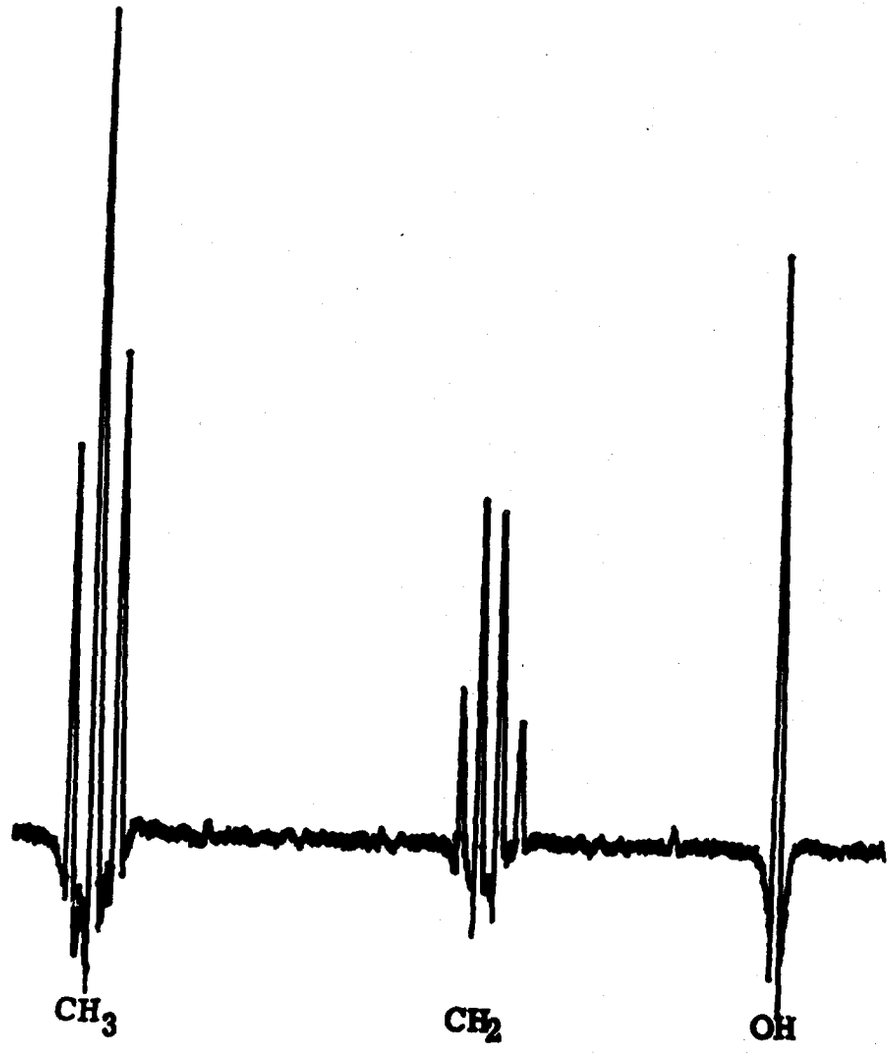

Figure 6. Spectrum of Ethyl Alcohol Obtained With New Rocketdyne Technique. Second Derivative Recorder Display

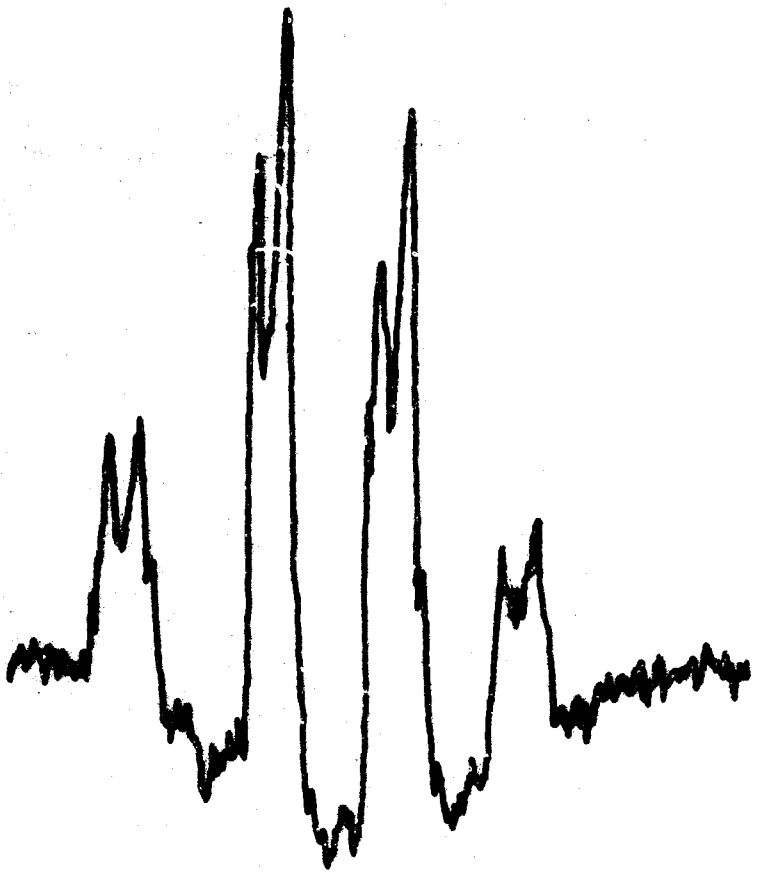

Figure 7. Spectrum of Ethyl Alcohol Methylene Group Quartet Obtained With New Rocketdyne Technique. Second Derivative Recorder Display

Figure 8. High-Resolution Spectrum of Ethyl Alcohol Methylene Group Quartet Run Just Before the Spectrum of Fig. 7 so as to Show Comparison of Resolution Obtainable by the Two Techniques

comparing a function of the ratio of central peak height to wing depth of the second derivative displayed spectrum. This procedure gives approximately a factor of eight in improved resolution over that obtained from the direct absorption mode display.

This is the first time that the use of broad-line techniques has been applied to the observation of high-resolution spectra. Thus the difference between the two techniques has been reduced to a semantic one.

Sensitivity enhancement can be achieved by using a low-frequency lock-in amplifier such as the PAR. Improvement in signal-to-noise ratio by a factor of about 350 over that available with ordinary high-resolution absorption mode display is easily achieved. However, the spectrum must be run much slower than were those reported here; it would take 24 hours to optimize the PAR spectrum, but considering the number of high-resolution scans (about 15 minutes per scan) required for a computer-averaging technique to duplicate such an enhancement, i.e., 350 squared = 120,000, it would take approximately 3-1/2 years.

Broad-Line H^1 n.m.r. Iron Nitrate Studies

The broad-line H^1 n.m.r. technique was improved during this report period and used (1) in an attempt to determine the presence of water in the synthetic iron nitrate which had been refluxed in wet N_2O_4, and (2) to ascertain the structure of the solid formed. Studies were made using a Varian DP-60 spectrometer operating at 60 MHz, an RF power of 0.5 watt, a modulating field of 1 gauss at 40 cycles, and a PAR lock-in amplifier. The RF receiver output to the lock-in amplifier was connected to the high-resolution recorder output so as to match the impedance better with that of the lock-in amplifier than can be done with the regular Varian cathode follower output used for the Varian output-control unit.

In Fig. 9 are shown the spectra of the empty sample tube, a single crystal of iron nitrate nonahydrate, and 0.5 gram of synthesized anhydrous iron nitrate (solvated with N_2O_4) which had been refluxed for 48 hours with 30 milliliters of N_2O_4 containing 0.2 percent added H_2O. Comparison of the spectrum of the refluxed sample with that of the empty tube (by subtracting the background signal algebraically) shows a signal in the same position as is seen for the (much larger) sample of known iron nitrate hydrate, and roughly in proportion to the known weights of the samples. On the basis of these spectra alone, it is possible to determine only that water is present in some amount but not how many water molecules are present per iron molecule. Reference to the e.p.r. studies in this report confirm that a change occurs on refluxing the synthesized anhydrous iron nitrate in wet N_2O_4.

The spectra obtained which are displayed on Fig. 9 have a poor signal-to-noise ratio primarily because the modulating field is not broad enough. During future studies this will be increased to approximately 10 gauss. There are strong indications that when the background signal (from the protons in the enamel of the transmitter and receiver coils and the Epoxy glue which is used to cement the various parts of the probe together) is subtracted from the observed signal, a good spectrum will be obtained with the use of a broader modulating field. The shape of the signal should allow calculation of the nature of the protons in the iron nitrate hydrate. Thus a broad single peak will indicate OH protons or an intact HNO_3 solvating species, while a broad doublet will indicate two protons close together as in the case of an H_2O molecule bonded through the oxygen to the iron. The other possibility, H_3O^+ in the crystal, would be distinguished by a broad triplet. Such conclusions must await spectra having a better signal-to-noise ratio.

e.p.r. Studies of Iron Nitrates

Solids. To investigate the possibilities of using e.p.r. techniques to determine structural parameters of the iron nitrate which causes flow stoppage in valves, four samples of iron nitrate were studied. All spectra were run at room temperature with a 9.5×10^9 Hz spectrometer on samples contained in 5-mm OD Pyrex tubes.

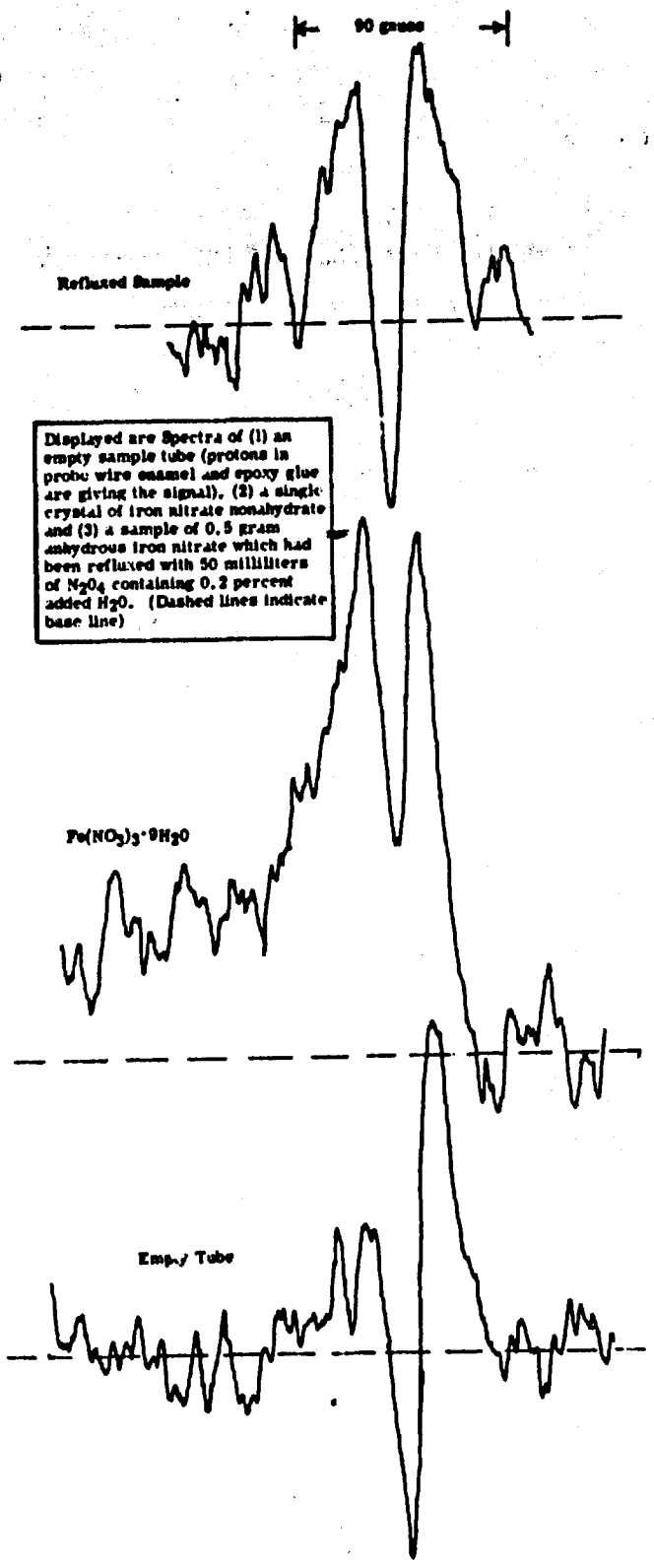

Figure 9. Broad-line H^1 n.m.r. Spectra at 60 MHz, RF Power 0.5 Watt, Modulating Field 1 Gauss at 40 Cycles, PAR Lock-in Amplifier, Varian DP-60 High Resolution Spectrometer

The spectrum of a sample of $Fe(NO_3)_3 \cdot 9H_2O$ is shown in Fig. 10. The sample was a large single crystal. It is expected that if a powdered sample were studied, the spectral structure at the higher fields would be broadened to correspond more closely in appearance to the spectra of the refluxed and purified samples displayed below it. The spectrum of a sample of iron nitrate, which had been purified (in Phase III) by precipitation of anhydrous iron nitrate dissolved in ethyl acetate by the addition of dry N_2O_4, is shown on the same illustration. For comparison, the spectrum of the same material is shown after a 0.5-gram sample had been refluxed with a 30-milliliter sample of N_2O_4 containing 0.2 percent H_2O. It is clear that the treatment with wet N_2O_4 caused structural changes. This evidence is compatible with the hypothesis that iron nitrate powder in equilibrium with wet N_2O_4 contains some water of hydration.

Solution. The e.p.r. spectrum of N_2O_4 containing 1.5 ppm Fe and 0.1 percent H_2O is shown in Fig. 11. The sample was taken from a carbon steel cylinder in which the N_2O_4 had been stored for several months. The large truncated central dispersion mode line is due to NO_2, and the asymmetric peak on the left of the spectrum is ascribed to Fe species.

An enlargement of the asymmetric peak which is ascribed to iron species in the solution is shown in Fig. 12. Because the peak has a good signal-to-noise ratio and was taken with a sample that analyzed 1.5 ppm Fe, it appears that the e.p.r. method will be a satisfactory analytical technique for use in Phase I. However, some reservations are necessary at the present time. It has not been established yet that the peak is due to iron, although analysis of samples stored in a carbon steel cylinder in the past has disclosed no other major transition metal impurities, and the peak cannot be due to species other than transition metals because of the high g value. It will be necessary to calibrate against known concentration samples, since the peak is asymmetric and overlapped partially (on the right) by the NO_2 resonance, so that a linear dependence of peak area vs concentration is not available.

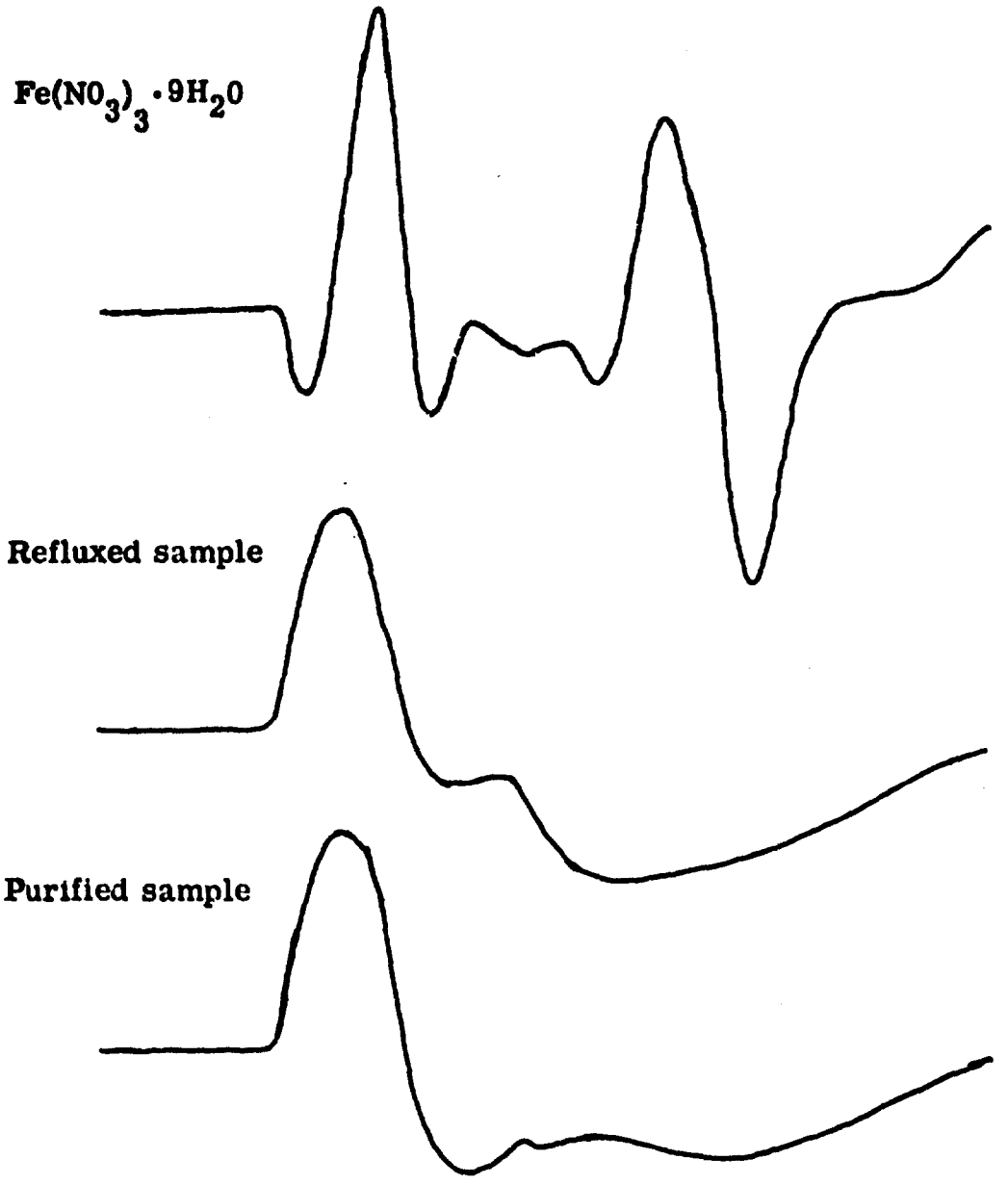

Figure 10. e.p.r. Spectra of a Single Crystal of Nonahydrous Iron Nitrate, Purified Anhydrous Iron Nitrate, and Purified Material Which Had Been Refluxed With N_2O_4 Containing 0.2 Percent H_2O. Ordinates are 0 to 6600 Gauss

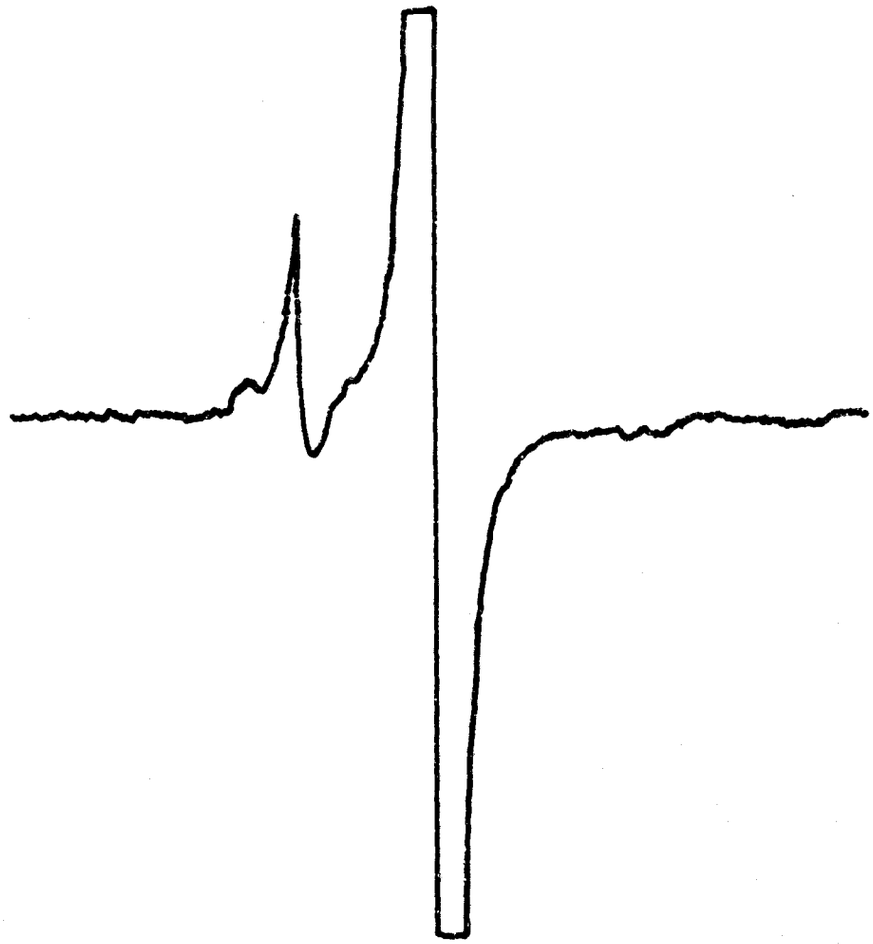

Figure 11. e.p.r. Spectrum of N_2O_4 Containing 1.5 ppm Fe and 0.1 Percent H_2O. Ordinates are 0 to 6000 Gauss. Truncated Central Dispersion Mode Line is Due to NO_2, and the Asymmetric Peak on the Left is Ascribed to Fe Species

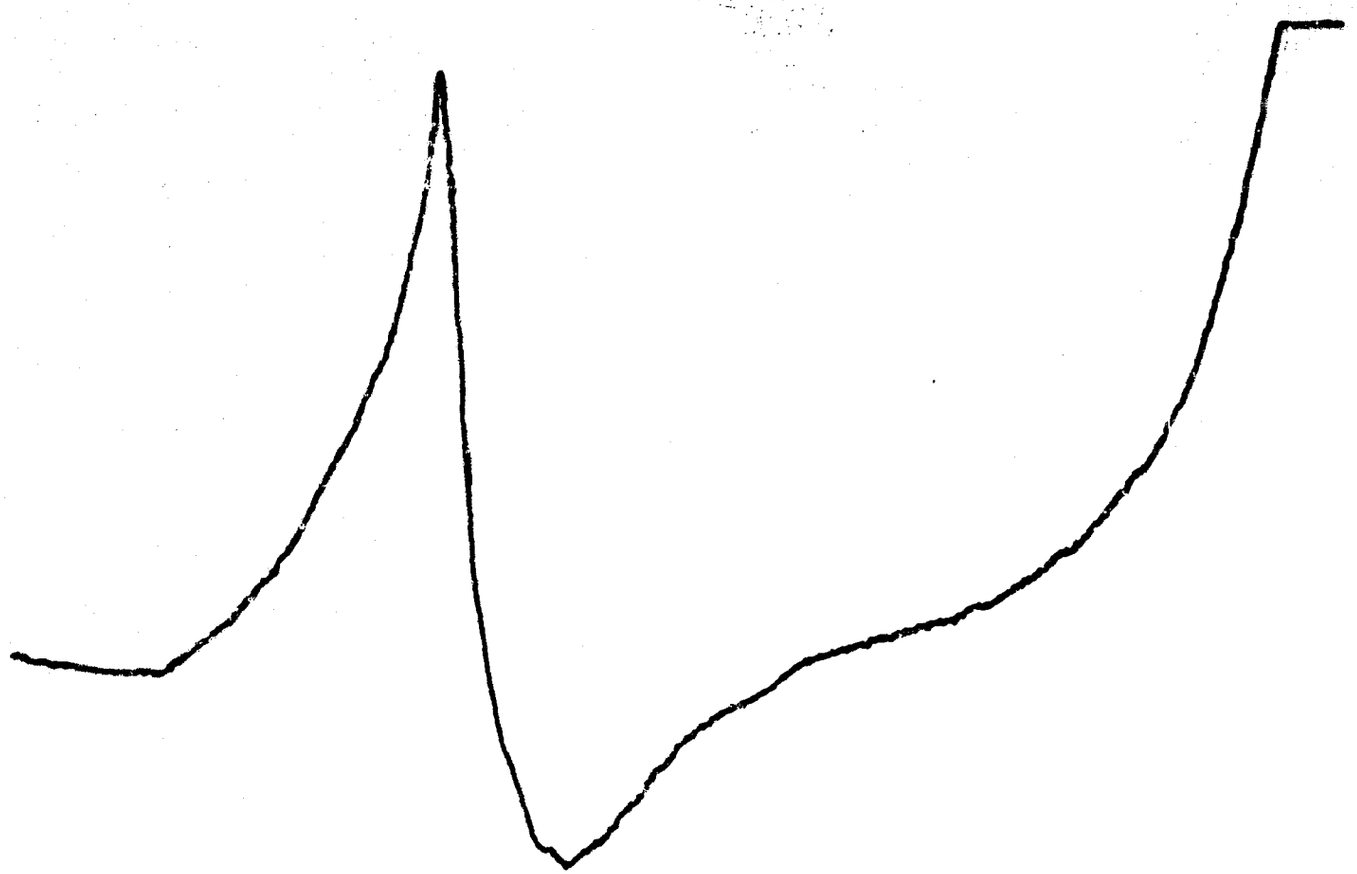

Figure 12. Enlarged Spectrum of the Iron Peak of 1.5 ppm Fe in N_2O_4. Truncated Peak on the Right is Due to NO_2

However, if the present assumption that the peak due to iron is correct, then it is clear that an asymmetric peak could not be due to a species such as $Fe(NO_3)_4^-$ in the solution, since such a species would be expected to have a cubic symmetry with a symmetric e.p.r. spectrum. Thus, this spectrum is evidence that the iron species in solution has more than one kind of attached ligand. Future studies with variation in the water content of the solution should establish whether the asymmetry of the spectrum is in fact due to water. A possible alternative explanation for the asymmetry is that the iron species is really colloidal. This question could be solved by ultrafiltration.

PHASE III: COMPOUND SOLUBILITY

The initial objective of Phase III was to prepare synthetically a compound of the composition $Fe(NO_3)_3 \cdot N_2O_4$, which had been shown previously to be identical with the flow-decay deposit. This objective has now been met with the successful preparation and purification of $Fe(NO_3)_3 \cdot N_2O_4$ in sufficient quantities that solubility studies with N_2O_4 can be conducted. During the solubility studies now in progress, the temperature of the N_2O_4 has been varied from 32 to 100 F. In addition, the concentrations of nitric oxide and water in the N_2O_4 are being varied from 0 to 1 percent and from 0.1 to 1 percent, respectively.

DISCUSSION AND RESULTS

The preparation of the anhydrous iron nitrate $Fe(NO_3)_3 \cdot N_2O_4$ has been described in the first quarterly progress report (Ref. 1). The next objective of this phase was to develop a method of purification for the crude $Fe(NO_3)_3 \cdot N_2O_4$. Investigations involving recrystallization from nonaqueous solvents, including N_2O_4 itself by cyclic extraction techniques, were undertaken. The cyclic extraction technique using N_2O_4 did produce a small amount of pure material. However, because the yield was very low and the method extremely time consuming, other methods of recrystallization were investigated. Solubilizing the crude material in ethyl acetate and then precipitating the solid by the addition of N_2O_4 has developed into an excellent method. A large amount of a pale cream-colored solid which was identical in all respects with the previously purified material (by cyclic extraction techniques using N_2O_4) has been obtained. Two separate purification runs have produced materials with the following empirical formulae: $Fe(NO_3)_{3.1} \cdot 1.03N_2O_4$ and $Fe(NO_3)_{3.1} \cdot 0.99N_2O_4$; on 98 to 99 percent mass balances.

With the preparation of sufficient quantities of pure "synthetic flow decay compound," solubility studies in N_2O_4 were begun. To establish a reference point of solubility and for purposes of comparison with propellant

grade N_2O_4, freshly distilled anhydrous iron-free N_2O_4 (< 0.1 pp Fe and 0.01 ppm water) was utilized. The N_2O_4 was also pretreated with oxygen to preclude the possible presence of traces of NO.

The solubility determinations were made in specially constructed glass apparatus. Solubility runs were carried out at controlled temperatures (constant temperature baths) of 32, 86, and 100 F. Solubility was established by withdrawing liquid samples periodically and then having the samples analyzed for iron. Based on the analytical results obtained thus far, the tentative conclusion is that the solubility of $Fe(NO_3)_3 \cdot N_2O_4$ in N_2O_4 is quite low, on the order of 0.5 ppm to 1.5 ppm (in terms of Fe concentration). The solubility results have been quite erratic, probably because of inherent errors in the sampling procedures and the procedures involved in the analysis of a trace component. However, these experiments will be repeated using a slightly modified apparatus and by taking larger samples for analyses; it is anticipated that some of the difficulties in the analytical procedures will be alleviated.

The investigation of the effect of the presence of small amounts of nitric oxide and water on the solubility of the flow-decay compound in N_2O_4 has been initiated. The NO was purified just prior to being used by fractional condensation. The purity was then checked by infrared and mass spectrometry. The $NO-N_2O_4$ mixture was made in the solubility apparatus itself whereas the $H_2O-N_2O_4$ mixture was made in a separate vessel and then added to the solid in the solubility apparatus. These experiments are in the initial stages, and no results are available at the present time.

EXPERIMENTAL

Purification of $Fe(NO_3)_3 \cdot N_2O_4$

The recrystallization of the iron nitrate from ethyl acetate for a 2-gram sample was described in the first quarterly report (Ref. 1). The analysis of the purified solid, however was pending. The following analytical

results are now available:

Fe, 16.0 w/o; NO_3^-, 55.2 w/o; N_2O_4, 27.2 w/o

A larger sample of crude iron nitrate (6.5 grams) was similarly purified. The analytical results on a sample of this second batch of purified material were as follows:

Fe, 16.5 w/o; NO_3^-, 55.2 w/o; N_2O_4, 26.9 w/o

The infrared spectra, as mulls in halocarbon oil, of these two batches were identical. Their physical appearances (pale cream powders) and their reactivities with moisture (rapidly becoming wet and the evolution of gases accompanied by bubbling effect) were also identical.

Solubility of $Fe(NO_3)_3 \cdot N_2O_4$ in Distilled N_2O_4

The solubility apparatus consisted of a glass vessel equipped with a Teflon-covered stirring bar and two Teflon needle valves (Fig. 13). The apparatus was calibrated and dried thoroughly prior to use. The solid $Fe(NO_3)_3 \cdot N_2O_4$ was placed in the apparatus through the needle valve A in an inert atmosphere (drybox). The N_2O_4 was distilled into the solubility apparatus through valve A using a glass-vacuum system. The apparatus was then immersed in a constant-temperature bath in such a fashion that only the valves remained above the liquid level of the bath. The N_2O_4-iron nitrate mixture was stirred by means of a magnetic stirrer.

Sampling was accomplished by means of a U-shaped glass vessel equipped with Teflon needle valves (Fig. 13). The sampler was directly attached to the solubility apparatus through an O-ring joint. A Teflon O-ring was used for this purpose. The section between valve B and valve D was evacuated and then refilled with dry nitrogen. The presence of the nitrogen provided back pressure and thus minimized the vaporization of the

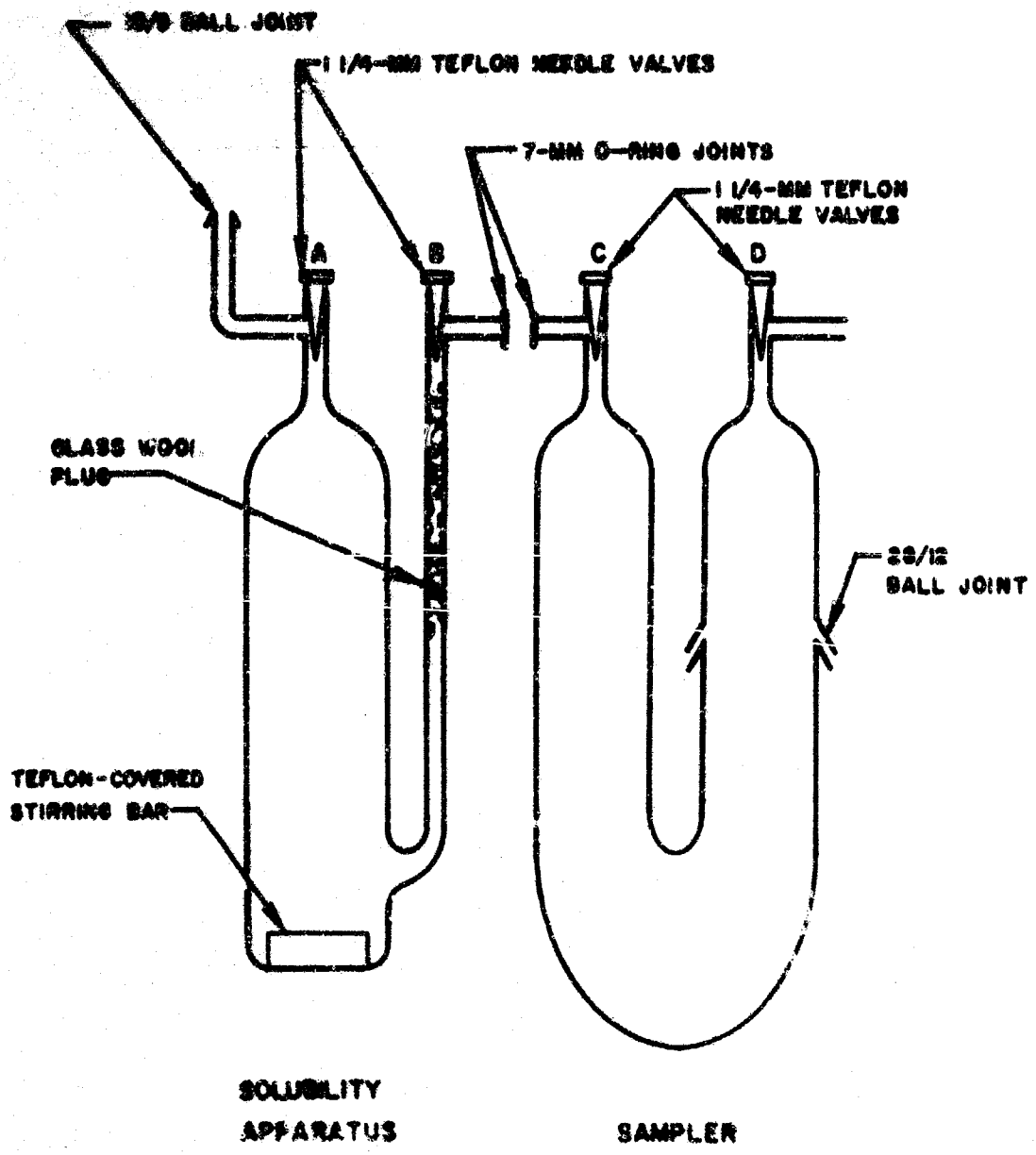

Figure 13. Solubility Apparatus and Sampler

N_2O_4. The sampling was done with a -78 C bath around the sampler. At low temperatures, pressurization of the solubility apparatus with dry nitrogen was necessary to force the liquid out through the opening in valve B. A glass-wool plug prevented any solid particles from being carried over into the sampler. During the sampling, the solubility apparatus was kept in the constant-temperature bath, thus assuring that a truly representative liquid sample was being taken. The weights of the N_2O_4 samples were obtained by determining the difference in the weights of the U-sampler before (evacuated) and after (N_2 removed) the sampling. The hydrolyses of the N_2O_4 samples were accomplished directly in the U-sampler by the addition of ice-cold water (deionized). Aliquots of these hydrolysates were then submitted for iron analyses. The results are presented in Table 1.

TABLE 1

SOLUBILITY OF $Fe(NO_3)_3 \cdot N_2O_4$ IN N_2O_4

Temperature, F	Values in ppm of Fe						
	Duration of Studies, Days						
	2	5	9	14	24	28	38
32				0.55		0.65	
86		*			1.37		0.57
100	0.89	0.06	0.46	0.25	1.75		

*Sample taken at this period gave an exceptionally high value, and the result was discarded

NO Additive to N_2O_4-Iron Nitrate Mixture

Nitric oxide was purified by passing it through a -156 C trap several times, and the purity was checked by infrared and mass spectrometry and by vapor pressure measurements. The solid iron nitrate (65 milligrams) was placed

in the solubility apparatus in the manner described previously. The gaseous NO (162.5 cc) was then placed in the apparatus by condensing it in a narrow sidearm added to the apparatus shown in Fig. 13. The N_2O_4 (100.7 grams) was then distilled into the apparatus using the vacuum system and a cooling bath of ice-brine mixture. With the completion of the addition of the N_2O_4, the sidearm was slowly warmed, thus allowing the NO to vaporize and dissolve in the N_2O_4. The apparatus was then placed in a constant-temperature bath held at a temperature of 25 C. This experiment is in progress at the present time, and sampling will be done as described previously.

Water Additive to N_2O_4-Iron Nitrate Mixture

Water (0.10 gram) and N_2O_4 (97.0 grams) were mixed in a 200-milliliter glass bulb equipped with a Teflon needle valve. This mixture was directly added to the solubility apparatus containing the solid iron nitrate. This was accomplished by affixing the bulb containing the mixture to the solubility apparatus by means of an adapter through which the adjoining sections could be evacuated. The apparatus was then immersed in a constant temperature bath at 25 C. This experiment is in the initial stages, and no results are available.

PHASE IV: COMPOUND ELIMINATION

Investigations on appropriate coordinating agents as means of eliminating flow-decay compounds is the major task of this phase of the program. In an effort to render the metal compound soluble in N_2O_4, the effects of these coordinating agents on the synthesized flow-decay compound and its N_2O_4 solutions are being studied.

DISCUSSION AND RESULTS

Investigations of the reactivity of the synthesized iron nitrate with various coordinating agents have been continuing. The iron nitrate-N_2O_4 complex was found to be soluble in the following additional reagents: benzonitrile, benzaldehyde, acetophenone, and acetone. The complex was found to be insoluble in trifluoroacetonitrile, hexafluoroacetone, n-pentane, Freon 113, and silicone (XF 1000) liquid. The last three reagents gave not only a test for solubility, but also an indication of the ionic nature of the iron nitrate-N_2O_4 complex (ionic substances are unlikely to be soluble in nonpolar solvents).

The reactivity of the preceding reagents when added in small quantities to N_2O_4 under ambient conditions was tested. No visible reactivity was noted when the following reagents were mixed with N_2O_4 (N_2O_4 was always in large excess): trifluoroacetonitrile, hexafluoroacetone, n-pentane, and Freon 113. In addition, other workers (Ref. 4 and 5) have reported that benzonitrile, benzaldehyde, acetophenone, and acetone can be added to N_2O_4 without gross reaction. A vigorous reaction, with the evolution of a great deal of gas, took place when silicone (XF 1000) liquid was mixed with N_2O_4.

The results of the above experiments have thus added new candidates (benzonitrile, benzaldehyde, acetophenone, and acetone) to the previous list of candidates for further investigations in flow-decay compound elimination.

Similar screening of various other reagents will be conducted in the near future.

Preliminary investigation of the solubility of the iron nitrate in N_2O_4 in the presence of a candidate-coordinating reagent has been made. The addition of acetonitrile to a mixture of $Fe(NO_3)_3 \cdot N_2O_4$ (40 ppm of Fe) and N_2O_4 at room temperature was found to completely solubilize the solid $Fe(NO_3)_3 \cdot N_2O_4$. Practically all of the solid was insoluble under these conditions before the addition of acetonitrile. Such a solution was also found to maintain its integrity (no apparent change) during a temperature cycling over the range of 32 to 100 F.

Although the $Fe(NO_3)_3 \cdot N_2O_4$ was found to be insoluble in CF_3CN alone, it was found to be soluble (0.7 w/o of solid $Fe(NO_3)_3 \cdot N_2O_4$) in a mixture of CF_3CN and N_2O_4. No change in the solution was observable over the temperature range of 32 to 100 F. However, a very high concentration of additive was used in this test (10 percent). CF_3CN would probably not be a satisfactory additive because of its high volatility. Further tests at a more realistic additive level will be carried out with other less volatile perfluoroalkyl nitriles.

It is anticipated that similar solubility phenomenon as in CF_3CN-N_2O_4 mixture will be found with CF_3COCF_3-N_2O_4 mixture. This will be tested shortly. The results of the CF_3CN experiment may lead to new additives for the flow-decay compound elimination. Reagents which do not dissolve the solid $Fe(NO_3)_3 \cdot N_2O_4$ by themselves may still be effective as long as they are compatible with N_2O_4.

EXPERIMENTAL

The solubility and compatibility tests were carried out essentially as described in Ref. 1.

The solubility of the iron nitrate in N_2O_4 in the presence of a candidate-coordinating reagent (acetonitrile) was carried out in the following manner. The solid $Fe(NO_3)_3 \cdot N_2O_4$ was placed in a small glass bulb equipped with a Teflon-covered stirring bar and a Teflon needle valve. The weight of the solid was obtained by determining the difference in the weights of the evacuated bulb before and after the addition of the solid. N_2O_4 was then condensed over the solid. The mixture was allowed to warm to room temperature and was stirred (magnetic stirrer) overnight. Most of the solid was observed to be insoluble during this period. Acetonitrile (0.2 w/o) was then condensed into the bulb, and the mixture was allowed to warm to room temperature. After 1 hour of stirring, the amount of insoluble solid had decreased considerably. After overnight stirring, all of the solid had dissolved. The resulting solution was subjected to a temperature cycling by immersion in baths from 32 to 100 F.

PHASE V: EFFICIENCY OF ELIMINATION

Construction of the flow test system started during this quarter, but activity was temporarily discontinued pending the availability of a better test location. The flow system is now being installed in an entirely separate test bay of the Propellant Engineering Laboratory. This new site represents a considerable improvement in the larger space now available for system components, and in the greater freedom from other laboratory activities, thus providing for more efficient flow-test operations.

At present, the test bay has been made ready for occupation by the flow test system. The nitrogen gas system to be used for N_2O_4 tank pressurization has been installed. Supporting structures for the tankage and for the flow-line components have been built. Installation of the flow line is under way; this includes, in downstream sequence, the on-stream heat exchanger, the test hardware, which will be initially a sight-gage needle valve previously utilized at Rocketdyne for N_2O_4 flow-decay observations, a flowmeter, and a metering valve for flowrate control independent of the decay process. Three temperature bath containers have been prepared, one for batch temperature conditioning at the N_2O_4 source tank, a second for stream temperature conditioning with the flow-line heat exchanger, and a third to provide for circulating flow of adequately large cooling or heating capacity to either of the others. Preliminary testing of these temperature-conditioning units is being carried out.

The design requirements for the on-stream heat exchanger are problematic. This heat exchanger is being constructed to provide reasonably precise selection of emerging stream temperatures for all flow conditions of interest. Conditions of potential interest include cooling from 165 F to near 15 F at flowrates of several gallons per minute, requiring a long heat exchanger of large surface area. Such a unit is not a localized flow restriction and would not be expected to participate directly in

flow decay. However, the large cold area could conceivably act as a scavenger of flow-decay material ahead of the t st hardware. If this possibility materializes, efficient stream temperature control may have to be abandoned in favor of larger flow decay effects

APPENDIX A

IRON ANALYSIS PROCEDURE

The analysis for trace amounts of iron in N_2O_4 has been carried out using 1,10-phenanthroline as the color-developing reagent. Using sample sizes of 10 grams of N_2O_4, the ideal range covered by this technique is 0.2 to 2.0 ppm of iron. By increasing or decreasing sample size, the range can be extended at either end. Therefore, the use of 4,7-diphenyl derivative (Ref. 1) of ortho-phenanthroline has not been required, and all analyses carried out during this period have utilized orthophenanthroline. The analytical procedure used for the analyses is described in the following paragraph.

The weighed sample of N_2O_4 is hydrolyzed slowly in a closed container using excess (30 to 50 cc) water at 0 C. The aqueous solution is quantitatively transferred to a 100-milliliter beaker, 2 milliliters of concentrated sulfuric acid are added, and the solution slowly boiled to dense SO_3 fumes to remove nitric and nitrous acids. The cooled sample is then transferred to a 50-milliliter volumetric flask, and Fe^{III} reduced to Fe^{II} using 2 milliliters of 10 percent hydroxylamine hydrochloride. The rate of reduction is increased by heating the flasks to 60 C for 10 minutes. The pH is then adjusted to 3 to 5 with 2 M sodium acetate and 1:1 amonia solution. One milliliter of 1,10-phenanthroline (0.1 percent in 10 percent ethanol) is added, and the solution is set aside for 30 minutes. The flask is then diluted to the mark, and the absorbance is measured at 510 millimicrons against a reagent blank. Calibration standards are prepared by adding known amounts of iron to 1:1 nitric acid solution and carrying out the analytical procedure in the same manner as the unknowns.

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13. ABSTRACT

Second quarter progress is reviewed on a 12-month program to ascertain methods for the elimination of the corrosion products in N_2O_4 (iron-nitrate-containing species) which are responsible for the phenomenon of "flow decay." Studies on the rate and mechanism of solution of iron in anhydrous N_2O_4 are described. Nuclear magnetic resonance and electron resonance spectroscopy studies of the solvated iron nitrate species are presented. Compounds of the type $Fe(NO_3)_3 \cdot xN_2O_4$ have been synthesized and purified. The properties of these materials have been found to match the properties of the flow decay substance. Solubility studies of the "synthetic" flow decay material in anhydrous N_2O_4, N_2O_4 containing NO, and N_2O_4 containing small quantities of H_2O have been initiated and are discussed in detail. Preliminary experiments have indicated possible candidate coordinating agents for further investigation. A flow bench designed to study this phenomenon is being constructed. Design considerations are discussed.

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