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Iron Containing Contaminants in N_2O_4

Prepared by H. H. TAKIMOTO, G. C. DENAULT, and P. A. MARSH
Aerodynamics and Propulsion Research Laboratory

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Laboratory Operations
AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
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FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract F04701-68-C-0200.

This report, which documents research carried out from August 1967 through April 1968, was submitted on 14 October 1968 to Lieutenant John F. Turk, II, SMTTP, for review and approval.

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G. W. King
Operations General Manager

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.

John F. Turk II

John F. Turk, II, 2nd Lt., USAF
Project Officer

ABSTRACT

The contaminants found in N_2O_4 causing flow blockage at the launch site have been analyzed and identified as nitrosyl tetranitratoferrate. An authentic sample of this material was synthesized in the laboratory for comparison purposes. The corrosive action of the oxidizer on the iron containing materials of constructions results in the formation of this contaminant.

CONTENTS

FIGURE

I. INTRODUCTION

The contaminants present in nitrogen tetroxide can seriously affect the performance of bipropellant rocket motors. The deposition of impurities in the oxidizer can cause decreased N_2O_4 flow by partially or completely clogging injectors, screens, and filters in the propellant line. One such contaminant believed to be present in any N_2O_4 that has come in contact with iron-containing materials is nitrosyl tetranitratoferrate (NTNF). Although the presence of this compound in N_2O_4 has been shown in the laboratory, its actual isolation from the oxidizer used in the field has not been previously reported. This report describes the identification of NTNF as a major constituent in the gel-like material that causes blockage of a filter in the transfer line between the oxidizer transport trailers and the ready storage vessel at Vandenberg AFB.

II. EXPERIMENTAL

The stainless steel filter containing the contaminants was obtained from SLC-IV West at Vandenberg AFB. Approximately 18,000 gal of N_2O_4 had been passed through this filter, which was located in the transfer line between the oxidizer transport trailers and the ready storage vessel. The filter and its contents had minimum exposure to moisture during removal and were placed in an air-tight stainless steel container while still copiously evolving NO_2. The container was transported to the laboratory at Aerospace Corporation and then opened in a dry box under nitrogen atmosphere.

Extraction of the filter contaminants with ethyl acetate and removal of the solvent yielded a dark amber-brown viscous material. The crude contaminants were purified by the following procedure: (1) dissolution in ethyl acetate, (2) filtration, (3) removal of the volatile from the filtrate, and (4) precipitation with fresh N_2O_4. This purification process was repeated several times while excluding moisture to yield a light amber-colored solid. The infrared spectrum of this compound (Fig. 1) was taken on a halocarbon mull between polyethylene films since NTNF reacted with NaCl when placed directly on the salt plate and gave extraneous absorptions. Characteristic absorption bands observed at 2225, 1597, 1550, 1280, 1013, 976, and 765 cm^{-1} are similar to that reported for NTNF. Further, an authentic sample of NTNF was prepared from the reaction of iron powder and N_2O_4 in ethyl acetate catalyzed by ferric chloride. This synthetic material yielded an infrared spectrum identical to that for the iron compound obtained from the filter.

In an analysis of $NOFe(NO_3)_4$ iron (Ref. 5), a known quantity of NTNF was dissolved in water. Aliquots were taken, and the iron content of the solution was determined colorimetrically using o-phenathroline as an indicator on a Beckman Spectrometer DK-2 at 510 mμ. The procedure described in ASTM E87-58 was followed. The values were obtained by a comparison with a calibration curve obtained on standard iron solutions:

Calculated: 16.8% Found: 16.8%

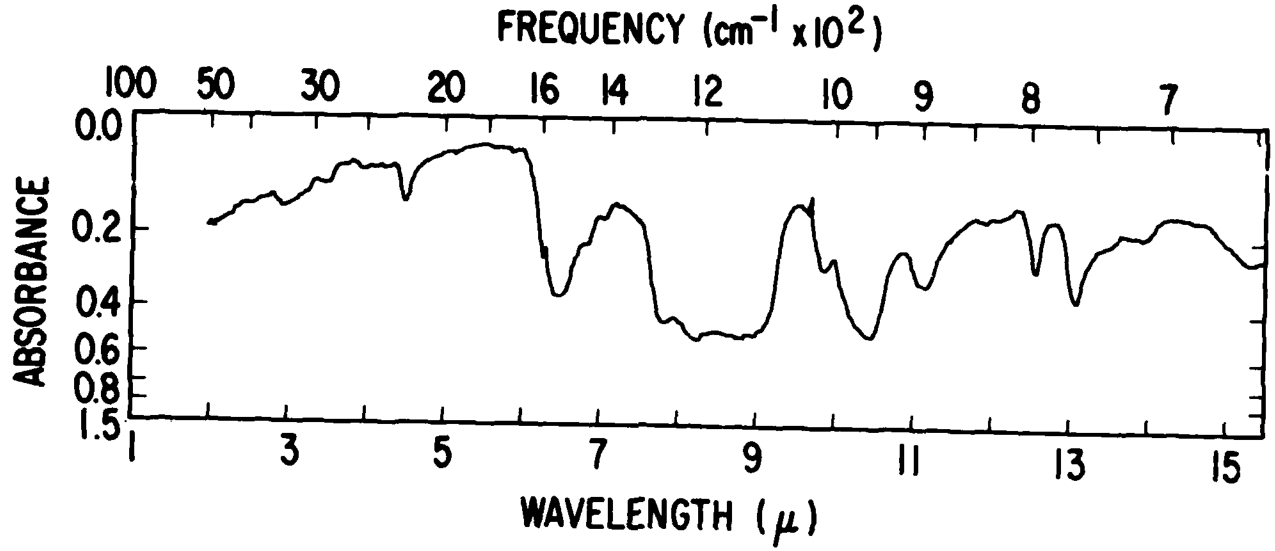

Figure 1. Infrared Spectrum of Nitrosyl Tetranitratoferrate.

III. RESULTS AND DISCUSSION

Addison, et al. (Ref. 1), have described the synthesis of NTNF by the reaction of N_2O_4 with either iron filings, ferric chloride, or iron pentacarbonyl. Of particular interest is the first reaction involving the metallic iron that resembles in part the corrosion process taking place between N_2O_4 and steel storage tanks. N_2O_4 is reported not to react with metallic iron unless a catalytic quantity of iron chloride is added. However, trace amounts of chlorides are known to be present in all propellant grade N_2O_4. Further, in a synthesis program such as that undertaken by Addison, where a relatively large amount of the product was expected, the formation of parts per million quantity of NTNF could be very easily overlooked. In fact Cain, et al. (Ref. 2), have reported that the presence of iron N_2O_4 can be detected a few hours after the oxidizer is in contact with the metal powder, stainless steel, or carbon steel. This reaction is limited by the solubility of NTNF in the oxidizer, and the reaction stops when the concentration of the iron compounds reaches 1 to 2 ppm (determined as iron).

The reaction product of N_2O_4 and iron, identified by Addison, was later verified by Cain as nitrosyl tetranitratoferrate (NTNF) having the following structure:

$$NOFe(NO_3)_4$$

This compound is frequently called ferric nitrate N_2O_4 "adduct" for simplicity. The presence of NTNF even in low concentrations can bring about flow restriction in the laboratory by complete blockage of a tiny orifice by the deposition of crystalline or gel-like contaminant (Ref. 3). Upon contact with moisture, it is readily converted to hydrated ferric nitrate, nitric acid, and nitrous acids.

The iron contaminants in N_2O_4 can take various forms, such as straw-colored solid, gel, or black oil (Ref. 4), depending on the purity of the material and the water content of the media. Although the exact conditions necessary for the flow restriction process to occur are not completely understood, two factors appear to be important, viz., reduction in temperature and the presence of small orifices in the propellant line. The former causes the separation of the adduct out of solution, and the latter, a location for the accumulation of the NTNF. Other factors such as configuration of the orifice, pressure drop, flow rate, and turbulence are also believed to influence the deposition of NTNF.

The isolation and identification of NTNF from the field is difficult due to its extremely hygroscopic nature. This compound is generally converted to hydrated ferric nitrate before it can be transferred to the laboratory for analysis. However, this compound together with other contaminants can be collected by passing a large volume of N_2O_4 through fine filters. In this study, by taking precautions to minimize exposure to moisture, the contents of the filter were transferred to the laboratory for analyses. NTNF was isolated and purifiedby extraction with dry ethyl acetate and reprecipitation with fresh N_2O_4. The infrared spectrum of this compound taken on a halocarbon mull between polyethylene film (Fig. 1) showed absorption bands essentially identical to that reported for NTNF. Its structure was further verified by comparison of the spectrum of an authentic sample of NTNF prepared by the reaction of iron powder with N_2O_4 in ethyl acetate.

Further substantiation of the NTNF structure was carried out by analyses for iron and nitrite ions after hydrolysis and determination of its equivalent weight by titration with a base. The results are in agreement with the structure $NOFe(NO_3)_4$.

In addition to NTNF, other contaminants were also found to be collected in the filter. The residue (approximately 20% of total contaminant), after extraction with ethyl acetate, was divided into a water soluble and insoluble portion. The former was found to be primarily ferric nitrate monohydrate, which probably resulted from the hydrolysis of NTNF. The water insoluble fraction consisted of brownish-black magnetic material. An x-ray diffraction pattern taken on this material showed this solid to be a mixture of Fe_3O_4 and Fe_2O_3.

The major contaminant trapped in the filter has been identified as the ferric nitrate N_2O_4 "adduct." A sufficient quantity of this material can be collected to result in flow restriction in the propellant line of the oxidizer loading unit at the rocket launch site. This iron compound results from the reaction of N_2O_4 with the iron containing material of construction. Since the oxidizer is manufactured in stainless steel apparatus and transported and stored in either stainless or carbon steel equipment, it appears that all N_2O_4 (unless specially purified) will contain NTNF. Further, if the oxidizer had undergone considerable fluctuation in temperature over an extended period of time, it may contain a much higher quantity of NTNF than realized from the solubility data. Under these conditions, it can exist as a separate phase in the oxidizer in the form of a solid, gel, or an oil.

The oxides of iron are believed to result from the action of wet N_2O_4 with carbon steel. Indications are available which show that when the water content of the oxidizer is high (such as incomplete drying of transport trailers after hydrostatic testing) a larger quantity of iron oxides is observed in the oxidizer.

An aqueous solution of NTNF in water was analyzed for nitrite ion (Ref. 6) by a colorimetric method using sulfanilic acid and α-naphthylamine (Griess reagent). The ferric ion which interferes with this analysis was complexed with the addition of 1% HF solution. Comparison of the absorption to a standard curve yielded the value for nitrite content.

Calculated: 13.8%   Found: 13.5%

In the determination of equivalent weight, a solution of NTNF can be titrated with base to a pH endpoint of 5.7 according to the following equation:

$$NOFe(NO_3)_4 + 5\ OH^- = Fe(OH)_3 + 4\ NO_3^- + NO_2^- + H_2$$

Equivalent weight of the iron-containing compound from the filter can be calculated by the above equation.

Calculated: 67.8%   Found: 67.3%

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