A STUDY OF THE CORROSION PRODUCT FORMED BY NITRIC ACID BASED PROPELLANTS IN CONTACT WITH STAINLESS STEEL

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Summary

Mixtures of highly concentrated nitric acid and dinitrogen tetroxide are used as the oxidiser component in certain liquid bi-propellant rocket systems. A low concentration of hydrogen fluoride is also added to these mixtures, and serves as a corrosion inhibitor. This type of oxidiser is commonly referred to as Inhibited Red Fuming Nitric Acid (IRFNA). When stored in stainless steel tanks for long periods of time, solid corrosion products form which may cause the blockage of propellant flowlines and injectors. This paper describes the isolation and identification of the corrosion product which is shown to be a novel form of iron fluoride.

1. Introduction

Many rocket propulsion systems are required to meet long term storage and/or operational lifetimes. Few liquid oxidisers are available which meet all the requirements of a storable propellant. Many energetic compounds which might be considered for use as propellants are intrinsically unstable and may decompose spontaneously. Among the more stable liquid oxidisers, mixtures of nitric acid and dinitrogen tetroxide have been used in a number of systems. The composition most frequently encountered is known as 'Inhibited Red Fuming Nitric Acid' (IRFNA) which is a 6:1 w/w mixture of highly concentrated nitric acid ($>97.5\%$ HNO_3) and dinitrogen tetroxide (N_2O_4). A second HNO_3/N_2O_4 based oxidiser known as 'High Density Acid' (HDA) has also been developed which has a much higher N_2O_4 content (1.3:1). Although IRFNA and HDA have many favourable characteristics as propellants, one major drawback which does affect the use of these oxidisers is their highly corrosive behaviour towards the stainless steel and aluminium alloys used in the construction of propellant systems. Attempts have been made to utilise protective linings of PTFE and

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similar materials but with limited success. N_2O_4 dissociates to produce NO_2 which quickly permeates thin sectioned polymers and leads to delamination of the lining from the substrate metal.

Development work during the 1950's revealed that corrosion by HNO_3/N_2O_4 mixtures can be greatly reduced by the inclusion of small concentrations of fluoride. This has usually been achieved by adding liquid hydrogen fluoride (0.7 wt.%) to the oxidiser [1, 2]. The presence of the fluoride corrosion inhibitor has been shown to reduce the rate of attack (in terms of loss of section) on steel and aluminium alloys to acceptable levels, but causes a secondary problem due to the formation of significant quantities of low-solubility corrosion products. These corrosion products are important because they do not remain adherent to the walls of the propellant tanks but tend to form semicolloidal suspensions in the liquid or settle as a sludge in the bottom of the oxidiser tank. In either case such material is dangerous since it has the capacity to cause clogging of the propellant feed system thereby affecting the performance of the rocket engine.

Although HDA is the more energetic propellant, experience suggests that it is also more susceptible to problems with corrosion products than IRFNA and this is one factor which may have restricted the use of HDA.

To date, the chemical identity of the corrosion products formed in IRFNA and HDA has not been well established. The problems caused by the formation of this material have been dealt with by such means as the inclusion of filtration devices in oxidiser feedlines, the avoidance of restrictive orifices wherever possible and the costly expedience of systems surveillance and refurbishment. Such measures could be assisted, however, by a more fundamental understanding of the chemical and physical nature of these corrosion products. The work described here has been undertaken in order to gain additional knowledge concerning the chemical identity and properties of these materials.

2. Experimental

Small amounts of 'authentic' corrosion product were obtained from tests in which 18/8 stainless steel was exposed to HNO_3/N_2O_4 mixtures for long periods of time. The amounts of material obtained by this route were sufficient to permit only a partial characterisation, but this enabled a 'synthetic' method of producing the corrosion product to be developed. The larger amounts of material available by this means allowed a more complete investigation to be undertaken.

2.1 Isolation of authentic corrosion products
Three experiments were performed in which type 321 stainless steel was exposed to inhibited HNO_3/N_2O_4 mixtures. These tests may be outlined as follows:

(a) a mixture of 56/44 w/w HNO_3/N_2O_4 (i.e. HDA) stored in a small steel tank for a period of 150 days,

(b) a mixture of 70/30 w/w HNO_3/N_2O_4 stored in a thick-walled PTFE vessel with two stainless steel specimens (bar, 18 mm dia., 14 mm long) for a period of 300 days,

and (c) 100% HNO_3 stored in a PTFE vessel with steel specimens as in (b) above, for a period of 220 days.

Each test utilised approximately 120 cm^3 of acid mixture so that the ratio of the surface area of exposed metal and the volume of liquid (i.e. the 'S/V' ratios) were of the same order as those found in actual propellant systems (1 cm^{-1} for test (a) and 0.2 cm^{-1} for (b) and (c)).

All three tests were maintained at ambient temperature (20–25 °C) and were terminated when visual inspection of samples of the liquid revealed the presence of particulate matter in suspension. Attempts were then made to isolate the solid product by expelling the liquid from the test vessel and passing it through a PTFE filter (pore size 100 μm). The filtration process was carried out using a closed-system technique so that the corrosion product was not exposed to contact with atmospheric moisture. Similarly, all subsequent handling of the material was performed so as to exclude contact with the atmosphere.

Although each test appeared to have resulted in the formation of many fine particles suspended in the liquid, only very small amounts of solid were obtained after filtration and drying. This material was characterised as follows:

(a) the filtered solid appeared dark green while wet and pale green when dry,

(b) examination of some of the solid using a scanning electron microscope (fitted with an energy dispersive X-ray analyser) showed it to be a homogeneous finely divided powder whose chief metallic content was iron, with only trace amounts of chromium and nickel,

(c) different samples of the corrosion product studied by X-ray powder diffraction revealed two different diffraction patterns which were matched with those previously reported for the compounds $FeF_3 \cdot H_2O$ and $FeF_3 \cdot 3H_2O$ [3,4],

(d) the infrared spectra obtained from the material is shown in Fig. 1 and is discussed in Section 2.2.

These results clearly indicated the corrosion product to be a form of iron (III) fluoride, but although both the infrared and X-ray data showed that the material was hydrated, the only form of iron (III) fluoride known to be green is the anhydrous form. The monohydrate is reported to be yellow [3] and the trihydrate is pale pink.

The evidence available suggested that the same material had formed in all three corrosion tests. In view of the difficulty in obtaining authentic corrosion product, it was decided to attempt to pursue the study by investigating the general chemical behaviour of iron (III) fluoride compounds in HNO_3/N_2O_4

solutions. As the X-ray diffraction pattern of the solid obtained from the HDA test showed it to be $FeF_3 \cdot 3H_2O$ it was decided to begin the study with this compound.

2.2 The reaction of $FeF_3 \cdot 3H_2O$ in HNO_3/N_2O_4 solutions

The reaction of commercial grade $FeF_3 \cdot 3H_2O$ in HNO_3/N_2O_4 solutions was investigated by adding a small amount of the dried solid (0.2 g) to small volumes (10 cm^3) of the following liquids: (a) uninhibited HDA, (b) inhibited HDA (containing 0.6 wt.% HF), (c) fuming (95 wt.%) nitric acid (FNA), and (d) N_2O_4.

The fluoride showed no visible signs of immediate reaction or dissolution in any of the liquids but over a period of a few days the solid material in each test was observed to change colour from pale pink to pale green. As fuming nitric acid is commercially available, it was decided to repeat the reaction with FNA on a larger scale (5 g of solid in 30 cm^3 acid).

After standing for several days, the solid was recovered by filtration under dry nitrogen, washed in fresh FNA and then dried by evacuation overnight. All subsequent handling of the solid was confined to a glove box (filled with dry nitrogen). In addition to chemical analysis, it was characterised by infrared spectroscopy, X-ray powder diffraction, Mössbauer spectroscopy and thermogravimetric analysis.

2.2.1 Chemical analysis

Duplicate analyses were performed giving the following results:

	Found	$FeF_3 \cdot H_2O$ requires	$FeF_3 \cdot 3H_2O$ requires
% Fe	44.0 44.1	42.8	49.6
% F	43.6 43.6	43.5	50.4
total	87.6%		

These analyses showed that the green solid had a composition close to the monohydrate, assuming that all of the remaining mass (12.4%) was accounted for by water, the approximate composition of this material was $FeF_3 \cdot 0.86H_2O$. (Iron determination was performed by dissolution of the compound in aqua-regia, followed by dilution and analysis by atomic absorption spectrometry. Fluoride determination was performed by fusion with KOH in a platinum crucible, followed by filtration and analysis of the filtrate using a selective ion electrode.)
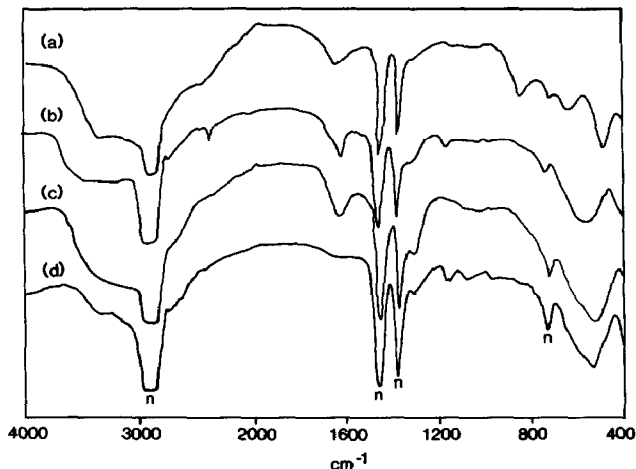
Fig. 1. IR spectrum of: (a) FeF$_3$·3H$_2$O, (b) authentic corrosion product, (c) the FNA reaction product and (d) FeF$_3$.

2.2.2 Infrared spectrum

The infrared spectrum of the FNA reaction product (c), together with those of (d) FeF$_3$, (a) FeF$_3$·3H$_2$O and (b) the corrosion product described in Section 2.1 are shown in Fig. 1. It can clearly be seen that the spectra of reaction product, the authentic corrosion product and FeF$_3$ are all very similar, showing a characteristic broad band at 530 cm^{-1}. In comparison, the spectrum of a sample of commercial grade FeF$_3$·3H$_2$O showed three sharper peaks at ca. 485, 630 and 850 cm^{-1}.

Assignment of IR absorption bands is as follows:

Absorption band (cm^{-1})	Assignment (Ref. 5)
3170	ν (O–H)
1635	δ (H–O)
530	ν (Fe–F) (FeF$_3$)
485 and 630	ν (Fe–F) (FeF$_3$·3H$_2$O)
850	δ (FeOH)

2.2.3 Mössbauer spectrum

The Mössbauer spectrum of the reaction product (at room temperature) showed a single symmetrical peak at 0.50 mm s^{-1}. In comparison, the Mössbauer spectrum of FeF$_3$ is reported to be a six line multiplet with an isomer shift of 0.49 mm s^{-1}, while both FeF$_3$·H$_2$O and FeF$_3$·3H$_2$O produce spectra showing doublets with isomer shifts of 0.21 and 0.40 mm s^{-1}, respectively (Refs.
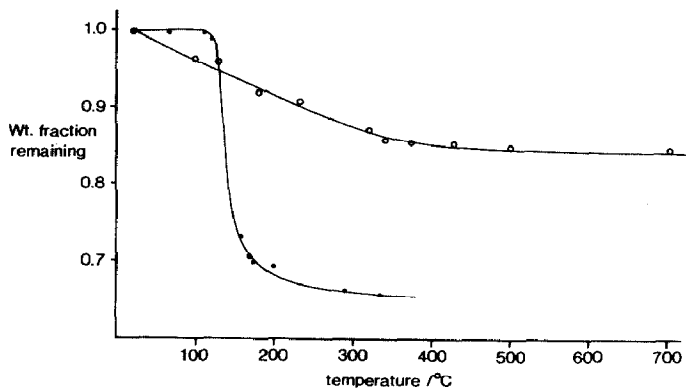
Fig. 2. Thermogravimetric decomposition analyses: ○ FNA reaction product and ● $FeF_3 \cdot 3H_2O$.

6, 7, 8). Although the signal is broad, it could not be resolved into a doublet even at the lower temperature of 77 K (Ref. 9).

2.2.4 X-ray powder diffraction

Two capillary tubes were loaded with finely ground samples of the reaction product but these samples produced diffraction patterns with only two detectable lines. The calculated d spacings (3.77 and 1.88 Å) could not be correlated with any reported form of iron (III) fluoride. Two further samples were prepared for X-ray diffraction using material subjected to even more intensive grinding than the first in order to try to improve the quality of the diffraction trace. These samples produced patterns matching that of $FeF_3 \cdot 3H_2O$.

2.2.5 Thermogravimetric analysis

The thermogravimetric decomposition of the FNA reaction product is shown in Fig. 2 and compared with that recorded for a sample of $FeF_3 \cdot 3H_2O$. It can be seen that the trihydrate compound exhibited a sharp and well defined decompositional change at 165–170°C. The mass fraction lost upto a temperature of 197°C was 0.3, corresponding to the loss of 2.8 molecules of water per formula unit.

In contrast, the FNA reaction product showed a much smaller loss of weight which occurred only gradually up to temperatures of $\simeq 400°C$. The mass fraction lost at 197°C, was 0.1, this corresponding to the loss of 0.64 molecules of water (assuming an initial compositon of $FeF_3 \cdot 0.86H_2O$).

A further thermal analysis was performed on a sample of the FNA reaction product after this had been exposed to the open atmosphere for three days (during which time the colour of the sample changed from green to pink) and this was found to match closely the decomposition profile of the trihydrate. This clearly suggests that the FNA reaction product reacts with atmospheric water to form the trihydrate.

3. Discussion

In a previous study of nitric acid based propellants the corrosion product formed by stainless steel was identified as a mixture of iron fluoride and iron oxide [2]. In the present work, no evidence has been obtained to suggest that any oxide species is formed, but rather, that the product formed is a low hydrate form of iron (III) fluoride. Two factors may account for this apparent difference in results:

(i) the previous study involved the use of a propellant mixture containing 3 wt.% water whereas the mixtures used in the present work contained <0.5 wt.%,

and (ii) the previous study involved the use of large surface areas of metal exposed to small volumes of liquid (i.e. a high S/V ratio) in order to accelerate the corrosion process. The S/V ratios used in the present work (0.2 and 1 cm^{-1}) are more representative of those found in actual propellant systems.

It is possible that these two factors may have influenced the corrosion chemistry in such a way as to favour the formation of oxides rather than fluorides. Using a high S/V, the amount of corrosion product which was reported to develop on the surface of the metal was so great, that it could be physically removed by scraping. In the present work, none of the corroded metal surfaces showed any visible sign of attack or the development of thick surface layers. The presence of fluoride reaction products on the surface of the steel could be detected only by the use of photoelectron spectroscopy, showing the layer to be of the order of $\leqslant 50$ nm in thickness [10].

The corrosion product isolated in the present study by filtration of the liquid gave reproducible analysis of the F : Fe ratios, within experimental error, of 3 : 1, and inspection of the X-ray diffraction data and Mössbauer spectrum exclude the possibility that any significant amount of oxide was present.

The degree of hydration of the fluoride was less readily established and the formulation of $FeF_3 \cdot 0.86H_2O$ seems unlikely to represent a distinct and unique phase. The possibility that the corrosion product might be a mixture of FeF_3, $FeF_3 \cdot H_2O$ and/or $FeF_3 \cdot 3H_2O$ is also excluded by the presence of only a single peak in the Mössbauer spectrum. Although different samples of the corrosion product produced X-ray diffraction patterns corresponding to different phases, none of the patterns showed a mixture to be present.

The evidence suggests that the material is actually a partial hydrate which is exceptionally hygroscopic and readily converts to $FeF_3 \cdot 3H_2O$ (as witnessed by the change of the diffraction pattern after prolonged powdering). Consequently, it is considered that it is best to represent the compound as $FeF_3 \cdot xH_2O$ where $0 < x < 1$ and it is possible that x may be variable to some degree. It is believed that this is the first reporting of this form of iron fluoride.

It is appropriate to note here that the reactions of metals (and anhydrous

metalchlorides) with HNO_3/N_2O_4 mixtures free of fluoride invariably result in the formation of hydrated metal nitrate compounds of the general formula $M(NO_3)_x \cdot H_2O$. In the absence of the inhibitor, the corrosion of 18/8 stainless steels by HNO_3/N_2O_4 mixtures eventually results in the precipitation of Ni $(NO_3)_2 \cdot 2H_2O$ [11, 12]. The water molecules in these reaction products originate from the self-dissociation of the HNO_3 molecule:

$$2HNO_3 \rightleftharpoons NO_3^- + NO^+ + H_2O$$
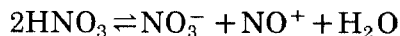
Consequently, the dehydrating effect of HNO_3/N_2O_4 solutions on $FeF_3 \cdot 3H_2O$ and the formation of a corrosion product which is only partially hydrated, is considered to be most unusual.

An important consequence of the identification of the corrosion product formed by stainless steel in contact with HNO_3/N_2O_4 mixtures inhibited with HF is that it may now be possible to assess its solubility in the propellant mixtures. This data, correlated with corrosion rate data, could be used to predict the occurrence of solids in the propellant and hence service lifetimes. Preliminary studies (at $20\,^\circ C$) showed that the solubility of $FeF_3 \cdot 0.86H_2O$ in HDA is ~ 700 ppm.

4. Conclusion

The corrosion of 18/8 stainless steel by the nitric acid based propellants IRFNA and HDA results in the formation of a solid reaction product which may be formulated as $FeF_3 \cdot xH_2O$ $(0 < x < 1)$. This compound is very hygroscopic and rapidly converts to $FeF_3 \cdot 3H_2O$ if exposed to atmospheric moisture.

Acknowledgement

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