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Problems in Storage and Handling of Red Fuming Nitric Acid

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Abstract. Design and development of the equipment for storing and handling red fuming nitric acid should take into consideration the special properties of the acid, particularly its high corrosive nature. The accuracy of the dosing system for such a highly fuming liquid depends upon the proper selection of pump and flow-meter. The properties of the acid and the corrosion resistance of various stainless steels are briefly discussed.

1. Introduction

Red fuming nitric acid (*RFNA*) is used as a liquid oxidiser both with xylidine fuel, as well as, unsymmetrical dimethyl hydrazine (*UDMH*) in liquid propelled missile systems. It is a dangerous, corrosive, toxic heavy liquid of red-brown colour containing extensive amount of oxides of nitrogen. Because of its high vapour pressure, considerable difficulties are experienced in pumping and handling this liquid. The components of the pumping and dosing equipment used in handling this liquid should satisfactorily withstand its corrosive action. Stabilised stainless steels and low carbon stainless steels are found suitable for this purpose. Teflon can serve as a suitable joint sealing material.

2. Properties of Fuming Nitric Acid

General

Red fuming nitric acid used in the role of oxidiser conforms to the following chemical composition (percent by weight) :

Nitrogen dioxide	Water	Nitric acid	Total solids as nitrates	Additives *HF*
14 ± 1	1.5 to 2.5	82.4 to 85.4	0.1	0.7 ± 0.1

Fuming nitric acids are highly reactive and will oxidise most organic materials and may produce fire with wood and cellulose products. These are very corrosive and cause yellow stain and severe burn in contact with the skin. Special protective clothing is required while handling *RFNA*.

Problems in storage of RFNA—Two chemical processes which cause problems in the storage of this widely used oxidant are

(a) The corrosion of metal containers causing weakening of metal, change in the composition of the acid and its contamination with metallic salts.

(b) Thermal decomposition of the acid lean in NO_2 and H_2O with accompanying high pressure and changes in the composition of the oxidant.

The presence of about 0.5% of hydrogen fluoride in the fuming nitric acid reduces the first problem of storage. The mechanism of passivation appears to be due to the formation of an impervious coating of insoluable metal fluoride on the surface of the metal. The second problem of thermal decomposition and correspondingly excessive storage pressure is eliminated in acid containing enough NO_2 (12 to 16%) to obtain the results desired without causing high partial pressure and enough H_2O (2 to $3\frac{1}{2}$%) to give satisfactory results without unduly diluting the oxidising power.

Excessive pressures arise because of formation of oxygen due to thermal decomposition. The thermal decomposition can be represented by the equation

$$2HNO_3 \rightarrow H_2O + 2NO_2 + \tfrac{1}{2}O_2$$

During the storage period, if corrosion and thermal decomposition occur, the composition of the acid changes continuously; thus the undesirable feature arises of having acid of variable composition available during this time for use as a rocket propellant.

3. Corrosion Resistance of Aluminium

Impurities in metals cause heterogeneity which decreases their corrosion resistance. Pure metals exhibit higher corrosion resistance than the impure ones. This is particularly true in the case of such highly electronegative metals as aluminium and magnesium. Even such minute amounts of impurities in aluminium as 0.02% iron and 0.005% nickel decrease its corrosion resistance by a factor of 100 to 500 in a solution of magnesium chloride. The removal of impurities reduces the number of possible local couples, resulting in much higher corrosion resistance. For maximum corrosion resistance high purity metals are often used, such as superpurity aluminium with higher than 99.99% aluminium content. In many cases it is not practical to produce a metal of high chemical purity because of cost considerations and because very pure metals have inadequate mechanical properties, being weak and soft. The advantage of increased corrosion resistance is thus offset by the greater thickness required and by the increased price of the superpure metal.

An increase in corrosion resistance of most commercial metals e. g., iron, nickel and copper is best secured by alloying them with suitable constituents. For maximum corrosion resistance such alloys should be completely homogeneous. Aluminium, magnesium and lead show little tendency to form homogeneous solid solutions with other elements. Hence an increase in their corrosion resistance can be achieved only by purification[1].

4. Stainless Steels

There are three basic types of stainless steels classified according to their micro-structure viz., martensitic, ferritic and austenitic. Austenitic stainless steels are noted for their excellent corrosion resistance in many media. They contain *Ni* and *Cr*, the basic composition being the well known 18/8 (18% *Cr* and 8% *Ni*). *Ni* greatly improves corrosion resistance over straight chromium. The most common grades are 304, 304*L*, 316, 316*L*, 321, 347 and for high temperature application 310, where *L* indicates low carbon content. Austenitic stainless steels are easily formable and readily weldable. However, some of these grades are susceptible to intergrannular corrosion after being welded or otherwise heated in the range of 425 to 900°C.

5. Intergrannular Corrosion

When austenitic stainless steels are held for a sufficient time between 425 to 900°C, chromium carbide $Cr_{23}C_6$ tends to precipitate preferentially at the austenitic grain boundaries, thus depleting the chromium content of the outer surface of the grain. In other words, this causes segregation of chromium. This type of precipitation is known as sensitisation. The ghost area with a low chromium content has a very low corrosion resistance and welds frequently fail or decay in bands adjacent to the weld bead. Intergrannular corrosion takes place when a sensitised material is exposed to sufficiently strong corrosive medium for a long enough time. It may be noted that stainless steel is stainless because of chromium, and chromium should be uniformly distributed.

As there is always some part of the metal container heated to the temperature range 425 to 900°C during welding operations, some means of curing or getting round this effect had to be found.

Methods for combating the intergrannular corrosion include (*i*) An anneal or soaking at 1000 to 1100°C followed by rapid cooling through the sensitisation range. This is done after welding in which process $Cr_{23}C_6$ gets dissolved. Subsequent operation of the part in the sensitisation range may resensitise the material, (ii) Addition of a stabiliser, a strong carbide former, which will preferentially form carbides leaving the chromium undisturbed. Elements like titanium, columbium are commonly used for this purpose. These are known as stabilised stainless steels (Example—*AISI* 321 347),

(iii) Use of stainless steels with very low carbon content less than 0.05%. If carbon is not available, carbide precipitation is obviously reduced. Thus the chromium depletion at the grain boundaries is kept within the safe limits (Examples—*AISI* 304*L*, 316*L*).

6. Selection of Suitable Grades for Welded Components

Types 304*L* and 316*L* are capable of avoiding sensitisation during welding. If the low carbon grades are not used, stabilised stainless steels of the types 321 and 347 are recommended for use in corrosive environments which may cause intergrannular attack where welded construction is employed and annealing is not practical. Out of these two types, type 347 is preferred since 321 type stainless steel is more susceptible to a phenomenon known as knife line attack due to the lower temperature of carbide dissolution. Titanium, present in type 321 is reactive with gases at welding temperatures so that it is partially lost during welding. Type 347 containing the less reactive columbium, is usually employed for weld rods in such applications. Molybdenum additions, as found in types 316 and 317, do not improve resistance to corrosion by nitric acid[2].

Cast stainless alloys—These are widely used in pumps, valves and fittings. These castings are designated under the Alloy Casting Institute System. All corrosion-resistant alloys have the letter *C* plus a second letter (*A* to *N*) denoting increasing nickel content. Numerals indicate maximum carbon. Typical members of this group are *CF*-8, similar to type 304 stainless steel and *CF*-8*M* or type 316.

Medium alloys—One group of alloys with somewhat better corrosion resistance than stainless steels are called medium alloys. A popular member of this group is the 20 alloy, made by a number of companies, under various trade names. It was originally developed to fill the need for a material with sulphuric acid resistance superior to the stainless steels.

7. Testing for Corrosion Resistance

Before fabricating any equipment or part for handling and storage of *RFNA*, it is essential to test the samples of materials of construction. The corrosion rate is measured by depth of linear penetration of a specimen and is usually expressed as penetration in mils per year or microns per year, but other units are also in use. The penetration can be calculated from determination of loss in weight of a metal specimen of a given area exposed to a certain corrosive environment for a definite period of time, using the following formula :

$$P = KW/\rho AT$$

where

- P is the average penetration
- W is the weight of the metal lost
- A is the area of the specimen
- T is the time of test
- ρ is the density of the metal
- K is a constant, the numerical value of which depends on the choice of units for P, W, A, T and ρ.

Susceptibility to intergrannular attack in stainless steels can be determined as per the standard recommended tests given in *ASTM A*262-77*a*. The recommended practice describes the procedure for conducting the boiling nitric acid test to measure the relative susceptibility of austenitic stainless steels to intergrannular attack. The test solution shall be 65 $\pm$ 0.2 Wt% as nitric acid as determined by analysis. The solution is prepared by adding distilled water to the concentrated nitric acid. For most consistent results, the test should consist of 5 boiling periods of 48 hrs each with fresh test solution being used in each period[3]. The authors have first hand experience in testing samples of *AISI* 304, 316, 321 and 446 as per this test procedure and it was found that type 321 had the lowest corrosion rate.

ASTM G 31-72 describes accepted procedures for and factors that influence laboratory immersion corrosion tests, particularly mass loss tests. If anticipated corrosion rates are moderate or low, the following equation gives the suggested test duration.

$$\text{Hrs} = \frac{2000}{\text{corrosion rates in mpy}}$$

where

mpy = mils per year

The most common testing periods are 2 to 7 days. The authors follow the practice of immersing specimens in *RFNA* for 7 days for selecting materials for handling and storage of *RFNA*.

ASTM D 543-67 covers the testing of all plastic materials, for resistance to chemical reagents. Different sealing materials were tested as per this standard. Teflon samples were found to withstand the action of *RFNA* satisfactorily.

8. Problems in Pumping and Metering

Bulk handling of *RFNA* containing excessive amount of NO_2 gases require special attention. Both reciprocating pumps and centrifugal pumps can be used in pumping this liquid. The material of construction should be a suitable grade stainless steel for pumps having welded construction. Alloy-20 or *CF*-8*M* is used for castings. The sealing can be achieved either by means of a mechanical seal or hydraulic sealing arrangement having auxiliary impellers.

Because centrifugal pumps are not self priming, some priming means is required on a suction lift. Either special self priming pumps may be used or auxiliary priming equipments may be installed. The auxiliary priming equipment may consist of a liquid reservoir on the pump discharge which holds priming liquid and serves as an air/fume separator. The liquid is being circulated from discharge to suction during priming. The circulation is stopped by means of a suitable valve after the pump primes. A hand pump or an ejector is required to be provided for filling the priming tank.

Reciprocating pump capable of giving a discharge of 30 litres/minute at a delivery head of 10 metres of liquid column has been successfully developed. It is available in both hand operated as well as motor driven versions. Centrifugal pump of 300 litres/minute capacity and 23 m of delivery head has also been developed. It is fitted with mechanical seal and priming tank on the discharge side and is operated at a speed of 1500 rpm. The pump has been developed after extensive trials in pumping *RFNA*. The authors have observed, during the course of the trials, that the higher speed pumps are not suitable for this application as vapour locks are caused due to churning action.

While metering and dosing, certain amount of fumes are likely to be measured along with the liquid which affects the accuracy of the dose. This necessitates the provision of arrangement for frequent checking of doses before passing the actual dose. Selection of a suitable type of flow-meter for the required high accuracy standards is also another important factor. Two types of flow-meters have been developed—one turbine type and another electro-magnetic type. The electro-magnetic type of flow-meter is suitable for conducting type of liquids. Turbine flow-meters are suitable for conducting as well as non-conducting types of liquids and are found to be more accurate than the electro-magnetic type.

Since the liquid to be handled is hazardous, it is necessary to provide remote control facility for carrying out pumping operation. Pneumatically operated valves have been developed for this purpose. Various measuring and indicating instruments used in such type of handling equipment are required to be protected from fumes.

9. Conclusion

Stainless steel grades *AISI* 304*L* and 316*L* are recommended as the materials of construction for the fabrication of the welded components, which come in contact with highly corrosive *RFNA* to avoid intergrannular corrosion. Suitable reciprocating pumps and centrifugal pumps have been indigenously developed for bulk handling of *RFNA*. The turbine type flow-meter is found quite accurate for dosing system used in filling liquid propelled missiles.

References

1. Jastrzebski, Z. D., 'Engineering Materials' (Wiley International Edition, 1959, p. 439.
2. 'Corrosion Resistance of the Austentitic Chromium-nickel Stainless Steels in Chemical Environments', issued by International Nickel Co Inc, New York.
3. Annual Book of *ASTM* Standards, Part 3, 1916 Race St., Philadelphia, Pa. 19103, USA, 1979.
4. Annual Book of *ASTM* Standards, Part 35, 1916 Race St., Philadelphia, Pa. 19103, USA, 1979.
5. Perry, J. H., 'Chemical Engineering Hand Book, Materials of Construction' (McGraw-Hill Kogakusha), 1963, p. 23.