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AN IMPROVED METHOD FOR APOLLO PROPELLANT SYSTEM DECONTAMINATION

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Summary
An improved, reliable method for removing residual hypergolic propellants from Apollo propulsion systems is described.

Vapor phase decontamination provides improved efficiency with lower residual contaminant levels, and requires less time and solvents than liquid flushing. The development and evaluation of this new method is discussed.

Introduction
This study was performed by The Dow Chemical Company under contract to NASA Manned Spacecraft Center.

Effective decontamination of the Apollo propulsion system containing nitrogen tetroxide as the oxidizer and a hydrazine mixture as the fuel is necessary for at least two important reasons: to eliminate the possibility of personnel exposure to toxic vapors when systems or components are being disassembled for inspection or maintenance, and to prepare a system for storage.

Numerous methods have been used to decontaminate assembled systems and components. At one time, the Tri-Flush method was popular. This method was based upon flushing with water solutions of a neutralizing agent followed by flushing with large volumes of organic solvents to complete the decontamination and remove the water. This procedure had several undesirable characteristics: (1) possible formation of salts in crevices from the reaction of the neutralizers with the propellants, (2) the requirement of large quantities of three flushing fluids in the launch area, (3) questionable effectiveness unless extensive flushings have been made, and (4) the possible formation of nitric acid. About the time The Dow Chemical Company was awarded this contract, the Tri-Flush cleaning method was abandoned in favor of the single-flush method, which did not have the objectionable features. This single-flush method used methanol for the fuel side and a fluorocarbon for the oxidizer side as the flushing solvents at ambient temperature. Recently, the use of methanol on the fuel side has been abandoned because of its possible detrimental effects upon titanium.

Objectives
The objective of this study was the development of a reliable, rapid decontamination method not involving large quantities of materials or complex equipment, with certain restrictions upon the choice of solvents. The use of aqueous solvent systems was considered undesirable because of the slow rate of drying and the danger of forming high local concentrations of nitric acid in crevices and capillaries of the oxidizer system. The solvents used must not react with the highly reactive propellants and the materials of construction, be relatively non-toxic, economical and sufficiently volatile for easy removal from the system.

Study Plan
The study program was set up in two phases—the first concerned laboratory scale development of candidate procedures and methods; the second consisted of the evaluation of these techniques on a sub-scale test unit.

Phase I included the identification and examination of critical problems in the decontamination process; studies of the compatibility of candidate solvents with system materials and propellants; determination of the relative efficiencies of these solvents; investigation of the effects of such factors as temperature and pressure within the limits of the system, i.e., temperatures to 93°C (200°F) and pressures from 1 to 160 PSIG; and consideration of various solvent reclamation methods.

Phase II consisted of the design, construction and operation of a test unit for the evaluation of candidate decontamination procedures. This test unit approximated the Apollo service module propulsion system in 1/20 scale and was fabricated of similar materials.

Results
Phase I
One task in this phase of the study concerned selection of compatible candidate solvents. Compatibility with the system materials was measured by standard screening tests such as evidence of corrosion or weight loss of metal specimens and evidence of swelling, elongation and loss in tensile strength in the case of elastomer samples.

Criteria for the compatibility of the solvents with the propellants included solubility tests and evidence of reaction or formation of an explosive mixture. As background here, it should be recalled that nitrogen tetroxide is a highly reactive oxidizing agent and with certain solvents, notably trichlorethylene, forms a mixture which may produce a high-intensity explosion. As a first precaution in the screening of solvents for service in the oxidizer system, therefore, a testing program was initiated which involved adding nitrogen tetroxide to the solvent and shocking the mixture with a blasting cap to determine if the mixture was explosive. These detonation tests were set up in an empirical manner and the results were judged by concussion and aural and visual observations. The tests were run in triplicate; the method proved sensitive and reproducible.

Similar detonation tests with the hydrazine fuel
mixture and fuel-solvent mixtures resulted in low intensity explosions in each case, with no discernible difference in magnitude, with or without a solvent. Compatibility of the solvents with the fuel, therefore, was based on the criteria of solubility and lack of evidence of reaction.

The results of this testing are summarized in Table 1. While this work was being conducted, screening tests were set up to evaluate decontamination methods. One of the problems was to demonstrate any significant differences in the cleaning efficiency of the various solvents. The approach was to start off with very simple systems which consisted principally of smooth, stainless steel surfaces. If no differences in the solvents could be detected, the systems were made more and more complex by the addition of capillary surfaces, crevices and elastomers until any latent differences in efficiencies of the solvents became apparent. This early work tended to give erratic and inconclusive results and did not demonstrate clearly any significant differences in the efficiencies of the various solvents tested. The principal point demonstrated was that difficulties in the decontamination process are due principally to the propellants absorbed into the semi-porous elastomers in the systems. Therefore, a study was initiated to determine the rate at which contaminants are removed from elastomer samples. Weighed and measured specimens of each elastomer were immersed in the contaminant, either nitrogen tetroxide or the hydrazine mixture, for several days and the weight gain recorded. After determining the contaminant content of each specimen, they were exposed to a measured quantity of the solvent under test. The contaminant content of the solvent was then determined at specified time intervals. In the first series of tests using nitrogen tetroxide as the contaminant, the solvents used were Freon MP®, Freon TFP® and carbontetrachloride; the elastomers used were Teflon FEP®, Teflon TFE®, Rulon®, and Kynar®. At ambient temperature, all of the solvents had approximately the same contaminant removal rate. Repetition of these experiments using gaseous nitrogen instead of a solvent showed approximately the same results. This is indicated in Figures 1, 2 and 3. Those results are presented by plotting the contaminants remaining in the sample, expressed in milligrams per square centimeter of surface, against time on a semi-log scale. The significant factor is the slope of these curves, which represents the rate of nitrogen tetroxide removal. The starting points differ due to differences in the initial amounts of contaminant absorbed on each sample specimen. Similar runs with the hydrazine mixture and the synthetic rubber elastomer used in the fuel side of the system gave similar results, as illustrated in Figure 4. The essentially straight-line relationship of these plots indicates that the amount of material removed from the elastomers per unit time is proportional to the amount present at that time. The removal of contaminants, then, follows a familiar first order reaction relationship. This relationship can be expressed by the equation:

\[
\frac{-dc}{dt} = k \cdot c
\]

where: 
- \( c \) = concentration of contaminant in the elastomer
- \( t \) = time
- \( k \) = a constant

\[
\frac{-dc}{dt} = \text{the rate the concentration in the elastomer decreases}
\]

Integration of this equation between the limits of concentration \( c_1 \) at time \( t_1 \) and concentration \( c_2 \) at time \( t_2 \) yields the equation

\[
K = \frac{2.303}{t_2-t_1} \log \frac{c_1}{c_2}
\]

where \( K \) = velocity constant or specific rate constant

These specific rate or velocity constants can be calculated for this data. This specific decontamination rate constant should be a specific characteristic, then, of each solvent with a particular elastomer.

The order of magnitude of the rate constants for all of the solvents and gaseous nitrogen was found to be about the same under the same conditions. This similarity is indicated by the similar slopes of the plots. This suggests that the removal rate of the contaminants from the elastomers is essentially independent of the solvent environment.

Figure 4 also illustrates the increase in decontamination rate caused by increasing the temperature. These data are for the removal of fuel mixture from a sample of rubber in methanol at 25°C and 65°C. This temperature dependence of the decontamination rate is a general relationship.

Figure 5 illustrates the increase in the decontamination rate constant with temperature increase for the oxidizer from an elastomer in gaseous nitrogen.

Results, such as those discussed here, indicated that developmental efforts should be concentrated on devising a procedure based upon raising the temperature of the system within acceptable limits while purging with an inert gas or vapor to remove the release contaminants from the system.

This work demonstrated that this was most readily accomplished by vaporizing a fluid through the system, since the latent heat of vaporization as well as the sensible heat is available to allow uniform heating throughout the system.

Because of the importance of reducing the total quantities of solvent required at the work site or the launch area, it seemed desirable to devise methods of removing the contaminants from the effluent solvent stream and recycling the regenerated solvent. Several methods were evaluated which offer possibilities of success. Procedures which seem most suitable for this use are based upon passing the used, contaminated solvent through adsorption columns. This recommendation is based upon simplicity of equipment requirements and reliability of operation. Hydrazine and unsymmetrical dimethylhydrazine may be

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removed efficiently from inert solvents by passing them through an adsorption column which has been packed with a cation exchange resin. Figure 6 illustrates the breakthrough curve for this procedure. Nitrogen tetroxide can be removed effectively from inert solvents by passing them through an adsorption column which has been packed with water-swollen and caustic-treated silica gel. Figure 7 illustrates the breakthrough curve for this method.

Phase II

The object of the work of this phase was to evaluate the methods developed in Phase I.

Laboratory work indicated that a decontamination procedure utilizing a vapor purge would have advantages over a liquid flush method using the same solvents. Therefore, a series of tests was set up to compare these two methods on a sub-scale test unit.

The test unit consisted of:

(1) a test vessel, fabricated of titanium, approximately 1/20 the size of an Apollo service module propellant tank; associated piping of stainless steel; appropriate soft-part samples.

(2) the decontamination equipment necessary to store, transfer, circulate, vaporize, condense and regenerate the solvent; provisions for drying with gaseous nitrogen; suitable instrumentation to measure temperature, pressure and the contaminant level of the exit gas and effluent solvent.

Figures 8, 9 and 10 illustrate this test unit.

Twelve tests were made in which the system was first contaminated with the hydrazine mixture fuel, then decontaminated by liquid flushing or vapor phase purging. The solvents used were methanol and n-propanol.

Ten tests were made in which the system was contaminated with nitrogen tetroxide, then decontaminated by liquid flushing or vapor phase purging. The solvents used were Freon 113 and Freon 114.

In each case, the liquid flushing procedures used were made to simulate as closely as possible those methods currently being used on the Apollo propulsion systems. This enabled us to establish a benchmark for comparison.

In the liquid flush tests, the system was filled with solvent and then allowed to soak for one hour. Eighteen gallons of solvent were used.

In the vapor phase purging tests, eight gallons of solvent were vaporized under 10 PSIG pressure and passed through the test unit over a 16-minute period.

In all cases, after this decontamination period, the system was purged with a moderate flow of nitrogen (one test vessel volume per minute). The concentration of contaminant in the gas was then measured at suitable time intervals. This measurement was made by wet chemical analysis of samples obtained by a scrubber method since this technique proved more accurate and reliable than instrumental methods.

The results of these tests are shown in Figure 11 (decontamination of a fuel system using methanol) and Figure 12 (decontamination of an oxidizer system using Freon 113). The latter figure also includes the results of one vapor phase run in which the procedure was modified. In this run, the pressure of the vapor phase purge was not held at a constant 10 PSIG but was cycled or pulsed between 45 PSIG and 5 PSIG. This pulsing further reduced the contamination level of the system.

Discussion

The propellants are not appreciably adsorbed on the metallic surfaces of the propulsion system. Most of the tenacious residual contamination is held within the elastomers and soft parts. The rate at which the contaminant is released from these elastomers is independent of the environment at a given temperature and pressure. No significant differences were noted in the efficiencies of the various solvents tested in removing the contaminants. Temperature is the major factor determining the decontamination rate. This rate was found to just about double for every 15°C increase in temperature. Heat may be introduced into the system by the vapors of a boiling solvent. This is a rapid, convenient method which is easily controlled within the system limits. The advantages of the vapor phase method are that the system is heated uniformly throughout and the surfaces are washed with a flowing film of condensed solvent.

In addition, the test data indicate that in comparison with liquid flushing, the vapor phase procedure reduces contamination to a lower level, and requires less time, less solvent, and less nitrogen.
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Figure 1.
DECONTAMINATION RATE OF N₂O₄ FROM TEFLO® FEP
BY VARIOUS SOLVENTS AT AMBIENT
Figure 2.
DECONTAMINATION RATE OF N₂O₄ FROM TEFLON® TFE
BY VARIOUS SOLVENTS AT AMBIENT
Figure 3.
DECONTAMINATION RATE OF \( \text{N}_2\text{O}_4 \) FROM KYNAR
BY VARIOUS SOLVENTS AT AMBIENT
Figure 4.
DECONTAMINATION RATE OF AEROZINE-50 FROM STILLMAN SR634-70 RUBBER BY METHANOL GN₂ AND STEAM AT 2.5°, 65° AND 119°C
Figure 5.

THE SPECIFIC RATE CONSTANT (K) VERSUS TEMPERATURE FOR THE DECONTAMINATION OF N₂O₄ FROM TEFLO® FEP BY GN₂

K = SPECIFIC N₂O₄ DEGASSING RATE CONSTANT

TEMPERATURE (°C.)
Figure 6.

COLUMN STUDY -
Adsorption of UDMH from Freon® 113 on Dowex® 50W-XB (H+)

Flow Rate - 1 ml/minute
Column - 3 mm x 97 min.
110 ml. volume

VOLUME OF EFFLUENT (BED-VOLUMES)

CONCENTRATION UDMH IN EFFLUENT (ppm)
Figure 7.
COLUMN STUDY
ADSORPTION OF N₂O₄ FROM FREON® 113
WITH SILICA GEL (NaOH TREATED) AT HIGH FLOW RATE

Average Flow = 11.1 ml/min.
I.D. = 0.342 in.
Figure 8.
BLOCK DIAGRAM OF TEST UNIT

CLEAN SOLVENT TANK

DRYING COLUMN

ABSORBENT COLUMN

CONTAMINATED SOLVENT TANK

HEAT EXCHANGER

FILTER

TEST VESSEL

CONDENSER

EXIT GAS SCRUBBER

PROPELLANT STORAGE

PUMP

PUMP
Figure 9.

Perspective Drawing of Test Unit

Note:
- N₂O₅ System operated after A-50 system was disassembled.
Figure 11.

REMOVAL OF AEROZINE 50 FROM TEST VESSEL

PARTS PER MILLION A-50 IN EXIT GAS

MINUTES

1000

100

10

1

100

200

300

LIQUID

VAPOR PHASE

8
Figure 12.

REMOVAL OF N₂O₄ FROM TEST VESSEL USING FREON® MF

MINUTES

N₂O₄ PPM IN EXIT GAS

1000

100

10

PULSATING VAPOR PHASE

LIQUID

VAPOR PHASE