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Nitrous Oxide Explosive Hazards (Preprint)

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Abstract

A recent incident caused us to evaluate the subject of nitrous oxide (N_2O) hazards. Use of N_2O for rocket propulsion seems to be a continuing interest. Accounts of serious, large system N_2O accidents are mysterious since technically satisfying explanation of how the incidents occurred seems lacking. Inadequacy of technical information for serious N_2O incidents indicates that safety practice understanding beyond current knowledge is needed. At a minimum, application of some safety practices used with high pressure oxygen systems, but not specified with N_2O operations, may provide some safety improvements. Experimental investigation to gain recognition of large quantity N_2O explosive and ignition traits may be the only way to ensure large N_2O system safety. Prior hazard and monopropellant decomposition studies largely indicated that N_2O was difficult to initiate into dangerous monopropellant decompositions. Based on prior studies and use of N_2O for decades in dental practice without serious incidents, many people have considered use of N_2O as safe. Early explosive hazard studies did not indicate a serious explosive nature for N_2O. Inadequacy of historical N_2O hazard study experiments was that they used too small volumes in their studies. Explosive hazards for N_2O are exacerbated by its extraordinary gas and liquid solvent properties that can lead to fuel/N_2O compositions where fuel material is normally considered insoluble. Organic resins can be extracted by contact with seals, and N_2O can dissolve like a plasticizer into organic materials. Transfer of N_2O monopropellant reaction from combustion sources, impact, or friction, through piping back to a storage tank seems a primary hazard for N_2O systems. A reaction trap structure in feed lines may be able to prevent monopropellant reaction through piping systems. Electrostatic discharge (ESD) has surfaced as a probable hazard for oxidizer flows over polymeric seals infused with high concentrations of N_2O. A test program is suggested that could answer questions about decomposition propagation control in large N_2O systems and hazards associated with N_2O/organic mixtures.

Introduction

The author lacks experience with large N_2O filled tanks. Material for this presentation has been derived primarily from review of available literature and experience with rocket propulsion hazard investigations. This presentation is intended to point out N_2O hazards and at the end to suggest need for developing means for stopping runaway monopropellant decomposition propagation through piping to N_2O storage tanks and for measuring increase in explosive sensitivity of fuel contaminated N_2O. Speculation about how or why the Mojave explosion occurred in July 2007 (1, 2) is not intended during this presentation. The author has only newspaper information about the

Mojave incident. When the Mojave explosive incident was reported, it stimulated our concerns about N_2O explosive hazards. N_2O has been used for decades in dental practice without accidents being widely publicized. Prior to the Mojave event little concern was raised over explosive safety of N_2O.

N_2O explosive events other than the one at Mojave in sizeable scale have been reported (4-6). Repeated appearance of N_2O explosive events indicates that present understanding of N_2O hazards and means to control such hazards is inadequate (13-15). Inadequate understanding of N_2O hazard issues was indicated by recent reference to "unknown voodoo" in a N_2O hazard behavior report (6). This discussion is intended to point out N_2O hazard concerns where experimental investigation and confirmation of operational safety are needed.

N_2O has been viewed as a nontoxic, "safe" oxidizer that might be used in rocket propulsion systems (8-12). That is, N_2O is a candidate "green propellant" oxidizer. Since N_2O is an energetic oxidizer, it should be treated with at least the level of respect given to high pressure gaseous oxygen systems (16-17). Of special note in gaseous oxygen hazard experience was infrequent fires in stainless valves using viton® or silicone seats (17). Although electrostatic discharge was not cited as a cause for gaseous oxygen valve fires, it is logical that an electric spark through oxygen infused plastic seats could have started the fires. Environmental conditions of fast gas flow over plastic seats, high pressure, and low temperature through large expansion of oxygen gas were fairly optimal for producing electrostatic discharge (ESD) activity (18, 19). Since N_2O can dissolve significantly in plastics, electrostatic sensitivity of such compositions seems probable (6).

Probability of hazardous behavior with N_2O in operational combustion uses has been recognized for decades. As a result, several explosive and fire studies have been supported by US Navy and AF organizations (20-25). Those N_2O hazard studies did not show any strong violence by N_2O runaway decompositions or continuation of monopropellant decompositions started by adiabatic compressions. Lack of violent events when N_2O was abused by initiating means was, perhaps, partly due to use of small volumes for experiments where wall effects were adequate for limiting N_2O speed or providing quenching for N_2O decomposition processes. Approaches for safely utilizing N_2O for rocket propulsion should involve measures countering N_2O's unique array of chemical and physical hazard characteristics. Concerns about pure liquid N_2O reaction initiation by "water hammering" and "bubble collapse" (6) seem unlikely due to liquid N_2O being a highly compressible liquid (8) and lack of response to 50 gram tetryl pellet detonation at 27 mm diameter (23). Main N_2O traits to be concerned about are positive heat of formation (9), close proximity of its critical temperature to normal ambient temperatures (pressures above 40 atmospheres), its extraordinary solvent capability for dissolving or plasticizing even complex organic materials (25-31), and, perhaps, sensitivity to ESD when N_2O flows rapidly over high electrical resistance materials, such as, viton® and silicone valve seats. Organic contaminated N_2O fluid (gaseous or liquid) compositions might be particularly hazardous due to their ease of fire/explosion initiation by ESD and minor explosive stimulation.

At this time I am involved in a research development effort aimed at demonstrating whether nitrous oxide monopropellant thrusters could be suitable for small space satellite propulsion. The Mojave explosive incident close to our Laboratory at Edwards AF Base was a wake up call to assess N_2O explosive hazards. Since a number of proposals to utilize N_2O as an oxidizer has arisen in recent years, members of the rocket propulsion community can benefit from a timely hazard assessment and a suitably supported and comprehensive N_2O experimental hazard assessment program.

Limited data are available from accounts of accidents (1-6) and studies of N_2O hazards and decompositions (20-27). Primary deficits of past hazard studies were that test systems were small for demonstrating N_2O explosive potential that could be posed by large volume tanks (4-6, 8) and that hazard measurements of threshold initiations for organically contaminated N_2O were not made.

Should we continue to consider use of N_2O as a rocket propellant oxidizer? Available evidence has indicated that safe operation may be possible. Propagation of monopropellant decomposition from a combustion source, e.g., rocket engine, through feed lines back to storage tanks must be prevented. How to do this is presently unknown. In addition, combustibility of N_2O/organic mixtures and N_2O/organic mixture responses to friction, impact, and ESD need to be investigated. ESD incidents have caused accidents in solid propellant operations. Causes for solid propellant accidents prompted hazard studies that elucidated causes for fire initiations and threshold conditions that were needed to provide solid propellant fires. Such work brought about means for avoiding future ESD incidents with solid propellants (18, 19). ESD ignitions have not been recognized as a potential problem for causing N_2O and gaseous oxygen fire incidents.

To have confidence that large volume N_2O systems can be used safely a test program is needed to provide critical data and understanding about the origin of explosions with large volume N_2O systems. A key item in such a study will be demonstrating that an line device, that might be called a "reaction trap", will stop propagation of N_2O monopropellant decomposition from one adequately large tank to another tank through a high flow rate feed line. Additional information is degree of seal and gasket material swelling in liquid N_2O and drop weight impact, friction and ESD tests on swelled seal and gasket material. Some organic resins may be solubilized by liquid N_2O to make a viscous "gunk". Such "gunk" should be subjected to drop weight impact, friction, and ESD tests and compared to results obtained with pure N_2O. Nitrous oxide in gas phase near its critical temperature can dissolve and transport nonpolymeric organic material, even those with negligible vapor pressure, and some low molecular weight oligomeric organic materials forming explosively hazardous compositions (6). Explosiveness of dilute motor oil solutions in N_2O with respect to combustion and hazard sensitivity seems also needing investigation. Today, support for such a N_2O hazard test program is not available.

<center>**Discussion**</center>

N_2O is an energetic oxidizer:

Compared to storable oxidizers nitric acid (HNO_3), nitrogen tetroxide (N_2O_4), and hydrogen peroxide (H_2O_2), N_2O is a "green" oxidizer. N_2O is storable up to about 500° C (27), non-toxic, and often considered as being quite safe. N_2O has suitable oxygen content for bipropellant combustion. For operational safety with N_2O systems adoption of methods and procedures such as with high pressure gaseous oxygen could be prudent. Nitrous oxide heat of formation, 19.61 kcal/mole (9), indicates energy stored in its molecular structure that provides extra energy for propulsion operations whether as monopropellant or as bipropellant oxidizer. Monopropellant decomposition of N_2O poses a hazard risk that is not available with most alternate oxidizers.

News reports and publications are readily available about use of N_2O as rocket propellant. Notable accounts of rocket operations and planning are by Scaled Composites Space Ship One using N_2O/hydrocarbon rubber hybrid rocket (12), H. K. Haussmann consideration of N_2O propulsion systems for JATO smokeless aircraft takeoffs in the arctic (8), and Vadim Zakirov, et. al., testing N_2O monopropellant thrusters of a size that could be considered for satellite maneuvering (10, 11). Haussmann discusses a range of propulsion options that included liquid bipropellants, N_2O/graphite hybrid, N_2O monopropellant, N_2O/hydrocarbon mixed monopropellants, and N_2O/liquid hydrocarbon explosives. Later, I will refer to Haussmann's observations about traits of N_2O propulsion systems in various environments and N_2O propellant hazard testing results.

Vadim Zakirov has been using metal oxides as decomposition catalysts for N_2O. Cobalt III oxide, CoO_3 was most active enabling N_2O decomposition at the lowest temperature. Copper oxide, Cu_2O was the next best catalyst, and ferric oxide, Fe_2O_3 was the least active decomposition catalyst. This information should provide warning that copper and iron piping should be avoided in N_2O plumbing since formation of metal oxides would reduce the initiating temperature for start of N_2O decomposition into nitrogen and oxygen gases.

Explosive incidents with N_2O:

The large explosion in July 2007 in Mojave, CA was a surprise to us that had considered N_2O a safe material (1-2). Our perception of N_2O safeness was partly due to its widespread use without publicized problems by medical practitioners. Medical use of N_2O has considerable safety features in small volume systems and utilization at pressures near one atmosphere. Nitrous oxide medical explosive risk is of low order in that structures are not blown apart. Primary risk with medical use of N_2O is with fire hazard rather than explosive risk. Medical risk with N_2O use most often occurs when oxygen-N_2O overflow from a patient mixes with fuel vapors near a combustion source (7). Use of N_2O in rocket applications has considerably greater risk than for medical applications,

in that, large N_2O volumes, massive flow rates, and greater pressures up to 50 atmospheres or more are likely. Seeing a need for assessing N_2O explosive hazards when considered as a monopropellant and oxidizer for rocket engine applications, we conducted a literature search to gain understanding about all N_2O characteristics. Interestingly, explosive accidents with N_2O were more common than we originally thought. Some articles were found about N_2O explosive accidents (1-6, 33-34) that provided some information about what circumstances were in place before explosive events.

To date no suitable explanation for the July 2007 explosion in Mojave, CA has appeared in news media accounts of the accident. OSHA fined Scaled Composites for not training their workers informing them about N_2O hazards, instructing them on safe procedures, and providing a safe workplace (3). OSHA news article did not indicate causes for the explosion nor what procedures would ensure worker safety.

Reports about N_2O accidents are a) Scaled Composites explosion at Mojave Site, California (1, 2, 3), b) N_2O trailer rupture at Einhoven, Netherlands, 2 July 2001 (4), c) tank explosion and fire in West Palm Beach, Florida during 1973 (5), and d) recent eruptive events in Switzerland prior to October 2007 (6). According to news reports an explosion of several tons of N_2O occurred involving a semitruck trailer tank rupture at Mojave, CA during liquid flow tests. Operators at the Mojave site considered the N_2O system without a hybrid motor firing as being "safe" for mildly refrigerated liquid flow tests. No description of how or why the explosion occurred has been publicized.

The Einhoven accident involved rupture of a semitruck trailer containing N_2O. N_2O in a large storage tank attached to a liquid delivery line upstream of the centrifugal pump was not exploded although many tons of N_2O in the storage tank was lost. Capacity of the centrifugal pump was about 7.5 cubic meters per hour (~14 gallons per minute). Since the semitruck trailer had a capacity of about 7.5 tons of N_2O, filling the trailer could take most of one hour to fill an empty trailer with the pump system being used. Thankfully, the truck operator was not killed since he went to a location some distance away to smoke a cigarette after starting filling of the semitruck trailer. The explosion was attributed to hot graphite bearings in a centrifugal pump that was started in a dry state. This explanation did not seem reasonable since the explosion occurred about five minutes after liquid flow had been initiated. By the time liquid flow of several minutes duration had elapsed hot bearings in the pump would have been expected to have cooled to a temperature near that of the liquid that was at -15° C in the storage tank. Without adequate description of materials, configuration, internal size of connecting pipes, and purity of N2O only speculations can be made at this point about what really caused the explosive event.

An encouraging feature for indicating that large N_2O systems can be made safe was lack of N_2O monopropellant runaway decomposition flashing back through connecting pipes to the delivery tank. The N_2O supply tank at Einhoven remained intact after the explosion although its position had been shifted by about 3 meters (~10 feet). Since N_2O in the supply tank was stored at temperature well above N_2O boiling point, -

15° C versus -88.5 C, all N_2O contents in the supply tank escaped once an open line to atmospheric pressure became available. What would prevent flashback of runaway N_2O decomposition through pipes connecting between rotary pump and supply tank?

A tank rupture and fire at West Palm Beach, Florida in 1973 was referenced in the Einhoven explosion viewgraphs. No other publications have been found that describe the West Palm Beach incident. Thus, details allowing analysis of what happened at West Palm Beach have not been available.

Recently, October 2007, Bruno Berger, Swiss Propulsion Laboratory, reported that he knew of several N_2O system eruptive events that produced at least one ruptured N_2O feed tank (6). His question was, "Is N_2O safe?" He mentioned decomposition flashbacks from combustion chambers in a N_2O hybrid motor and in a N_2O/alcohol bipropellant engine. Combustion instability and low pressure drop between N_2O injectors and combustion chambers were cited as causes for the flashbacks. Mr Berger mentioned that copper oxide contamination could lower initiation of N_2O monopropellant reaction from temperatures of above 500° C to as low as 250° C. Any material reducing N_2O initiation temperature should be avoided. He had concerns about water hammering and adiabatic compression as processes that might start N_2O monopropellant decompositions.

One of B. Berger's concerns was "**unknown voodoo**" that he had read about in a report by Rhodes (22). He quoted the following excerpt from the Rhodes article, "Anomalies ----- One disturbing observation during the gaseous test program was the rather frequent (about 10 per cent of the tests) occurrence of unexplained events in two categories, spontaneous ignitions and spontaneous temperature rises. In the first category, sudden temperature and pressure spikes were sometimes observed while N_2O was being vented from the pipe. These anomalies generally occurred at low-pressure conditions where steady-state decomposition cannot be sustained. The other category consisted of unusual increases in pipe wall temperatures (by 11° to 28° C or 20° to 50° F,) during filling operations without any sudden pressure rise of other indication of a decomposition reaction. Both of these anomalies remain unexplained."

In light of other information the Berger "**unknown voodoo**" and Rhodes "Anomalies" may be explainable. Since Rhodes did not describe his first anomaly ignitions by having visible flame or very high temperatures on the surface of his vent pipe, actual ignitions of N_2O monopropellant process may not have occurred. Mitigating against N_2O ignition were the conditions of low pressure and lack of energetic stimulus needed to start a decomposing flame process. Warm zone volumes with turbulent gas flow have been observed with oxygen passing through pipes and could explain his flashes of warmth (17). Mild pressure spikes in a depressurizing environment might be explained by formation of liquid blobs formed by gas expansion cooling and fast conversion of liquid blobs to gas when they entered warm zones produced from the gas turbulent environment. Formation of liquid during the venting process might depend upon considerable but temporary back pressure in a vent system having substantial gas flow resistance. Rhodes' first anomaly observation would be most likely where gas

temperature in his experimental was lowest. If the gas were being vented from an elevated temperature, such as, 100 C, formation of liquid globs would be much less likely. Added information about gas turbulence heating will be provided later with discussion of oxygen gas behavior. Rhodes' second anomaly of pipe wall temperature increases may be explained by adiabatic compression of N_2O gas in the bottom of a vessel being filled, gas turbulence zone heating, or a combination of both. By Rhodes' admission no indication of N_2O decomposition occurred. During Rhodes' anomalies lack of broken experimental equipment, absence of huge equipment displacing thrusts, or evidence of N_2O monopropellant decomposition testifies to absence of endangering physical hazards to personnel.

Small scale explosions have been observed during super critical N_2O extraction processes (33, 34). Super critical extraction explosions were related to organic materials mixed into the primary N_2O gas phase. In 1991, Sievers, et. al., reported that a mixture of N_2O, 9% ethanol, 0.9% tetraethoxy silane, 0.07% triethyl borate, and 0.07% triethyl phosphate spontaneously exploded under conditions of 143 atmospheres pressure and 40 C. Stainless steel fittings were shattered. Another supercritical N_2O event occurred at 680 atmospheres and 80° C while extracting one gram of ground coffee, Raynie, 1993. Power evidenced by shattering of stainless steel fittings could be expected since the quantity of combustible fuel in the N_2O would raise kinetic speed of reaction and output energies considerably above that could be produced by N_2O monopropellant decomposition. Higher temperatures from a combination of oxidizer fuel reaction and monopropellant reaction would produce acceleration for producing eruptive events. Small scale explosions with N_2O containing combustible organic material are evidence that N_2O/combustible material mixtures are very hazardous with respect to pure N_2O. Since N_2O does not have significant monopropellant decomposition until temperatures above 500° C are obtained, reduction of initial reaction temperature with N_2O/organic material mixtures to the 40° to 80° C range are particularly daunting.

Since explosive events seem relatively common with use of N_2O, methods are needed to eliminate explosive risk. Lack of understanding is evident when some available reports about N_2O eruptive incidents are read. As a start considering that N_2O is an energetic oxidizer with some similarity to gaseous oxygen, what safety procedures developed for use with high pressure, gaseous oxygen systems should be adopted for N_2O systems? N_2O is a high energy oxidizer that should be given as much respect for its hazard potentials as we do for gaseous oxygen. More will be given on this subject later.

Early N_2O hazard studies:

Hazard studies about N_2O have been reported more than thirty years ago (20-24). Additional N_2O hazard study results are provided by Haussmann (8). Listed hazard studies were supported by U. S. military services. The article by Rhodes (22) is notable and B. Berger referred to Rhodes paper "anomalies" as "unknown voodoo". Edse, et. al., conducted explosion experiments over a variety of temperatures and pressures with N_2O (20, 21). A principle problem with early N_2O hazard studies was that internal volumes of

experimental vessels was so small that wall energy absorption effects inhibited the N_2O monopropellant reaction process and the speed of the process.

Edse and coworkers (20, 21) used one reaction vessel that was 32 mm (1.25 inch) diameter by 114 cm (45 inches) length, 905 cc, and, more extensively used a vessel 38 mm (1.5 inch) diameter by 106 mm (4.06 inches) long, 117 cc. Edse used exploding bridgewires and glow wires for ignitions. Gas phase monopropellant reactions at elevated temperatures were slow even at 325 C. In Edse's 117 cc chamber an exploding bridgewire ignition would occur at pressures of ~47 atmospheres pressure (4.76 MPa, 690 psi) or greater at 25 C. Maximum measured conversion of N_2O to nitrogen and oxygen in monopropellant decompositions was 90% and often much less. Spontaneous reaction without ignition stimulation occurred at 762 C. Explosion experiments were not carried out with liquid N_2O.

Rhodes gas phase propagation trials (22) were mostly conducted with pipes ranging from 12.7 mm (½ inch) to 51 mm (2 inches) diameters. Most monopropellant propagation reaction tests used stainless steel tubes 50.8 mm (2 inches) in diameter by 30.5 cm (12 inches) long. A few propagation reaction quenching tests were conducted in a vessel 15 cm (6 inch) diameter by 25 cm (10 inches) long. Electric sparks (7.3 joules), exploding bridgewires, and number 6 dynamite caps were used to provide N_2O gas phase ignition. Rhodes obtained more violent results than Edse, probably, due to his larger diameter containers. High speed monopropellant reactions of N_2O in gas phase employed temperatures ranging from about 10 (50 F) to 762 C (1400 F). Adiabatic compression at a rate of 4.1 MPa/second (600 psi/sec) in 51mm (2" inch) diameter pipe at room temperature did not start N_2O decomposition. At a gas compression rate of about 6.9 MPa/second (1000 psi/second), monopropellant decomposition started but quenched as cool gas filling of the tube continued. When number 6 caps were set off in 51 mm (2 inch) diameter pipes filled with water the pipes swelled in diameter. Cap tests were conducted in 51 mm (2 inch) diameter pipes filled with liquid N_2O. Cracked pipes resulted in most of the liquid N_2O trials. This was taken as evidence for some monopropellant decomposition occurring, but the reaction was considered as being relatively mild. A problem with the liquid cap tests was that 1700 psi of gaseous nitrogen was used over the liquid N_2O. This invalidates the conclusion of lack of violent reaction from N_2O number 6 cap testing since nitrogen is very soluble in N_2O producing a diluted liquid N_2O/nitrogen mixture that would be expected to give less violent reaction under harsh stimulation. Rhodes might have picked up on reaction attenuating effect of nitrogen gas with liquid N_2O since he demonstrated monopropellant reaction quenching when helium was used to dilute gas phase N_2O. Nitrous oxide was found to be compatible with Buna-N, neoprene, delron, Teflon, nylon, Vespel, & AF E-124X rubber. That is, no chemical reactions were observed between liquid N_2O and tested materials. No attempt was made to check polymeric material swelling by exposure to liquid N_2O. No hazard tests were conducted with N_2O plasticized polymeric materials indicated above. Gas phase explosion hazards with N_2O did not seem to be a problem in 51 mm pipes since flame or reaction propagation rates were 30 times less than with propane (C3H8)/air mixtures. Minimum reaction propagation pressure in 51 mm pipe was 1.7 MPA (250 psi) at normal ambient temperature. Exploding bridgewire ignitions took

more than one second to accelerate. Rhodes conclusions were "that nitrous oxide may be safely handled under extreme conditions in the cooled liquid state, but that great hazards exist in the gaseous condition at elevated pressure and temperatures."

Rivovich, et. al. (23), reported that 50 gram tetryl explosive donor testing of liquid and solid N_2O did not produce any discernible explosive reaction. Tests were conducted in 26.64 mm (1.05 inch) internal diameter steel pipes of 3.38 mm (0.13 inch) wall thickness. Nitrous oxide lengths were about 510 mm, that is, a L/D charge ratio of about 19 was employed. These results demonstrated that pure, condensed phase N_2O despite its internally contained heat energy has considerable resistance toward explosive initiation.

Haussmann's (8) article had interesting observations about behavior of N_2O, particularly, interactions when mixed with combustible materials. That is:
- Glycerin is used as a lubricant in pumping N_2O and it has frequently been found in N_2O storage cylinders.
- Liquid N_2O will burn the skin because its lipoid solubility prevents a protective vapor layer from being formed, as with liquid air or carbon dioxide.
- Nitrous oxide is soluble in water and many organic compounds.
- Gas phases of all N_2O-fuel mixtures could be exploded by electric fuses.
- Liquid phases of N_2O-fuel mixtures exploded only by heavy detonator charges.
- Graphite tubes acted more or less as decomposition surfaces for the N_2O, and as flameholders rather than reactive fuel.
- Mixtures of N_2O and hydrocarbon are monopropellants that are easily transportable explosives, such as, N_2O and kerosene.
- Liquid N_2O can be compressed by about 40% near its critical temperature under 10.9 MPa (1580 psi) pressure. That is, liquid density was about 0.748 g/ml versus critical temperature density of 0.451 g/ml. Pressure was about 50% higher than critical pressure of 7.3 MPa (1054 psi).

Two potential modes of explosive initiation for liquid N_2O will be unable to provide adequate energy stress over a large enough volume to provoke a runaway decomposition process for pure N_2O. That is, water hammering and bubble collapse. Liquid N_2O compressibility would be a factor when subjected to a water hammer process where impact momentum of liquid against a hard surface might be considered as a method of getting N_2O initiated into a runaway monopropellant explosion. Ability to provide high pressure and temperature in a small volume would be enhanced where the liquid is essentially incompressible.   Since water hammering to produce high shock pressures with liquid N_2O would be cushioned by the extraordinary compressibility of liquid N_2O (8), capability to get initiation would not be easily accomplished since elevation of pressure and temperature by the process would be dispersed over a relatively large volume compared to other liquids. This action would minimize both pressure and temperature extremes. Bubble collapse in liquids has been suggested as a mechanism for attaining very high temperatures that could be capable of initiating liquid N_2O into a runaway decomposition reaction (6). In a bubble collapse process, where vapor would compressed to an infinitesimal point to attain high temperature, the high energy volume

would be very small. However, since application of a 50 gram tetryl pellet detonation to a 27 mm (1.05 inch) diameter column of pure liquid N_2O did not provide any reaction (23), the volume of highly energized N_2O that was thousands of times larger than could be achieved by a bubble collapse was unable to start a propagating, uncontrolled, N_2O decomposition reaction. Organic fuel contamination of, perhaps, both gaseous and liquid N_2O may be adequately sensitized versus pure N_2O to make water hammering and bubble collapse work as initiating methods for getting a combined, propagating, uncontrolled N_2O monopropellant and N_2O/fuel reaction.

In a review of N_2O investigations Cawthra (36) referred to NASA, White Sands mechanical impact testing in liquid N_2O with mixtures and solid materials. His referenced internal report document was not able to be accessed by a literature search. Since no emphasis was placed on hazardous results from the NASA mechanical impact testing, lack of ready ignitions by mechanical impact are assumed.

N_2O could be given respect equal to gaseous oxygen:

Both N_2O and oxygen are strong oxidizers. Strong oxidizers provide risk for hazardous combustion incidents. Hazardous fires and explosive eruptions with oxygen have been observed over many years and studied in detail. As a result, suggested industrial practices for using gaseous oxygen have evolved so that following industrial practice guidance can be used to minimize probability of serious incidents (16, 17). Nitrous oxide industrial use has a low experience base as compared with gaseous oxygen. Adoption of selected industrial practices used with gaseous oxygen for use with N_2O might be a way to readily improve N_2O operational safety. Avoidance of heated gas volumes with N_2O as is done with oxygen through avoidance of sharp pipe bends and minimization of gas turbulence seems prudent. Perhaps, a previously undesignated fire ignition hazard occurs with oxygen in valve fires, is electrostatic discharge (ESD). If ESD becomes known as a hazard cause for gaseous oxygen valve fires, it may also surface as a problem for starting N_2O fires. Table 1 below compares industrial practices assembled by the Compressed Gas Association for gaseous oxygen and N_2O (13, 15, and 17).

Table 1: Comparison of Industrial Practices

Gaseous Oxygen (16)	N_2O (13)
No oils or particulates	Yes
Minimum radii for bends should be1.5 x pipe I.D.	Not specified
Suggested velocity in 2" SS of 25 fps - 100 fps – in monel, nickel, brass	Not specified
Vortices, flow friction, oscillation concerns– Prompted by seat fires in valves (17)	Not specified
ESD is an unconsidered problem	Not considered

Since perception of safety is attributed to N_2O handling, strict adherence to tank and piping cleanliness up to gaseous oxygen standards may not always be as good as it should be with N_2O systems. Solid abrasive particle impact and gas turbulence heating effects are concerns for gaseous oxygen but not advised as a concern for N_2O. Minimizing gas turbulence and particle impact risks in gaseous oxygen systems is accomplished by using sweeping bends in pipes and limiting gas velocity in pipes. Maximal general purpose velocities for gaseous oxygen have been spelled out in preferred industrial practices but velocity restriction for N_2O has not been provided. Since oxidizer pipe flow velocity restrictions can not be used in rocket engine applications, safety prudence in selecting and shaping construction materials where high oxidizer velocities will occur seems advisable. Mild localized heating with gaseous oxygen due to turbulence has been observed (17), but turbulence heating has not been raised as a concern with N_2O (13). Electrostatic discharge (ESD) ignitions might be a concern with oxygen valve seat fires. This has not been considered for gaseous oxygen systems, but if it turns out to be a valid issue with gaseous oxygen it could become a major concern for liquid and gaseous N_2O systems (17).

An unsolved ignition problem has been observed with soft seat fires burning up stainless steel valves in gaseous oxygen systems in airplanes, dome loaded regulators, and scuba regulators. It seems that the valve ignition problems occur where polymeric seats are involved with pressures above 10.3 MPa (1500 psi) dropping to much lower pressures often in the vicinity of a few atmospheres. Valve seat materials were Viton®, Vespel®, and silicone rubber. Ignitions occurred after some time delay (17). Abrupt system changes had not occurred prior to the valve fires, and fires seemed to originate in polymeric seat material. Unanswered question was, "Why did the fires start when no known heating mechanism seemed present that could produce temperatures in excess of the autogeneous ignition temperature (AIT) for the polymers? Autogeneous ignition temperatures for Viton® is about 268° C, for Vespel® about 562° C, and for silicone rubber about 262° C.

NASA conducted experiments trying to find oxygen valve fire causes. In vortex tube effect heating maximum temperature was about 200° C. Polymeric seat materials seemed unaffected by the elevated temperature. Torsion cold working experiments with nylon fibers attained peak temperature of about 260° C, but nylon was fatigued to failure during rotational bending, but no ignitions were obtained despite peak temperature approaching its ignition temperature just above its melting point. Internal friction was tested as an ignition source where rapid polymer oscillations were used. Inelastic bonds during oscillations should produce heat. No ignitions were obtained. External friction fires were produced when massive friction was produced by motor rotation of 12.7 mm (0.5 inch) diameter polymer rods were rotated against a metal surface. However, energetics of about 60 watts for the friction tests were much larger than could be conceived within flow valve operation. NASA tests into flow friction ignitions in an atmosphere of pure oxygen involved great vigor that did not produce ignitions except where total energy at polymer rod surface was greatly in excess of that available in small flow control valves. Silicone rubber and Viton® are known to dissolve considerable oxygen at high pressures. To explain valve seat ignitions impregnated with internal

dissolved oxygen some low level energy source that involves high enough temperature to produce a combustion reaction is needed. A probable answer to oxygen valve ignition problem might be electrostatic discharge (ESD). B. Berger (6) referred to ESD during injection as a probable hazard, but he did not provide any observations of behavior or explanations why ESD might occur.

Why should ESD (an electrical spark) be considered as an ignition initiator for oxygen valve fires? Electric sparks have extremely high temperatures although they can maintain the high temperatures only briefly in a very small volume of material. Electric spark temperatures are easily adequate for initiating fires under favorable conditions. If the volume of materials heated to high temperature by an electric spark is extremely small, overall spark energies can be quite small. Valve fire ignitions with oxygen started after some time of normal operation. Electrostatic charges often build up to higher voltages (higher energy) over a period of time. Low temperatures are favorable for getting ESD sparks. As polymeric materials are cooled their electrical resistance rises to high values and humidity effects attenuating ESD are minimized. Large gas pressure differentials across a valve constriction or regulator device will produce quite low temperatures. Charge build-up and cooling are changes that will reach their maximum effects over some finite period of time. Silicone and Viton® rubbers are known to strongly absorb oxygen under elevated pressures (17). Oxidizer within a fuel matrix produces a likely combination for ease of fire initiation and support of continued combustion, especially, when surrounding atmosphere is an elevated pressure oxidizer. High electrical resistance materials being separated or flowing over each other can generate high voltages. Silicone and Viton® rubbers can generate high electrostatic charges in flow processes. In oxygen valve fires conditions for charge generation, low temperatures, and very high electrical resistance materials are favorable for producing ESD events.

The triboelectric effect is the generation of electrostatic charges when differing materials are separated or rubbed or flowed over one another (37). With highly insulating materials and large surface areas voltages can become quite large. Highly insulating materials might be those having an electrical resistance above 10^{10} ohms per centimeter. Solid propellants having electric resistances above 10^{10} ohms per centimeter can be sensitive to electrostatic ignitions while solid propellants having electrical resistance below 10^{10} per centimeter are insensitive to fire ignition by ESD sparks (19). Nitrous oxide is a material that has very high electrical resistance in both gas and liquid states. Liquid nitrogen stream over a solid propellant surface can readily build up to 200,000 volts (18). Nylon, silicone rubber, Viton®, and Teflon® are known to be quite effective in generating static electricity when rubbed with other common materials. As gas pressure is increased, ignition energies for initiation of fire with solid propellants can diminish dramatically. Threshold electrostatic discharge voltage for getting a solid propellant ignition between one atmosphere (0.10 MPA, 14.7 psi) and 40 atmospheres (4.1 MPa, 600 psi) can reduce by a factor of 30 (19). Since spark energy is proportional to voltage squared, the spark energy for propellant ignition at 40 atmospheres pressure was about one thousandth $(1/30^2)$ that required for propellant ignition at one atmosphere pressure. Since N_2O vapor pressure at 20° C is about 50 atmospheres (5.2 MPa, 750 psi)

(8), pressure conditions are fairly optimal for having ESD events occurring that might attain combustion ignitions with fuel/oxidizer mixtures.

Special N₂O hazard traits:

Nitrous oxide has traits that exacerbate combustion and explosive hazards that are not found with oxygen. A primary factor is its positive heat of formation. This portends possibility of attaining a runaway monopropellant decomposition reaction. If N_2O decomposition reaction can propagate from a combustion process or other adequately vigorous thermal source through piping to a storage tank, dire trouble will happen with large amounts of N_2O. Runaway reaction might be expected both in liquid and gas phases. Since N_2O vapor pressure at 20° C is about 50 atmospheres (9), material mass density in the gas phase is quite high. As might be suspected, explosion hazard in N_2O gas phase is greater than for the liquid phase that has a heat of vaporization impediment to runaway decomposition reaction. Added explosive hazard in the N_2O gas phase has been demonstrated by experiment (22). Adiabatic temperature for N_2O decomposition starting from 20 C is about 1650° C (8). When N_2O is converted into one mole of nitrogen plus 0.5 mole of oxygen, standard gas volume will increase by 50%. If N_2O gas initially at 50 atmospheres (5.2 MPa, 750 psi) was converted adiabatically in a strong tank, the resulting pressure could reach about 430 atmospheres (43.7 MPa, 6300 psi) pressure. If the N_2O storage tank would break at 100 atmospheres (10.4 MPa, 1500 psi), a violent eruption producing explosive air shock would occur.

As a result of its positive heat of formation, N_2O will decompose once temperatures become adequately high. Rhodes (22) reported that adiabatic compression into 51 mm (2 inch) tubes at about 10° C (50° F) temperature would not start monopropellant decomposition at compression rates of 4.1 MPa/second (600 psi/second), but monopropellant decomposition starts would occur at gas compression rates near 6.9 MPa/second (1000 psi/second). In the 51 mm tubes N_2O monopropellant decomposition was observed to quench as added cool N_2O gas was admitted to the reaction vessel. Decomposition reaction quenching would be expected to be less likely as container being pressurized became larger in diameter. Threshold adiabatic compression rate to initiate N_2O decomposition at 20° C would be expected to attain a fixed minimum value once some vessel diameter was exceeded. That vessel diameter is unknown, but the diameter is likely to exceed the 51 mm diameter (2 inch) that was used during testing. Threshold minimum pressurization rate at 20° C in a larger diameter would likely fall to a value less than the 6.9 MPa (1000 psi/second) observed at the 51 mm (2 inch) diameter employed during Rhodes' adiabatic compression testing.

Despite having a number of explosive hazard studies with pure N_2O that showed relatively low explosive hazards (20-24), examples of serious accidents (1, 2, 4-6) keep appearing. The accidents indicate that nitrous oxide in those incidents was more hazardous than demonstrated by N_2O explosive hazard studies, presumably using pure N_2O. Fuel contamination appears to be a likely suspect. What is a better way to get lowered threshold stimulations to release a combination of N_2O internal contained energy and combustive energy where a dissolved fuel is burned? Haussmann's article (7) said

that while pure N_2O vapor at 20° C may not give monopropellant decomposition with 7 joule electric spark stimulation, but that gas phases of all N_2O-fuel mixtures could be exploded by electric fuses. Easy initiation of all N_2O/fuel mixtures demonstrated extra sensitivity for N_2O with mixed in fuels.

Fuel contamination of N_2O is a far more likely event than most would suspect. The primary reason for capability of getting soluble fuel contamination in N_2O is the fact that N_2O may be the best solvent known for organic materials and even many polar materials, such as, ammonia (8). Extraordinary solvent power for N_2O has been demonstrated in its use as a supercritical solvent (28-34). Supercritical N_2O is an even better solvent than supercritical carbon dioxide that was first used as a gas solvent for negligible vapor pressure organic materials (29). Any polymeric material that can dissolve oxygen gas such as, silicone rubber and Viton® (17), will even more readily absorb N_2O. Nitrous oxide in gas phase near its critical temperature can pick up (dissolve) and transport nonpolymeric organic material, and, perhaps, low molecular weight oligomeric organic materials to form explosively hazardous compositions (6). At 20 C temperature gas phase N_2O has a high enough density to have some supercritical type of solvent capability. That is, N_2O gas can be expected not only to dissolve materials based on their 20° C vapor pressure but, also, through solvent power to pick up high boiling materials that have negligible vapor pressure at 20° C. Materials, such as, low molecular weight components of cured epoxy glue might transfer with N_2O vapor even if distilled at 20° C into a cooled. B. Berger (6) in his presentation said that N_2O is a swelling agent for polymeric materials. Nitrogen dioxide, NO_2, has been noted to solvate into Teflon® membranes without chemical reaction and be emitted out the other side (38). Nitrous oxide with its higher solvent power than nitrogen dioxide will similarly be able to pass through Teflon® without chemical reaction.

Haussmann's (8) article had interesting observations about behavior of N_2O as a solvent to form mixtures with combustible materials. One example was that glycerin was used as a lubricant in pumping N_2O and that it was frequently found in N_2O storage cylinders. Whether N_2O obtained in recent times contains glycerin is unknown. A frustrating problem with trying to remove a high boiling organic material contamination, such as, glycerin from N_2O is that simple vapor transfer of N_2O from a tank at 20° C into a cooled container may not reduce glycerin concentration to low value. This would occur due to solvent power of dense N_2O vapor to carry over some glycerin despite a large difference between boiling points of N_2O and glycerin. This behavior would be a consequence of dense N_2O gas being not only capable of mixing with vapors but, also, having a solvent carrying nature similar to that of liquid solvents where high boiling materials will form solutions. Nitrous oxide was said to be soluble in water and many organic compounds. Mixtures of N_2O and hydrocarbons were described as being monopropellants that were easily (safely) transportable explosives, such as, N_2O and kerosene. Another indication of liquid N_2O solvent capability was the statement that: "liquid N_2O will burn the skin because its lipoid solubility prevents a protective vapor layer from being formed, as with liquid air or carbon dioxide."

Liquid N_2O at 20° C due to its higher density than the gas phase at the same temperature will have stronger solvent and solute power than for gaseous N_2O. Some chemical compatibility studies between silicon rubber, Viton®, Vespel®, Buna-N, neoprene, delron, Teflon®, nylon, and AF E-124X rubber were conducted by exposure to liquid N_2O (22, 24). Tested materials above were compatible in that no chemical reactions were observed with liquid N_2O. Typically, tested materials were recovered essentially unchanged. AF E-124X rubber was incompatible in that physical properties changed during exposure to liquid N_2O. Since compatibility trials were conducted in nontransparent, pressure capable vessels, investigators did not record or, perhaps, even see swelling of any materials while in liquid N_2O. Recovered polymeric compatibility trial samples may have been examined after plasticizing N_2O within them had escaped as vapor. One of B. Berger's (6) warnings was to test polymeric seals intended to be used in N_2O systems for swelling in liquid N_2O. Prudence in employing polymeric seals in liquid N_2O systems would be to use those that had minimal combustibility, such as, Kalrez, a perfluorocarbon ether elastomer. Where possible, seals of annealed nickel have been suggested for N_2O system service (13).

Evidence obtained in N_2O hazard discussions and studies showed that N_2O mixtures containing dissolved fuels were recognized as being more readily ignited or exploded than when pure N_2O was tested under the same conditions. Explosive incidents with N_2O where strong energetic stimuli seemed absent need explanation. Since fuel contamination of N_2O is easily obtained, at least some mysterious explosive incidents were likely to involve fuel contamination. However, explosions in small volume equipment using supercritical N_2O at mild temperatures, 40° to 80° C, showed that organic contamination in N_2O is a greatly sensitizing method for explosive events (33, 34). If spontaneous combustion/explosion has not yet occurred, the best candidate for a low energy level stimulation to promote fuel contaminated N_2O combustion and explosions is ESD.

N_2O hazard test effort to gain understanding of safety issues:

As stated above, technical explanation of causes for serious N_2O fire and explosive incidents seem inadequate and/or missing in accounts for such incidents (1, 2, 4-6). Understanding of how and why such incidents occur is obviously needed before large scale use of N_2O as a propellant material can be conducted with confidence about adequate control and elimination of safety issues. Understanding of N_2O system safety will require an experimental effort. Concerns of such an experimental study might be:

a) Determining energetic stimulus reaction thresholds for tests in vessel diameters of practical size. As vessel cross section is enlarged muting effects, primarily, through heat transfer to container surfaces will become less important for inhibiting N_2O gas phase monopropellant decomposition. Some sub-scale N_2O container size as compared to an operational system can be used, but certainly larger than the 51 mm diameter vessels used in the Rhodes study (22). Vessel diameters found with 20 liter (5 gallon) containers should be adequate. This would correspond to about 25 cm (10 inch) test vessel diameter. Types of tests could be by exploding bridgewires, multijoule electric

sparks, adiabatic compressions, and dynamite caps. Such larger diameter tests would demonstrate whether runaway N_2O monopropellant reaction in the gas phase could be readily transferred into the liquid phase at normal ambient temperatures.

b) Develop a suitable structure to quench N_2O monopropellant decomposition propagation from one tank, possibly with 20 liter volumes, to another through connecting pipes. A flame holder or reaction trap structure for N_2O-hydrocarbon fuel combustion at one atmosphere pressure is described by Muscat, et. al. (35). Very small diameter pipes may work, but single small pipes would not permit flow rates appropriate for conducting a modest sized rocket engine firing. Attenuating system in connecting pipe from one reaction vessel to another needs to be capable of rocket engine fluid flow rates if used in useful combustion equipment. Both gas and liquid monopropellant reaction quenching tests needs to be accomplished.

c) Test relative threshold sensitivity of N_2O containing organic fuel contamination as in a) above with fuel concentrations ranging from approximately 0.5 to 5%. Compare contaminated N_2O threshold test results with that for pure N_2O.

d) Test vapor and liquid N_2O containing fuels for threshold, propagating reactions by electrostatic discharge. Compare electrostatic discharge initiating jolts with results using pure N_2O.

e) Check ESD threshold sensitivies of polymeric materials, such as, Viton®, HTPB rubber, polymethylmethacrylate (PMMA), Buna-N, cured epoxy resin, Bakelite®, nylon, Teflon®, and silicone rubber immersed in saturated N_2O vapor and liquid at temperatures close to 20° C. Since ESD fire initiations in polymeric materials are assumed to boot strap from very small dimensions, swelled polymeric material threshold ESD trial samples can be very small in dimension. Cross sections as small as 1 mm across may be adequate. Conduct a few swelling measurements for some polymeric compounds in list above to determine volume changes in liquid N_2O at 20° C. Swelling tests could be with very small samples encased in heavy glass tubing by measuring increases in visual length and diameter. .

Conclusions and Recommendations

Large explosive events with N_2O systems occur at infrequent intervals (1, 2, 4-6). Satisfying, insightful engineering and chemical analysis for these accidents seems lacking. Nitrous oxide hazards tests with pure N_2O did not indicate why such explosive events could take place in cases where no vigorous energetic initiation events were apparent. Mysterious explosive initiating events need to be explained before large N2O combustion systems can be used with confidence in their safety. A focused hazard study of N_2O explosive thresholds in suitable size, development of reaction quenching structures, and examination of hazards associated with N_2O – fuel mixtures whether in liquid or infused solid phases is needed to provide safety understanding. Some accidents, Mojave, Einhoven, and oxygen valve fires occurred with some time delays (1, 2, 4, 17).

Electrostatic discharge probabilities are likely to increase over time as charge buildup develops, perhaps, over seconds to many minutes. Once electric charge rose to some critical value, an ESD event might take place. Mojave was reputed to initiate after about 3 seconds, Einhoven after about 5 minutes, and oxygen and scuba valve fires after many minutes (2, 4, 17). This is a mild clue that ESD might be involved in the fire and explosion event initiations. Adiabatic compression ignitions and water hammering initiations might be expected to start relatively fast with fire and explosive reaction occurring almost immediately after fluid flow began.

Propagating, runaway N_2O monopropellant decompositions from a hot source through pipes back to N_2O storage tanks is a primary risk of using large volume N_2O systems. In the Einhoven explosion propagation of N_2O monopropellant decomposition reaction from rotary pump to semitruck trailer occurred. Hope for eventual safe use of N_2O in large systems was provided by the fact that propagation backwards from the rotary pump to the larger storage tank did not occur (4).

B. Berger raised questions about safety of polymeric materials containing infused N_2O. He thought polymeric components considered for use in a N_2O system should have their swelling in liquid N_2O determined. Further concern was water hammering and adiabatic compression of small gas bubbles (6). According to Rhodes (22) flame speed of N_2O monopropellant decomposition in the gas phase was about 30 times slower than with a mixture of propane and air at the same initial temperature and pressure. Haussmann indicated that N_2O at conditions close to its critical temperature was amazingly compressive (8). Pure N_2O's slow flame speed and liquid compressibility indicates almost no safety concern about water hammering and adiabatic compression of gas bubbles. In addition, since Rivovich, et. al. (23) reported that 50 gram tetryl explosive donor testing of liquid and solid N_2O did not produce any discernible explosive reaction at 27 mm (1.05 inch) diameter, production of very small, extremely hot volumes produced by bubble collapse would have zero probability of initiating a bootstrapping explosion in pure liquid N_2O. Berger also worried about Rhodes "strange voodoo" that upon examination did not seem to pose any physical hazard (6, 22).

Hazard testing by Rhodes of pure N_2O showed it to be explosively inert (22) except under great provocation. Saturated gaseous N_2O at 20° C did not initiate into propagating monopropellant reaction by 7 joule electric spark although an exploding bridgewire (EBW) could initiate a propagating reaction in 51 mm diameter tubes at 20 C. Flame speed of the reaction front was about 30 times slower than with a stoichiometric mixture of propane and air. Adiabatic compression at 20° C in 51 mm diameter tubes could initiate N_2O monopropellant reaction at 6.9 MPa per second at beginning of compression process but reaction quenched with continued admission of cool N_2O gas. Adiabatic compression of gaseous N_2O at 20° C and compression rate of 4.1 MPa per second did not initiate decomposition reaction. Rhodes' dynamite cap tests with liquid N_2O in 51 mm diameter tubes were invalid due to heavy dilution of N_2O with nitrogen (Rhodes, 22). Nitrogen gas was introduced to sample tubes at 115 atmospheres (11.7 MPa, 1700 psi) prior to dynamite cap tests. Drop weight impact and friction tests conducted by NASA for liquid N_2O and liquid N_2O – fuel mixtures did not exhibit

sensitivity (24). In an overall assessment, explosive safety of liquid N_2O was excellent, and 20° C N_2O saturated vapor could be initiated into propagating reaction only with considerable difficulty. Rhodes conclusion was that use of pure N_2O is explosively safe except at high temperatures. Fundamental criticism of available N_2O explosive study reports was that test vessel cross sections (51 mm for most tests) may have been too small to exhibit true explosive nature of N_2O.

In contrast to safety in using pure N_2O are organic materials - N_2O mixtures that are quite sensitive to initiations of fire and explosions. Rhodes could not initiate saturated N_2O vapor at 20° C with heavy electric spark, but all tested N_2O-fuel mixtures could be readily ignited in 51 mm diameters (22). An even more enlightening example about explosive sensitivity of N_2O – fuel mixtures are spontaneous explosions produced in small volume, super critical, N_2O extractions at temperatures in the 40° to 80° C range (33, 34).

An experimental hazard program for N_2O and N_2O – fuel mixture has been proposed. Goals of the proposed N_2O hazard study are to conduct threshold, pure N_2O hazard tests in suitably large sizes, develop flame trap structures to prevent N_2O monopropellant decompositions from propagating from a hot source like a liquid engine back through pipes to a N_2O storage tank, investigate threshold explosive initiation of N_2O - fuel mixtures, and to elucidate whether ESD with N_2O – fuel mixtures provides an extraordinary, low energy method for fire/explosion starts for N_2O – fuel mixtures.

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Nitrous Oxide Explosive Hazards

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Nitrous Oxide Explosive Hazards
Topics of Discussion

Nitrous oxide (N_2O) is energetic oxidizer

Accidents with N_2O systems

Prior N_2O hazard studies

N_2O should be respected as well as gaseous oxygen

Special N_2O hazard traits

N_2O hazard test effort to gain understanding of issues

Nitrous Oxide Explosive Hazards
As Oxidizer, N_2O is Attractive

"Green" oxidizer

- **Nontoxic when released to the atmosphere**
- **Contains adequate oxygen content**
- **Positive heat of formation adds to combustion energies** [1]

Recently considered as rocket propellant

- **Hybrid rocket motor oxidizer by Burt Rutan** [2]
- **Considered for small monopropellant thrusters** [3,4]

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Nitrous Oxide Explosive Hazards
N_2O Explosive Incidents

Lack of hazard understanding is evident:

- Scaled Composites, Mojave, CA, Aug 2007, 3 killed by "safe" system associated with space access vehicle. (5)

- Einhoven, Netherlands, Jul 2001, semitrailer tank used for transfer of N_2O to medical facilities. (6)

- Tank explosion, N_2O, Pratt & Whitney, W. Palm Beach, 1973. (6)

- Recent Swiss Propulsion Lab engine/motor flashbacks, 2007. (7)

(5) "SS2 Slip", Guy Norris, Aviation Week & Space Technology, August 6, 2007. http://www.bakersfield.com/102/story/198908.html.

(6) "Nitrous Oxide Trailer Rupture", July 2, 2001, The Netherlands, Eindhoven.pdf file; Report at CGA Seminar, "Safety and Reliability of Industrial Gases, Equipment and facilities", Konrad Munke, St. Louis, Missouri, October 15-17, 2001.

(7) "Is nitrous oxide safe?" Pdf file, Bruno Berger, Swiss Propulsion Laboratory (SPL), presentation 5 October 2007.

Nitrous Oxide Explosive Hazards

Eindhoven, Netherlands N_2O explosion – Semitrailer exploded down stream of centrifugal pump but N_2O storage tank survived intact. (7)

- Hot pump unlikely cause for explosion since incident did not occur until five minutes after pumping started.

No flashback to storage tank indicates large N_2O systems could be safe.

trailer tank

N_2O supply tank

(6) "Nitrous Oxide Trailer Rupture", July 2, 2001, The Netherlands, Eindhoven.pdf file; Report at CGA Seminar, "Safety and Reliability of Industrial Gases, Equipment and facilities", Konrad Munke, St. Louis, Missouri, October 15-17, 2001.

Nitrous Oxide Explosive Hazards
N_2O Explosive Incidents

Small scale explosions in supercritical N_2O:

- **Mixture N_2O, 9% EtOH, 0.9% $(EtO)_4Si$, 0.07% $(EtO)_3B$, & 0.07% $(EtO)_3P$ at 143 atmospheres pressure & 40° C exploded shattering SS fittings, 1991 (8)**

- **Supercritical N_2O at 680 atmospheres pressure & 80° C exploded when extracting one gram of ground coffee, 1993 (9)**

Spontaneous explosions!!

(8) "Supercritical fluid nitrous oxide explosion," Sievers R. R.; Hansen B., Chem. Eng. News, 69 (29), p. 2, July 1991.

(9) "Warning Concerning the Use of Nitrous Oxide in Supercritical Fluid Extractions", Douglas E. Raynie, Cincinnati, Ohio, Anal. Chem 65, pp 3127-3128, 1993.

Nitrous Oxide Explosive Hazards
Prior N$_2$O Explosive Hazard Studies

Studies of N$_2$O decomposition & explosiveness did not exhibit violent activity (blow tanks apart) (10, 11, 12, 13)

- Fast decompositions required high temperatures (10)

- Decompositions started by adiabatic compression died in 51 mm pipe with continued gas admittance (13)

(10) "The Thermal Decomposition of Nitrous Oxide at Pressures up to Forty Atmospheres", E. Hunter, Proceedings of the Royal Soc, v.144, n.852, pp 386-412, 29 Mar.1934.

(11) "Explosion Limit Studies of Nitrous Oxide and Nitrous Oxide – Nitrogen – Air Mixtures to 200 Atm. And 1800 R.", Juris O. Krisjansons, Doren E. Bollinger, and Rudolph Edse, ARL 62-431. September 1962.

(12) "Detonability of Nitrous Oxide at Elevated Initial Pressures and Temperatures", James A Laughrey, Loren E. Bollinger, Rudolph Edse, ARL 62-432, September 1962.

(13) "Investigation of Decomposition Characteristics of Gaseous and Liquid Nitrous Oxide," G. W. Rhodes, AD-784 802, AFWL-TR-73-299, Air Force Weapons Laboratory, Kirtland AFB, NM 87117, July 1974.

Nitrous Oxide Explosive Hazards
Prior N_2O Hazard Studies Shortcomings

- Volumes were too small to get runaway N_2O monopropellant decomposition and complete reaction starting at room temp.

- Did not look at N_2O decomposition propagation between two substantial volumes through connecting piping

- Did not use velocity and minimum radius practices such as used for today's high pressure oxygen systems

- Did not recognize need to study resin and plastic solubility in N_2O or N_2O swelling of resins and plastics

- Didn't check fire sensitivity of N_2O containing low levels of organic materials

- Didn't check ESD sensitivity of resins and plastics that had absorbed substantial N_2O

Nitrous Oxide Explosive Hazards
Is N_2O Safe?

"Unknown Voodoo": Bruno Berger words about description by G. W. Rhodes (7) & (13)

"One disturbing observation during the gaseous test program was the rather frequent (about 10 percent of the tests) occurrence of unexplained events in two categories, spontaneous ignitions and spontaneous temperature rises. In the first category, sudden temperature and pressure spikes were sometimes observed while N_2O was being vented from the pipe. These anomalies generally occurred at low-pressure conditions where steady-state decomposition cannot be sustained. The other category consisted of unusual increases in pipe wall temperatures (by 20° to 50° F) during filling operations without any sudden pressure rise or other indication of a decomposition reaction. Both of the anomalies remain unexplained." G. W. Rhodes

Nitrous Oxide Explosive Hazards
B. Berger"'s Unknown Voodoo by Rhodes (7,13)

Category 1, occasional sudden temperature and pressure spikes during N$_2$O venting under non-decomposition conditions. (13)

- High pressure gas cools during venting. With flow restriction in vent blobs of liquid could intermittently impede gas venting.

- Gas turbulence (vortices) in high pressure oxygen can provide warm pipes. (15) Why shouldn't N$_2$O provide heating?

- Gas turbulence can provide hot spots and liquid hitting hot spots can provide pressure spikes without decomposition rx.

Category 2, increases in pipe wall temperature (by 20 to 50 F) during filling operations. (13)

- Gas turbulence heating such as observed with oxygen. (15)

(15) "Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eleventh Volume," D. Hirsch, R. Zawierrucha, T. Steinberg, and H. Barthelemy, Editors, ASTM Stock Number: STP1479, "Flow Friction Fire History and Research," pp. 151-162, October 2006.

Nitrous Oxide Explosive Hazards
Comparison of Industrial Practices

Gaseous Oxygen	N_2O
No oils or particulates (14)	Yes (16)
Minimum radii for bends (1.5 x I.D.) (14)	Not specified
Suggested transfer velocity (25 fps in (14) 2" - SS, 100 fps – in monel, nickel, brass)	Not specified
Vortices, flow friction, oscillations (15) (Seat fires in valves)	Not specified
ESD may be unconsidered problem	Not considered

(14) "Industrial Practices for Gaseous Oxygen Transmission and Distribution Piping, " Compressed Gas Association (CGA), Publication CGA G-4.4-1993;

(15) "Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eleventh Volume," D. Hirsch, R. Zawierrucha, T. Steinberg, and H. Barthelemy, Editors, ASTM Stock Number: STP1479, "Flow Friction Fire History and Research," pp. 151-162, October 2006.

(16) "Standard for Nitrous Oxide Systems at Systems, Customer Sites," fourth edition, Compressed Gas Association (CGA), Publication GCA 8.1-2007.

Nitrous Oxide Explosive Hazards
Explosive Hazard Contrasts

Pure N_2O	Tests	Contaminated N_2O
No rx., condensed	Heavy Donor	Can be strong expl.
No rx., liquid	Dynamite cap	Transportable expl.
Slow rx. , gas	Dynamite cap	Fast rx.
No rx., gas & liquid	Electric Spark	All mixtures ignite
No problem	Mechanical impact	No documented prob.
No problem	Friction	No documented prob.
Above 500° C	Spontan. Decomp.	As low as 40° C
Rx. rate 30x less than propane-air	Adiabatic Compress.	Sens.? - lack data

Nitrous Oxide Explosive Hazards
Why Consider Electrostatic Discharge Hazards?

Oxygen valve fires:

- Occurred after considerable flow time [6]

- Large pressure drops on aircraft and scuba regulators

- No visible highly energetic inputs

- Silicone and Viton® seats

- Oxygen is highly soluble in silicone and viton at high pressures

- Conditions favorable for promoting electrostatic discharge

(15) "Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eleventh Volume," D. Hirsch, R. Zawierrucha, T. Steinberg, and H. Barthelemy, Editors, ASTM Stock Number: STP1479, "Flow Friction Fire History and Research," pp. 151-162, October 2006.

Nitrous Oxide Explosive Hazards
Why Consider Electrostatic Discharge Hazards?

Electrostatic charges are generated by flowing over or separating differing materials -- Triboelectric effect (17)

- **Voltages produced can be very large with insulating materials**

- **Low temperatures increase electrostatic sensitivity**

- **Electric spark temperatures are capable of dissociating molecules**

Examples:

- **Liquid nitrogen stream over solid propellant readily gave 200,000 volts electric charge (18)**

- **Threshold spark ignition energy for solid propellant can be reduced by 1000 by increasing pressure from 1 to 40 atm. (19)**

- **Typical ambient vapor pressure of N_2O is about 50 atm.**

(17) "Triboelectric Charging of Common Objects," Jones, T.B., University of Rochester, December 1999.

(18) Claude Merrill, unpublished incident investigation

(19) "ESD Traits of Bulk Propellant Under Pressure," C. I. Merrill and J. A. Askins, JANNAF Propulsion Systems Hazards Subcommittee Meeting, Silver Springs, Maryland, CPIA 582, Volume 1, pp 131-144, 17 April - 1 May 1992.

Nitrous Oxide Explosive Hazards
Hazards Peculiar to N_2O

N_2O can undergo exothermic decomposition into O_2 and N_2 [13]
- Positive heat of formation, 19.6 kcal/mole [13]
- Adiabatic compression ignition [13]
- Runaway reaction hazard is greater for larger volumes

N_2O excellent solvent trait can create ignition & explosive haz.
- Better solvent than supercritical CO_2 [20]
- Swiss concerns over infusion into grease, HTPB, plastics [7]
- How about silicones, Viton®, epoxies?

High solubility trait makes oxidizer/fuel mixtures easily obtained.
- Excluding organics within N_2O is a key hazard issue

(7) "Is nitrous oxide safe?" Pdf file, Bruno Berger, Swiss Propulsion Laboratory (SPL), presentation 5 October 2007.
(13) "Investigation of Decomposition Characteristics of Gaseous and Liquid Nitrous Oxide," G. W. Rhodes, AD-784 802, AFWL-TR-73-299, Air Force Weapons Laboratory, Kirtland AFB, NM 87117, July 1974.
(20) "Supercritical Fluid Extraction of Fungal Oil Using CO_2, N_2O, CHF_3, and SF_6," Keiji Sakata, Toshihiro Yokochi, Osamu Suzuki, and Toshikatsu Hakuta, JAOCS, Vol. 67, no. 9, pp. 553-557, September 1990.

Nitrous Oxide Explosive Hazards
What Data Would be Suitable for N_2O Hazards Effort?

In 25 cm diam. find threshold, N_2O adiabatic compression initiations, measure rx. velocities from EBWs, dynamite caps, and multijoule electric sparks. Repeat for N_2O – fuel mixtures and compare,

Demonstrate that N_2O decomposition propagation can be stopped by multiple small size orifices between 20 liter tanks; gas and liquid.

Investigate N_2O solubility or swelling of typical resin and seal materials

Study hazard effects with about 0.5 to 5% hydrocarbon & soluble resins
   - Check thermal reactivity at 125º C
   - Threshold ESD sensitivity of above

Measure electrostatic charging from N_2O liquid and gas flow over typical plastics, rubbers, and graphite

Nitrous Oxide Explosive Hazards
Conclusions

N_2O explosive incidents are mysterious

Need to know what/how low energy stimulus can start explosions

Need to stop N_2O decomposition propagation through pipes

Organic contamination in N_2O is a prime suspect

N_2O testing is needed for hazard understanding and safety control
- Conduct hazard tests in about 25 cm diameter
- Find adiabatic compression threshold for decomposition
- Repeat above for dilute N_2O/organic fuel solutions
- Develop reaction propagation blockage system for pipes
- Conduct threshold ESD tests for N_2O/organic mixes