# Nitrous Oxide Explosive Hazards (Preprint)

**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. $N_2O$/organic mixtures.

**Subject Terms**

Nitrous Oxide Explosive Hazards, $N_2O$, Rocket Propulsion, Hazard Studies, Monopropellant Decomposition.

**Distribution / Availability Statement**

Approved for public release; distribution unlimited (PA #08247A).

**Supplementary Notes**

May 2008

Nitrous Oxide Explosive Hazards (Preprint)

Claude Merrill

Air Force Research Laboratory, Edwards AFB, CA

Abstract

A recent incident caused us to evaluate the subject of nitrous oxide (N\textsubscript{2}O) hazards. Use of N\textsubscript{2}O for rocket propulsion seems to be a continuing interest. Accounts of serious, large system N\textsubscript{2}O accidents are mysterious since technically satisfying explanation of how the incidents occurred seems lacking. Inadequacy of technical information for serious N\textsubscript{2}O 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\textsubscript{2}O operations, may provide some safety improvements. Experimental investigation to gain recognition of large quantity N\textsubscript{2}O explosive and ignition traits may be the only way to ensure large N\textsubscript{2}O system safety. Prior hazard and monopropellant decomposition studies largely indicated that N\textsubscript{2}O was difficult to initiate into dangerous monopropellant decompositions. Based on prior studies and use of N\textsubscript{2}O for decades in dental practice without serious incidents, many people have considered use of N\textsubscript{2}O as safe. Early explosive hazard studies did not indicate a serious explosive nature for N\textsubscript{2}O. Inadequacy of historical N\textsubscript{2}O hazard study experiments was that they used too small volumes in their studies. Explosive hazards for N\textsubscript{2}O are exacerbated by its extraordinary gas and liquid solvent properties that can lead to fuel/N\textsubscript{2}O compositions where fuel material is normally considered insoluble. Organic resins can be extracted by contact with seals, and N\textsubscript{2}O can dissolve like a plasticizer into organic materials. Transfer of N\textsubscript{2}O monopropellant reaction from combustion sources, impact, or friction, through piping back to a storage tank seems a primary hazard for N\textsubscript{2}O 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\textsubscript{2}O. A test program is suggested that could answer questions about decomposition propagation control in large N\textsubscript{2}O systems and hazards associated with N\textsubscript{2}O/organic mixtures.

Introduction

The author lacks experience with large N\textsubscript{2}O 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\textsubscript{2}O hazards and at the end to suggest need for developing means for stopping runaway monopropellant decomposition propagation through piping to N\textsubscript{2}O storage tanks and for measuring increase in explosive sensitivity of fuel contaminated N\textsubscript{2}O. 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 \( \text{N}_2\text{O} \) explosive hazards. \( \text{N}_2\text{O} \) 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 \( \text{N}_2\text{O} \).

\( \text{N}_2\text{O} \) explosive events other than the one at Mojave in sizeable scale have been reported (4-6). Repeated appearance of \( \text{N}_2\text{O} \) explosive events indicates that present understanding of \( \text{N}_2\text{O} \) hazards and means to control such hazards is inadequate (13-15). Inadequate understanding of \( \text{N}_2\text{O} \) hazard issues was indicated by recent reference to “unknown voodoo” in a \( \text{N}_2\text{O} \) hazard behavior report (6). This discussion is intended to point out \( \text{N}_2\text{O} \) hazard concerns where experimental investigation and confirmation of operational safety are needed.

\( \text{N}_2\text{O} \) has been viewed as a nontoxic, “safe” oxidizer that might be used in rocket propulsion systems (8-12). That is, \( \text{N}_2\text{O} \) is a candidate “green propellant” oxidizer. Since \( \text{N}_2\text{O} \) 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 \( \text{N}_2\text{O} \) can dissolve significantly in plastics, electrostatic sensitivity of such compositions seems probable (6).

Probability of hazardous behavior with \( \text{N}_2\text{O} \) 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 \( \text{N}_2\text{O} \) hazard studies did not show any strong violence by \( \text{N}_2\text{O} \) runaway decompositions or continuation of monopropellant decompositions started by adiabatic compressions. Lack of violent events when \( \text{N}_2\text{O} \) was abused by initiating means was, perhaps, partly due to use of small volumes for experiments where wall effects were adequate for limiting \( \text{N}_2\text{O} \) speed or providing quenching for \( \text{N}_2\text{O} \) decomposition processes. Approaches for safely utilizing \( \text{N}_2\text{O} \) for rocket propulsion should involve measures countering \( \text{N}_2\text{O} \)’s unique array of chemical and physical hazard characteristics. Concerns about pure liquid \( \text{N}_2\text{O} \) reaction initiation by “water hammering” and “bubble collapse” (6) seem unlikely due to liquid \( \text{N}_2\text{O} \) being a highly compressible liquid (8) and lack of response to 50 gram tetryl pellet detonation at 27 mm diameter (23). Main \( \text{N}_2\text{O} \) 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 \( \text{N}_2\text{O} \) flows rapidly over high electrical resistance materials, such as, viton® and silicone valve seats. Organic contaminated \( \text{N}_2\text{O} \) 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$_2$O explosive hazards. Since a number of proposals to utilize N$_2$O 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$_2$O experimental hazard assessment program.

Limited data are available from accounts of accidents (1-6) and studies of N$_2$O hazards and decompositions (20-27). Primary deficits of past hazard studies were that test systems were small for demonstrating N$_2$O explosive potential that could be posed by large volume tanks (4-6, 8) and that hazard measurements of threshold initiations for organically contaminated N$_2$O were not made.

Should we continue to consider use of N$_2$O 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$_2$O/organic mixtures and N$_2$O/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$_2$O and gaseous oxygen fire incidents.

To have confidence that large volume N$_2$O 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$_2$O 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$_2$O 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$_2$O and drop weight impact, friction and ESD tests on swelled seal and gasket material. Some organic resins may be solubilized by liquid N$_2$O 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$_2$O. 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$_2$O with respect to combustion and hazard sensitivity seems also needing investigation. Today, support for such a N$_2$O hazard test program is not available.
Discussion

N₂O is an energetic oxidizer:

Compared to storable oxidizers nitric acid (HNO₃), nitrogen tetroxide (N₂O₄), and hydrogen peroxide (H₂O₂), N₂O is a “green” oxidizer. N₂O is storable up to about 500º C (27), non-toxic, and often considered as being quite safe. N₂O has suitable oxygen content for bipropellant combustion. For operational safety with N₂O 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 N₂O poses a hazard risk that is not available with most alternate oxidizers.

News reports and publications are readily available about use of N₂O as rocket propellant. Notable accounts of rocket operations and planning are by Scaled Composites Space Ship One using N₂O/hydrocarbon rubber hybrid rocket (12), H. K. Haussmann consideration of N₂O propulsion systems for JATO smokeless aircraft takeoffs in the arctic (8), and Vadim Zakirov, et. al., testing N₂O 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, N₂O/graphite hybrid, N₂O monopropellant, N₂O/hydrocarbon mixed monopropellants, and N₂O/liquid hydrocarbon explosives. Later, I will refer to Haussmann’s observations about traits of N₂O propulsion systems in various environments and N₂O propellant hazard testing results.

Vadim Zakirov has been using metal oxides as decomposition catalysts for N₂O. Cobalt III oxide, CoO₃ was most active enabling N₂O decomposition at the lowest temperature. Copper oxide, Cu₂O was the next best catalyst, and ferric oxide, Fe₂O₃ was the least active decomposition catalyst. This information should provide warning that copper and iron piping should be avoided in N₂O plumbing since formation of metal oxides would reduce the initiating temperature for start of N₂O decomposition into nitrogen and oxygen gases.

Explosive incidents with N₂O:

The large explosion in July 2007 in Mojave, CA was a surprise to us that had considered N₂O a safe material (1-2). Our perception of N₂O safeness was partly due to its widespread use without publicized problems by medical practitioners. Medical use of N₂O 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 N₂O is with fire hazard rather than explosive risk. Medical risk with N₂O use most often occurs when oxygen-N₂O overflow from a patient mixes with fuel vapors near a combustion source (7). Use of N₂O in rocket applications has considerably greater risk than for medical applications,
in that, large N\textsubscript{2}O volumes, massive flow rates, and greater pressures up to 50 atmospheres or more are likely. Seeing a need for assessing N\textsubscript{2}O explosive hazards when considered as a monopropellant and oxidizer for rocket engine applications, we conducted a literature search to gain understanding about all N\textsubscript{2}O characteristics. Interestingly, explosive accidents with N\textsubscript{2}O were more common than we originally thought. Some articles were found about N\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O accidents are a) Scaled Composites explosion at Mojave Site, California (1, 2, 3), b) N\textsubscript{2}O 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\textsubscript{2}O occurred involving a semitruck trailer tank rupture at Mojave, CA during liquid flow tests. Operators at the Mojave site considered the N\textsubscript{2}O 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\textsubscript{2}O. N\textsubscript{2}O in a large storage tank attached to a liquid delivery line upstream of the centrifugal pump was not exploded although many tons of N\textsubscript{2}O 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\textsubscript{2}O, 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\textdegree\ C in the storage tank. Without adequate description of materials, configuration, internal size of connecting pipes, and purity of N\textsubscript{2}O only speculations can be made at this point about what really caused the explosive event.

An encouraging feature for indicating that large N\textsubscript{2}O systems can be made safe was lack of N\textsubscript{2}O monopropellant runaway decomposition flashing back through connecting pipes to the delivery tank. The N\textsubscript{2}O supply tank at Einhoven remained intact after the explosion although its position had been shifted by about 3 meters (~10 feet). Since N\textsubscript{2}O in the supply tank was stored at temperature well above N\textsubscript{2}O boiling point, -
15° C versus -88.5 C, all N₂O contents in the supply tank escaped once an open line to atmospheric pressure became available. What would prevent flashback of runaway N₂O 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 N₂O system eruptive events that produced at least one ruptured N₂O feed tank (6). His question was, “Is N₂O safe?” He mentioned decomposition flashbacks from combustion chambers in a N₂O hybrid motor and in a N₂O/alcohol bipropellant engine. Combustion instability and low pressure drop between N₂O injectors and combustion chambers were cited as causes for the flashbacks. Mr Berger mentioned that copper oxide contamination could lower initiation of N₂O monopropellant reaction from temperatures of above 500° C to as low as 250° C. Any material reducing N₂O initiation temperature should be avoided. He had concerns about water hammering and adiabatic compression as processes that might start N₂O 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 N₂O 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 N₂O monopropellant process may not have occurred. Mitigating against N₂O 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 N₂O gas in the bottom of a vessel being filled, gas turbulence zone heating, or a combination of both. By Rhodes’ admission no indication of N₂O decomposition occurred. During Rhodes’ anomalies lack of broken experimental equipment, absence of huge equipment displacing thrusts, or evidence of N₂O monopropellant decomposition testifies to absence of endangering physical hazards to personnel.

Small scale explosions have been observed during super critical N₂O extraction processes (33, 34). Super critical extraction explosions were related to organic materials mixed into the primary N₂O gas phase. In 1991, Sievers, et. al., reported that a mixture of N₂O, 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 N₂O 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 N₂O would raise kinetic speed of reaction and output energies considerably above that could be produced by N₂O 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 N₂O containing combustible organic material are evidence that N₂O/combustible material mixtures are very hazardous with respect to pure N₂O. Since N₂O does not have significant monopropellant decomposition until temperatures above 500° C are obtained, reduction of initial reaction temperature with N₂O/organic material mixtures to the 40° to 80° C range are particularly daunting.

Since explosive events seem relatively common with use of N₂O, methods are needed to eliminate explosive risk. Lack of understanding is evident when some available reports about N₂O eruptive incidents are read. As a start considering that N₂O 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 N₂O systems? N₂O 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 N₂O hazard studies:**

Hazard studies about N₂O have been reported more than thirty years ago (20-24). Additional N₂O 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 N₂O (20, 21). A principle problem with early N₂O hazard studies was that internal volumes of
experimental vessels was so small that wall energy absorption effects inhibited the N₂O 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 N₂O 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 N₂O.

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 N₂O gas phase ignition. Rhodes obtained more violent results than Edse, probably, due to his larger diameter containers. High speed monopropellant reactions of N₂O 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 N₂O 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 N₂O. Cracked pipes resulted in most of the liquid N₂O 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 N₂O. This invalidates the conclusion of lack of violent reaction from N₂O number 6 cap testing since nitrogen is very soluble in N₂O producing a diluted liquid N₂O/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 N₂O since he demonstrated monopropellant reaction quenching when helium was used to dilute gas phase N₂O. Nitrous oxide was found to be compatible with Buna-N, neoprene, delron, Teflon, nylon, Vespel, & AF-124X rubber. That is, no chemical reactions were observed between liquid N₂O and tested materials. No attempt was made to check polymeric material swelling by exposure to liquid N₂O. No hazard tests were conducted with N₂O plasticized polymeric materials indicated above. Gas phase explosion hazards with N₂O 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 N₂O 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 N₂O despite its internally contained heat energy has considerable resistance toward explosive initiation.

Haussmann’s (8) article had interesting observations about behavior of N₂O, particularly, interactions when mixed with combustible materials. That is:
- Glycerin is used as a lubricant in pumping N₂O and it has frequently been found in N₂O storage cylinders.
- Liquid N₂O will burn the skin because its lipid 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 N₂O-fuel mixtures could be exploded by electric fuses.
- Liquid phases of N₂O-fuel mixtures exploded only by heavy detonator charges.
- Graphite tubes acted more or less as decomposition surfaces for the N₂O, and as flameholders rather than reactive fuel.
- Mixtures of N₂O and hydrocarbon are monopropellants that are easily transportable explosives, such as, N₂O and kerosene.
- Liquid N₂O 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 N₂O will be unable to provide adequate energy stress over a large enough volume to provoke a runaway decomposition process for pure N₂O. That is, water hammering and bubble collapse. Liquid N₂O 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 N₂O 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 N₂O would be cushioned by the extraordinary compressibility of liquid N₂O (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 N₂O 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 N₂O did not provide any reaction (23), the volume of highly energized N₂O that was thousands of times larger than could be achieved by a bubble collapse was unable to start a propagating, uncontrolled, N₂O decomposition reaction. Organic fuel contamination of, perhaps, both gaseous and liquid N₂O may be adequately sensitized versus pure N₂O to make water hammering and bubble collapse work as initiating methods for getting a combined, propagating, uncontrolled N₂O monopropellant and N₂O/fuel reaction.

In a review of N₂O investigations Cawthra (36) referred to NASA, White Sands mechanical impact testing in liquid N₂O 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.

**N₂O could be given respect equal to gaseous oxygen:**

Both N₂O 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 N₂O might be a way to readily improve N₂O operational safety. Avoidance of heated gas volumes with N₂O 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 N₂O fires. Table 1 below compares industrial practices assembled by the Compressed Gas Association for gaseous oxygen and N₂O (13, 15, and 17).

<table>
<thead>
<tr>
<th>Table 1: Comparison of Industrial Practices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous Oxygen (16)</td>
</tr>
<tr>
<td>No oils or particulates</td>
</tr>
<tr>
<td>Minimum radii for bends should be 1.5 x pipe I.D.</td>
</tr>
<tr>
<td>Suggested velocity in 2” SS of 25 fps - 100 fps – in monel, nickel, brass</td>
</tr>
<tr>
<td>Vortices, flow friction, oscillation concerns– Prompted by seat fires in valves (17)</td>
</tr>
<tr>
<td>ESD is an unconsidered problem</td>
</tr>
</tbody>
</table>
Since perception of safety is attributed to $\text{N}_2\text{O}$ handling, strict adherence to tank and piping cleanliness up to gaseous oxygen standards may not always be as good as it should be with $\text{N}_2\text{O}$ systems. Solid abrasive particle impact and gas turbulence heating effects are concerns for gaseous oxygen but not advised as a concern for $\text{N}_2\text{O}$. 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 $\text{N}_2\text{O}$ has not been provided. Since oxidizer pipe flow velocity restrictions cannot 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, but turbulence heating has not been raised as a concern with $\text{N}_2\text{O}$ (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 $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ 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 N₂O 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 N₂O. Runaway reaction might be expected both in liquid and gas phases. Since N₂O 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 N₂O 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 N₂O gas phase has been demonstrated by experiment (22). Adiabatic temperature for N₂O decomposition starting from 20°C is about 1650°C (8). When N₂O is converted into one mole of nitrogen plus 0.5 mole of oxygen, standard gas volume will increase by 50%. If N₂O 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 N₂O 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, N₂O 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 N₂O monopropellant decomposition was observed to quench as added cool N₂O 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 N₂O 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 N₂O 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 N₂O explosive hazard studies, presumably using pure N₂O. Fuel contamination appears to be a likely suspect. What is a better way to get lowered threshold stimulations to release a combination of N₂O internal contained energy and combustive energy where a dissolved fuel is burned? Haussmann’s article (7) said...
that while pure N$_2$O vapor at 20$^\circ$ C may not give monopropellant decomposition with 7 joule electric spark stimulation, but that gas phases of all N$_2$O-fuel mixtures could be exploded by electric fuses. Easy initiation of all N$_2$O/fuel mixtures demonstrated extra sensitivity for N$_2$O with mixed in fuels.

Fuel contamination of N$_2$O is a far more likely event than most would suspect. The primary reason for capability of getting soluble fuel contamination in N$_2$O is the fact that N$_2$O may be the best solvent known for organic materials and even many polar materials, such as, ammonia (8). Extraordinary solvent power for N$_2$O has been demonstrated in its use as a supercritical solvent (28-34). Supercritical N$_2$O 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$_2$O. 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$^\circ$ C temperature gas phase N$_2$O has a high enough density to have some supercritical type of solvent capability. That is, N$_2$O gas can be expected not only to dissolve materials based on their 20$^\circ$ C vapor pressure but, also, through solvent power to pick up high boiling materials that have negligible vapor pressure at 20$^\circ$ C. Materials, such as, low molecular weight components of cured epoxy glue might transfer with N$_2$O vapor even if distilled at 20$^\circ$ C into a cooled B. Berger (6) in his presentation said that N$_2$O 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$_2$O as a solvent to form mixtures with combustible materials. One example was that glycerin was used as a lubricant in pumping N$_2$O and that it was frequently found in N$_2$O storage cylinders. Whether N$_2$O 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$_2$O is that simple vapor transfer of N$_2$O from a tank at 20$^\circ$ C into a cooled container may not reduce glycerin concentration to low value. This would occur due to solvent power of dense N$_2$O vapor to carry over some glycerin despite a large difference between boiling points of N$_2$O and glycerin. This behavior would be a consequence of dense N$_2$O 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$_2$O and hydrocarbons were described as being monopropellants that were easily (safely) transportable explosives, such as, N$_2$O and kerosene. Another indication of liquid N$_2$O solvent capability was the statement that: “liquid N$_2$O 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\textsubscript{2}O 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\textsubscript{2}O. 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\textsubscript{2}O (22, 24). Tested materials above were compatible in that no chemical reactions were observed with liquid N\textsubscript{2}O. Typically, tested materials were recovered essentially unchanged. AF E-124X rubber was incompatible in that physical properties changed during exposure to liquid N\textsubscript{2}O. 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\textsubscript{2}O. Recovered polymeric compatibility trial samples may have been examined after plasticizing N\textsubscript{2}O within them had escaped as vapor. One of B. Berger’s (6) warnings was to test polymeric seals intended to be used in N\textsubscript{2}O systems for swelling in liquid N\textsubscript{2}O. Prudence in employing polymeric seals in liquid N\textsubscript{2}O 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\textsubscript{2}O system service (13).

Evidence obtained in N\textsubscript{2}O hazard discussions and studies showed that N\textsubscript{2}O mixtures containing dissolved fuels were recognized as being more readily ignited or exploded than when pure N\textsubscript{2}O was tested under the same conditions. Explosive incidents with N\textsubscript{2}O where strong energetic stimuli seemed absent need explanation. Since fuel contamination of N\textsubscript{2}O is easily obtained, at least some mysterious explosive incidents were likely to involve fuel contamination. However, explosions in small volume equipment using supercritical N\textsubscript{2}O at mild temperatures, 40° to 80° C, showed that organic contamination in N\textsubscript{2}O 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\textsubscript{2}O combustion and explosions is ESD.

**N\textsubscript{2}O hazard test effort to gain understanding of safety issues:**

As stated above, technical explanation of causes for serious N\textsubscript{2}O 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\textsubscript{2}O as a propellant material can be conducted with confidence about adequate control and elimination of safety issues. Understanding of N\textsubscript{2}O 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\textsubscript{2}O gas phase monopropellant decomposition. Some sub-scale N\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O-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\textsubscript{2}O containing organic fuel contamination as in a) above with fuel concentrations ranging from approximately 0.5 to 5%. Compare contaminated N\textsubscript{2}O threshold test results with that for pure N\textsubscript{2}O.

d) Test vapor and liquid N\textsubscript{2}O containing fuels for threshold, propagating reactions by electrostatic discharge. Compare electrostatic discharge initiating jolts with results using pure N\textsubscript{2}O.

e) Check ESD threshold sensitivities 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O explosive thresholds in suitable size, development of reaction quenching structures, and examination of hazards associated with N\textsubscript{2}O – 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$_2$O monopropellant decompositions from a hot source through pipes back to N$_2$O storage tanks is a primary risk of using large volume N$_2$O systems. In the Einhoven explosion propagation of N$_2$O monopropellant decomposition reaction from rotary pump to semitruck trailer occurred. Hope for eventual safe use of N$_2$O 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$_2$O. He thought polymeric components considered for use in a N$_2$O system should have their swelling in liquid N$_2$O determined. Further concern was water hammering and adiabatic compression of small gas bubbles (6). According to Rhodes (22) flame speed of N$_2$O 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$_2$O at conditions close to its critical temperature was amazingly compressive (8). Pure N$_2$O’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$_2$O 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$_2$O. 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$_2$O showed it to be explosively inert (22) except under great provocation. Saturated gaseous N$_2$O 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$_2$O monopropellant reaction at 6.9 MPa per second at beginning of compression process but reaction quenched with continued admission of cool N$_2$O gas. Adiabatic compression of gaseous N$_2$O at 20° C and compression rate of 4.1 MPa per second did not initiate decomposition reaction. Rhodes’ dynamite cap tests with liquid N$_2$O in 51 mm diameter tubes were invalid due to heavy dilution of N$_2$O 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$_2$O and liquid N$_2$O – fuel mixtures did not exhibit
sensitivity (24). In an overall assessment, explosive safety of liquid N$_2$O was excellent, and 20° C N$_2$O saturated vapor could be initiated into propagating reaction only with considerable difficulty. Rhodes conclusion was that use of pure N$_2$O is explosively safe except at high temperatures. Fundamental criticism of available N$_2$O 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$_2$O.

In contrast to safety in using pure N$_2$O are organic materials - N$_2$O mixtures that are quite sensitive to initiations of fire and explosions. Rhodes could not initiate saturated N$_2$O vapor at 20° C with heavy electric spark, but all tested N$_2$O-fuel mixtures could be readily ignited in 51 mm diameters (22). An even more enlightening example about explosive sensitivity of N$_2$O – fuel mixtures are spontaneous explosions produced in small volume, super critical, N$_2$O extractions at temperatures in the 40° to 80° C range (33, 34).

An experimental hazard program for N$_2$O and N$_2$O – fuel mixture has been proposed. Goals of the proposed N$_2$O hazard study are to conduct threshold, pure N$_2$O hazard tests in suitably large sizes, develop flame trap structures to prevent N$_2$O monopropellant decompositions from propagating from a hot source like a liquid engine back through pipes to a N$_2$O storage tank, investigate threshold explosive initiation of N$_2$O - fuel mixtures, and to elucidate whether ESD with N$_2$O – fuel mixtures provides an extraordinary, low energy method for fire/explosion starts for N$_2$O – fuel mixtures.

References:

18. One author, C. Merrill, has conducted extensive study of electrostatic discharge ignitions of solid propellants. Unpublished investigations, C. Merrill.
26. “A Comparison between the Homogeneous Thermal Decomposition of Nitrous Oxide and Its Heterogeneous Catalytic Decomposition on the Surface of Platinum”, Cyril
38. Nitrogen dioxide was observed to pass through Teflon® membrane while acting as project monitor for effort developing a positive expulsion bladder for use with dinitrogen tetroxide, Claude Merrill.
Nitrous Oxide Explosive Hazards

Claude Merrill

Air Force Research Laboratory, Edwards AFB, CA
Nitrous Oxide Explosive Hazards
Topics of Discussion

Nitrous oxide (N$_2$O) is energetic oxidizer

Accidents with N$_2$O systems

Prior N$_2$O hazard studies

N$_2$O should be respected as well as gaseous oxygen

Special N$_2$O hazard traits

N$_2$O hazard test effort to gain understanding of issues
Nitrous Oxide Explosive Hazards
As Oxidizer, N₂O is Attractive

“Green” oxidizer

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

Recently considered as rocket propellant

- Hybrid rocket motor oxidizer by Burt Rutan
- Considered for small monopropellant thrusters

Nitrous Oxide Explosive Hazards
N₂O 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 N₂O to medical facilities. (6)

- Tank explosion, N₂O, Pratt & Whitney, W. Palm Beach, 1973. (6)

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


Nitrous Oxide Explosive Hazards

Eindhoven, Netherlands N\textsubscript{2}O explosion – Semitrailer exploded down stream of centrifugal pump but N\textsubscript{2}O 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\textsubscript{2}O systems could be safe.

Nitrous Oxide Explosive Hazards
N$_2$O Explosive Incidents

Small scale explosions in supercritical N$_2$O:

- Mixture N$_2$O, 9% EtOH, 0.9% (EtO)$_4$Si, 0.07% (EtO)$_3$B, & 0.07% (EtO)$_3$P at 143 atmospheres pressure & 40$^\circ$C exploded shattering SS fittings, 1991 (8)

- Supercritical N$_2$O at 680 atmospheres pressure & 80$^\circ$C exploded when extracting one gram of ground coffee, 1993 (9)

Spontaneous explosions!!


Nitrous Oxide Explosive Hazards
Prior N₂O Explosive Hazard Studies

Studies of N₂O 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)

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

- Volumes were too small to get runaway N$_2$O monopropellant decomposition and complete reaction starting at room temp.

- Did not look at N$_2$O 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$_2$O or N$_2$O swelling of resins and plastics

- Didn’t check fire sensitivity of N$_2$O containing low levels of organic materials

- Didn’t check ESD sensitivity of resins and plastics that had absorbed substantial N$_2$O
Nitrous Oxide Explosive Hazards
Is N₂O 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 N₂O 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 N₂O 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 N₂O 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)

## Nitrous Oxide Explosive Hazards
### Comparison of Industrial Practices

<table>
<thead>
<tr>
<th>Gaseous Oxygen</th>
<th>N₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>No oils or particulates</td>
<td>Yes</td>
</tr>
<tr>
<td>Minimum radii for bends (1.5 x I.D.)</td>
<td>Not specified</td>
</tr>
<tr>
<td>Suggested transfer velocity (25 fps in 2” - SS, 100 fps – in monel, nickel, brass)</td>
<td>Not specified</td>
</tr>
<tr>
<td>Vortices, flow friction, oscillations</td>
<td>Not specified</td>
</tr>
<tr>
<td>ESD may be unconsidered problem</td>
<td>Not considered</td>
</tr>
</tbody>
</table>


# Nitrous Oxide Explosive Hazards

## Explosive Hazard Contrasts

<table>
<thead>
<tr>
<th>Pure $\text{N}_2\text{O}$</th>
<th>Tests</th>
<th>Contaminated $\text{N}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No rx., condensed</td>
<td>Heavy Donor</td>
<td>Can be strong expl.</td>
</tr>
<tr>
<td>No rx., liquid</td>
<td>Dynamite cap</td>
<td>Transportable expl.</td>
</tr>
<tr>
<td>Slow rx., gas</td>
<td>Dynamite cap</td>
<td>Fast rx.</td>
</tr>
<tr>
<td>No rx., gas &amp; liquid</td>
<td>Electric Spark</td>
<td>All mixtures ignite</td>
</tr>
<tr>
<td>No problem</td>
<td>Mechanical impact</td>
<td>No documented prob.</td>
</tr>
<tr>
<td>No problem</td>
<td>Friction</td>
<td>No documented prob.</td>
</tr>
<tr>
<td>Above 500(^\circ) C</td>
<td>Spontan. Decomp.</td>
<td>As low as 40(^\circ) C</td>
</tr>
<tr>
<td>Rx. rate 30x less than propane-air</td>
<td>Adiabatic Compress.</td>
<td>Sens.? - lack data</td>
</tr>
</tbody>
</table>
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

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$_2$O is about 50 atm.

(18) Claude Merrill, unpublished incident investigation
Nitrous Oxide Explosive Hazards
Hazards Peculiar to N₂O

N₂O can undergo exothermic decomposition into O₂ and N₂ (13)
- Positive heat of formation, 19.6 kcal/mole (13)
- Adiabatic compression ignition (13)
- Runaway reaction hazard is greater for larger volumes

N₂O excellent solvent trait can create ignition & explosive haz.
- Better solvent than supercritical CO₂ (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 N₂O is a key hazard issue

Nitrous Oxide Explosive Hazards
What Data Would be Suitable for N\textsubscript{2}O Hazards Effort?

In 25 cm diam. find threshold, N\textsubscript{2}O adiabatic compression initiations, measure rx. velocities from EBWs, dynamite caps, and multijoule electric sparks. Repeat for N\textsubscript{2}O – fuel mixtures and compare,

Demonstrate that N\textsubscript{2}O decomposition propagation can be stopped by multiple small size orifices between 20 liter tanks; gas and liquid.

Investigate N\textsubscript{2}O 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 125\textdegree{} C
- Threshold ESD sensitivity of above

Measure electrostatic charging from N\textsubscript{2}O liquid and gas flow over typical plastics, rubbers, and graphite
Nitrous Oxide Explosive Hazards

Conclusions

$\text{N}_2\text{O}$ explosive incidents are mysterious

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

Need to stop $\text{N}_2\text{O}$ decomposition propagation through pipes

Organic contamination in $\text{N}_2\text{O}$ is a prime suspect

$\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$/organic fuel solutions
- Develop reaction propagation blockage system for pipes
- Conduct threshold ESD tests for $\text{N}_2\text{O}$/organic mixes