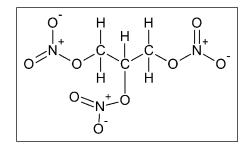
67. Nitroglycerin

CHEMICAL NAME = propane-1,2,3-triyl trinitrate CAS NUMBER = 55-63-0MOLECULAR FORMULA = $C_3H_5N_3O_9$ MOLAR MASS = 227.1 g/mol COMPOSITION = C(15.9%) H(2.2%) N(18.5%) O(63.4%) MELTING POINT = 13.2°C BOILING POINT = 13.2°C BOILING POINT = decomposes between 50° and 60°X DENSITY = 1.6 g/cm³



Nitroglycerin is an oily, poisonous, clear to pale yellow, explosive liquid. It was first prepared in 1846 by the Italian chemist Ascanio Sobrero (1812-1888), who nitrated glycerol using a mixture of nitric acid and sulfuric acid. Sobrero, who was injured in an explosion doing his research, realized the compound's danger and abandoned work on nitroglycerin. Twenty years after Sobrero's discovery, Alfred Nobel (1833-1896) developed its use commercially. Nobel was born in Stockholm Sweden, where his father, Immanuel Nobel (1801-1872), ran a heavy construction company. When Alfred was four, his father's company went bankrupt and Immanuel left for St. Petersburg, Russia to pursue new ventures. Immanuel rebuilt a successful business in Russia, in part because of his ability to develop and sell mines to the Russian Navy for use in the Crimean War. Alfred and the rest of his family joined his father in Russia when Alfred was nine, where he received an excellent education with private tutors. He studied in the United States and Paris, where he met Sobrero. Nobel studied chemistry, literature, and mechanical engineering as his father groomed Alfred to join him in the construction and defense industry. After another downturn in his fortune, Immanuel and his sons Alfred and Emil returned to Stockholm in 1859 to start another business. It was at this time that Alfred began to experiment with nitroglycerin, seeking a safe method for its use as an explosive. Nobel mixed nitroglycerin with other substances, searching for a safe way to transport it and make it less sensitive to heat and pressure. Several explosions at Nobel's laboratory, one of which killed Emil in 1864, prompted the city of Stockholm to ban nitroglycerin research inside the city and forced Nobel to move his studies to a barge in a lake just outside the city limits.

In 1864, Nobel had developed an explosive that was almost eight times as powerful as gunpowder on a weight basis and began mass producing nitroglycerin. Early shipments and use of nitroglycerin were made with nitroglycerin in its unstable liquid state. It was shipped in zinc cans, which were often packed in crates using sawdust as packing material. Nitroglycerin could detonate when disturbed, and the probability of an explosion increased with temperature and the presence of air bubbles in the liquid nitroglycerin. Furthermore, impurities in the form of residual acids used in nitroglycerin's production could corrode the zinc shipping containers and also produce gases that could trigger an explosion. Numerous deaths were attributed to nitroglycerin when it was first marketed, and Nobel continued to experiment with methods to make nitroglycerin safer. One of these was mixing nitroglycerin with materials to make a solid form of nitroglycerin. Nobel discovered that when nitroglycerin was mixed with a silica-based diatomaceous earth material called kieselguhr, a relatively stable product resulted. The mixture produced a paste that Nobel could pack into cardboard tubes; these could then be inserted into holes drilled into rock structures and detonated. In 1867, Nobel patented his mixture and called it dynamite, a name derived from the Greek word *dunamis*, meaning power. Nobel also perfected a blasting cap made from mercury fulminate $(Hg(ONC)_{2})$ and potassium chlorate (KClO₃) to detonate the nitroglycerin. Nobel's business expanded rapidly, as dynamite was increasingly used for construction and defense purposes. Although Nobel's fame and fortune were based on his invention of dynamite, he was an able inventor and chemist. Over the years he received 355 patents, including ones for synthetic rubber and artificial silk. His will requested that the bulk of his fortune, which approached \$10 million, be used to fund annual prizes in the areas of chemistry, physiology or medicine, physics, literature, and peace.

Nitroglycerin is made by nitrating glycerol. Early industrial processes used a batch process in which glycerol was added to a mixture with approximately equal volumes of nitric acid and sulfuric acid. The sulfuric acid serves to ionize the nitric acid and removes water formed in the nitration process. Removing the water formed in nitration increases the yield of nitroglycerin. Acids and water must be removed from the desired nitroglycerin through a washing process. The production of nitroglycerin is highly exothermic, and it is important to keep the temperature below room temperature to prevent an explosion. Early production methods used cooling coils in the nitration vessels to regulate the temperature. During the latter half of the 20th century, safer continuous production methods replaced batch processes. In these methods much smaller reactors are required, as glycerol is reacted with the acids.

The explosive power of nitroglycerin is related to several factors. Each molecule of nitroglycerin contains three nitrate groups, which serve as oxidizing agents for the hydro-carbon groups to which they are bonded. The hydrocarbon groups provide the fuel and the nitrate groups provide the oxidizer necessary for combustion. In typical combustion reactions involving hydrocarbons, oxygen does not come from the molecule but from air or another source external to the molecule. Glycerin contains both the fuel and oxidizer bonded together. The detonation of nitroglycerin can be represented by the reaction: $4C_3H_5(ONO_2)_{3(l)} \rightarrow 12CO_{2(g)} + 10H_2O_{(g)} + 6N_{2(g)} + O_{2(g)}$. Four moles of liquid nitroglycerin produces 29 moles of gaseous products in this reaction. Also, the production of stable products results in a highly exothermic reaction. The hot gaseous products produce a rapid expansion in volume,

producing a shock wave that propagates throughout the material, causing an almost instantaneous reaction. This is contrasted with combustion where the flame moves through the material as the fuel and oxygen react.

Nitroglycerin has medicinal use as a vasodilator. Workers in the original nitroglycerin plants developed headaches, which led to the discovery that nitroglycerin is a vasodilator. The main medical use of nitroglycerin is to treat angina pectoris. Angina pectoris is a condition in which the heart does not receive sufficient blood (oxygen) supply, producing a tight sensation in the chest. This lack of oxygen supply may be due to arthrosclerosis, thickening of the arteries. Nitroglycerin was first used to treat this condition in the late 19th century. It is prescribed today in various forms (tablet, ointment, patches, and injection) for patients who suffer from angina pectoris. Nitroglycerin is marketed under various trade names: Nitro-Dur, Nitrostat, Nitrospan, Nitro-Bid, and Tridil. When used in medications, the name glyceryl trinitrate is often used instead of nitroglycerin.