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Hazards in the Manufacture of RDX and HMX

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Abstract. Manufacture of cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) by the modified Bachmann process involves the nitrolysis of hexamine in glacial acetic acid with a solution of ammonium nitrate in nitric acid, in the presence of excess of acetic anhydride. Fire, explosion and toxic hazards during the manfacture of these explosives are reviewed and discussed.

1. Introduction

Currently RDX and HMX are the two high explosives extensively used for various military applications, particularly high explosive compositions for warheads to produce mass destructive effect and as an additive to produce high energy in the most advanced solid propellants for guns and rockets. One of the common methods for the manufacture of RDX is the Bachmann process[1]. A modified Bachmann Process is also the main method of production of HMX[2]. Both these processes involve the use of same starting materials but the process conditions in the two cases are different. RDX is formed at a temperature of 75°C whereas at 45°C HMX formation takes place. The chemicals viz : (i) a solution of hexamine in glacial acetic acid (ii) a solution of ammonium nitrate in nitric acid and (iii) acetic anhydride are mixed in the nitrators, equivalently and simultaneously to produce these explosives. It has been reported recently[3] that in the modified Bachmann processes for manufacturing of RDX and HMX, certain combinations of Bachmann chemicals, when mixed in an unconfined, insulated vessel, initially at ambient temperatures were found to generate fires spontaneously and other combinations generate spontaneous explosions when mixed in a closed vessel. Very limited studies seem to have been conducted on the hazards involved in the manufacture of RDX and HMX and a detailed review on the subject in open literature is not available. In the present paper an attempt has been made to review the hazards of Bachmann chemicals and the specific reactivity hazards due to inadvertent mixing of these chemicals. The toxic effects of RDX and HMX are also discussed.

2. Fire and Explosion Hazards

The various chemicals used in the production of RDX and HMX involve mainly three types of hazards viz (i) fire (ii) explosion and (iii) toxic effects. It will be in the fitness of things, therefore, to mention first of all the hazards involved in the chemicals used for the manufacture of these explosives

(*i*) *Hazards of Chemicals*

Ammonium nitrate has turbulent history of unpredictable fire and explosion hazards. It gets sensitized to thermal and mechanical shock by heat and nitric acid. Contaminants like carbonaceous materials, nitrated organic bodies and nonexplosive impurities like sulphur, coal, paraffin, flour and cereals tend to sensitize ammonium nitrate[4]. Explosion hazard is considerably increased with traces of oxidizable metallic powders like zinc, cadmium, brass, nickel and magnesium by lowering the decomposition temperature. The main physiological hazard is reported to be lowering of blood pressure on continued exposure[5].

Nitric acid is a well known oxidizing agent increasing the likelihood of ignition and the intensity of the subsequent fire when in contact with combustible materials. It combines explosively with metallic powders, carbides, acetic anhydride, alcohols and other oxidizable organic chemicals. Vapours of the acid cause deep tissue burns to the skin and permanent damage to the eyes[4].

Acetic acid is dangerous when in contact with oxidizers. Vapours of the acid are harmful to the eyes and lungs. Acetic anhydride is a known water-reactive corrosive flammable liquid.

Hexamine is also combustible when exposed to heat or flame and can react with oxidizing materials. It is a mild skin irritant and the side effects are urinary tract irritation, skin rash and digestive disturbances[6].

Acetone, used for the recrystallisation of the crude explosives, is a well known inflammable solvent. Its vapour in contact with flame may cause explosion. It causes skin irritations and headache due to prolonged inhalation.

(*ii*) *Hazards Involved in Mixing of Chemicals during Manufacture of RDX and HMX*

As in the case of starting materials, uncontrolled mixing of chemicals can also result in fire and explosion hazards. Leach and co-workers were the first to work out the specific reactivity hazards on the Bachmann system of chemicals[3]. They developed an ASTM Chemical Thermodynamic and Energy Release Evaluation (CHETAH) computer programme to evaluate the hazards of inadvertent mixing of chemicals at Holston Army Ammunition Plant, USA, in modified Bachmann processes for the manufacture of RDX and HMX. Preliminary reactivity tests and remotely controlled mixing experiments in confined and unconfined conditions were conducted. The predictions of CHETAH have been verified experimentally by these authors.

When mixed in an unconfined, insulated vessel, certain combinations of Bachmann chemicals initially at ambient temperatures were found to generate fires spontaneously. The fires at 29°C or higher ambient temperatures are considered to be the result of (i) formation of hexamine dinitrate which can bring the mixture near boiling (ii) the ensuing oxidation and or decomposition of hexamine dinitrate or its fragments by excess nitric acid and (iii) finally by exothermic decomposition of ammonium nitrate. Such vigorous reactions were not observed when small quantities of hexamine/acetic acid solution and nitric acid/ammonium nitrate solution were mixed in the laboratory at 21°C. They observed that certain proportions of Bachmann chemicals in confined space at temperatures ranging from 90°C to 150°C caused explosions probably due to the accumulation and subsequent explosive decomposition of acetyl nitrate. This was conclusively proved by studying layered systems of nitric acid/ammonium nitrate — acetic anhydride.

(*iii*) *Hazards due to Crude Products*

The crude RDX and HMX contain unstable polymorphic forms of HMX which are very sensitive and may cause explosion. Johnson et. al.[7] reported that the sensitivity of crude RDX can be controlled to a satisfactory value by the conversion of unstable polymorphic forms of HMX contained therein to its stable β form by holding the crystals under equilibrium conditions in contact with the mother liquor for at least 0.5 hr at <150°C. It is reported[8] that the crude HMX product exists in the unstable α form which is more sensitive to impact and friction[9] and this gets converted into stable β form by slow crystallization from acetone.

In addition to the factors discussed above, reaction mixture obtained in the preparation of RDX and HMX contains many undesirable by-products which may cause explosion. Aristoff et. al[10] mentioned eleven possible by-products during the nitrolysis of hexamethylenetetramine, all of which may not necessarily be present in the final product. According to Bachmann[11] these by-products can be converted to water soluble and volatile products by digesting the mixture at 90-100°C for 1-24 hr in the presence of water.

3. Toxicity of RDX and HMX

A number of research workers have worked out the toxicity and potential dangers of RDX and HMX during manufacture. Carpenter et. al.[12] attempted to define the specific air pollutants generated during the production of RDX and HMX together with their attendant raw material manufacture and recovery processes based on the chemical and toxicological characteristics of known emitted compounds. Von Oettingen reported that when RDX was fed to rats and dogs, no lesions were found in the brain although some action apparently was exerted on the central nervous system[13]. Sklyanskaya[14] found that RDX acts chiefly on the central nervous system interfering with blood formation and causing changes in vascular walls, accompanied by secondary degeneration of nerve cells. These authors attribute the toxicity of RDX to its nitrated amine groups, since the $C\text{-}NO_2$ linkage does not have a spasmodic action. According to Timofievskaya, et. al.[15] RDX did not show any effect on animals when applied to the skin in 33% ointments. Taylor[16] has predicted the toxicity of RDX for dogs and outlined the probable symptoms of acute and chronic toxicosis. The study conducted by Hathaway[17] demonstrated limited autoimmune disease and failed to identify any abnormalities of the hematol, hepatic systems in employees with 8 hr time weighted exposures to RDX $\leqslant 1.57 mg/m^3$. Urbanski[18] mentioned that breathing RDX dust gives rise to tonic-clonic spasms. The acute toxicity of HMX has been studied by Bentley and co-workers[19] using aquatic organisms and they found no adverse effects of exposure upto 0.32 mg/L among any of them.

4. Conclusion

From the account of the reported work as discussed it is apparent that although a number of attempts have been made to find out the various causes of hazards involved during mixing, manufacture, handling etc., the field is still open for systematic study, particularly with reference to the isolation, identification of intermediates and by-products, their thermal stability and the variations in the experimental conditions during scaling up of RDX and HMX from laboratory to production via pilot-plant.

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