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Review on thermal decomposition of 50% Hydroxylamine/water solution under different condition using adiabatic calorimeter.

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Abstract

This review paper examines thermal stability and decomposition hazards associated with 50% Hydroxylamine (HA)/water solutions, highlighting catastrophic explosions at Concept Sciences in USA and Nissin Chemical in Japan, resulting in multiple fatalities underscore the importance of understanding effects of contaminants on 50% Hydroxylamine/water solution stability. Studies using adiabatic calorimeter test assess the influence of various impurities including metals, metal ions, acids, and bases on thermal decomposition behaviour of hydroxylamine solutions indicating that presence of iron or carbon steel significantly lowers onset temperature and accelerates decomposition process. Also, environmental conditions, such as air versus vacuum, have minimal impact on the thermal decomposition parameters. The paper concludes that stringent safety measures must be implemented during handling and storage of hydroxylamine to mitigate the risks associated with its explosive potential, emphasizing the need for careful monitoring of impurities and process conditions to prevent catastrophic incidents.

Key Words: 50% hydroxylamine/water, Adiabatic calorimeter, APTAC.

1. Background

Pure hydroxylamine is a colourless to white solid which is hygroscopic and has needle like crystals. It may ignite spontaneously in air if large surface area is exposed and heating above 70°C, due to safety concerns only HA derivative salts were manufactured and sale till 1982.Growing demand of HA and its derivative in various industries like Nylon, Ink, paints, pharmaceutical, agrochemical and photographic development in late 1970 & 1980. Also, HA had important application in semiconductor manufacturing industry using HA solution in cleaning formulation to strip process residue from integrated circuit devices. To fulfil this market demand by utilizing opportunity Nissin chemical started manufacturing and sales of 50% HA/water solution in 1982 and increased its manufacturing capacity to 8000 tonnes per year by 1988.Nissin Chemical Company was the only provider of HA in the world. BASF Aktiengesellschaft opened a new HA manufacturing plant in Germany at the beginning of 1999. Concentrated HA solutions demand grown in the market. In 1999, Concept Sciences Inc. would have been the first business in the US to produce this product in large numbers for sale.[1]

Due to lack of information regarding thermal stability and decomposition hazard resulted in catastrophic hydroxylamine (HA) explosion occurred on February 19, 1999, at the Concept Sciences, Inc. (CSI), facility in Pennsylvania reported 14 injuries and the fatality of four CSI personnel and one employee of a nearby company. The building was totally destroyed and several other nearby companies had serious property damage. Additionally, blast also shattered windows of homes in a nearby residential area with property damage of ~$4 million. CSI began its first distillation to produce 50 wt-percent HA from charge tank contained approximately 9,000 pounds of 30 wt-percent HA required time 30 hours of distillation was required to complete the batch under normal conditions. Next day evening process was shut down for maintenance as reported water had leaked into the charge tank through broken tubes in the heater column. The necessary repairs were made by next 2 days, and the distillation process was restarted. concentration of liquid solution in the charge tank was 56 wt-percent. The distillation process was resumed when the required repairs were completed during the next two days, concentration in charging tank's liquid solution was recorded to be 56 wt-percent. Again, following day distillation process was shut down for maintenance to replace 1.5-inch feed line to the heater column with a 2-inch line, which delayed startup and the liquid solution's concentration in the charge tank at the time was around 57 weight percent HA. It steadily increased throughout the day and last recorded concentration of liquid solution in the charge tank was 86 wt-percent HA. AS CSI management knew crystal of HA formed with HA concentration greater than 80 wt-percent are unstable and potentially unstable. CSI personnel visually monitored the distillation system for the formation of crystals. At approximately 7:45 pm, distillation was shut down and cleaned with 30 percent HA to wash away crystals that may have formed and after approx. 30 min explosion occurred and second phase of distillation was never started. The explosive energy of HA is essentially equivalent to TNT on a weight basis. Approximate to 667 pounds of TNT of HA was present in the tank as per Hazards Research corporation [2]. Fourteen months following the CSI incident, on 10 June 2000 a catastrophic explosion at the Nissin plant in Japan took place during manufacturing of 50% Hydroxylamine/water solution resulting in fatality of 4 persons and 58 injuries residing near the factory. Nine buildings fell, two partially collapsed, and four structures were physically damaged by fire. Two buildings collapsed, five structures partially collapsed, and 286 buildings sustained damage outside the plant. Fifty-five automobiles and machinery sustained damage. Several hours were spent disconnecting a high-voltage wire. A feedstock of crude 50% solution of hydroxylamine contaminated with 40-50 ppb ferrous ion that was charged into the circulating line in the column where it was evaporated to obtain product less 1 ppb ferrous ion. Some amount of the hydroxylamine was evaporated by heating the hydroxylamine solution. Then, an 80% hydroxylamine solution fell to the bottom of the column, while 50% hydroxylamine vapor went to the top of column. As a ferrous ion contained in feedstock at about 50 ppb is reduced to 1 ppb or less in the product, part of the circulation liquid was drawn out from the bottom circulation line. Below bottom circulation piping an emergency blow down piping with block valve was installed near branching point and dead-end short piping path between branch to block valve. At the re-distillation column bottom, hydroxylamine was concentrated to 80-85% causes explosive decomposition by itself or by reacting with a ferrous ion as high HA concentration greater than 80% has dangerous tendency to decompose explosively at high temperature and also at ambient temperature if the ferrous ion concentration increases [3].

2. Introduction

The tragic incident at Concept Sciences Inc, USA and Nissin chemical, Japan explosion resulting from higher concentration of HA during process (>80%) and causing the death of nine people. Potassium hydroxide was used as raw material to react with hydroxylamine sulphate to produce hydroxylamine at concept sciences Inc and distillation of 50% HA solution at Nissin chemical to achieve ferrous ion concentration to 1 ppb. The effect of contamination is often considered as one the cause of industrial incident. This review paper focuses on the effect on different contaminant that can be present in form of impurities during process on thermal stability and decomposition hazard of 50% Hydroxylamine/water solution. Thermal decomposition parameter like onset temperature, maximum temperature and maximum pressure studied under adiabatic condition using adiabatic calorimeter APTAC (Automatic pressure tracking adiabatic calorimeter) is discussed. The catalytic effect of containments like metals, metal ions, acid, base and also thermal behaviour of 50% Hydroxylamine/water solution between two environments with air and without air (vacuum) is explained using result of adiabatic calorimeter APTAC which is important to identify potential reactive hazards under process conditions and provide guidelines for safety and control measures accordingly [4].

3. Presence of Carbon Nail.

Carbon steel generally composed of iron, 97-99 % & graphite, <2 % which is a common industrial contaminant that is found in nails, wire, or structural components. Cisneros et al. [5] reported the impact of carbon steel nail on decomposition of 50% Hydroxylamine/water solution (with stabilizer and without stabilizer) by performing APTAC experiment using glass test cell and Teflon coated thermocouple to ensure only catalytic material was carbon steel nail by maintaining metal surface contact area to sample volume ratio of 0.022 ± 0.002 mm^{-1}. Test resulted that the decomposition reaction of 50% Hydroxylamine/water solution with and without stabilizers is majorly impacted by carbon steel. The presence of the nail resulted in greatly lowered onset temperatures (Tonset), from 133-136°C to below 50°C, increased self-heat rates from no greater than 5°C/min to 13°C/min for sample without stabilizer and

31°C/min for sample with stabilizer. After the tests, sample and nail remains were inspected and both 50% Hydroxylamine/water solution sample were bluish colour. Nail had changed from grey to black for 50% Hydroxylamine/water solution with stabilizers and sample with stabilizers had no nail colour changed.

4. Presence of Air and vacuum

Thermal decomposition of Hydroxylamine mentioned Sax's dangerous properties of industrial materials handbook reports the decomposition of hydroxylamine into nitrogen oxide (NO_2), ammonia gas (NH_3), hydrogen gas (H_2) and NOx gases. Understanding the possible mechanism for hydroxylamine's byproduct release requires demonstrating whether oxygen from air contributes significantly to the reaction. This is essential for designing process safety measures during handling. Cisneros et al. [6] reported the impact of oxygen from air on the thermal breakdown of a 50% hydroxylamine/water solution by employing an adiabatic calorimeter APTAC to measure the overall kinetics, onset temperature, non-condensable pressure, time to maximum rate, and heat and pressure rate under vacuum conditions. The results were compared with those obtained for hydroxylamine decomposition in air. Typical Heat-Wait-Search method for the performed experimental replicas with air (7 run) and without air (6 run), showed that the thermal decomposition of 50% Hydroxylamine/water solution has no significant impact by the presence of air above the sample.

Test result showed no major difference for the experiments performed with and without air with Tonset = 117.5 & 118.5°C and Tmax = 273 & 274°C respectively. Pmax is high 6212 kPa in air and 6316 kPa in vacuum also vapour pressure of water at Tmax is approximately 6019 kPa which suggests Pmax is due to water and heat produced in the reaction was used to vaporize water having large heat of vaporization which classify the system to be hybrid system. Non condensable pressure end of experiment is relatively low 352 kPa in air and 393 kPa in vacuum and sample residue had no difference in physical appearance with air and evacuated environment. In most experiments, residues obtained where crystal clear liquid expect some residue turn blue when removed at end of experiment from calorimeter. 165 ppm of copper was measured in the liquid residue samples using atomic absorption. Tube heater assembly of the calorimeter was the source of copper. A thin layer of a white solid attached to the glass sample cell. which was not soluble in water, acid, or basic solutions and could not be removed. Cameka electron microprobe used to examine solid residue detected majorly of Si. It is a well-documented fact that silica (SiO_2), the main component of the glass sample cells, has increased solubility as pH increases explaining dissolution of part of glass cell at higher temperature during runaway reaction and the high pH of the solution and then re-crystallized to form the white solid residue [6].

5. Presence of Acid and Base

As mention earlier, catastrophic hydroxylamine explosion occurred on 19 February 1999, at the Concept Sciences, Inc., potassium hydroxide was being used to react with hydroxylamine sulfate in the hydroxylamine production processes. Furthermore, according to the National Oceanic and Atmospheric Administration's (NOAA) chemical reactivity worksheet [7], mixing KOH and hydroxylamine exhibits no reaction. The effect of acid and base contamination can be considered to be cause of incidents in the chemical industry, hence understanding the mechanism behind the runaway reaction is important. Wei et al. [8] used RSST and APTAC calorimeter study thermal runaway reaction of hydroxylamine in different concentration of KOH (base) and HCl (acid). The RSST study reported for 6 ml of 8N KOH solution with two concentration 43 mass % and 38.5mass % showed significant decrease in onset temperature from ~139°C to ~86°C in 43 mass% and ~46°C in 38.5 mass% indicating significant decrease in onset temperature and apparently activation energy of thermal decomposition of hydroxylamine/water mixture. The concentration of KOH has a greater effect on the onset temperature than the concentration of hydroxylamine in the mixture. In industry it is common to encounter containment of 0.1-2 mass% during process and storage condition. Wei et al. [2003] further explain impact of lower concentration of KOH (0.1N and 1N) in 3 gm of 50% hydroxylamine/water solution resulting in hydroxylamine concentration of 43 mass% in HA/KOH mixture. This mixture of 0.1N and 1N hydroxylamine/KOH was tested in APTAC adiabatic calorimeter in heat-wait-search with 2°C/min heating rate in glass test cell reporting onset temperature of ~123.4°C and heat release of ~113.8 KJ/mol for Hydroxylamine/water mixture without KOH. 0.15 mass% KOH mixture showed nearly similar decomposition behaviour as of hydroxylamine without KOH with heat release of ~114.2 KJ/mol and onset temperature of ~122.6°C. For mixture of 1.5 mass% KOH, the onset temperature decreases by approximately 11°C to ~112.7°C, and 18% more heat is released to ~134.3KJ/mol compared to those of hydroxylamine without KOH. Additionally, the maximum pressure is increased and also increased is the non-condensable gas pressure at 50°C. Due to corrosive nature of KOH, a white residue was observed in glass test cell because of SiO2 from glass cell particle was dissolved in the basic media at high temperature.

For understanding impact of Acidic impurity on thermal decomposition on 50% hydroxylamine/H2O solution, Wei et al. [8] performed Adiabatic calorimeter test using APTAC by adding 1N (0.5mass%) and 2N (1mass%) hydrochloric acid solution to 50% hydroxylamine/H2O solution making concentration of hydroxylamine in resulting 3 ml mixture to 43 mass%. Except onset temperature lower than 10°C in 1 mass% HCl remaining decomposition behaviour results were similar to 0.5 mass% mixture. The maximum self-heat rate and pressure rate also increase significantly. The liquid products of these tests were clear and there was smell of ammonia. Additionally, hydroxylamine without HCl has slightly lower non-condensable gas pressures than mixtures containing acidic impurities. Wei et al. [8] further performed APTAC test by adding 1M KCl solution to 50% hydroxylamine/H2O solution resulting thermal decomposition characteristics where very close to that of HCl. The decomposition of hydroxylamine was not catalysed by potassium ions, but chlorine took part in it and was oxidized by it, increasing the maximum pressure and self-heat rates. Based on overall comparison addition of 1N KOH solution decreases the onset temperature by 10°C due to presence of hydroxide ion and the addition of 1N HCl solution increases the maximum self-heat rate and pressure rate due to presence of hydrogen ion. Concluding that even small amount of hydrochloric acid and potassium hydroxide presence can accelerate the thermal decomposition of hydroxylamine at the elevated temperatures and mixing with hydroxylamine should be avoided during process and storage conditions.

6. Presence of Iron or Iron Ion.

It is important to known the catalytic effect of iron or iron ion on thermal decomposition behaviour of 50 mass % hydroxylamine/water solutions. since it is a common industrial contaminant, which can cause uncontrollable runaway reactions that may lead to incidents. References like Chemical risk analysis A practical handbook states that, hydroxylamine does not have a dangerous reaction with transition metals, metal halides (FeCl3, for example), or metal oxides which contradicting to Cisneros et al. [9] reported on thermal decomposition behaviour of 50 mass % hydroxylamine/water solutions (HA) when contacted with iron in the form of ferric oxide, ferrous ion, and ferric ion using adiabatic calorimeter APTAC using spherical sample cells of 130 cm3 nominal volume and of borosilicate glass to measure onset temperature, non-condensable pressure, time to maximum rate, heat and pressure rate.

6.1 Heterogenous Iron catalyst

Rust one of the common industrial contaminants which is not very soluble in water. Cisneros et al. [9] used iron (III) oxide in water to prepare dark red suspension of ferric oxide (Fe2O3) or rust and contacted with 50 mass% hydroxylamine/water solutions (HA) in APTAC experiment as heterogenous Iron catalyst resulted in onset temperature of the decomposition of HA in the presence of 0.0004 mol % (10 ppm) iron oxide was 111°C which decreased by 9°C when the iron oxide concentration increased 0.0088 mol % (200 ppm). Also, time to the maximum rate was reduced significantly (around 4.7 times) from 223 min in iron oxide concentration of 10 ppm to 51 min in iron oxide concentration of 200 ppm. Non-condensable pressure of 751 kPa remained unchanged in both concentration indicating only dynamic parameter were affected by the amount of contaminant and static parameters remained unchanged. White residue observed at end of experiment possible identify as the precipitate of iron (II) hydroxide [Fe(OH)2] during reaction.

6.2 Homogeneous Iron catalyst

As rust is not very soluble in water, it was hypothesized that the ions in solution produce a more violent reaction than the heterogeneous iron reaction (Fe2O3) due to higher ion availability, hence Cisneros et al. [9] further studied impact of homogeneous iron catalyst using yellowish ferric ion solution, (Fe3+), prepared using ammonium iron (III) sulfate dodecahydrate and greenish ferrous ion, (Fe2+) solution prepared using iron (II) sulfate hydrate. The solutions of Fe2+ are known to oxidize in the presence of air to Fe3+, so special care was taken to use the solution as quickly as possible. A minor incident occurred in the laboratory during the ferrous ion experiment while adding 1ml of 0.52mol % (16000 ppm) Fe2+ solution (from iron (II) sulfate hydrate) in 8 gm of 50 mass% hydroxylamine/water solutions (HA). The formation of a brown precipitate was followed immediately by a rapid reaction that produced a bubbling system with little vapor-liquid disengagement. The heated reaction mass was scattered up to two meters, and the sample cell was nearly empty at the end of the reaction. Since the pressure generated inside the sample cell will create a huge pressure differential across the sample cell wall, which most likely will lead to the mechanical failure of the glass sample cell, a ruptured cell could result from a closed cell experiment or a higher concentration of iron ions, which will increase the pressure generation rate. ferric oxide (Fe2O3) or iron hydroxide (FeO) (OH), which are both dark brown or blackish precipitates that are typical of Fe3+ compounds. In any case, the oxidation of Fe2+ to Fe3+ was a part of the reaction, and iron oxidation may have been the initial stage in the reaction because the brown colour was seen just before the reaction become severe. Therefore only 0.0004 mol % (10 ppm) Fe2+ & Fe3+ was used to measured decomposition parameters in contact with 50 mass% hydroxylamine/water solutions (HA). It is important to note that the reaction started immediately after the injection of the experiments run with ferric as well as ferrous ion. The good data reproducibility of 5 run recorded, initial injection of the iron ion triggers the first reaction, which liberates enough thermal energy to heat the reaction mixture to the onset temperature of the second exotherm. Maximum Temperature and pressure of ~260°C and ~6688KPa.The blue residue is explained by copper contamination from the tube heater assembly, since an analysis for one of the samples (Fe3+) revealed 100 ppm of copper. It seems that the same precipitate is formed irrespective of the initial oxidation state of the iron ion. Iron hydroxide [FeO(OH)] or rust [Fe2O3] is a possible identity for this precipitate.

7. Conclusion

From this review, adiabatic calorimeter APTAC, result shows 50% Hydroxylamine/water solution decomposes exothermically with an onset temperature of ~133–136°C (W & WO stabilizer). The presence nail resulted significantly reducing the onset temperatures from 133–136°C to below 50°C and raised the maximum self-heat rates from 5 to 13°C/min (WO) and 31°C/min (W), and increased self-heat rates overall. These tests demonstrated that carbon steel act as strong catalyst in the decomposition reaction of a 50% hydroxylamine/water solution, both with and without stabilizers. Also, an iron ion (Fe3+ or Fe2+) in a 50% hydroxylamine/water solution will react violently, even at very low concentrations of 10 ppm, creating a bubbling system with very little vapor-liquid disengagement at ambient temperature liberating energy in a very short period of time, which will result in boiling of the reaction mass.

Rust will cause heterogeneous catalysis of the reaction, which is not as violent as iron homogeneous catalysis. Homogeneous catalysis of 50% Hydroxylamine/water solution takes place in two well defined exothermic reactions, the first being more aggressive than the second. In both air and vacuum, the thermal decomposition of HA solutions produced nearly identical Tonset, Tmax, Pmax, heat rates, and pressure rates. This suggests that the presence of air above the sample had no discernible effect, and the oxidation products (NO, N2O) that were found were mostly formed by the oxygen present in the hydroxylamine molecule. The hydrogen ion can raise the maximum rates of self-heating and pressure, while the hydroxide ion can lower the onset temperature and produce more gas derivatives. At lower temperatures, hydroxylamine can release energy if it accidentally mixes with impurities, so it must be handled and stored carefully. Because glass dissolves at higher temperatures, the integrity of equipment lined with glass may be jeopardized during a 50% hydroxylamine/water solution runaway or process disruption. The presence of an acid or base affects the thermal decomposition behaviour of a 50% hydroxylamine/water solution.

Hydroxide ions can lower the onset temperature and produce more gas products & hydrogen ions can raise the maximal self-heat and pressure rates. Hydroxylamine should be managed and stored carefully since unintentional mixing with contaminants can create a hazardous release energy release at low temperatures. In the event of a runaway or process upset with a 50% Hydroxylamine/water solution, the integrity of glass-lined equipment may be at risk because glass can dissolve at elevated temperatures. Another important process safety related result is that the heat produced by the runaway reaction vaporized a solvent with a large heat of vaporization that tempered the reaction. If hydroxylamine is used in another solvent, with a lower heat of vaporization, then temperature and pressure increase should be higher.

8. Reference

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