

Case History

EXPLOSION DURING DISTILLATION OF 4-CHLORO-2-METHYLANILINE

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Summary

During the final stages of 4-chloro-2-methylaniline (CMA) distillation in a batch still under vacuum an unexpected reaction took place accompanied by the evolution of gas leading to an explosion of the still. Experimental studies identified the gas as HCl which was produced by the decomposition of CMA in the presence of CuCl_2 . The CuCl_2 was formed from Cu_2O carried forward from the reactor, HCl and air leaked into the still. The quantity of HCl which could be produced was about three times that necessary to reach the estimated bursting pressure of the still of 18 kg/cm^2 . The still temperature at the time of the explosion was in excess of 260°C .

The main conclusion from the studies is that for safe operation, distillation of chlorinated aromatic amines should be carried out in the presence of alkali under air-tight conditions.

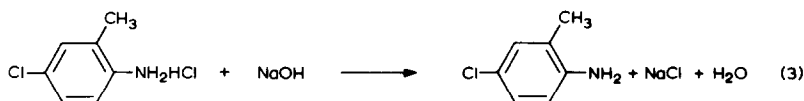
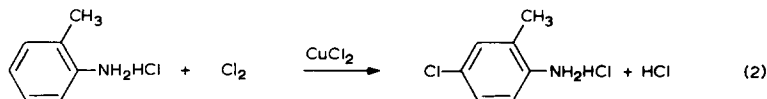
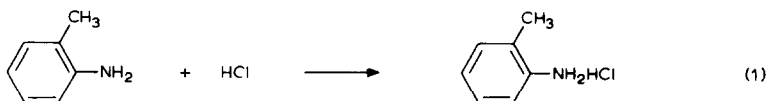
Introduction

At 9.39 a.m. of December 4th, 1973 a residue still of a vacuum distillation plant burst in the Kashima factory of Asahi Electrochemical Industries Inc. The accident occurred during the stripping of CMA (m.p. 30°C , b.p. 240°C) from higher boiling residue. Three operators were killed and two seriously injured.

Description of the process

(a) Synthesis of CMA

CMA is produced in a three stage reaction from *o*-toluidine (eqn. 1-3). The crude CMA is purified by vacuum distillation. The chlorination catalyst, CuCl_2 is recovered as Cu_2O by neutralisation of the filtrate from the CMA-HCl centrifuging. Some Cu_2O is however carried through to the distillation stage with the crude CMA.



(b) CMA distillation

The distillation plant is shown in Fig. 1. Crude CMA is charged to the steam heated rectifying still B where it is distilled until contents have been reduced to approximately $\frac{1}{3}$ of the original charge. The residual material is then transferred to the steam jacketed agitated residue still C and distilled to recover remaining CMA until the viscosity of the residue reaches a certain value. The temperature in the still is about 160°C at a pressure of 70 Torr. When the distillation is completed the still is isolated by closing valve F and the vacuum broken with nitrogen. The residue is discharged through the discharge valve E.

Description of the accident

The operation of the plant progressed normally from the previous night. At 4.40 a.m. (5 hours before the accident) the contents of the rectifying still were transferred to the residue still and distillation commenced. At 6.40 a.m. the operator observed that the CMA distillate, which is normally colourless, was discoloured. The colour changed from pink to brown and finally to black. Suspecting contamination caused by entrainment, the operator diverted the distillate to the rectifying still. Judging by the distillation rate, the distillation was completed at 8.30 a.m. by which time some 500 litres of contaminated CMA was collected in the rectifying still. The operator attempted to discharge the tar from the residue still but without success since the discharge line was blocked from the previous run. The operator continued distillation in order to remove the final traces of CMA so that after cooling he could enter the still and remove the solidified tar, as practiced on previous occasions.

At 9.10 a.m. the agitator stopped owing to the increase in the viscosity of the tar. At the same time the operator noticed that the still temperature and pressure were much higher than normal. At 9.30 a.m., the supervisor was summoned to the plant and he observed that the indicated pressure was 700 Torr and the temperature 220°C , although the vapour line was open. He ordered the operator to open the transfer valve D to the rectifying still to

regain vacuum and to cool the residue still with water on the outside. This was not effective as the vapourline and the transfer lines were already blocked with tar.

At 9.39 a.m. the residue still ruptured at the lid flange. The lid was blown upwards causing extensive damage. At the time of the explosion, a black smoke was observed around the still and a white smoke around the vapour line. There was no fire. A pungent odour could be detected near the still after the explosion. The bursting pressure of the still was calculated to be 18 kg/cm^2 .

Facts established after the accident

The inspection revealed the following facts:

- There was no evidence of fire in any part of the plant and the conclusion was that the rupture was due to gas pressure in the still.
- The temperature record Fig. 2 shows that contaminated CMA passed from the rectifying still to the residue still at 9.15 a.m. as a result of the operator opening the transfer line valves some 5 minutes after the agitator stopped.
- The transfer line and the vapour lines (dotted lines Fig. 1) were filled with black porous tar (tar A).
- The ball valve (Figs. 3 and 4) showed deterioration and cracks in the teflon covered packing and a part of internal asbestos gasket was missing indicating a source of air leak.
- The chlorine content of tar A was higher for samples situated further away from the still. The metals present were Na, Fe and Cu. There was no evidence of the presence of crystalline Cu compounds as shown by X-ray analysis. Copper-like reddish powder was observed on the surface of tar in the still.

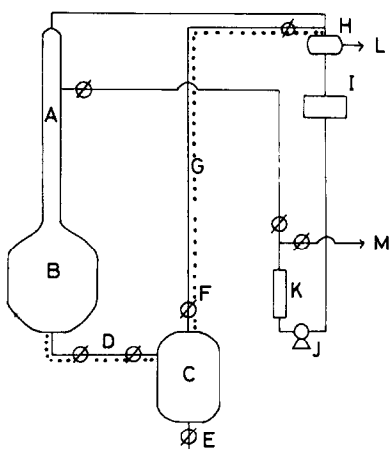


Fig. 1. Diagram of distillation plant.

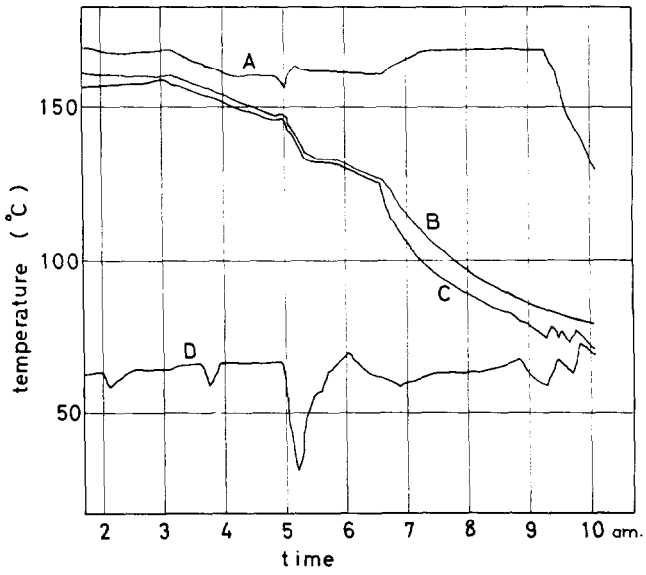


Fig. 2. Temperature record before explosion.

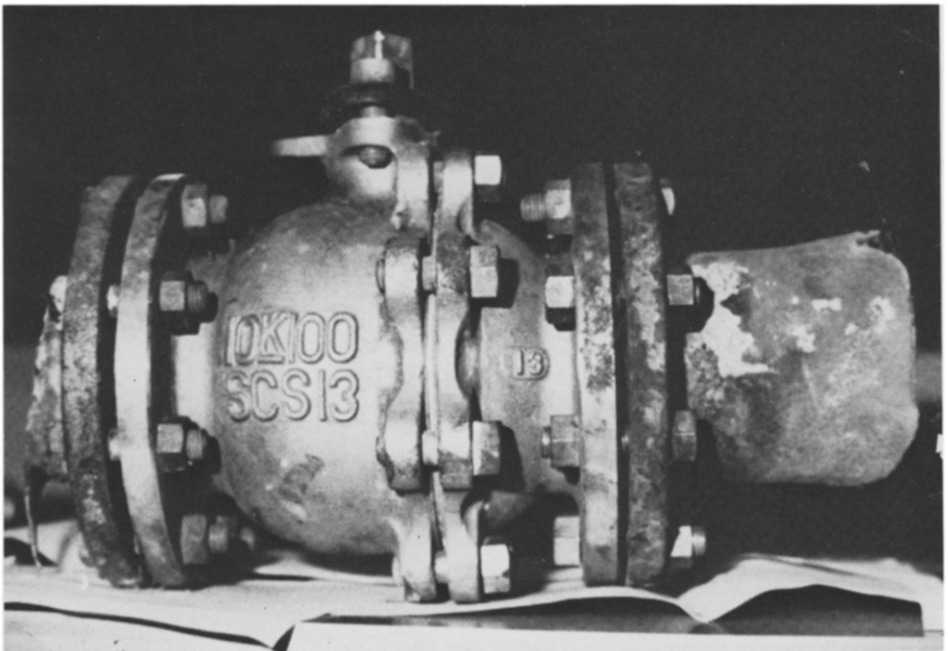


Fig. 3. Ball valve.



Fig. 4. Ball valve gasket.

- Lustrous black tar (tar B) covered the underside of the lid and filled the pressure gauge line as well as the space below the ball valve F.
- From the layer-like appearance of the solid deposit it was concluded that tar B was formed before tar A.

Experimental investigation

The committee considered the processes leading to the accident in two stages. In Stage 1 some exothermic reaction occurred in the residue. In Stage 2 some unknown gas evolution reaction took place after CMA entered the residue still containing hot tars.

(a) Stage 1

Two possibilities exist, either an exothermic reaction set in when residue was held for a period of time at the distillation temperature, or CMA, or residue was oxidised by air which leaked into the plant.

Examination of all possible combinations of substances known to be present in the residue by differential thermal analysis did not show any significant exothermic reaction. CMA, when contacted with air at the distillation temperature became discoloured and produced a small rise in temperature. However, residue completely stripped of CMA undergoes oxidation with marked evolution of heat when contacted with air.

(b) Stage 2

Experiments were carried out in the laboratory to investigate the possible reactions responsible for the gas evolution. Samples of tar were collected from the top of the vapour line (tar B) and some black viscous CMA was removed from the rectifying still. This CMA is referred to as 2/9 CMA.

Air was blown into a mixture of 500 g of tar and 250 g of 2/9 CMA for 30 minutes at 180°C in a 2 litre flask. The unreacted CMA was removed by distillation under vacuum. The residual tar is referred to as 2/9 tar. When the temperature of the residual tar reached 290°C, 550 g of 2/9 CMA were added to the residue and the contents sealed at atmospheric pressure. Figure 5 shows the temperature and pressure record. The flask burst after 75 minutes due to pressure of HCl gas. The tar from the upper part of the vapour line showed also much the same pressure curve as 2/9 tar.

To elucidate the reaction in more detail further experiments were carried out in a 160 ml pressure pyrex tube equipped with a pressure gauge. The tube was immersed in a salt bath at 239°C. A standard test mixture consisted of 3 g of redistilled CMA and 3.3 mmoles of various additives. All materials were dried and degassed under vacuum. The tube was evacuated, filled with nitrogen at atmospheric pressure, sealed and immersed in the salt bath. The pressure in the flask was recorded every minute. After the completion of the experiment the tube was cooled and the total gas evolved was calculated from the final pressure. The gas and the contents were analysed.

The experimental results show that 2/9 tar, or 2/9 CMA alone, do not produce any gas. A mixture of 2/9 tar and pure CMA shows the same pressure

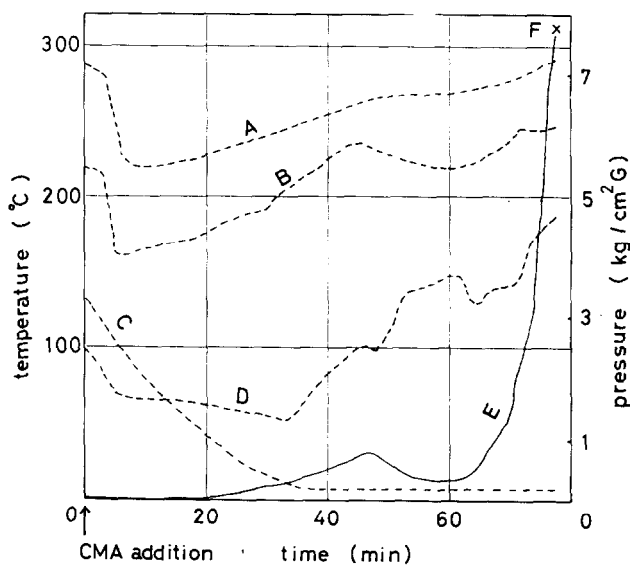
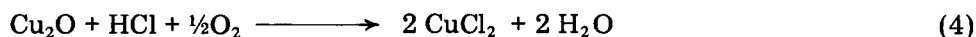


Fig. 5. Temperature and pressure records of first experimental run.

curve as a mixture of tar with impure CMA. The gas produced in all cases was HCl. The contents of the tube expand with the evolution of HCl by a factor of 10. Further experiments were conducted to establish which of the tar components was responsible for the gas evolution. The composition of the tar is given in Fig. 6. NaCl, NaOH, amine polymer, Fe powder and Fe_2O_3 do not react with CMA. Fe compounds may react but without the evolution of gas. On the other hand tests carried out with Cu powder, Cu_2O , CuO, CuCl and CuCl_2 showed that each produced CMA—HCl salt but only CuCl_2 generated HCl gas. The pressure curve for CuCl_2 —CMA mixture is similar to that of 2/9 tar and 2/9 CMA system (Fig. 7). Basically there is no difference between the formation of CMA—HCl salt and HCl gas. HCl gas produced will react with CMA to form salt as long as free CMA is present. CuCl_2 is obviously capable of producing more HCl than the other Cu compounds.

Source of CuCl_2

CuCl_2 is not likely to be present in crude CMA since the reaction mixture is neutralised and crude CMA is adjusted to pH 12. However, a clue to the formation of CuCl_2 can be gained from the reaction used for the regeneration of CuCl_2 from Cu_2O (eqn. 4).



This reaction would take place if there were an air leak into the still and the contents were acidic. When air was blown into a mixture of 6 g CMA and 6.6 milliatoms of Cu as Cu_2O at 239°C , the mixture turned into a lustrous black tar after 30–40 minutes. Some CMA—HCl salt was deposited on the walls. The mixture finally solidified creeping up the walls of the tube. The solid resembled tar B. A mixture of 3 g of this tar and 3 g of CMA when heated

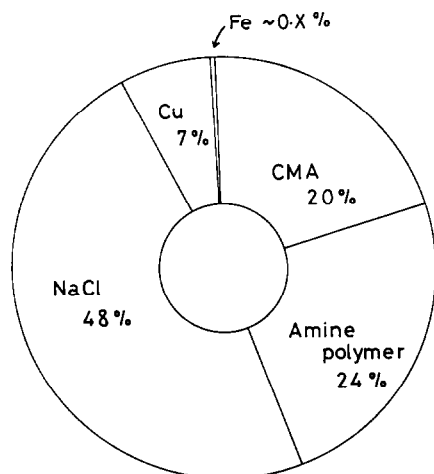


Fig. 6. Composition of tar.

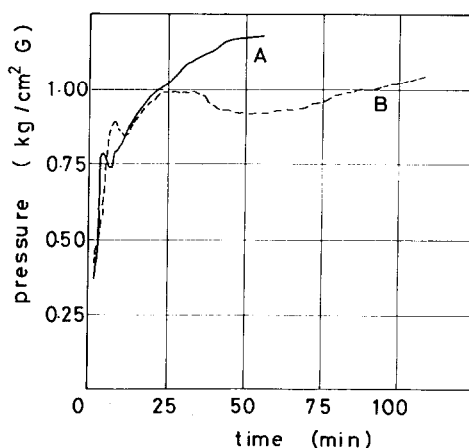


Fig. 7. Pressure curves for CuCl_2 —CMA and tar—CMA systems.

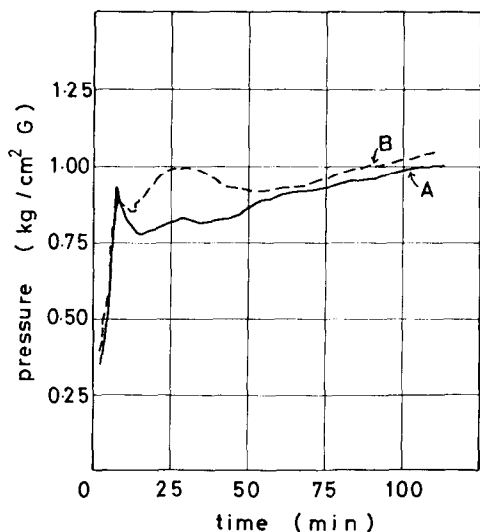


Fig. 8. Pressure curves for two tar-CMA systems.

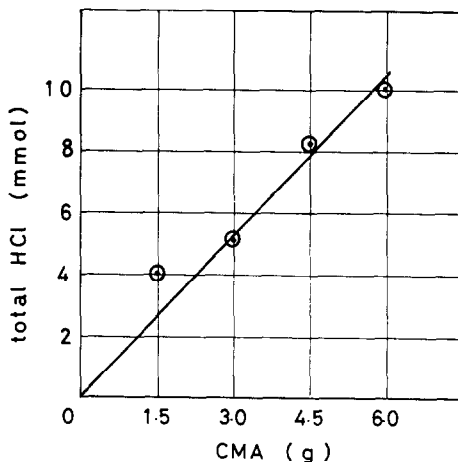


Fig. 9. Quantity of HCl generated.

under standard conditions produced a pressure curve similar to that for 2/9 tar and CMA (Fig. 8).

Potential quantity of HCl produced

Further experiments were conducted in which various amounts of CMA were reacted with 3.3 mmoles of CuCl_2 . The results in Fig. 9 show that the amount of HCl generated as CMA-HCl salt and HCl gas is proportional to the quantity of CMA employed.

The estimated quantity of material present in the still at the time of rupture was approximately 600 kg. The Cu content of tar type A was ca. 7.5% so that the amount of Cu in the still was 45 kg, or 700 g moles. The ratio of CMA to Cu in the tar corresponds to that of 3 g CMA in Fig. 9 giving 5 mmoles of HCl per 3.3 mmoles of Cu^{++} . This would be capable of producing $5/3.3 \times 700 = 1050$ g moles of HCl, assuming that all the Cu ions were in the divalent state.

The volume of the still was 1300 litres, the contents approximately 600 litres giving the net empty volume of 700 litres. The estimated bursting pressure of the still was 18.5 kg/cm^2 . The still temperature was at least 200°C . Thus the number of moles of HCl required to reach the bursting pressure is:

$$\frac{(18.5 + 1) \times 700}{0.082 \times 473} = 351 \text{ moles}$$

The potential quantity of HCl which could be produced in the still is thus three times that required to burst the still. The effect of temperature on the

reaction rate of CuCl_2 with CMA was also investigated (Fig. 10). An Arrhenius plot is shown in Fig. 11. It is seen that the reaction rate at 160°C , the normal operating temperature is very low. It is estimated that the reaction temperature necessary to produce enough HCl to burst the still in 24 minutes, the time elapsed between CMA entering the still and the explosion, would be in excess of 260°C .

Summary of the probable course of the accident

The discolouration of the CMA distillate which was observed at 6.40 a.m. can be attributed to an air leak into the residue still. It has been observed in the past that entrainment produces black distillate immediately, whereas an air leak causes a gradual change in colour from pink via brown to black. There is also evidence that the ball valve F was not in a satisfactory condition and is suspected as the source of air leak. Experimental results show that an air leak would start an exothermic reaction in the residue still forming tar B, raising the viscosity of the contents and causing an increase in the temperature. Since the tar has a tendency to creep up the wall in the still it is likely that the thermometer pocket would be out of the still contents and not indicate the correct temperature. It is presumed that at about 9.15 a.m., just prior to the opening of the transfer line valves, the still temperature was far higher than 260°C .

When the transfer line valves were opened to reduce the still pressure at 9.15 a.m., CMA, which was previously directed to the rectifying still, would enter the residue still and mix with the hot tar containing CuCl_2 . This led to the generation of HCl gas causing the residue to swell, and force it up the vapour and transfer lines where it solidified, blocked the outlet lines and led to the rupture of the still.

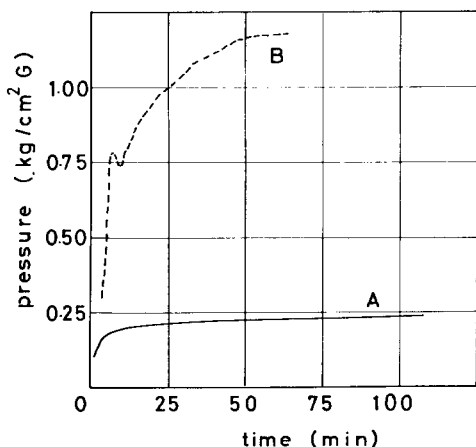


Fig. 10. Pressure curve for CuCl_2 -CMA reaction.

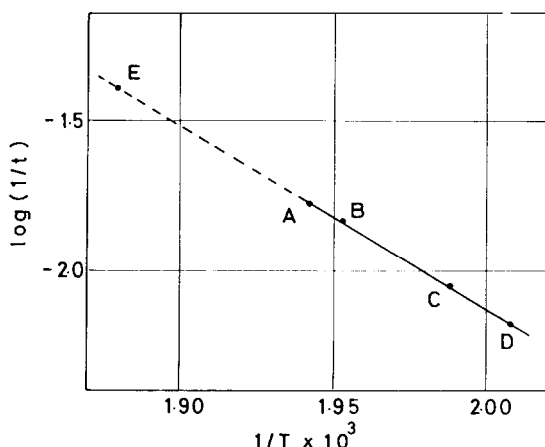


Fig. 11. Arrhenius plot for CuCl_2 -CMA reaction.

Conclusions

There are obvious lessons to be learned from the accident. It is essential that when developing a new process the properties and reactivities of substances involved are examined in detail for possible thermal effects or unexpected reactions between the components or impurities. In fact, the investigation that followed the accident should have been carried out before full scale operation was undertaken. Moreover, several abnormal occurrences e.g., overheating of residue which did not result in an accident were apparently observed on previous occasions. These should have been thoroughly investigated before manufacture was restarted.

Specifically, the investigation showed that for safe distillation of chlorinated aromatic amines as produced by the chlorination of *o*-toluidine, the following measures should be taken:

- (a) Ensure air tight plant to prevent ingress of air.
- (b) Install a suitable safety valve, or a bursting disc.
- (c) Eliminate, or drastically reduce copper compounds from crude CMA.
- (d) Distil under alkali conditions (Ref. 1, 2).
- (e) Consider the use of inhibitors.

Acknowledgement

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References

- 1 U.S. Patent 2,911,340
- 2 U.S. Patent 3,324,011