NOx Containing Process Streams

Fluid Catalytic Cracking (FCC) units often export an olefins containing "light ends" stream to ethylene plants for separation. This refinery gas typically contains nitric oxide (NO) which is formed during regeneration of the catalytic cracker catalyst. Regeneration consists of burning coke which contains varying amounts of nitrogen depending upon FCC unit feed. N2O and NO2 can be completely removed in amine and caustic scrubbers. N2O3, however, dissociates to NO and NO2. Low levels of oxygen react with NO to form nitrogen dioxide:

$$2NO + O2 \text{ ------- } 2NO2$$

Nitrogen dioxide reacts with nitric oxide to from nitrogen trioxide:

$$NO2 + NO \text{ ------- } N2O3$$

Formation of NOx Gums

NOx compounds will react with 1-3 butadiene or cyclopentadiene to form an amorphous gummy polymeric material. These compounds are unstable and will ignite or explode at low temperatures.

Incident

On February 22, 1990, Shell's Berre, France ethylene plant experienced an explosion inside their cold box. As a result, the plant was out of service for 5 months. The cause of the explosion has been attributed to the deflagration of gums present in the low-pressure methane pass of their cold box. The gums contained 14-21% nitrogen with numerous nitro and nitrosocomponents on short hydrocarbon chains.

Precautions

Ethylene plants should not process FCC streams without special treatment to remove nitrogen and nitric oxides.

Reference

"Cold Box Explosion at Shell Steam Cracker in Berre, France", by Jacques Kohler.

AIChE Spring National Meeting, April 7-11, 1991

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COLD BOX EXPLOSION AT SHELL STEAM CRACKER IN BERRE, FRANCE

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FOR PRESENTATION AT

AIChE Spring National Meeting

Houston, Texas, April 7 - 11, 1991

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COLD BOX EXPLOSION AT SHELL STEAM CRACKER IN BERRE, FRANCE

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ANUSCRIPT CTR.

MAR 7 1991

ABSTRACT

An emergency shutdown occured on February 22nd 1990 at the Shell Berre 420 000 tonnes/year steamcracker in Southeast France after an explosion inside the cold box. As a result, the plant was out of operation for nearly 5 months, the cold box having to be completely replaced. After an investigation by a team of experts and exchanges with other relevant industrial specialists, the cause of the cold box explosion has been attributed to the deflagration of gums present in the lov-pressure methane pass, inside one of the fin-plate heat exchangers of a twin pair. The gums contained 14 to 21% of nitrogen with numerous nitro and nitroso components on short hydrocarbon chains. The source of NOx was identified as NOx components present in the catalytic cracker dry gas which had been part of the Berre steam cracker feed since 1982. Corrective measures have been taken to avoid a similar incident.

INTRODUCTION

The Berre cracker had been taking refinery gas from the neighbouring Shell refinery since 1982 as part of its feed, at the level of the cracked gas compressor, upstream of the caustic vash tover. This stream included gas from one Fluid Catalytic Cracking unit (FCC) from 1982 to 1987 and of two FCC units since the end of 1987 to the day of the incident. The Berre cracker is of a standard Lummus design with no front-end deethaniser before the cold box. No special treatment was applied to these refinery gases, like a dedicated cold box, to remove methane, nitrogen or hydrogen and nitric oxides . The practice generally applied by the steamcracker industry (ref.1) was used, especially during the shutdowns (every four years) and the resulting cold-box thavs.

I. BACKGROUND

1. CHARACTERISTICS OF THE FCC GAS CONTAMINANTS

The concentration levels of the contaminants in the two gas streams did not differ significantly.
Lov levels of nitrogen oxides, known to be present in these refinery gases, vere measured using the GRIESS-SALTZMAN method. Nitrogen dioxide (NO2) vas never measured (detection limit 0,01 ml/m3). Lov levels of nitric oxide (NO), ranging between 0,02 and 0,3 ml/m3, vere currently observed.

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In general, the ammonia (NH3) concentration was below 0,1 ppm but values of 2 to 4 ppm were encountered. Also, concentrations of around 10 ml/m3 of oxygen were found to be present in these gases.

2. COLD BOX STATUS BEFORE FEBRUARY 22nd 1990

A scheme of the Berre cold box is given in Appendix 1.

No real abnormal temperature or pressure profile through the cold box had been noticed before the last shutdown in March 88 However in 1987, a slight decrease of the hydrogen purity had been observed due to higher temperatures in V 308 (- 155°C versus a design of - 165°C), as well as some difficulties to evacuate the liquid stream of V307 to the demethaniser. A procedure, consisting of heating the cold box, downstream of V306, to -95/-100°C was applied, in order to melt or sublimate any NOx present. Then flushing with a counter flow of methane from the demethaniser through E 308 to the liquid draining header, permitted the recovery of the right temperature profile.

During the March 88 shutdown and the resulting cold box thaw at ambient temperature, up to 35 ppm of NOx were measured in V 307, working normally at - 129°C and a very small amount of NOx gums was recovered on a E 309 inlet filter (deposit 0 in appendix 1).

In May 88, the presence of "blue liquid" was observed for the first time in the LRCV of V 308 and a procedure to purge this valve with nitrogen was applied.

From May 88 to the day of the incident, fouling of the LRCV of V 307 and V 308 occured several times resulting in difficulties to evacuate the liquid from these vessels and an increase of 2,3 bar of the differential pressure between V 307 and the demethaniser was observed. Also the hydrogen purity decreased, and temperature of V 308 was more often at - 157°C.

Two trials to recover the design conditions by heating the last parts of the cold box to - 95°C and purging with methane from the demethaniser did not result in the intended reduction of differential pressure between V 307 and the demethaniser.

II. DESCRIPTION OF THE INCIDENT

The incident occured after an upset of the steam-cracker operation which resulted from the opening of a cracked gas compressor relief valve. After one hour with the cracked gases essentially to the flare and with the cold columns on total reflux, the cold box temperature increased by 25°C. At that moment, both ethylene and propylene compressors tripped, due to high liquid levels in the suction vessels, and remained out of operation.

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About one hour before the explosion, and 3 hours after the start of the incident, the pressure of the demethaniser was lowered by 2 bars, in order to empty the vessels V 304 to V 308 which had high levels of liquid.
The intention was also to heat the downstream part of the cold box to about -70°C in order to get rid of the high differential pressure between V 307 and the demethaniser.
During the investigation, it was established that during that period, a flow of 30 to 60 metric tons per hour of cracked gases entered the cold box, creating a heat front which warmed up the cold box (see appendix 2) and that the temperatures of V 307 and V 308 increased at first to - 58°C (a temperature higher than originally intented). When, finally, the exchangers E 310 - E 311 and 313 lost their liquid ethylene hold-up, the temperature rose at a higher rate (about 4°C/min) to - 25 / - 30°C for the coldest parts of the cold box, and the explosion occured.

Operators immediately located the origin of the explosion at the cold box. A gas cloud estimated at 20 tons of hydrocarbons plus the perlite, escaped and covered a large part of the steamcracker. The cloud was confined by water spraying, especially from the furnaces which had been tripped immediately. Larger quantities of NOx were measured (up to 200 ppm) around E 308 and the first visual inspection of the cold box could only take place 2 weeks after the incident due to continous NOx release over that period.

The visual inspection showed that the explosion had occured inside the E 308N (see photo 1 and appendix 1) which presented a large spherical cavity. The E 308S was damaged by the explosion of E 308N, the LP methane header was torn away and broken in pieces. The casing and frame of the cold box were distorted by the explosion (See photo 2).
At a first look, the other exchangers seemed less damaged, but a more thorough inspection showed the necessity to replace the entire cold box.

III. DETERMINATION OF THE CAUSES OF THE EXPLOSION

The investigation was done by a team of Shell experts both from Shell CHIMIE and Shell Internationale Chemie Maatschappij. Where required, advice was sought from outside specialists and laboratories familiar with explosive reactions and the analysis of components causing explosive reactions.

1. EQUIPMENT AND EXPLOSION STUDIES

The first results of the investigations confirmed that the burst was not the result of a rupture by overpressure or thermal constraint.

The explosion had occured in the low-pressure methane pass, inside one of the fin-plate heat exchangers of a twin pair (the E 308N). The melting temperature of aluminium (660°C) was reached at specific points of the damaged heat exchanger.
A study was later done to evaluate :

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- the quantity of product (in TNT equivalent) which created the explosion.
- the type of the explosive reaction

To quantify the explosion power, various calculations have been done, taking into account :

- the level of the sound of the explosion perceived in the control room.
- the study of the perlite impact
- the study of the deformation of the frame of the cold box and of an experimental model exposed to an explosion.

The conclusions of these studies were that the explosion phenomenon was of a deflagration type with a most probable equivalent mass of TNT between 17 and 28 kg.
However some local detonations could also have taken place.
The perlite had a very important damping effect during the explosion.

2. ANALYSIS OF THE DEPOSITS

Two different deposits were recovered (see appendix 1)

Deposit 1 : on a filter in the bottom line from V 307 to E 308, at the entrance of E 308.

Deposit 2 : at the entrance of E 308 in the low pressure methane line coming from E 309 (See photo 3).

The deposit 1 has very clearly been identified as ammonium salts. It consists essentially of nitrite, bicarbonate and small quantities of nitrate of ammonium. It is completely soluble in water.

The deposit 2 looks like a red-brown gum, with a honey like consistency. This unstable product decomposes slowly at ambient temperature, releasing NOx. This deposit is very heterogeneous, which explains the fact that the different laboratories involved found a nitrogen content varying from 14 to 21%.
The product can be divided into a water soluble inorganic phase, and an organic phase.
The inorganic phase has a pH of 2 to 3 and contains essentially ammonium nitrate.(Ionic chromatography - IR spectrometry)

The volatile fraction of deposit 2 has been characterized by gas chromatography coupled with mass spectrometry.
Of about 10 products, appearing on a total ionic chromatogram, about 8 have been identified (see Appendix 3)

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IV. EXPLANATION OF THE CONDITIONS LEADING TO THE EXPLOSION

1. FORMATION OF AMMONIUM SALTS

The deposit 1, which plugged the filter at the entrance of E 308, was mainly responsible for the differential pressure increase between V 307 and the demethaniser. The heating and methane purging procedure, previously described in I-2, had no effect on the ammonium salts.
With the presence of ammonia in the refinery gas, the formation of ammonium nitrite can occur following the reaction :

$$2\ NH_3 + N_2O_3 + H_2O \quad \leftrightarrows \quad 2\ NH_4NO_2 \qquad (1)$$

and that of ammonium nitrate, following the reaction :

$$2\ NH_3 + 2\ NO_2 + H_2O \quad \leftrightarrows \quad NH_4NO_3 + NH_4NO_2 \qquad (2)$$

As for the formation of ammonium bicarbonate, it was explained by a small leakage, in January 1990, of CO2 in the cracked gases out of the caustic tower :

$$CO_2 + NH_3 + H_2O \quad \leftrightarrows \quad NH_4HCO_3 \qquad (3)$$

2. NOx ACCUMULATION IN THE COLD BOX

The NOx in refinery gas is essentially nitric oxide (NO). It is formed during the regeneration of the catalytic cracker catalyst when combustion of coke containing variable amounts of nitrogen (depending on the residue fed to the FCC unit) takes place. N2O and NO2 should be completely removed by the dry gas treatment (DEA + caustic) and N2O3 is, at ambient temperature, entirely dissociated into NO+NO2.
Low levels of oxygen are present in refinery gas resulting in oxygen concentration, in the stream entering the cold box, one or twice the level of the nitric oxide concentration. Oxygen reacts with nitric oxide to form nitrogen dioxide :

$$2\ NO + O_2 \quad \leftrightarrows \quad 2\ NO_2$$

Both the rate and equilibrium of this reaction are favoured by the cryogenic temperatures and relatively high pressure in the cold box. According to W.M. HENSTOCK (ref.2) not all the nitric oxide is oxidised to nitrogen dioxide, the reaction being rate limited rather than equilibrium limited. Therefore nitrogen dioxide reacts with the excess nitric oxide to form nitrogen trioxide :

$$NO_2 + NO \quad \leftrightarrows \quad N_2O_3$$

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The equilibrium for this reaction favors N203 at lov temperatures and high pressure. Nitrogen trioxide is solid at temperatures < - 102°C and insoluble in the hydrocarbons present. At the prevailing cold box temperature, it will be present as a solid, inducing plugging in the coldest parts of the cold box.

In conclusion, since the untreated FCC gases always contained small quantities of NO and oxygen, and in viev of the physical properties of the NOx (see Appendix 3), it was unavoidable to find NOx in the cold box. This was recognized after 1987 when partial plugging and "Blue liquid" appeared. N203 was therefore present in V 307 and V 308, plugging from time to time the LRCV of these vessels.

3. FORMATION OF NOx GUMS

It is well known that NOx compounds in general and nitrogen dioxide in particular, will react with certain unsaturated hydrocarbons to form amorphous gummy polymeric material, generally called "NOx gums" (see Ref.3).

Studies (See Ref.4) have also been done on the reaction of unsaturated hydrocarbons with nitric oxide, nitrogen dioxide and mixtures of nitric oxide and oxygen.
They noticed that the reaction rate between mono-olefins, propadiene or acetylene and NOx vas very slov and that ignition vas not possible below 0°C.

They shoved also that unstable nitro and nitroso compounds could be formed when NO2 or N203 reacted with conjugated dienes like 1-3 butadiene or cyclopentadiene and that these compounds were apt to ignite or explode at lov temperatures.

V. COLD BOX EXPLOSION HYPOTHESIS

NOx had accumulated in the coldest parts of the cold box since the last shutdown in March 1988.

The heating procedure of V 306 - V 307 - V 308 at a temperature of - 95°C may have displaced monoolefins like ethylene, propylene, 1-butene or acetylene from V 306 downtream and may have formed some "stable gums"as partially identified in components of Appendix 3.

During the steamcracker upset of 22 February and the resulting cold box heating , the composition of the different vessels V 308 to V 304 was enriched in heavier components and most likely, as simulations showed afterwards, in components like 1-3 butadiene and 1-3 cyclopentadiene.

This meant that unstable gums could have been formed.

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When, finally, the temperature of the coldest parts of the cold box increased at a fast rate to - 25°C, due to the loss of the ethylene refrigerant, most probably the unstable NOx gums exploded followed by the stable gums, since no product was subsequently found in the exploded E 308 N. For some unknown reasons, the twin exchanger E 308 S, which presumably vent through the same treatment and which contained NOx gums, did not explode.
This explanation is well supported by the literature where explosions have occured in other cryogenic gas processing units (Ref 4.5.6). These explosions were attributed to the presence of unstable nitrogen compounds which had been formed also from the reaction between trace amounts of NOx and hydrocarbons accumulated over time, with concentration sometimes lower than 1 ppm (Ref 7).

CONCLUSIONS

NOx compounds, when present at the entrance of a cold box, will accumulate in the coldest part of the cryogenic equipment. If during a partial heating or cooling procedure of the cold box or during a plant upset, the concentration profile of the various mono and diolefins in the different parts of the cold box is changed, these NOx may form stable or unstable gums with the hydrocarbons.
At that moment, the potential for a very violent reaction exists, and an explosion can then occur, initiated for example by a fast heating rate of the cold box, as in the Berre case.

To prevent the occurence of a similar incident in the Berre cracker, it has been decided to eliminate the presence of NOx in the cold box.
The direct consequence of this decision means that FCC gases will not be taken back as feed to the Berre cracker until a process can be developed which will remove NOx from these gases.

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REFERENCES

1. Plant Operations Progress Vol 6, N°4, October 1987.

2. Henstock, W.H., "NOx in the cryogenic section of an ethylene plant" 1989 AICHE Spring National Meeting ; April 4, 1989, Houston, Texas.

3. Henstock, W.H., "NOx in the cryogenic Hydrogen Recovery Section of an Olefins Production Unit". Plant Operations Progress Vol 5, N°4, October 1986.

4. Haseba, S, et al., "Nitric Oxide Explosion", Chemical Engineering Progress, 62 (4), P.92 (1966).

5. Bohlken, S.F., "Heat Exchanger Explosion at a Nitrogen Wash Unit", Chemical Engineering Progress, 57 (4), P.49 (1961).

6. Alexander, D.S. and C.M. Finigan, "Inert Gas + Poor Piping = Explosion", Petroleum Refiner, 38 (5), P.285 (1959).

7. Haseba S, Kubo, Kitagawa, "The Danger of Nitrogen Oxides in Cryogenic Gas Separating Plant", Anzen Kagaku (Safety Engineering), Vol 8, N°1, P.22 (1969).

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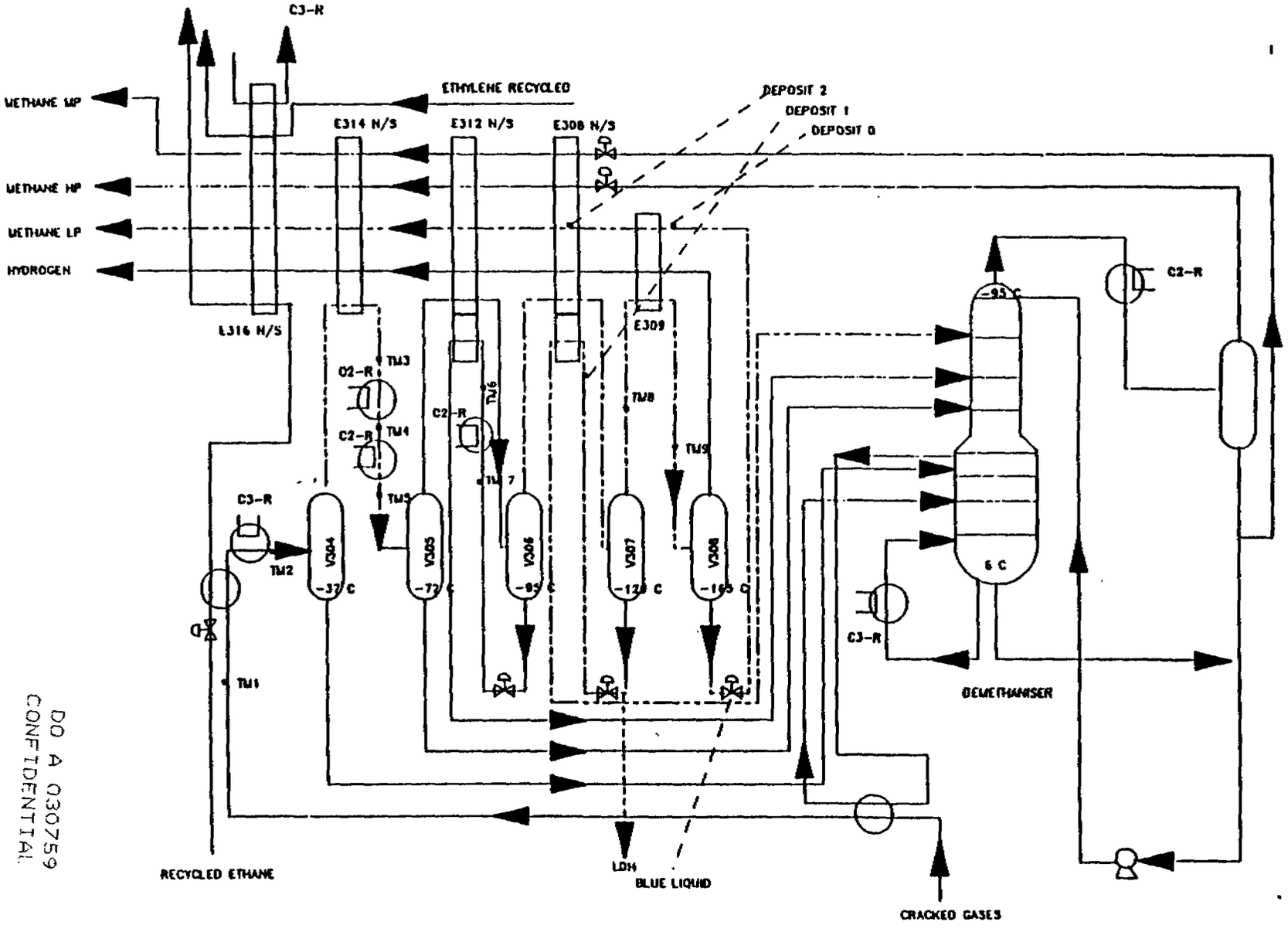
APPENDIX 1 : AUBETTE COLD BOX



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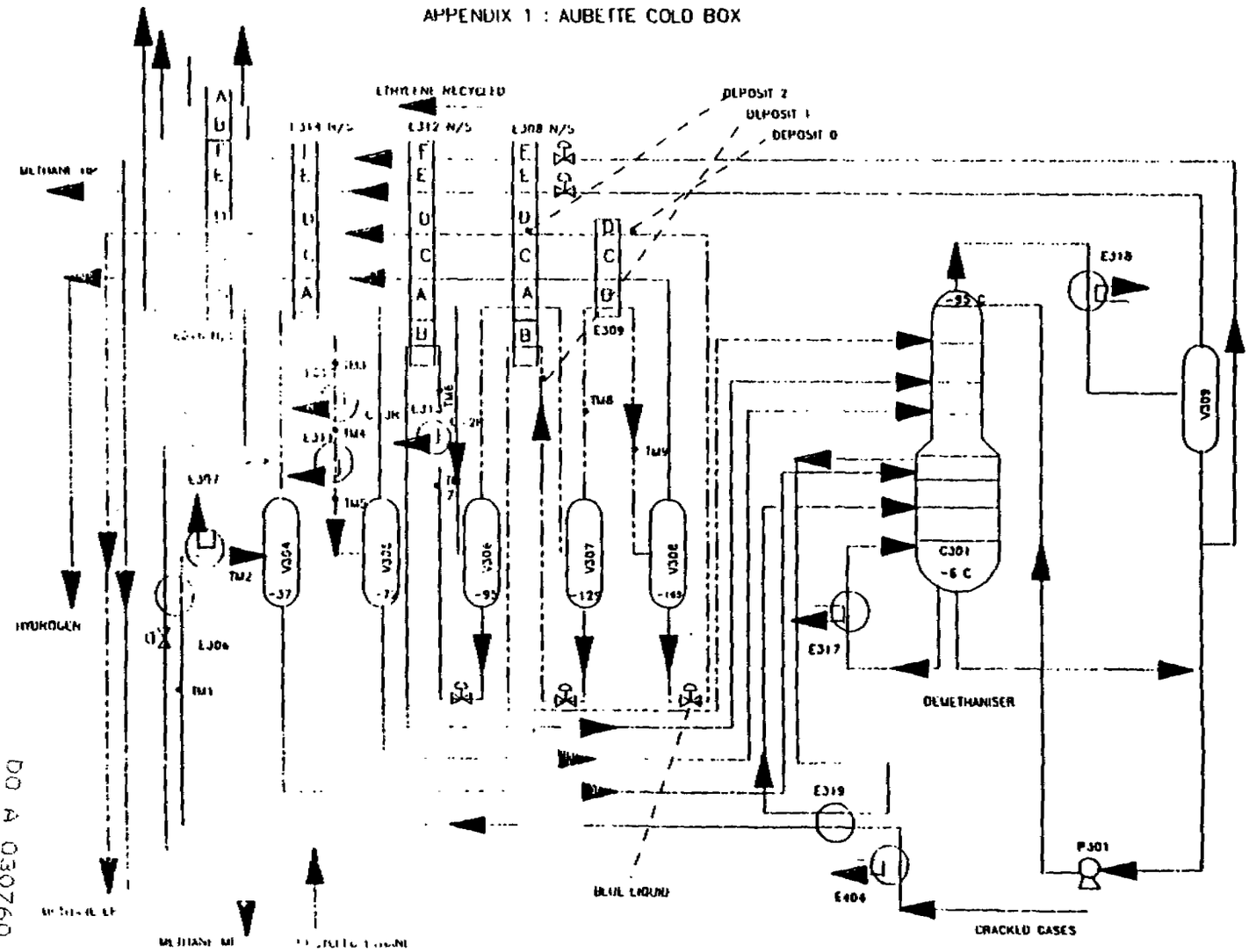
APPENDIX 1 : AUBETTE COLD BOX



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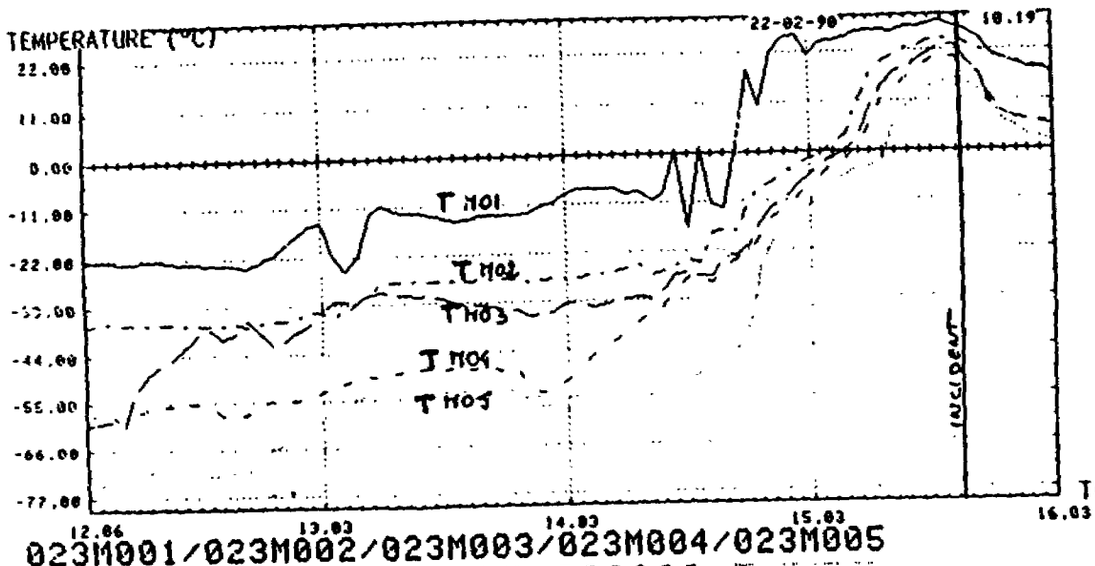
APPENDIX 2 : COLD BOX TEMPERATURE PROFILE



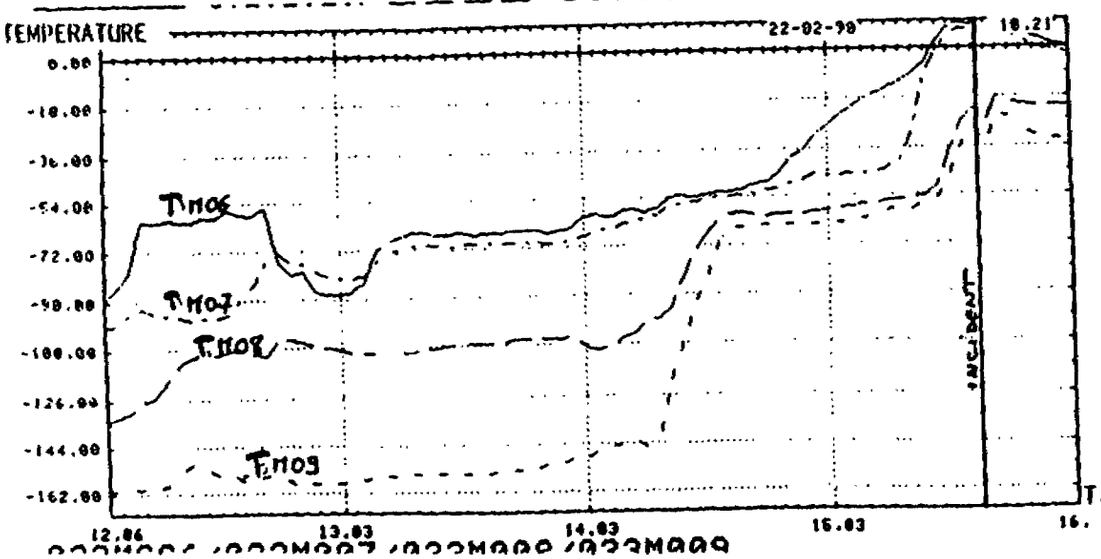
T M01 . CRACKED GASES TEMPERATURE INLET E306

T M02 . CRACKED GASES TEMPERATURE TO V304

T M03 . CRACKED GASES TEMPERATURE INLET E310

T M04 . CRACKED GASES TEMPERATURE INLET E311

T M05 . CRACKED GASES TEMPERATURE TO V305



T M06 . CRACKED GASES TEMPERATURE INLET E313

T M07 . CRACKED GASES TEMPERATURE TO V306

T M08 . TEMPERATURE TOP V307 TO V308

T M09 . TEMPERATURE INLET V308

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APPENDIX 3

NOx GUMS COMPONENTS

1) FORMIC ACID

2) ACETIC ACID

3) $C_3H_7ONO_2$ or $CH_3CH(CH_3)CH_2ONO_2$

4) C_3H_7 O-COOH

5) $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$ (proposed structure)

6) NO_2 O $CH_2(CH_2)_n$ O NO_2 n=1,2...

7) NO_2 O $CH_2-CH(CH_3)-ONO_2$

8) CF_3 CH_2 O NO_2

****

PHYSICAL PROPERTIES OF NOx

	MELTING PT	BOILING PT	
		(At Atm P)	(At Working P)
NO	- 161° C	- 151° C	- 108° C
NO_2	- 9,3° C	+ 21° C	-
N_2O_3	- 102° C	+ 3,5° C	-

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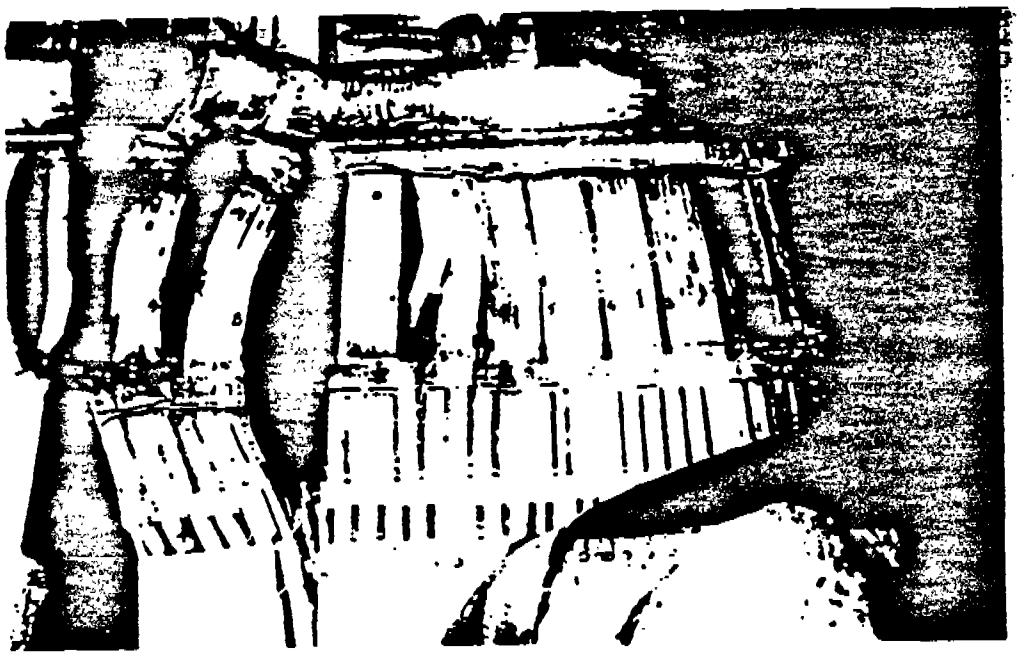

PHOTO 1

E 308 N AFTER EXPLOSION

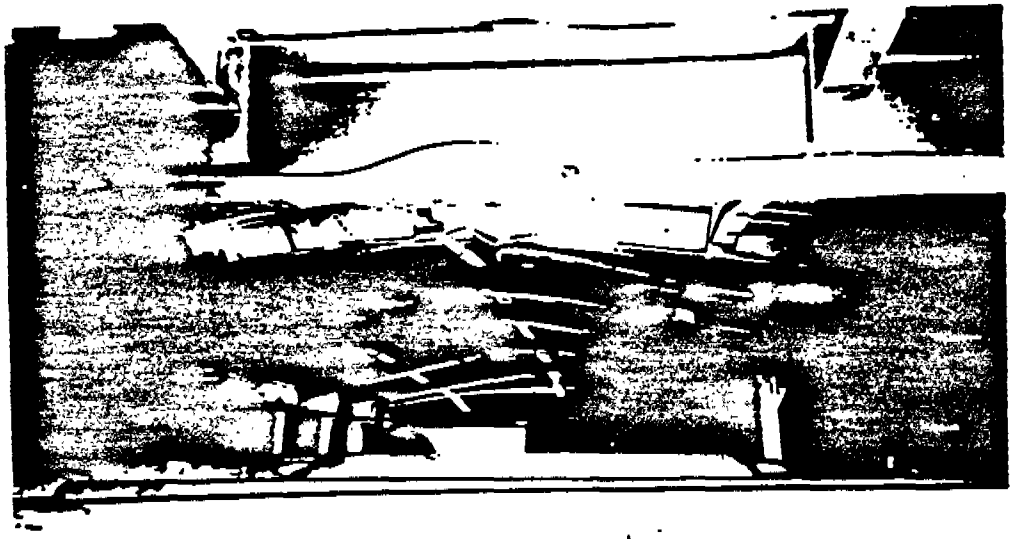

PHOTO 2

COLD BOX FRAME AFTER EXPLOSION

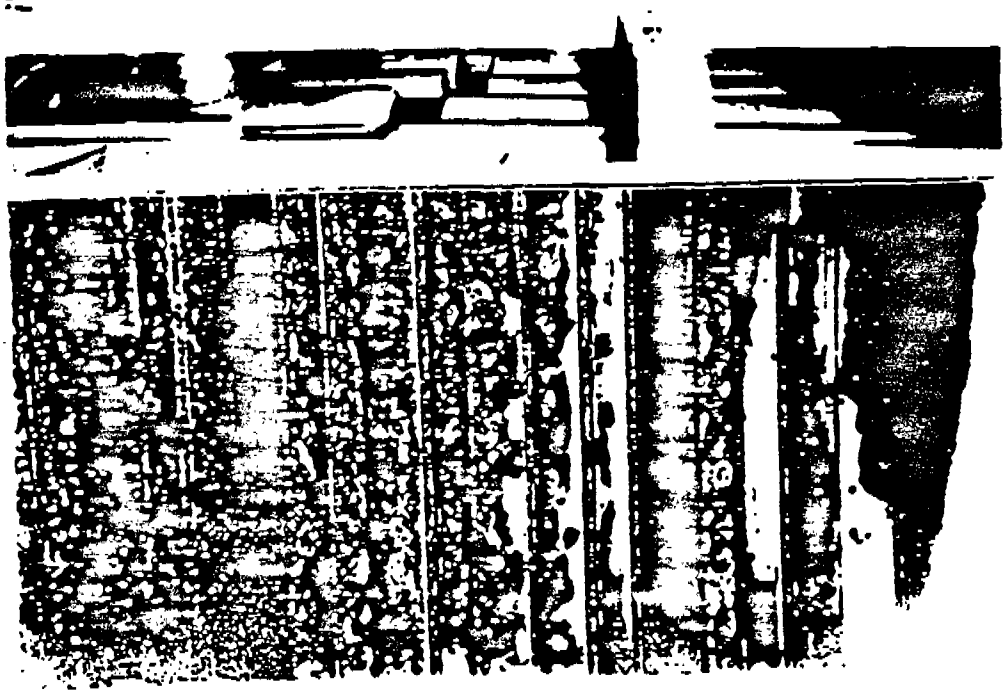

PHOTO 3

DEPOSIT 2 ON E 308 S

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