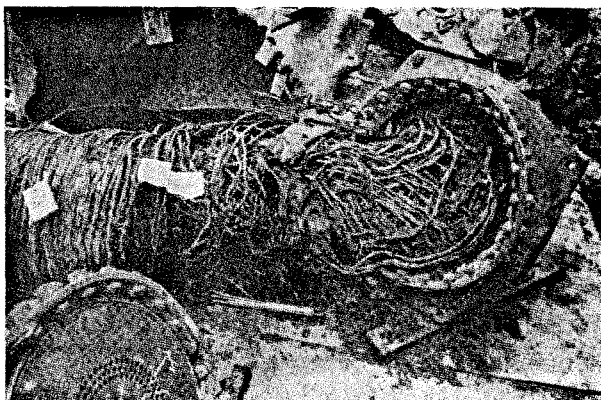# Nitric oxide explosion

Coils of the second heat exchanger damaged by the explosion.

As a result of an incident involving a nitrogen wash unit, an excellent method of removing NO from the gas stream using an adsorbent was developed.

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THERE ARE MANY EXAMPLES OF EX-plosions in the warming step of a liquid nitrogen wash unit or coke oven gas splitter. These explosions usually involve resinous substances. In fact, these substances are apt to decompose and explode mainly in the warming step. However, it is the intention here to show that these substances are also capable of ignition under normal operating conditions.

About six years ago, an explosion occurred in a second heat exchanger of a liquid nitrogen wash unit during normal operation at Kyowa Chemicals, Ltd., Japan; at almost the same time, a similar explosion occurred at Mekog, Holland (1), Table 1. Immediately following the explosion in Japan a thorough investigation was made to discover the cause and means of prevention of such accidents. The investigation committee consisted of the manufacturer of the unit, Kobe Steel, Ltd., the user of the unit, Kyowa Chemicals, Ltd., and, finally, several university specialists.

Process description

The process at Kyowa for producing ammonia synthesis gas at the time of the explosion was as follows: A gaseous mixture was obtained by partial oxidation of crude oil using steam and oxygen. The sulfur compounds in the gas were removed by means of Thylox process and an FeS packed dry chamber, after which the CO was converted. The gas was then compressed in reciprocating compressors to a pressure of 12 kg./sq. cm. gauge (170 lb./sq. in. gauge).

The 10,000 std. cu. m./hr. of gas at 170 lb./sq. in. gauge and ambient temperature was then fed to a water scrubbing tower, where the carbon dioxide was removed, and, subsequently, washed with caustic solution after which 6,700 std. cu. ft./-hr. of gas remained.

The main components of the gas, thus, obtained were 93.0 vol. % of H_2, 4.2% of CO, 1.0% of CH_4, and 1.8% of N_2. This gas then passed into the liquid nitrogen wash unit which consisted of two parallel in-terchangeable precoolers (ambient temperature to $-10°C$), ammonia cooler (-10 to $-40°C$), first heat exchangers (-40 to $-120°C$), second heat exchanger (-120 to $-160°C$), third heat exchanger (-160 to $-180°C$), and then into the CO vaporizer and wash column. Other associated apparatus consisted of an ethylene pool, positioned between the first and second heat exchangers, and a methane pool, positioned at the bottom of the third heat exchanger. The heat exchangers contained vertical tube coils, the incoming gas passing through the space around the tubes.

The explosion unexpectedly occurred in the second heat exchanger during normal operation in the temperature range of -100 to $-180°C$.

Explosion damage

At the bottom of the second heat exchanger, each 8/10 mm. (0.32/0.4 in.) copper tube in the tube coils was crushed by a high external pressure, Introductory Figure. The bottom of the exchanger, a round brass plate 60 mm. (2.4 in.) thick and 610 mm. (2 ft.) in diameter, was domed outwards. The shell of the exchanger was cut off into two parts, a part opened outwards along the welded seams and another torn off.
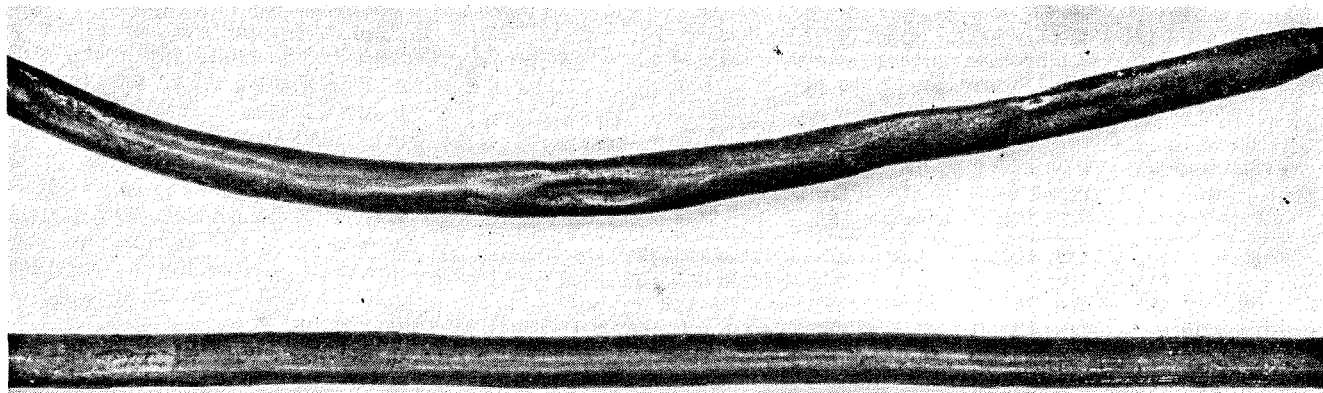
A calculation made by an explo-

Figure 1. Copper tube crushed by the explosive power of the reaction between 1,3-butadiene and oxides of nitrogen.

sives expert indicated that the tubes had experienced pressures of 70 to 450 kg./sq. cm. (1,000 to 6,400 lb./sq. in.) minimum. These facts show that 5 to 7 kg. (11 to 15.4 lb.) of solid explosives had accumulated around the tube coils and at the bottom of the second heat exchanger.

Investigations were made to confirm the possible causes of the explosion, and it was found that oxides of nitrogen and dienes in the gas had caused the explosion.

Analyzing for hydrocarbons

It was assumed that the hydrocarbons which existed in the gas in parts per million to parts per billion concentrations played an important role in the cause of the explosion. At the time of the explosion, in 1959, it was a difficult problem for us to analyze hydrocarbons existing in such low concentrations. After studying how to analyze them quantitatively, a suitable method was found. The principle of this analytical method being as follows (2): While sample gas was passed through a glass tube in-which small particles of fire brick (40 to 60 mesh in size) were packed at the temperature of liquid O_2 ($-183°C$), the small content of hydrocarbons in the gas could be completely collected on the surface of the fire brick. In order to analyze 1 ppb (0.001 ppm) of hydrocarbons, for example, 40 to 60 l. of sample gas was required. After this process, the hydrocarbons collected were warmed to room temperature and introduced along with pure H_2 into

Table 1. Plant conditions at the explosion time.

	KYOWA N₂ WASH UNIT		MEKOG** N₂ WASH UNIT
Gas load, std. cu. m./hr.	6,700		10,500
Pressure, kg./sq. cm. gauge	12		16
Gas impurities			
NO, ppm	0.2–0.8 max 1.8		0.1–0.5 max 0.8
O_2, %	0.3		0.1
C_2H_4, ppm	50–100 max 400		1–7
C_3H_6, ppm	2–3		<0.5
C_2H_2, ppm	1–3		0.01
1,3-C_4H_6, ppm	[0.1–0.3]*		0.01
Allene, ppm	0.1–0.2		—
Unsaturated C_4-C_6	0.1–0.2		—
Saturated C-H, excl. CH_4, ppm	3–6		2–7
N_2O	—		Present
Max. NO load, g.	Unit 1	Destroyed unit	
Before explosion	2,300	5,600	5,000
After explosion	1,000	1,000	1,000

*1,3-Butadiene content in the bracket was obtained when NO content was 0.005 to 0.01 ppm. It had been less than 0.01 ppm when NO content had been 0.2 to 0.8 ppm.
**An explosion occurred at Mekog, Holland (1). The situation at the explosion time was quite similar to that of Kyowa.

Table 2. Distribution of gas impurities.

COMPONENTS	BEFORE CO CONVERTER, PPM	BEFORE 1ST HEAT EXCHANGER, PPM	AFTER 2ND HEAT EXCHANGER, PPM	IN ETHYLENE POOL, VOL. %
C_2H_4	25–150	50–100 max 400	0.1–1 max 30	80–85
C_2H_6	2–5	2–5	0.2–0.5	2–3
C_3H_6	1–2	2–3	0.1–0.3	5–6
C_3H_8	0.2–0.5	0.5–1	0.05–0.1	0.1–0.3
C_4H_{10}	—	0.02–0.04	<0.001	0.01–0.02
Butenes	—	0.2–0.4	0.001–0.1	0.1–0.3
Pentenes	—	0.02–0.04	<0.001	0.01–0.03
C_2H_2	30–50	2–3	0.001–0.02	2–3
1,3·C_4H_6	—	0.1–0.5	0.01–0.05	0.05–0.03
Allene	—	0.2–0.3	0.01–0.05	0.1–0.2
O_2*	100	0.2–0.3% (100 ppm)	0.2–0.3% (100 ppm)	0.1–0.5 (0.01–0.05)
NO*	0.005	0.4–0.5 (0.02–0.08)	0.005 (0.005)	0.01–0.02

*Before 1962, when Kyowa employed a scrubbing method with As_2O_3 solution for CO_2 removal, O_2 and NO had originated in the CO_2 scrubbing water (8).
The values in the bracket indicate the contents obtained after employing the new process.

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a gas chromatograph, having D.M.S. as its stationary phase. A trouble with this method was that dienes could not be detected when NO and O_2 coexisted with them in the sample gas. However, one succeeded in analyzing for them by using an adsorbent of NO, one which could only remove NO from the sample gas. The details of the adsorbent will be described later.

With this analytical method, the distribution of the hydrocarbons in the process was checked, as indicated in Table 2. It was found that dangerous components such as acetylene, 1,3-butadiene and allene existed in the crude gas in the order of 2 to 3 ppm, 0.2 to 0.5 ppm, and 0.2 to 0.3 ppm, respectively. It was confirmed that 60 to 90% of these components were deposited in the second heat exchanger (—100 to —160°C). These data are quite in accord with the calculation based upon the vapor-liquid equilibria relation of A. Toyama, et al. (8).

Analyzing for NO

No reliable analytical method could be found for detecting NO, especially at concentrations in the order of 0.005 to 1 ppm. In Japan, a committee consisting of representatives from 13 major fertilizer manufacturing companies was formed to study the analytical method for detecting NO in low concentrations. The principle, of the method adopted, was that NO was to be first oxidized with permanganate and sulfuric acid and then detected calorimetrically with the Griess-Saltzman reagent (3, 4). This method was thoroughly examined in the concentrations between 0.005 to 1 ppm of NO, after which a modified method (5) was introduced. It was to be employed by most organizations in Japan.

With this method, the distributions of NO in the process was checked. It was found that more than 90% of NO entered the unit accumulated in the second heat exchanger, as shown in Table 2, and most of the NO was oxidized to NO_2 or N_2O_3, which is much more reactive with hydrocarbons than NO.

Reactions studied

In order to confirm the possibility of the spontaneous ignition in the second exchanger, a series of experiments were carried out. These included the following:
1. The reacting phenomena between unsaturated hydrocarbons found in the gas and oxides of nitrogen at low temperatures.
2. The possibility of their igniting and exploding.
3. The explosive power of the reaction products.

Oxides of nitrogen used in this study were nitric oxide (NO), nitrogen dioxide (NO_2), and the mixture of nitric oxide and oxygen. Hydrocarbons used were ethylene, propylene, α-butylene, acetylene, pro-

Table 3. Reaction between hydrocarbons and oxides of nitrogen at low temperatures.

KINDS OF HYDROCARBONS AND AMOUNT, G.	KINDS OF OXIDES OF NITROGEN	AMOUNT OF NO OR NO_2, G.	RE-ACTION TIME, HR.	REACTION TEMP., °C	EXIST-ENCE OF IGNI-TION	IGNITION TEMP., °C
Ethylene (0.5)	1%NO	1.2	10	−160 to −180	No	
(3.0)	1%NO_2	6.2	96	−120 to −140	No	
(2.0)	1%NO_2	0.8	120	−183	No	
(5.0)	1%NO+1%O_2	2.8	48	−120 to −160	No	
(10.0)	1%NO+1%O_2	4.4	72	−120 to −160	No	
Propylene						
(2.0)	1%NO_2	2.5	4	−120 to −130	No	
(1.0)	1%NO_2	4.9	8	−150 to −160	No	
α-Butylene						
(2.0)	1%NO_2	0.8	4	−180	No	
(2.0)	1%NO_2	4.9	8	−140 to −150	No	
Propadiene						
(0.5)	1%NO_2	2.5	4	−140 to −160	Yes	+40
(1.0)	1%NO_2	3.2	8	−130 to −140	No	
(1.0)	1%NO_2	4.9	24	−120 to −160	No	
Acetylene						
(2.0)	1%NO_2	3.0	5	−150 to −180	No	
(3.0)	1%NO_2	4.8	8	−170 to −180	Yes	+50
(4.0)	1%NO_2	6.0	10	−120 to −180	Yes	+30
Cyclopentadiene						
(1.5–2.5)	1%NO_2	0.4	2	−145 to −155	Yes	−105
(1.5–2.5)	1%NO_2	0.6	2.5	−140 to −150	Yes	−35
1,3-Butadiene						
(1.0)	1%NO	0.4	2	−130 to −150	No	
(1.0)	1%NO	0.6	3	−130 to −150	No	
(1.0)	1%NO	0.6	3	−130 to −150	No	
(1.0)	1%NO_2	0.3	1.5	−140 to −150	Yes	−115
(1.0)	1%NO_2	0.6	2.5	−140 to −150	Yes	−80
(1.0)	1%NO_2	0.4	14	−140 to −150	Yes	−110
(5.0)	0.009%NO_2	0.13	12	−110 to −120	Yes	−90
(1.0)	1%NO_2	5.5	72	−120 to −130	Yes	−115
(1.0)	1%NO+1%O_2	0.6	3	−160 to −170	Yes	−90
Ethylene+ 1,3-Butadiene						
(5+5)	1%NO+1%O_2	2.9	72	−120 to −140	Yes	−40, +70
(10+1)	1%NO+1%O_2	2.9	144	−140 to −160	Yes	−48, +70 to +90
(10+0.1)	1%NO+1%O_2	2.9	96	−160 to −170	Yes	−50, +70, +115
(10+1)	1%NO+1%O_2	30.0	144	−140 to −160	Yes	−105, +68
(10+0.1)	1%NO+1%O_2	30.0	144	−130 to −150	Yes	−102, +90

Table 4. Composition of reaction products between oxides of nitrogen and conjugated dienes.

MOLECULE	ANALYZED AT KYOWA	ANALYZED AT KOBE	ANALYZED (6) BY PIERRAIN	ANALYZED (7) BY HOLLINGS
C	20 – 38	24 – 60	26 – 60	26 – 70
H_2	4 – 6	4 – 6	4 – 6	4 – 9
N_2	5 – 11	2 – 6	4 – 8	3 – 10
O_2	30 – 50	20 – 40	20 – 40	12 – 35
Ash	13 – 25	0 – 20	0 – 50	0 – 31
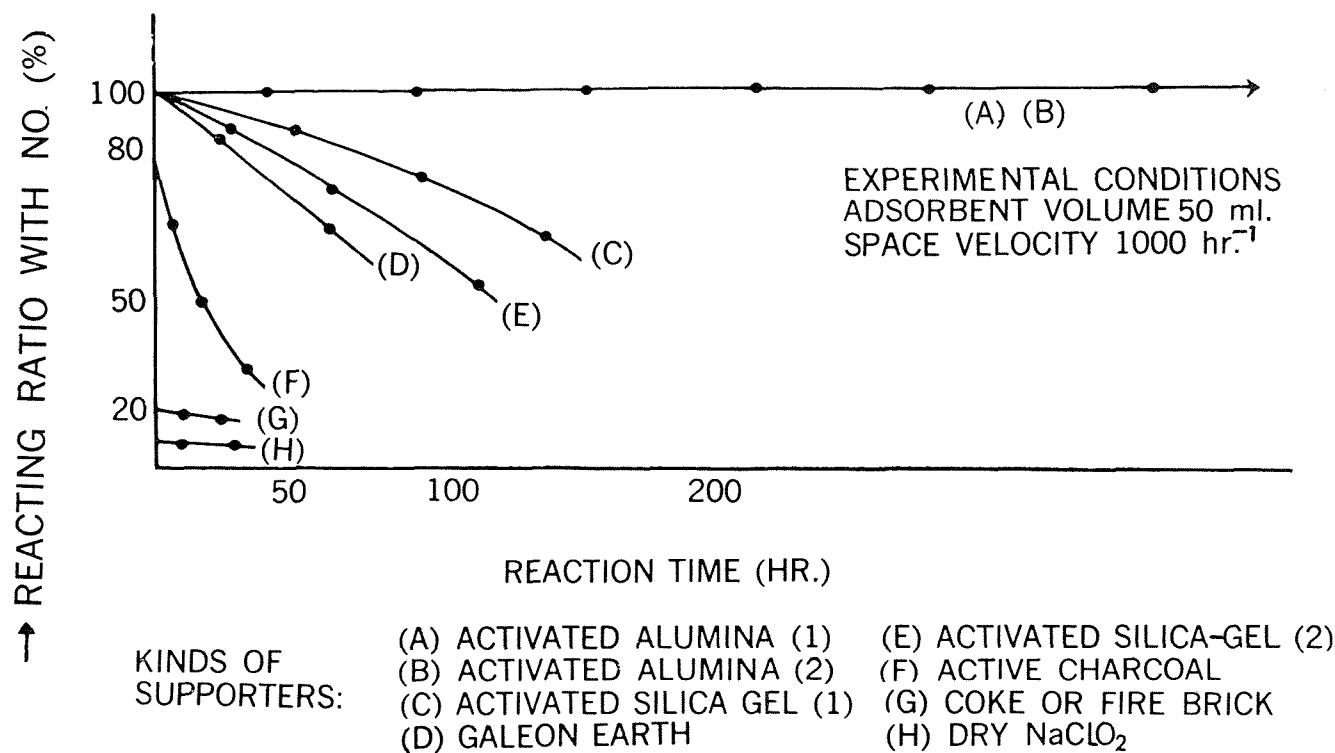
Figure 2. Comparison of the reaction ratio with NO using different supports.

EXPERIMENTAL CONDITIONS
ADSORBENT VOLUME 50 ml.
SPACE VELOCITY 1000 hr.$^{-1}$

KINDS OF SUPPORTERS:

(A) ACTIVATED ALUMINA (1)
(B) ACTIVATED ALUMINA (2)
(C) ACTIVATED SILICA GEL (1)
(D) GALEON EARTH
(E) ACTIVATED SILICA-GEL (2)
(F) ACTIVE CHARCOAL
(G) COKE OR FIRE BRICK
(H) DRY $NaClO_2$

REMARKS:
(A) $NaClO_2$ + NaOH OR Na_2CO_3 SUPPORTED ON Al_2O_3
(B) $NaClO_2$ SUPPORTED Al_2O_3
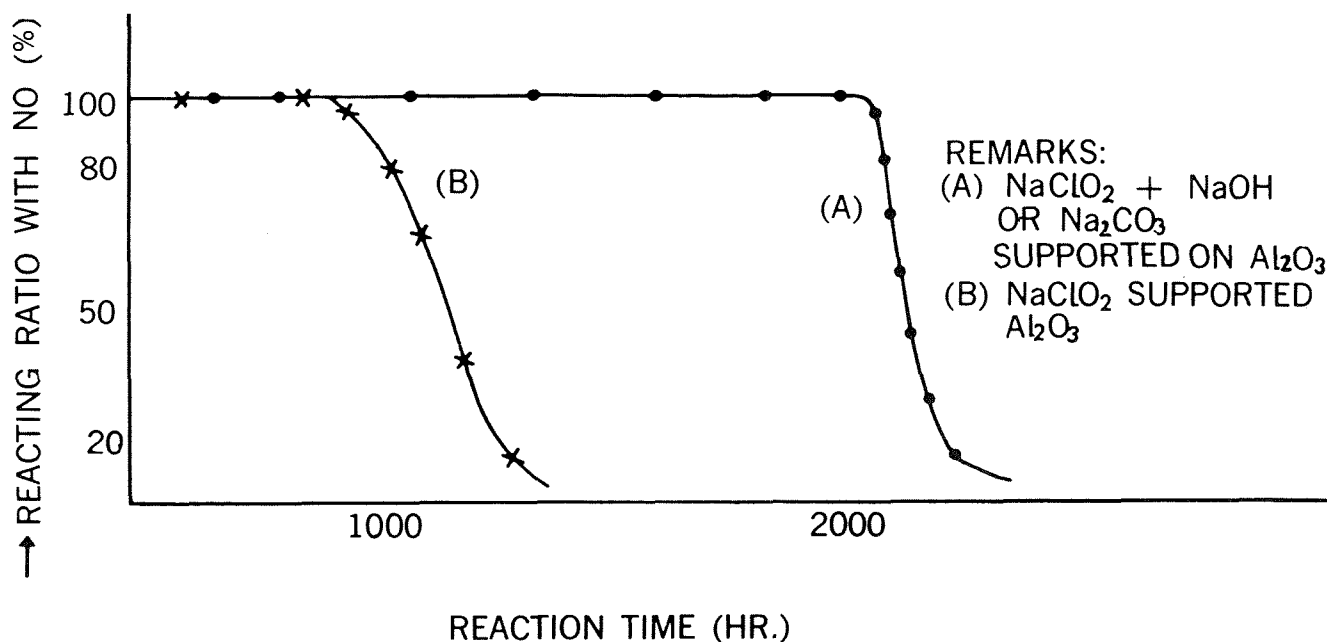
Figure 3. Adsorptivity of NO.

padiene, 1,3-butadiene, and cyclopentadiene, Table 3.

The reactions were carried out primarily in the temperature range of −180 to −100°C. The reaction products were gradually warmed up to +200°C at atmospheric pressure.

The results, summerized in Table 3, showed that unstable nitro or nitroso compounds could be formed in the temperature range of −180 to −100°C when NO_2 or N_2O_3 re-

acted with the conjugated dienes and that the compounds were apt to ignite or explode spontaneously in the temperature range of −115 to −50°C. It was also confirmed that ignition became more intense and that ignition temperature decreased when NO_2 or N_2O_3 existed in larger quantities than that of the hydrocarbons and that the explosive power of the reaction products was as powerful as that of

TNT, Figure 1.

On the other hand, it was noticed that the reaction velocity between mono-olefins, propadiene or acetylene and oxides of nitrogen was very slow and that ignition was not possible below 0°C.

In order to confirm whether nitrogen oxides reacted with 1,3-butadiene in the second heat exchanger and in the ethylene pool, attempts were made to analyze the

Table 5. Effects of other components.

COMPONENTS REACTIVE WITH THE ADSORBENT

COMPONENTS	REACTING RATIO, (%)
NO	100
NO_2	100
H_2S	100
SO_2	100

COMPONENTS NON-REACTIVE WITH THE ADSORBENT

H_2O (vapor), O_2, N_2, CO, CH_4, CO_2, CS_2, NH_3,
C_2H_5, C_2H_4, C_2H_2, C_3H_8, C_3H_6
C_4H_{10} (n-C_4H_{10}, iso-C_4H_{10})
C_4H_8 (n-C_4H_8, iso-C_4H_8, cis-C_4H_8, trans-2-C_4H_8)
1,3-C_4H_6, C_5H_{12} (n-C_5H_{12}, iso-C_5H_{12})
C_5H_{14}, C_6H_6

Table 6. Operational data of pilot plant.

Volume of adsorbent, l.	1
Gas volume treated, std. cu. m.	34,990
Period of operation, days	372
Temperature, °C	20–35
Pressure, kg./sq. cm. gauge	12
Gas compon-ents	As shown in Table 1 and 2
Plus CO_2	1–5 ppm
NO 0.04–0.08 ppm	
SO_2 H_2S	<0.1

reaction products which were extracted from 8% NaOH solution used for washing the unit. The result is shown in Table 4, which indicates the clear evidence of the formation of the reaction products between nitrogen oxides and conjugated dienes.

Preventing explosions

The following steps were taken to prevent further explosions:

1. Preventive chemicals, such as $Na_2Cr_2O_7$ or Cl_2 gas, were used in the CO_2 wash water circuit, in order to eliminate NO. However, Kyowa found that this caused inconveniences in their daily routine and so employed a scrubbing method with As_2O_3 solution in 1962, which replaced the water scrubbing circuit for the removal of CO_2. The NO content decreased to 0.02 to 0.06 ppm, which still originated in caustic solution tower. (In the CO_2 wash water, extremely small quantity of NO_2^- and NO_3^- ions produce NO by catalytic reduction on the surface of the slime. In the same way, NO can be produced from caustic soda solution used for the removal of small quantity of CO_2. Accordingly NO_2^- and NO_3^- free chemicals should be used for the CO_2 scrubbing circuit (8).

2. The NO content was analyzed once daily.
3. The unit was to be cleaned with caustic solution when 1,000 l. of NO were accumulated in it.

NO adsorption

No further explosions have been experienced since the 1959 accidents. However, the above-mentioned measures cannot be said to be the final solution for the removal of NO, which is the most dangerous factor, if present in any amount.

Several methods exist for the removal of NO from oil cracked gas or coke oven gas. However, all of them have some disadvantages; for example, a catalytic method requires large heat exchangers to warm the gas stream and catalyst bed, and scrubbing systems require high construction costs. To overcome these disadvantages, an attempt was made to discover a chemical adsorbent to remove NO at ambient temperature and with easy maintenance.

From 160 kinds of chemicals screened, an excellent adsorbent for NO removal was found. The adsorbent consists of sodium chlorite ($NaClO_2$) and several kinds of alkali, such as NaOH, Na_2CO_3 or K_2CO_3, supported on 4 to 6 mesh activated particles.

Experimental data indicates that dry $NaClO_2$ hardly reacts with NO, but that $NaClO_2$ readily reacts with NO provided that it is supported on activated particles, especially activated aluminas. It was shown that such supports work catalytically for the reaction between $NaClO_2$ and NO, Figure 2. In addition, it was found that alkalies worked as a stabilizer on their reaction to produce a longer working life, Figure 3.

With this adsorbent, NO existing in oil cracked gas, coke oven gas, or similar gases can be removed almost completely. Laboratory tests indicated that certain other impurities (less than 1 ppm in the gas) were adsorbed by the adsorbent to

shorten its life, however, most of the other components did not affect the life of the adsorbent, as shown in Table 5.
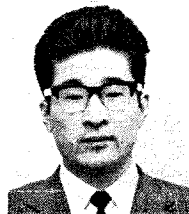
Pilot plant data

In order to test the adsorbent, in actual industrial gas service, a pilot plant was installed at Kyowa Chemical's Ube plant. The pilot plant was positioned at the inlet side of the liquid nitrogen wash unit. The operation of this pilot plant has proved satisfactory for 372 days. At the outlet side, NO content was below the limits of detection (less than 0.001 ppm). In addition, harmful components, such as NO_2, ClO_2, or NOCl, were not detected in the outlet gas stream. Operational data are given in Table 6. An additional pilot plant, to test the adsorbent in coke oven gas, is now under construction. #
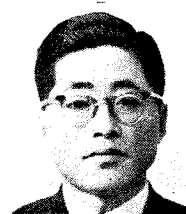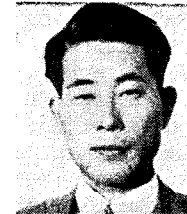
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