ERNST KARWAT *Linde Co.* (Germany)

Hydrocarbon contro **in** air separators

Adsorption at cold end of regenerators is effective; precombustion methods also offer advantages.

AN EXPLOSION IN A LINDE-FRÄNKL apparatus in which the presence of sufficiently large quantities of acetylene was defhitely excluded gave cause for a renewed investigation of the behavior of C_2 and C_3 hydrocarbons in **air** separators. The results showed that primarily C_8H_8 is unaffected by the conventional safety measures and consequently constitutes a potential source of danger.

This article deals with known and

novel safety measures, especially **with** regard to whether C_3H_8 present in the air can be rendered innocuous in the separator or prevented from entering the separator.

What caused the explosion

The explosions occurred **as liquid** 0, was being run off from **the** separator into **a** bucket, resulting in **severe** damage to pieces of electric apparatus and electric switchgear. Somewhat

less violent was the explosion inside the $C₂H₂$ separator which stretched the separator about 11 cm. and destroyed a number of tubes of the auxiliary vaporizer.

For weeks before the explosion, analytical checks of the main condenser O_2 had shown only C_2H_2 contents of a few hundredths ppm. Higher C_2H_2 contents could not be detected at the time of the explosion in a number of air separators operating in the same plant. Hence, there was no doubt that the force of the explosion was attributable to hydrocarbons other than C_2H_2 even though the presence of small quantities of solid $C₂H₂$ acting as a triggering substance did not need to be excluded.

Subsequently, over the course of several weeks, the impurities in the main condenser, in the gaseous O₂, and in the C_2H_2 separator were determined, the values for which are listed in Table 1. There were very small quantities of dissolved hydrocarbons which, in the light of earlier investigations (1) may be regarded as harmless. C_3H_6 and C_2H_2 are practically absent in the main condenser, although the air behind the regenerator and the high-pressure column liquid contained both. In addition, C_2H_6 , C_3H_8 , and C_2H_4 are present.

It is worthy of note that about 40- 80% of the C_2H_6 and C_2H_4 introduced into the auxiliary vaporizer is removed by the gaseous $O₂$. A liquid phase in equilibrium with this gaseous 0, (pressure, 1.1 kg./sq. cm.; content, 2 ppm C₂H₄) should contain about 650 ppm C_2H_4 . The liquid found in the \overline{C}_2H_2 separator, however, contained only 70 ppm C_2H_4 . Apparently this liquid must be regarded as a mixture of C_2H_4 -rich evaporation esidues with C_2H_4 -poor surplus liquid, just as the final content of 2 ppm C_2H_4 for gaseous O_2 may be considered as having emanated from a mixture of gas streams of varying C_2H_4 content.

Propane concentration hazardous

The C_3H_8 content of the gaseous $O₂$ is below the limits of detection. This is understandable, for at the $\frac{1}{\text{saturation}}$ limit (9800 ppm C_3H_8) the tension of the C_sH_s from the saturated solution amounts to only a few

^Ain the **02-rich** liquid of the pressure column.

B in the liquid **0,** of the main condenser. **C** in the gaseous **0,** after the separator. D in the unevaporated surplus liquid of the separator.

Typical oxygen plant of Linde (Germany).

dred times lower over solutions containing only ^{1/2} to 30 ppm C₃H₈. On the other hand, the partial pressures of C_2H_4 and C_2H_6 from their solutions are about 10 to 100 **times** higher.

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In early investigations, **we** tried to judge whether such hydrocarbons are retained in the auxiliary vaporizer by hydrocarbon material balances around the auxiliary vaporizer. We concluded, however, that the sums of all the errors deriving from sampling, gas chromatography, and fluctuations in the hydrocarbon content of the processed air make such calculations unreliable.

Therefore, after operating periods of different lengths, we sealed off the inlet and outlet of the auxiliary vaporizer and then heated its tubes from outside. We subsequently flushed the O_2 evaporating chambers with N_2 , and measured the impurities carried out by the flushing gas. In the case of eight measurements, no C_2H_4 or C_2H_6 could be found but C_8H_8 was always present in varying quantities up to 400 liters. As far as the explosive potential (free energy of combustion) is concerned, such a quantity of C_8H_8 is enough to be considered a hazard. This situation is rendered less serious, however, by the fact that simultaneously there was always present several kg. of $CO₂$ in the auxiliary vaporizer $(1).$

During the tests, surplus liquid in the auxiliary vaporizer amounted to 1% of the quantity of vaporized $O₂$. In no case of such supervised deriming was a large enongh quantity of hydrocarbons found in the auxiliary vaporizer and C_2H_2 separator that the force of the explosion could be explained by their presence alone.

Particularly it could not be proved that the exploded hydrocarbon was C,H,, but investigation had shown hat of all the C_2 and C_3 hydrocarbons only $\rm C_sH_s$ has a tendency to accumulate in the auxiliary vaporizer and C_2H_2 separator. Scarcely any C_3H_6 is present, and the two C_2 hydrocarbons, C_2H_4 and C_2H_6 are comparatively highly volatile.

Hydrocarbon adsorption study

Investigations of adsorption in the liquid and gaseous phases were undertaken to gain an understanding of the basic relationships in order to better consider safety measures. This data supplements earlier measurements of vapor pressure, solubility, and explosiveness of the hydrocarbons $(\overline{1})$.

The load curves of various hydrocarbons in Figure 1 show the standard cu. cm. of a hydrocarbon adsorbed (ordinate) by one gram of widepored silica gel from a liquid-O₂ solution of that hydrocarbon as a function of the concentration in the solution in ppm (abscissa). According to these curves the hydrocarbons are divided mto two groups: in the group of un saturated hydrocarbons $(C_2H_2, C_3H_6,$ and C_2H_4) the adsorptivity varies much less with their concentration in the solution than in the group of the saturated hydrocarbons $(C_3H_8$ and C_2H_6). In the range of concentrations most frequently encountered in practice, namely 0.1 to 5 ppm, wide-pored silica gel takes up almost 1000 times more unsaturated hydrocarbons than C_3H_8 or C_2H_6 .

The load curves in Figure 1 end (in circles) with the maximum adsorptivity of the gel at the saturation point of the solution. At this point the solution, the pure hydrocarbon, and its vapor are in equilibrium with the gel. Hence, at this quadruple point the amount of hydrocarbon adsorbed from the solution is identical with that adsorbed from the gaseous phase. This mdicates that such hydrocarbons, which emerge at the cold end of the regenerator with dew point concentration can be more efficiently ad sorbed there from the gaseous phase than from their solution after total liquefaction, *i.e.*, from the O₂-rich liquid in the high pressure column. From the equilibriums it follows that **.I** layer of gel saturated in contact with the gaseous phase can be desorbed by washing it with pure liquid O_{α} .

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Mixtures influence sorption

In the air separator we always have to deal with hydrocarbon mixtures, not with individual hydrocarbons. Consequently the adsorption of mixtures was subjected to investigations which showed the highly important influence of sorption displacement. Consider a liquid- O_2 solution of a mixture of 40 ppm each of C_2H_6 , C_2H_4 , C_3H_8 , and \widetilde{C}_3H_6 passed over gel until the same mixture passed out the exit side. When the gel was desorbed, the components of the mixture were not in proportion to their adsorbability as shown in Figure 1, but in entirely different proportions: 83% $\mathrm{C_3H_6}$, 10% C_2H_4 , 5% C_3H_8 , and 2% C_2H_6 . The C_3H_6 has practically completely prevented the adsorption of C_2H_6 , very much restricted the adsorption of C,H,, and considerably impaired the adsorption of C_2H_4 .

We have also investigated the interaction of the hydrocarbons with the constantly present air impurities N_2O and $CO₂$, both during the equilibrium measurements and with respect to the break through of the various substances. From these studies we could understand the observations made during the practical operation of the $C₂H₂$ adsorber of an air separator.

The first C_2H_6 passes through a freshly regenerated C_2H_2 adsorber only 15 min. after being put into operation. Propane is found from 30 to **45** min. later in the main condenser, and from this point onwards all the fluctuations of the C_3H_8 content in the O_2 -rich liquid of the pressure column are encountered half an hour later in the main condenser.

 $10¹$

Figure 2 shows the concentration of C_3H_8 in the enriched liquid air of the high pressure column and in the main condenser. Hills and valleys of the two lines follow each other in **k-hr.** distance. The increase in C_2H_4 behind the adsorber takes somewhat longer than that of C_3H_8 , but it also ended long before the first traces of C_2H_2 and C_3H_6 breaking through make it advisable to change the adsorber.

In the gas-phase adsorption of the various hydrocarbons, the usual phenomena are encountered: extensive independence of the gel's adsorptivity for a hydrocarbon on temperature and pressure along the hydrocarbon's vapor pressure curve *(i.e.,* at its dew point), but marked diminution of the gel's adsorptivity when the temperature is raised above dew point temperature while maintaining a constant partial pressure. The sequence in which **the** hydrocarbons displace each other from the gel is somewhat different from that observed in the case of liquidphase adsorption. Here, too, \hat{C}_2H_6 passes from the adsorber most **quickly,** and then is followed by $C_2\overline{H}_4$ and carbonic acid, and then by C_3H_8 .

The various substances according to the degree of adhesion with which they are bound by the gel and the sequence of their break-through **for** liquid-phase adsorption are as follows:

$$
C^{}_z H^{}_z\!\!-\!C^{}_s H^{}_6\!\!-\!\!C O^{}_z\!\! <\!\! \sum\limits_{C^{}_z H^{}_4\! >\! C^{}_s H^{}_s
$$

 $-C₂H₆$ (first to break-through)

For gas phase adsorption, these are as follows:

$$
\begin{array}{c} \mathrm{C_{3}H_{6}} \\ \mathrm{C_{2}H_{2}} \end{array} > \mathrm{C_{3}H_{8}-N_{2}O-C_{2}H_{4}-} \\ \mathrm{C_{2}H_{6}} \overset{\text{}}{\longrightarrow} \mathrm{CO_{2}} \overset{\text{}}{\longrightarrow}
$$

It is remarkable that in gas-phase adsorption C_3H_8 relative to other hydrocarbons is bound stronger than **in** liquid-phase adsorption.

Evaluation of safety methods

¹We tried to evaluate various **safety** measures, some of known and some of a novel nature, particularly with re-I gard to C,H,. Focussing attention **on** $\mathrm{\bar{C}_3H_8}$ does not mean we classify it as the number two enemy behind C_2H_2 . The free energies of combustion and the destructive power of explosive oxidation reactions of both do not differ
greatly. However, there is a great difference in spontaneity of self-decom-

 N_2 ^O

Figure 1. Adsorption of various hydrocarbons dissolved in liquid oxygen on wide-pored silica gel.

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position, which renders the explosionprobability (1) of C_3H_8 less than that of C_2H_2 (provided that no C_2H_2 is admixed to the C_3H_8). On the other side, the lower adsorbability in gaseous or dissolved state of \dot{C}_3H_8 compared to C_sH_s and its lower fugacity compared to C_2H_4 and C_2H_6 compel us to classify C_3H_8 as more dangerous than the C_2 -hydrocarbons. In our opinion, it would be best to keep C_sH_s away from O_2 -rich liquids.

It is of interest to compare the safety properties of C_4H_{10} with those of C_3H_3 . The vapor pressure of C_4H_{10} is only 1% and the solubility in liquid
O₂ only 2% of those of C_3H_8 . The adsorbabilites are nearly the same. It
adsorbabilites are nearly the same. It is only 1% and the solubility in liquid O₂ only 2% of those of C_3H_8 . The adsorbabilites are nearly the same. It enters the rectification set-up mainly by entrainment. We classify C_4H_{10} in the same class as C_3H_8 relating to its safe handling.

The safety measures we tried to evaluate are as follows:

Method **1.** Intensified flushing of the auxiliary vaporizer with surplus liquid prevents the accumulation of vaporization residues. When the surplus amounts to *2%* of the 0, output it becomes necessary to recycle the liquid surplus through an adsorber to avoid impermissible refrigeration losses. A properly functioning C_2H_2 adsorber retains C_2H_2 and \breve{C}_3H_6 almost completely, thus the circulating liquid contains chiefly C_2H_4 , C_2H_6 , and C_3H_8 . The conditions for adsorption in the circulation-type adsorber are favorable since the concentrations of the hydrocarbons in question have increased due to the preceding boiling of the liquid $O₂$ in the auxiliary vaporizer or are raised by the circulation. As can be seen from Figure 1, the adsorptivity of the gel increases with the concentration of C_3H_8 . As a result of sorption displacement, $C.H₆$ breaks through fairly quickly, C₃H₈ concentration rises slowly, and C_2H_4 does not break through until near the end of the adsorbers period of operation. With an ample circulation of liquid, such a system gives improved safety in the auxiliary vaporizer and the separator.

Method **2.** Removing hydrocarbons from the air before the high pressure column by washing with small quantjties of liquefied air was evaluated. The high solubility of C_2H_6 , C_2H_4 , and $C₃$ -hydrocarbon (3000 to 120,000 ppm) allows limiting the quantity of washing agent to 0.2% of total air throughput. The washing liquid can be vaporized without risk over hot water outside the separator with sacrifice of its refrigeration value. If pre-washing is ntended to prevent C_2H_2 from entering the rectification columns, the

pressure column and in the liquid oxygen of the main condenser.

theoretical minimum quantity of washing agent is about 4% of air throughput. If the air is saturated with C_2H_2 behind the regenerator, the quantity of washing agent will have to be at least doubled to avoid saturated $C₂H₂$ solutions. The cold content of such a large quantity of liquid cannot be sacrificed.

The liquid must be purified with an adsorber which would contain roughly about 75% of the quantity of gel used in the usual C_2H_2 adsorber for the high pressure column liquid. C_2H_6 , $C_3\breve{H}_8$, and C_2H_4 will break through just as quickly as in the customary adsorber. On the whole, pre-washing presumably would not increase safety as compared with the usual adsorption between the highand low-pressure columns.

Better methods needed

A disadvantage of the first two

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"Diplom-Ingenieur"

and "Doktor-Ingeni-
eur" as a physical
chemist in 1920 and 1923 from the Technische Hoch-

schule, Breslau,
Silesia. He joined paqment of the German Linde Corp. and became Head of the Department in **1939.** He has worked on basic scientific problems as well as develop- mental work in the fields of low and methods is that all the fluctuations in the hydrocarbon content of the air, especially its content of C_2 hydrocarbons and C_3H_8 (the fluctuations in the content of C_2H_2 and C_3H_6 are damped by the acetylene adsorber), would markedly show in the main condenser, the vaporizer, and adsorber cycle. The frequent variations in analytical findings would probably make supervision rather difficult.

In the trend of technological development O₂ plants will soon be automated, and then the measures taken relative to hydrocarbons in air separators will have to be such that hydrocarbons, with the exception of CH, and C_2H_6 , are no longer encountered where there are liquid, O_2 -rich mixtures. This requirement is not satisfied by the two safety measures described.

Method **3.** Hydrocarbons can be removed more effectively with an adsorber located in the gaseous phase between regenerator and pressure column. In gas-phase adsorption the gel extracts a large multiple of the hydrocarbons removed by adsorption in the liquid phase. The identical concentrations of 0.2 ppm C_3H_8 in gaseous air or 0.4 ppm in O₂-rich liquid air are in equilibrium either with a load of 50 cu. cm. or **0.04** cu. cm. C,H,/gin. of silica gel, or about thousand times more in the case of gas-phase adsorption.

An adsorber for the air behind the high temperatures, in the use of oxy- regenerator will have a fairly large gen for metallurgical and gasification cross section and also a large quantity processes. Since 1956 he has been working with the A.I.Ch.E. Committee of gel. It gives excellent protection on safety problems in air and amm on safety problems in air and ammonia against penetration of $C_2\tilde{H}_2$, C_3H_6 , plants. and also C_3H_8 . The C_2H_6 breaks

figure 3. Temperature curve in the re- generator with a gel layer.

through after a short time, and the $\mathbb{C}_2\mathbb{H}_4$ a little later. Operational periods of several months can be achieved up to the break-through of C_3H_8 and even longer periods for C_2H_2 and C_3H_6 .

Method 4. The most effective way of removing all air impurities is by gel layers located near the cold end of the regenerators (2). The impurities adsorbed from the air during the warm period are taken up during the cold period by the stream of N_2 passing over the gel. This method of egenerative adsorption and desorption was investigated in the laboratory and in full-scale tests. The chief measuremepts on the full-scale regenerator concerned the thermal variations resulting from the introduction of gel, while chemically, only the adsorption and desorption of $CO₂$ was observed. The laboratory measurements dealt with the behavior of the hydrocarbons.

In the regenerator, the gel layer achieves equilibrium with the pressurized air during the warm period and with the stream of N_2 during the cold period. In the warm period, an O_2 -rich O_2 -N₂ mixture is taken up **hv** the gel, this mixture being given off again when the pressure is reduced and during the ensuing cold period. The respective quantities of adsorption and desorption heat are distributed between the gel and the gas. lleat taken up after leaving the gel laver is given off by the air to the filling mass, and from there it is taken up again by the recycled N_2 ,

thus compensating for part of the desorption heat which causes the N_2 to be cooled over the gel. These are the reasons why the temperature curve in the regenerator at the gel layer is S-shaped, Figure 3. An appropriate S-shaped, Figure 3. An appropriate separator should reduce the C_3H_8 to quantity of heat storing material must 0.02 ppm (10% of the concentration quantity of heat storing material must 0.02 ppm (10% of the concentration
be placed adjacent to the gel layer that would pass through the cold end be placed adjacent to the gel layer that would pass through the cold end for the exchange of adsorption and of the regenerators). This requirement for the exchange of adsorption and of the regenerators). This requirement desorption heat. The quantity of O_2 is high, but is possible if the initial desorption heat. The quantity of O_2 is high, but is possible if the initial taken up by the gel and given off content of C_3H_8 in the air does not to the N_2 stream amounts to about 0.5 to 0.75% of the production.

carbons in regenerative adsorption and 50 to 100°C higher than usual for the desorption, air at a pressure of 5 atm.; combustion of C_2H_2 , C_3H_6 , and C_2H_4 . a temperature of 100° K; and contain-
ing about 1 ppm C_2H_2 , 1 ppm C_2H_3 , changers for outlet and inlet air can 0.3 ppm C_3H_s , 0.7 ppm C_2H_s , and a be built cheaply enough. surplus of CO₂ was passed over a layer A great advantage of the precom-
of alumina gel or sovabeds in one bustion method would be that the of alumina gel or sovabeds in one bustion method would be that the direction for a period of 15 min. Sub-
air separation processes could be subdirection for a period of 15 min. Sub- air separation processes could be sub-
sequently the same quantity by weight iected to changes in gas and liquid sequently the same quantity by weight jected to changes in gas and liquid of pure N_2 at the same temperature flow to obtain desired results, without and about atmospheric pressure was passed over in the opposite direction. passed over in the opposite direction. in each case. The safety measures dis-
These operations were repeated alter-cussed under previous methods do not nately over the course of several weeks. The air remained practically free from hydrocarbons. The hydro- LITERATURE CITED carbons, with the exception of small $\frac{1}{1}$, $\frac{1}{1}$ carbons, with the exception of small
amounts of C_2H_2 , were found in the
recycled N_2 . We concluded from these 2. German Patents 533, 277, and 534, 555, on
experiments that it is possible by this
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and 837 , experiments that it is possible by this

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LOW TEMPERATURE s method to achieve maximum possible

purification of the air in full-scale plants.

Method 5. Total combustion of the hydrocarbons before the air enters the content of C_3H_8 in the air does not exceed 10 ppm.

5 to 0.75% of the production. \qquad If the bulk of the C₂H₆ is to be con-
To check the behavior of the hydro-verted, the temperature must be set To check the behavior of the hydro-verted, the temperature must be set carbons in regenerative adsorption and 50 to 100° C higher than usual for the combustion of \check{C}_2H_2 , C_3H_6 , and C_2H_4 .
This will not be difficult if heat exing about 1 ppm C,H,, 1 ppm **C,H,,** changers for outlet and inlet air can

> flow to obtain desired results, without having to devise new safety measures cussed under previous methods do not fulfill this requirement.

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6. T. WRIGHT Dominion Foundries *and* Steel *Ltd.* **(Canada)**

Oxygen plant vaporizer explosion

An analysis of the causes led to plant changes for improving safe operation.

Hrai PURITY OXYGEN SUPPLIED by three units with a total capacity of 350 tons/day is required by the Dominion Foundries and Steel, Ltd. for producing steel. At 8:10 P.M., September 30, 1959, the vaporizer in No. **2** unit exploded, wrecking the vaporizer and surrounding parts of the cold box, Figures 1 and 2. No one was injured and production loss was minimized because the No. **3** spare 150 ton unit had gone on stream three weeks earlier.

Plant description

The No. 2 plant is a 100 ton/day

split cycle-type. The intake **air** is filtered through a 10-ply paper filter and then compressed to 75 Ib./sq. in. gauge in a turbo compressor. It is water scrubbed to remove soluble impurities. Two thirds of this air passes through aluminum-filled regenerators, then into the high pressure column. The rest of the air is compressed to 350-550 Ib./sq. in. gauge, goes through caustic scrubbers, heat exchangers, then through an expansion engine, and into the high pressure column. Rich liquid, produced in the high pressure column, then passes through silica-gel filters into the low

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