At the Oxygen Plant Safety Conference held in connection with A.I.Ch.E.'s Boston Annual Meeting, E. Karwat of The Linde Co., Munich, Germany, read a statement which is the basis for the following communication.

OXYGEN PLANT SAFETY

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Gesellschaft für Linde's Eismaschinen A. G. wishes to express to A.I. Ch.E. its appreciation for the opportunity to inform the chemical engineering profession about some of the experiences we have had in the field of safety involving almost 1,200 air separation plants of the tubular heat exchanger type and of almost 200 tonnage oxygen plants of the regenerator type.

I would like to open this discussion of hazards with comments on whether acetylene in solid state is particularly hazardous. A statement to the effect that it is not dangerous has appeared recently (1). Our opinion is that solid acetylene suspended in liquid oxygen exists in a high state of instability. Surely, the suspension in the violently boiling liquid is distributed in minute-sized crystals. In such cases (and we believe this happens quite frequently) one or another of such crystals may react with oxygen. Such small occurrences need not necessarily affect all floating crystals. Experiments, however, have shown that if with such a suspension there is introduced a strong initiating impact, e.g., by the explosive reaction of some tenths of a gram of solid acetylene or by the detonation of a primer cap, then all suspended little crystals will explode.

During a standstill, single crystals accumulate to greater bulks. This may happen in the upper part, in the middle section, or in the lower part of a vessel, according to the degree of admixture of solid CO_2 and the adherence of gas bubbles. Each particle reaction of a little crystal will then affect the whole bulk of the acetylene and become an explosion. We have observed that the explosion of 100 grams of solid acetylene with liquid oxygen smashes heavy thick-walled vessels.

In addition, we have come to regard with suspicion even dilute solutions of acetylene in liquid oxygen which are free from crystals. For, just as the boiling of a salt-solution creates a ring of crystals on the heated wall of the container, it is likewise possible that acetylene crystals will gradually deposit on surfaces where the boiling oxygen only periodically comes into contact with parts of the nitrogen condenser tube surfaces. These acetylene crystals will from time to time be wetted by liquid oxygen, with thin films remaining on their surfaces, and it is in just this state that a stoichiometric-explosive reaction will, as observed, most easily occur. Prior to the use of acetylene adsorbers, we occasionally observed accidents where every tube in the nest in the main condenser was demolished by acetylene explosions at exactly the height of the liquid level.

Causative Agents Most Important

In discussing explosion hazards, we believe it important to focus more attention on the causative agents providing the explosive medium rather than on the mechanism that serves to trigger or initiate the explosion to take place. A causative agent would be an explosive material, e.g., acetylene or butylene. Triggering or initiating effects can be manifold: mechanical influences, jerky evaporation after periods of standstill, formation of sparks caused by electrostatic charging, drying up of solutions in cavities, diminutive primary-ignitions, and finally the presence of specifically reactive substances which have likewise been referred to (1), such as radicals, nitrosates, and ozone. We are also of the opinion that their number is so great that, after having explored 20 different initiating effects, no one could be sure whether there would not be another still undiscovered.

Approaching the problem on the basis of initiating effects means then that there is no safety. Safety, however, is to be had when the explosive causative agents are eliminated and when unstable explosive materials are removed until only a harmless amount remains. Therefore, we attach great importance to achieving possibly complete removal of acetylene as the most unstable of all hydrocarbons—without disregarding other substances explosive with oxygen, such as hydrocarbons condensing in solid form (e.g. propane, butane, and in addition, hydrogen sulphide and carbon oxysulfide). The explosive limit of ozone in liquid oxygen is about 18 per cent by volume. As an explosive material by itself in air separation plants, therefore, ozone is out of question, although we agree that it is dangerous as an initiating agent when acetylene is present in liquid oxygen. Ozone has been found in krypton plants but not, to our knowledge, in liquid oxygen of tonnage oxygen plants. We are, however, concerned with the unstable compounds of ozone known as ozonides, and believe that efforts should be intensified to identify and remove them if they do exist in oxygen plants.

The hypothetically dangerous products of photochemical reactions of nitrogen oxides with organic materials (2) have mostly high molecular weights, with vapor pressures from 4 to 7 decimal points lower than those of acetylene and other light hydrocarbons. Up to concentrations of 0.001 p.p.m. they should be readily condensed in the regenerators and evaporated like the carbon dioxide in those cycles which employ regenerators. It might be expected that the non-condensed portion would be retained in the acetylene adsorber and that remaining traces would leave the separator via the auxiliary condenser and acetylene separator. The organic nitrogen dioxide compounds are of acid character and should be washed out by caustic, if the removal of carbon dioxide is effected by means of caustic. These, however, are

only assumptions. Until now, such organic nitrogen compounds have not been found by our organization in the main condensers of air separators. In my opinion it is desirable to prove their presence in liquid oxygen prior to their being presumed to be a cause of explosions and work in this direction should be undertaken. Until such proof is established, I must insist that the oxygen plant's enemy number one is acetylene.

Nitrogen oxides are normally present in waste gases and thus also in industrial air. They are found in the liquid oxygen of the air separator and mostly in the acetylene separator in p.p.m. concentrations. It has, however, been observed for a long time (without any hazard resulting) that they have been present in such large quantities as to impart to the liquid oxygen a greenish-blue tint, and to appear in the desorbed gas of the acetylene adsorbers as clouds of brown vapors. However, it must be considered that a stoichiometric mixture of NO with liquid oxygen will react after initiation with a primer cap, but only with low free energy. Whether or not they would react in the bath of liquid oxygen with unsaturated hydrocarbons at the very low temperature is being studied at present; ethylene does not react. They are, however, disagreeable because of their corrosion effects and possible reactions succeeding corrosion (e.g. formation of Cu_2C_2).

Comprehensive information has been gathered on vapor pressures at very low temperatures of the C_1 to C_4 saturated and unsaturated hydrocarbons, on their solubility in liquid oxygen, on their gas-liquid partition in solution, on the explosion behavior of single-phase liquid solutions and of the two-phase systems solid-solution or liquid-liquid, on the mutual solubility of such hydrocarbons at liquid-oxygen temperature, and on their adsorption from solutions—all of which data are available to us for discussing hydrocarbon problems. I will not endeavor to elaborate on this point except for a few details: the higher the C number the lower the solubility (from CH_4 ∞ to nC_4H_{10} ~ 175 p.p.m.); a double-bond will lower the solubility (C_2H_6, 12%; C_2H_4, 1.8%); mixtures of propane and oxygen show a two-phase liquid system with ~1% C_3H_8 in liquid oxygen.

The explosion violence of a hydrocarbon in liquid oxygen solution diminishes with decreasing concentration. Therefore the real danger comes from the two phase system: solid-liquid or liquid-liquid.

No general rule can be given for all of these "light" hydrocarbons; each of them should be treated individually. This means also that analytical work on the contamination of air or liquid oxygen must show each hydrocarbon individually and not only an average C-number. Gas chromatography lends itself as an appropriate method.

Design Factors

As to precautionary measures to prevent plant explosions, the adsorption of the acetylene on silica gel as in use in our plants since 1943 is of primary importance, according to our experience. In the vicinity of carbide plants, where acetylene accumulates in the air, we use adsorbers arranged after the air stream passes through the first cooling steps with good results. The adsorbers not only remove all of the carbon dioxide from the air, making caustic scrubbing unnecessary, but also reduce high concentrations of acetylene to traces.

Vaporizers

We have been installing in all of our major air separation facilities since 1927 (with good results) vertical-tube auxiliary condensers for liquid oxygen located away from the main columns for their protection. We safeguard the auxiliary condensers against accumulation of solid acetylene in the course of oxygen evaporation by the operating rule that, in large plants, the acetylene content in the main condenser must be kept below 0.1 p.p.m. and that, in addition, 0.1 to 0.5 per cent of the produced oxygen must be withdrawn from the separator in liquid form.

Vertical tube evaporators at which the liquid oxygen is boiling within the tubes while gaseous nitrogen is brought to condensation at the outside of the tubes were installed by us into several small installations in 1928. This system, however, proved to be more sensitive to acetylene than did the normal evaporators with the liquid oxygen bath boiling outside and gaseous nitrogen condensing within the vertical tubes.

As far as safety is concerned, the forced-feed countercurrent film-vaporizer system referred to in a previous publication (1), appears to us to afford no advantage but actually certain disadvantages in apparent higher acetylene concentration in the vaporizer and the trays of the low pressure column compared to the gravity-fed main condenser with a vertical-tube auxiliary vaporizer system.

Lubrication Oil

The formation of acetylene in air compressors has been investigated. Quantities of acetylene formed from oil were found to be so insignificant that, compared to the natural acetylene, they are believed to be of no importance. Entrainment of oil into the separation apparatus is but of little importance where gaseous oxygen only is produced, but it is exceedingly disagreeable when producing liquid oxygen. For, when treating liquid oxygen containing oil, considerable efforts must be made to avoid oil explosions in the gaseous high pressure oxygen after evaporation.

Catalytic Removal of C_2H_2

Catalytic oxidation of the hydrocarbons prior to the air separation has been investigated by us for some time. It appears that, from a technical point of view, it can be done well. However, catalytic plants are still too expensive.

We are thus compelled to design separation plants so that concentrations of acetylene higher than 1 p.p.m. can be tolerated. With regard to tonnage plants with regenerators, a variety of new problems arise: condensation and evaporation of hydrocarbons (especially acetylene) on the filling mass of the regenerators, thickness of condensate films, their sensibility to sparks in the presence of gaseous or liquid air, and means for preventing unforeseen accumulation of dangerous material. We are studying these problems. It seems that in relatively simple cases practical industrial solutions can be proposed.

In standard medium air separation plants silica-gel adsorbers inserted in the air stream precooled to its carbon dioxide dew point offer good protection against hazards even from highly contaminated air, besides dispensing with the use of caustic scrubbing for decarbonization as already mentioned.

Literature Cited

1. Kerry, F. G., Chem. Eng. Progr., **52**, 11, 443 (1956).
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