# SAFETY MEASURES IN LOW TEMPERATURE SEPARATION OF ACETYLENE-CONTAINING GAS MIXTURES

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Coke oven gas contains 600 - 2000 ppm acetylene. In refinery gases for ethylene production, the concentration of acetylene can amount to several percent. In discussions about the safety of low temperature gas separation plants the question was raised whether the presence of acetylene in a gas mixture makes necessary special safety measures, because of the tendency of the acetylene to self-decomposition of its tendency to form explosive carbides.

An answer to this question will in the first line have to show the physical limits and chemical conditions for safe handling of acetylene-containing gas mixtures at their low-temperature separation.

During the low temperature separation process, acetylene can be present in all three states of aggregation: gaseous, liquid and solid. It is known by Reppe that in the gaseous phase the partial pressure of acetylene at room temperature should not exceed values of 20 - 30 psia because, at higher pressures, self-decomposition of the acetylene molecule might occur.

In coke oven gas plants resp. ethylene plants with working pressures of 170 resp. 425 psia the above shown limit values are not reached.

In the liquefied $C_3$ and $C_4$ fractions, acetylene exists in the dissolved state. It is of importance to know that diluting the acetylene with the components of the $C_3$ resp. $C_4$ fractions does not deprive completely the acetylene of its tendency to self-decomposition.

## Explosive limits

In the literature and in patent specifications the opinion occasionally can be found advocated that the addition of a few percent of $C_2$ or $C_3$ hydrocarbons to acetylene will make the liquid mixture proof against explosion. This is not correct. A liquid homogeneous mixture of ethylene, ethane and acetylene in which the acetylene content is 42% or more, can be exploded, using a primer as initiator, whereas, in mixtures of lower acetylene content only the primer explodes, but not the solution.

In design and operation of gas separation plants, measures are to be taken to prevent that hydrocarbon mixtures with more than 42% acetylene might form anywhere within the separation device during process steps like rectification or boiling down.

Solid acetylene is often referred to as being sensitive to mechanical impact; probably remembering the high sensibility of solid acetylene moistened with liquid oxygen. In the absence of oxygen especially in a reducing atmosphere solid acetylene cannot even be exploded by blows of hammer.

Deposits of solid acetylene in gas separation plants may nevertheless cause troubles, the nature of which, however, will be the same as caused by other solid deposits, e.g. obstruction of cross sections, increasing pressure drop etc.

For normal design of a coke-oven-gas-separator a relation $C_2H_4 : C_2H_2 = 20$ can be considered as sufficient for preventing precipitating of solid acetylene. Lower relations down to 8 can be balanced out by special design of the cooling device regarding the process steps of condensation and re-evaporation.

In order to prevent that cross sections of the lines through which passes the evaporating methane-fraction become obstructed by solid acetylene the acetylene-content of the methane-fraction is limited to a few parts per million.

It is not necessary to remove the acetylene from the coke oven gas by hydration prior to the low temperature separation. The safety of the separation plant for acetylene containing coke oven gas is fully ensured if the limits indicated above, are adhered to.

## Copper apparatus

Certain chemical facts, however, will have to be taken into consideration in case the separation apparatus is made of copper.

In solvents of sufficient dielectric strength the acetylene molecule under the uncompensated charges of its triple bond, splits off one or two protons which can be substituted by monovalent metallic ions e. g. $Cu^+$ ions, thus forming carbides e. g. copper acetylide.

A most brisant species of copper acetylide can be obtained in the laboratory by reacting at low temperature (—40 degrees C) an ammoniacal solution of cuprous salt with acetylene. The precipitated copper acetylide after filtering and drying can be exploded even by the smoothest touch.

Divalent ions like $Fe^{++}$ do not react with dissolved acetylene and consequently iron can be used as a construction material e. g. for heat exchangers of the precooling systems (down to —45 C).

For the protection of a separating apparatus made of copper two kinds of measures are taken: Firstly as to construction: those parts of the inner surface, which come in contact with acetylene-containing gases, are tinned; and the outside surfaces of columns, heat exchangers and so on are covered with a temperature-stable painting. This is done in order to prevent corrosion and formation of cuprous salts. Secondly as to operation: corrosive gaseous constituents are held away from the separator e. g. the $NH_3$ content of the raw gas is limited to a few ppm, and sulphur-free insulating material like atone wool is preferred to sulphur containing material.

A thin cover of copper acetylide on the outside of unprotected columns as results from sulphur corrosion has no destructive power. However the sparks formed on rubbing or scratching might ignite gas-air-mixtures in the wool. Such ignition of gas air mixtures in the wool from sparkling copper acetylide during repair work has been observed. Therefore as a measure of precaution in repair work the air should be driven out by rinsing the wool and an eventual working hole, with nitrogen.

In the course of 30 years in which coke oven gas plants have been built we have experienced no explosion of copper acetylide. This shows that the formation of copper acetylide under the precautions described above is very limited and that the safety of the gas separator is but little influenced.