Patented Sept. 1, 1931

1,821,170

UNITED STATES PATENT OFFICE

RICHARD LINDE, OF MUNICH, GERMANY, ASSIGNOR TO GESELLSCHAFT FUR LINDE'S EISMASCHINEN A. G., OF HOLLRIEGELSKREUTH, GERMANY, A CORPORATION OF GERMANY

PROCESS FOR FRACTIONATION OF COKE OVEN GAS

No Drawing. Application filed April 23, 1928, Serial No. 272,355, and in Germany May 2, 1927.

In the fractionation of coke oven gas by partial liquefaction at low temperatures very troublesome disturbances have arisen in practice because of the separation of solid constituents and particularly because of the occurrence of explosions inside the separating apparatus. Against the supposition that the cause of these explosions is to be sought in the acetylene content of the gases to be separated, is the observation that solid acetylene, either alone or admixed with liquid hydrocarbons, cannot be caused to explode by friction, sparking nor shocks in general. That the formation of copper-acetylene is not the cause of the explosions is indicated by the fact that this substance cannot be formed by the direct action of acetylene even on finely divided copper.

In spite of these facts it has been found that the troubles described entirely disappear if, by suitable pretreatment according to the present invention, hydrocarbons containing triple bonds are substantially completely removed from the gases to be treated.

It is noteworthy that a quantitative removal of these hydrocarbons, which would be very difficult on a large scale with the means heretofore available, is not necessary, but that it is sufficient to so decrease their amount that on cooling the gases there is no separation of acetylenes in the solid state. This result is attained by reducing the content to about 1/100%, which amount can be obtained without difficulty by the known methods of removing acetylene.

Experiments have lead to the conclusion that contrary to expectations, the presence of acetylene hydrocarbons is the cause of the explosions, and indeed it has been found, that, in the presence of auxiliary agents which attack copper, such as ammonia or nitric oxide, these hydrocarbons can form explosive compounds with the copper of the separating apparatus. This reaction takes place particularly at ordinary temperature or slightly lower. If an explosion takes place in the presence of solid acetylene the latter takes part in the explosion and greatly increases the effect. Besides the heretofore known metallic- or copper-acetylene compounds there are formed high-molecular compounds of high boiling point—polymerization products of diacetylene, nitro compounds, etc.—which can likewise take part in the explosions, and which can cause a gradual encrustation of the separating apparatus. For these reasons a separation of large amounts of solid acetylenes in the separating apparatus is to be avoided. On the other hand a slight residue of acetylenes in the gases is unharmful as it is dissolved in the other hydrocarbons present on cooling the gases and is continually removed from the apparatus in solution. The term "separating apparatus" is used herein to mean the whole apparatus including the apparatus which the gas to be treated enters at a temperature of approximately −40° C., the heat exchangers and the fractionating apparatus proper.

To attain more certain security against the above mentioned disturbances two additional means may be utilized:

First the impurities present in the gases which favor the reaction of acetylene hydrocarbons with copper, particularly ammonia, nitric oxide and water vapor, can be removed as far as possible with known absorption means, such as concentrated sulfuric acid.

Further, all parts of the separating apparatus which consist of copper or copper alloys can be given a protective coating against the effect of acetylene. I have found that such a coating is effectively produced by a thin layer of tin, lead or alloys of these metals. These metals would have seemed to be unsuitable, since they are readily attacked by the traces of sulfur compounds present in all gases. However, it has been found by experiment that in spite of this apparent disadvantage, the coatings of these metals completely resist the chemical and mechanical action to which they are subjected in the separating apparatus, while on the other hand the certainty and ease with which completely covering coatings may be formed, is a particular advantage of the metals named.

The removal of acetylene-hydrocarbons may be accomplished by passing the compressed gases, after sulfur compounds and carbon dioxide have been removed in the usual manner and before entering the separating apparatus, over heated catalysts, which causes a hydrogenation or a decomposition of acetylene. Other chemical processes may also be used, such as polymerization of the acetylenes with heated copper, precipitation of the acetylenes with metal salt solutions, oxidation of the acetylenes, etc. Physical methods, for instance absorption in solvents, such as water or acetone, may also be applied.

The process of the above mentioned German application G. 69,937 is essentially as follows:

The gas mixture containing acetylene is passed before cooling at atmospheric or higher pressure over suitable catalysts heated up to 100–400° C., for instance over partially dehydrated hydroxides of aluminium or iron. By this procedure the acetylene-hydrocarbons are either decomposed or hydrogenated.

The decomposing effect consists in the formation of carbon and hydrogen from the acetylene, while the hydrogenating reaction, giving mainly ethylenes from acetylenes results in the presence of an excess of hydrogen for instance in the case of coke-oven gas. In this latter case the ethylene-hydrocarbons contained in the original gas are not altered.

By this process even the smallest traces of acetylene hydrocarbons are removed quantitatively from the treated gases.

The process may be carried out in an apparatus comprising periodically reversible regenerators for the inflowing and outflowing gases which are to be brought into heat interchange with one another, means for supplying the necessary additional heat in this process, and a reaction chamber filled with catalyst and arranged between the regenerators, all heated parts being insulated from heat interchange with the surroundings.

I claim:

1. A preliminary treatment preparatory to the fractionation of coke oven gases at low temperatures which comprises separating from said gas hydrocarbons containing triple bonds, before any portion of the gases are liquefied, to such an extent that the said hydrocarbons are not deposited in solid form in the subsequent liquefaction and fractionation.

2. A preliminary treatment preparatory to the fractionation of coke oven gases at low temperatures which comprises separating from said gas hydrocarbons containing triple bonds, before any portion of the gases are liquefied, to such an extent that the said hydrocarbons are not deposited in solid form in the subsequent liquefaction and fractionation and also removing from said gases compounds which activate the action of acetylene with copper.

3. A preliminary treatment preparatory to the fractionation of coke oven gases at low temperatures which comprises separating from said gas hydrocarbons containing triple bonds, before any portion of the gases are liquefied, to such an extent that the said hydrocarbons are not deposited in solid form in the subsequent liquefaction and fractionation and also removing from said gases ammonia nitric oxide and water vapor.

In testimony whereof, I affix my signature.

DR. RICHARD LINDE.