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PROCESS FOR REMOVING NITRIC OXIDE FROM GASES CONTAINING UNSATURATED HYDROCARBONS

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The present invention describes a process for removing nitric oxide from cracked gases, especially those which contain more than 10% by volume of unsaturated hydrocarbons and which are obtained by pyrolyzing hydrocarbons at high temperature. By the process of the invention, the nitric oxide included in the gas is transformed into nitrogen dioxide and removed by washing under superatmospheric pressure, but at a low temperature.

Cracked gases of the type described above generally contain a great proportion, for example 10% by volume, of lower unsaturated hydrocarbons, and a further proportion of higher unsaturated hydrocarbons. In the processing of these cracked gases, it is disadvantageous that the nitrogen included in the crude gases partially reacts during the pyrolysis at the high temperature used with the oxygen required for producing the carrier gas, and partially is transformed into nitric oxide. The rate of transformation is the greater the higher the maximum temperature used. In the starting phase of high temperature pyrolysis, the temperature is as high as about 2500° C. If, immediately after the cracking, the cracked gas is "frozen" in the state of equilibrium corresponding to that high temperature, by sudden cooling, for example direct cooling by injection of water as usual in the manufacture of acetylene and ethylene, the cracked gas obtained will also include a certain proportion of nitric oxide, which may be as high as, for example, 0.001 to 0.2% by volume and depends on the composition of the starting materials and the cracking temperature. In the processing of the cracked gases, which generally takes place after compression to 2 to 50 atmospheres, the nitric oxide and the residual oxygen always included in the gas first react to form nitrogen dioxide, which then undergoes further reaction with the unsaturated, higher hydrocarbons to form resinous compounds, the so-called nitro-resins. These resins deposit predominantly in valves and pipe contractions and produce operational disturbances. Experience has shown that these reactions, prior to compression, appear only to a slight, tolerable degree.

The present invention provides a process which substantially avoids the formation of nitro-resins, wherein nitric oxide included in the gas mixture in a proportion of about 0.001 to 0.2% by volume is partially oxidized with the oxygen included in or introduced into the cracking gas to form nitrogen dioxide, and then removed by washing during and/or immediately after compression to about 2 to 50 atmospheres, preferably 7 to 16 atmospheres, at a temperature of 0 to 50° C., preferably 10 to 40° C., and/or immediately after oxygen has been added to the compressed gas. The words "immediately after" as used herein are intended to mean that the time which elapses before the washing operation is short enough to avoid the formation of nitro-resins. It is surprising that in the presence of a large amount of unsaturated, highly reactive substances, the relatively small amounts of oxygen included in the cracked gas are sufficient to permit complete removal of the nitric oxide. As washing agent, which should have a pH-value of at least 7, there may be used water or more advantageously an alkaline solution, for example a solution of sodium or potassium acetate, hydroxide, carbonate or bicarbonate. The solution is used in a concentration for example, of 1 to 10%, preferably 2 to 6%. It has been found that washing at a relatively low temperature, for example about 30° C., is more convenient than at a relatively higher temperature, for example a temperature higher than 60° C., because the reaction $2NO+O_2 \rightarrow 2NO_2$ proceeds more rapidly at a lower temperature than at a raised temperature.

It is an essential requirement for the present reaction that the proportion of oxygen included in the cracked gas be sufficiently high, and amount to at least 0.5% by volume. In view of the danger of explosion, the upper oxygen limit should not exceed 1.5% by volume. The preferred proportion of oxygen is within the range of 0.8 to 1.2% by volume.

It is also advantageous to wash the gas immediately after it has been compressed so that nitro-resin cannot at all form from the nitrogen dioxide obtained. It is therefore advantageous to use a compressor in which the individual compression stages are separated from one another by a sealing liquid. One of this type of compressors is known under the designation "liquid piston type rotary blower," which may be used as the only or as an additional washing means. The sealing liquid may be one of the aforesaid washing liquids. Alternatively, compressors of different type may be provided with washing means and then used in the process of this invention.

The present process is also applicable to gas mixtures other than of cracked gases, for example coal distillation gases, such as they are obtained in gas works or coke works. The process of this invention is especially applicable to the processing of gas mixtures containing more than 10% by volume of unsaturated hydrocarbons.

With reference to the following examples it is stated that the disturbances mentioned above which are produced by nitro-resins in the processing of cracked gases were not observed when the proportion of nitric oxide in the cracked gas was reduced to less than 0.0001% by volume. The proportions of nitric oxide indicated in the examples were measured by a method as modified and described by Seebaum and Hartmann in "Brennstoffchemie," vol. 16, page 41 (1935), and which indicates 0.0001% by volume as the lower detectable limit under the conditions prevailing in cracked gases.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

Example 1

31.5 cubic meters per hour (measured at N.T.P.) of a cracked gas composed as follows (percent by volume):

H_2	28.7
CO	15.5
CH_4	11.7
C_2H_6	0.8
C_2H_4	16.5
CO_2	11.6
C_2H_2	6.2
C_3H_6	1.2
Allene	0.3
Butadiene	0.5
Methylacetylene	0.6
N_2, I_2 and other ingredients (of which 0.015% by volume is nitric oxide)	6.4

were processed in the following manner:

The gas mixture was introduced through a tube into a liquid piston type compressor (manufactured by Messrs. Siemens-Schuckert Werke) and compressed to 7.5 atmospheres absolute. About 2000 liters/hour washing liquid (water) were cycled in the compressor at about 30° C. The gas mixture was then conveyed together with the

washing liquid to a wash column filled with Raschig rings, where the liquid was separated, for example with the aid of a cyclone. In the wash column, the wash liquid flowed counter-currently to the gas. The mixture of gas and wash liquid was allowed to remain in the wash column for a period of 50 seconds. After that time, a sample of the issuing gas was tested to determine the proportion of nitric oxide still included in the gas.

(A) Before the compression, the cracked gas contained 0.45% by volume oxygen. Both the compressor and the wash column were rinsed with water. Under these conditions only as little as 10% of the nitric oxide were removed, the content of nitric oxide being reduced from initially 0.015 to 0.0135%.

(B) The proportion of oxygen included in the cracked gas was increased from 0.45% by volume to 1.15% by volume, the other conditions remaining the same. The content of nitric oxide determined after washing was less than 0.0001% by volume, i.e. below the detectable limit. Formation of a nitro-resin from the washed gas was not observed.

Example 2

The gas mixture and the conditions were the same as in Example 1, but the water used as washing liquid in the compressor and the wash column was replaced by a 2% potassium bicarbonate solution. The gas issuing from the wash column was tested. Its content of nitric oxide was below the detectable limit.

We claim:

1. A process for the removal of nitric oxide from cracked gases which contain 0.001 to 0.2 percent by volume of nitric oxide and more than 10 percent by volume of unsaturated hydrocarbons, which comprises compressing the cracked gases in the presence of at least 0.5 percent by volume of molecular oxygen to about 2 to 50 atmospheres and washing, at a temperature between 0 and 50° C., the nitrogen dioxide formed from the gases with an alkaline to neutral aqueous medium.

2. A process according to claim 1, wherein the concentration of oxygen in the gas mixture is in the range of 0.8 to 1.5 percent by volume.

3. A process according to claim 1, wherein nitric oxide is partially oxidized during the compression of the gases.

4. A process according to claim 1, which comprises washing the oxidized nitric oxide from the gases with an aqueous alkaline solution of 1 to 10 percent by weight of an alkali metal compound.

5. A process according to claim 1, wherein the alkaline washing solution contains 2 to 6 percent by weight of an alkali metal compound.

6. A process according to claim 5, wherein the alkali metal compound is potassium bicarbonate.

7. A process according to claim 1, wherein the cracked gases are compressed to about 7 to 16 atmospheres.

8. A process according to claim 1, wherein the washing temperature is in the range between 10 and 40° C.

9. A process as defined in claim 1 wherein said gases are simultaneously compressed and washed.

10. A process as defined in claim 1 wherein said gases are washed immediately after being compressed.

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