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PRODUCTION OF ACETALDEHYDE

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The present invention relates to an improved process for producing acetaldehyde from gases containing acetylene.

It has already been proposed to convert concentrated acetylene into acetaldehyde by treating it with solutions of iron sulphate in sulphuric acid, the said solutions containing mercury. The acetylene used in excess is led in circulation. The iron salt solution, which contains the major portion of the iron in the ferric stage at the commencement of the reaction, is reduced to the ferrous stage during the formation of the acetaldehyde. The continuous preparation of acetaldehyde is carried out by adding to the iron salt solution in a given time only such an amount of iron in the ferric stage as is reduced in the same time. Generally speaking the procedure is such that with the progressive addition of ferric sulphate solution and the continuous withdrawal of exhausted solution, only very little ferric sulphate is present in the solution because the amount of ferric sulphate added in the unit of time is immediately converted into ferrous sulphate.

In the case of gases having a comparatively low content of acetylene (up to about 20 per cent by volume), such as have been produced recently in electric arc plants, acetaldehyde can only be obtained in moderate yields with the iron salt solutions described above. Strongly diluted acetylene mainly passes unchanged through the iron salt solution and is thus lost as far as conversion into acetaldehyde is concerned. It is necessary, however, since the gas containing acetylene cannot be led in circulation without difficulty by reason of its strong dilution, to convert the acetylene as completely as possible into acetaldehyde by a single passage through the iron salt solution, because otherwise the process is useless from an economic point of view.

In the copending application Ser. No. 83,069, filed June 2nd, 1936, one of the present inventors has described an improved process for the manufacture of acetaldehyde from gases containing up to about 20 per cent of acetylene by means of an acid solution containing mercury according to which process the gas to be treated is led through the reaction vessel in the same direction as the catalytic liquid itself, the latter being led in a cycle at the same time and preferably so that a multiple of the amount of liquid present in the reaction vessel is circulated per hour. In the example of the said co-pending application Ser. No. 83,069 the catalytic liquid comprises a certain amount of iron in the form of ferrous and ferric sulphate.

We have now found that gases of the said kind containing acetylene in an amount of up to about 20 per cent by volume can be worked up with special advantage into acetaldehyde when the ratio of ferric sulphate to ferrous sulphate in the iron salt solution is not allowed to fall below a certain limit. Care should be taken that more than about 20 per cent of the total amount of iron is always present in the ferric stage. For example it is advantageous to use a solution which contains between 25 and 100 grams of iron per liter, about 30 per cent being in the form of ferric sulphate and the remainder in the form of ferrous sulphate. Depending on the nature of the gases containing acetylene employed, the content of other unsaturated hydrocarbons of which varies according to the hydrocarbon mixture serving for the preparation of the acetylene, it may be necessary to vary the said ratio of the ferric stage to the ferrous stage, i. e. to increase or decrease the proportion of ferric sulphate in the solution. In this manner it is easy to adapt the degree of efficiency of the solution to the gas mixture to be worked up. A higher content of unsaturated hydrocarbons in the initial gas necessitates a higher proportion of ferric sulphate. In this way the conversion of acetylene into acetaldehyde is rendered as complete as possible and at the same time too high a content of ferric sulphate in the solution, which may give rise to undesirable side reactions, is avoided.

The procedure may be for example that the reduction of the iron salt at first only present in the ferric stage taking place during the addition of water to the acetylene is allowed to proceed until the desired proportion of ferric sulphate to ferrous sulphate has been set up. There is then continuously added to the iron salt solution such an amount of ferric sulphate solution that the ferric sulphate content does not fall below the desired limit of 20 per cent. Naturally a corresponding amount of the reduced solution must be always withdrawn in order to maintain unchanged the effective amount of iron of for example 35 grams per liter and the volume of the salt solution. Atmospheric or also increased pressures may be employed.

When the ratio of ferric sulphate to ferrous sulphate does not fall below the above-specified limit, there is not only the advantage that for the first time the economic working up of gas mixtures containing acetylene is rendered possible but there is the further advantage that me-

tallic materials without protective coverings, as for example rubber, may be used for the construction of the parts of the vessels which come into contact with the hot sulphuric acid iron salt solutions. There are then suitable as constructional materials nickel chromium steels which may be welded at any time when it is necessary, this being impossible with parts of vessels which are coated with rubber or lined with brickwork. Indirect transfer of heat for the heating or cooling of the salt solution may also be carried out without difficulty. Furthermore parts coated with rubber may be replaced by parts of the said materials in cases where rubber-covered walls might be rubbed through, as for example in towers which are charged with filler bodies.

The following example, given with reference to the accompanying drawing which shows diagrammatically an arrangement of apparatus according to this invention, will further illustrate the nature of this invention but the invention is restricted neither to this example nor to the specific arrangement shown.

Example

150 liters of a solution which contains 24.5 grams of iron in the form of ferrous sulphate and 10.5 grams of iron in the form of ferric sulphate per liter and also contains 3 per cent of free sulphuric acid are charged into the vessel A. Into this solution there are blown through the pipe G 11 cubic meters per hour of a gas containing acetylene which in addition to hydrogen and methane and propane contains 18 per cent by volume of acetylene and 1.45 per cent by volume of other unsaturated hydrocarbons. The gas containing acetylene moves in the same direction as the salt solution. The solution itself is led in circulation over metallic mercury situated in the container B and/or in the parts of the tower A and/or C in such manner that by the circulation the volume of the said solution contained in the tower A is renewed several times per hour whereby the salt solution always remains saturated with mercurous and mercuric sulphate. The escaping gas which leaves the tower is under an excess pressure of one atmosphere. In order to maintain the composition of the salt solution, an amount of the solution corresponding to the amount of ferrous sulphate formed is withdrawn through the pipe D, the ferrous sulphate is converted in the vessel E into ferric sulphate and returned through the pipe F. A 94 per cent conversion of the acetylene is thus obtained. If, on the other hand, the amount of ferric sulphate in relation to the amount of ferrous sulphate is allowed to fall below 20 per cent of the total amount of iron, the conversion of acetylene continually diminishes and a yield of scarcely 70 per cent is attained. By increasing the ferric sulphate content to the former value (30 per cent of the total iron), the high conversion value of 94 per cent may be immediately obtained again. The residual gas together with the acetaldehyde formed and the water vapor carried along with it leave the vessel A through the pipe H. The acetaldehyde may be readily separated from the gas mixture by cooling and washing with water.

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