

PATENT SPECIFICATION

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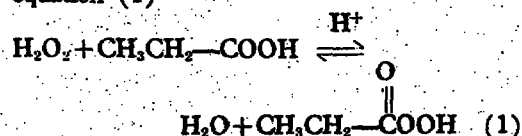
(54) PROCESS FOR THE PREPARATION OF PERPROPIONIC ACID SOLUTIONS

(71) We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT

Roessler, a body corporate organised under the laws of the Federal Republic of Germany, of Frankfurt/Main, Federal Republic of Germany, and BAYER AKTIENGESellschaft, a body corporate organised under the laws of the Federal Republic of Germany, of Leverkusen Bayerwerk, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of perpropionic acid from hydrogen peroxide and propionic acid.

The synthesis of perpropionic acid from hydrogen peroxide and propionic acid is known (Swern, Organic Peroxides I, Wiley 1970, page 369—372). The reaction of hydrogen peroxide with propionic acid takes place in the presence of an acid catalyst according to equation (1)



to give an equilibrium mixture which contains perpropionic acid, propionic acid, hydrogen peroxide, water and the acid catalyst. The concentration of perpropionic acid depends on the concentration of the feed materials and the molar feed ratio of hydrogen peroxide and propionic acid. In general, hydrogen peroxide is used in concentrations of 30 to 90% by weight, preferably 50 to 70% by weight. Propionic acid is preferably employed in the pure form or as an aqueous solution.

Suitable acid catalysts are the mineral acids, for example sulphuric acid, acid salts, such as sodium bisulphate, or cation exchangers based on sulphonated, partially crosslinked poly-

styrenes in the H⁺ ion form. The amount of these catalysts can vary within wide limits.

The mixtures formed according to the equation (1) can be used in a known manner for oxidation reactions.

The equilibrium mixtures formed according to equation (1) also arise as intermediates in processes for the preparation of anhydrous perpropionic acid solutions (DT-OS (German Published Specification) 2,262,970).

It is therefore extremely important to be able to prepare and handle the said reaction mixtures under explosion-proof conditions.

It is known that aqueous hydrogen peroxide, especially in a concentrated form, can form, with organic substances, mixtures which are capable of explosion and which present an explosion hazard. The explosibility of the lower percarboxylic acids in bulk and in their solutions is also known. Surprisingly, however, it was shown that reaction mixtures such as are formed by the reaction of hydrogen peroxide with propionic acid in the presence of sulphuric acid according to equation (1) present an explosion hazard even when 50% strength by weight hydrogen peroxide, that is to say a ratio by weight of hydrogen peroxide: water = 1, and anhydrous propionic acid are used.

It has now been found, surprisingly, that perpropionic acid can be prepared by reaction of hydrogen peroxide with propionic acid in the presence of sulphuric acid under explosion-proof conditions when the reaction is carried out using a molar ratio of hydrogen peroxide: propionic acid employed of from 0.8 to less than 1.4:1, the reaction temperature is restricted to a maximum of 60°C and the weight ratio of hydrogen peroxide (100% by weight): water before the start of the reaction with propionic acid, is restricted to from 1.0 to 1.22:1, the sulphuric acid concentration in the reaction mixture being 10 to 40% by weight.

Contrary to all expectations it has been found, when the reaction mixtures, under con-

ditions of partial, well defined enclosure in steel bombs, are exposed to heat and when the reaction mixtures are subjected to the detonation shock of a primer charge whilst enclosed in a steel tube (Explosivstoffe 9, 4 (1961)), that reaction mixtures such as are formed according to equation (1) are explosion-proof when the molar ratio of hydrogen peroxide: propionic acid employed is restricted to 0.8 to less than 1.4:1, preferably 0.8—1.3:1, the reaction temperature is restricted to a maximum of 60°C and the weight ratio of hydrogen peroxide (100% by weight):water before the start of the reaction with propionic acid is restricted to from 1.0 to 1.22:1, the sulphuric acid concentration in the reaction mixture being 10—40% by weight. An increase of the molar ratio of hydrogen peroxide:propionic acid for example from 1.3 to 1.5, at the same feed concentration of hydrogen peroxide, already results in a reaction mixture which at 60°C exhibits the properties of a high blasting explosive.

The reaction temperature in the preparation of the reaction mixtures is generally between 20 and 60°C, preferably 30—45°C and preferentially 35—40°C.

The present invention is illustrated by the tests which follow and the term explosion hazard, which is used there, is also explained.

Example.

There are various methods for assessing the explosion hazard of materials. For the present invention, the behaviour of the reaction mixtures when exposed to heat under conditions of partial, well-defined enclosure and the behaviour when subjected to the detonation shock of a primer charge were used to assess the explosion hazard of reaction mixtures which are formed by the reaction of hydrogen peroxide with propionic acid in the presence of sulphuric acid.

A method for determining the sensitivity of explosive materials towards exposure to heat, which leads to differentiated, comparable numerical values, is to heat the materials in a steel bomb which is closed off by a nozzle plate with a well-defined orifice. The steel bomb is fabricated from deep-drawing sheet metal and has an internal diameter of 24 mm, a length of 75 mm and a wall thickness of 0.5 mm. At its open end, the bomb is provided with a collar. The bomb is closed by a circular nozzle plate provided with a bore. Nozzle plates having the following diameters for the cylindrical outlet orifice for the gases produced by the decomposition are used:

1; 1.5; 2; 2.5; 3; 3.5; 4; 5; 6; 8; 10; 12; 14; 16 and 20 mm.

The materials to be investigated are introduced into the steel bombs and, in order to prevent the initiation of a catalytic decomposition, the walls of the steel bomb can be provided with a coating of e.g. polyethylene. The volume of the material sample is about 27 ml. The samples are exposed to heat by supplying heat in an amount of, on average, 2.4 kcals/sec from 4 Teclu-burners. With 3 tests, at least one explosion must take place, the bomb being split into 3 or more parts ("limiting diameter"). The limiting diameter determined in this way is to be regarded as a measure of the heat sensitivity of the material examined. The higher the limiting diameter, the higher is the heat sensitivity. Values of 2—2.5 mm are to be regarded as transition values into the dangerous range, values in excess of 2.5 mm indicating that the reaction is dangerously heat-sensitive.

The results of the investigations carried out on the reaction mixtures by the method described above are shown in the table which follows.

In order to obtain further data on the explosion hazard of the reaction mixtures, the behaviour of the reaction mixtures when subjected to the detonation shock of a primer charge, under conditions of enclosure, was investigated. For this purpose about 940 ml of the reaction mixtures were exposed, while enclosed in a 2 inch steel tube, to the detonation shock of a primer charge of 50 g of cyclonite with 5% of wax. In the present case, the conditions were further intensified by the temperature being raised to 60°C and the reaction mixtures being treated with oxygen gas by adding quartz pebbles coated with palladium. Seamless drawn 2" steel tubes having a wall thickness of 5 mm and a length of 500 mm and with a welded-on base were used for the experiments. A cap was screwed to the open end and the auxiliary charge was fastened to the inside of the cap. The cap has a bore for the electric fuse with the detonator. This method gives a clear result with regard to the explosibility of a material and it indicates whether the explosion induced was propagated wholly, partly or not at all or whether the tube was disintegrated into splinters. The reaction mixtures tested were prepared from hydrogen peroxide of the indicated concentration using anhydrous propionic acid and concentrated sulphuric acid. The proportion of sulphuric acid was 30% by weight, relative to the mixture of aqueous hydrogen peroxide and propionic acid.

The results of the steel bomb tests and of the 2" steel tube tests are given in the table which follows:

Example No.	Ratio by weight of hydrogen peroxide:water in the hydrogen peroxide charged	Molar ratio of hydrogen peroxide: propionic acid employed	Steel bomb limiting diameter (mm)	2" steel tube with primer charge
1	1.0	0.8	—	no explosion
2	1.0	1.0	2	no explosion
3	1.0	1.2	—	no explosion
4	1.0	1.5	2.5	complete explosion
5	1.22	0.8	2	no explosion
6	1.22	1.0	2	no explosion
7	1.22	1.2	2.5	no explosion
8	1.22	1.3	—	no explosion
9	1.22	1.4	—	complete explosion
10	1.22	1.5	4	complete explosion

As can be seen from the table, the range in which there is an explosion hazard is reached when the ratio by weight of hydrogen peroxide:water in the hydrogen peroxide charged is restricted to a maximum of 1.22, but the molar ratio of hydrogen peroxide:propionic acid employed is increased to 1.4—1.5.

We are aware of Specification No. 1,014,361 which describes and claims a process of producing a saturated aliphatic percarboxylic acid containing 1 to 3 carbon atoms comprising reacting hydrogen peroxide with

the corresponding aliphatic carboxylic acid in the ratio of 0.3 to 5.0 moles of hydrogen peroxide per mole of acid at 20 to 80°C in a reaction mixture containing 5 to 20% by weight of a strong water-entraining acid, preferably sulphuric acid, and 20 to 75% by weight of water, vaporizing together from the resulting reaction mixture, at a pressure of 15 to 350 mm of Hg, and at a temperature of 20 to 80°C, a reaction product containing peracid, aliphatic acid and water, and collecting said reaction product.

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The disclosed process is said to produce reaction products which are non-detonatable mixtures which can be handled safely and with no special precaution. Also, there is said to be rapid production of peracid in a system which is safe from hazard. The process, however, is exemplified only in terms of the production of peracetic acid and there is no appreciation in the context of the production of perpropionic acid of the critical nature of the ratio by weight of hydrogen peroxide to water in the hydrogen peroxide charged and the molar ratio of hydrogen peroxide to aliphatic acid employed. The broad ranges for these two ratios as disclosed would lead in the production of perpropionic acid to explosive mixtures in the absence of any appreciation or teaching of the critical nature of maintaining them within the very narrow limits of the present invention.

Moreover, it is to be noted that in all of the exemplified processes there is present dipicolinic acid as an active oxygen stabilizer. Such a material is not used in the process of the present invention.

WHAT WE CLAIM IS:—

1. A process for the preparation of per-

propionic acid comprising reacting hydrogen peroxide with propionic acid in the presence of from 10 to 40% by weight of sulphuric acid at a temperature not greater than 60°C, using an initial molar ratio of hydrogen peroxide:propionic acid of from 0.8 to less than 1.4:1, and an initial weight ratio of hydrogen peroxide (100% by weight):water of from 1.0 to 1.22:1.

2. A process according to claim 1 wherein the reaction is carried out at a temperature of from 30 to 45°C.

3. A process according to claim 1 substantially as hereinbefore described.

4. A process for the preparation of perpropionic acid substantially as hereinbefore described in any one of Examples 1 to 3 and 5 to 8.

5. Perpropionic acid prepared by a process according to any one of claims 1 to 5.

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10 of perpropionic acid of the critical nature of
the ratio by weight of hydrogen peroxide to
water in the hydrogen peroxide charged and
the molar ratio of hydrogen peroxide to ali-
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maintaining them within the very narrow
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Moreover, it is to be noted that in all of the
exemplified processes there is present dipico-
linic acid as an active oxygen stabilizer. Such
a material is not used in the process of the
25 present invention.

WHAT WE CLAIM IS:—

1. A process for the preparation of per-

propionic acid comprising reacting hydrogen
peroxide with propionic acid in the presence
of from 10 to 40% by weight of sulphuric 30
acid at a temperature not greater than 60°C,
using an initial molar ratio of hydrogen per-
oxide:propionic acid of from 0.8 to less than
1.4:1, and an initial weight ratio of hydrogen
peroxide (100% by weight):water of from 1.0 35
to 1.22:1.

2. A process according to claim 1 wherein
the reaction is carried out at a temperature of
from 30 to 45°C.

3. A process according to claim 1 substan- 40
tially as hereinbefore described.

4. A process for the preparation of per-
propionic acid substantially as hereinbefore
described in any one of Examples 1 to 3 and
5 to 8. 45

5. Perpropionic acid prepared by a process
according to any one of claims 1 to 5.

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