

PATENT SPECIFICATION

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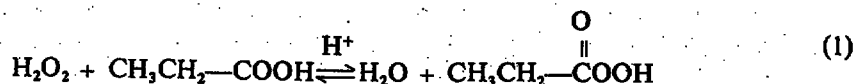
(54) PROCESS FOR THE PREPARATION OF PERPROPIONIC ACID SOLUTIONS

(71) We, DEUTSCHE GOLD-UND
 SILBER-SCHNEIDANSTALT Vormal
 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 Lever-
 kusen Bayerwerk, Federal Republic of Ger-
 many, 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 concentrations of the
 feed materials and on the molar ratio of
 hydrogen peroxide and propionic acid in
 the feed. In general, hydrogen peroxide is
 used in concentrations of from 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 polystyrenes in the H⁺ ion form.
 The amount of these catalysts can vary
 within wide limits.

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

The equilibrium mixtures formed
 according to equation (1) also arise as inter-
 mediates in processes for the preparation of
 anhydrous perpropionic acid solutions

(DT—OS (German Published Specifica-
 tion) 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 prop-
 ionic 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 an acid,

preferably sulphuric acid, under explosion-proof conditions when the reaction is carried out using a molar ratio of hydrogen peroxide:propionic acid employed of more than 3.5:1, 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 a maximum of about 0.82:1, the sulphuric acid concentration in the reaction mixture being 10—40% by weight.

Contrary to all expectations it has been found, when the reaction mixtures, under conditions 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 more than 3.5:1, preferably 3.8—10:1, 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 a maximum of about 0.82:1. Where sulphuric acid is used as catalyst, its concentration in the reaction mixture is 10—40% by weight.

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 when exposed to heat under conditions of partial, well defined enclosure was used to assess the explosion hazard of the 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 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 mixture is dangerously heat sensitive.

The reaction mixtures investigated were prepared from hydrogen peroxide of the indicated concentration using anhydrous propionic acid and concentrated sulphuric acid. The results of the steel bomb tests are given in the table which follows.

As can be seen from the table the range in which there is an explosion hazard is already reached when the ratio by weight of hydrogen peroxide:water in the hydrogen peroxide charged is increased from 0.82 to 1.0.

Example No.	Ratio by weight of hydrogen peroxide: water in the hydrogen peroxide charged	Molar ratio of hydrogen peroxide: propionic acid employed	Proportion of sulphuric acid %	Limiting diameter (mm)
1	0.82	5	20	2.5
2	0.82	7	20	1.5
3	0.82	10	20	1.0
4	0.82	5	30	2.5
5	0.82	7	30	2
6	0.82	8	30	2
7	0.82	10	30	1.5
8	0.67	6	20	1.5
9	0.67	10	20	1
10	0.67	5	30	2.5
11	0.67	6	30	2
12	0.67	7	30	2
13	0.67	10	30	1
14	0.54	4	30	2
15	0.54	6	30	1
16	1.0	5.6	20	5
17	1.0	6.7	20	5
18	1.0	9.4	20	4
19	1.0	4.2	30	5
20	1.0	6.2	30	5
21	1.0	8.4	30	4

WHAT WE CLAIM IS:—

1. A process for the preparation of perpropionic 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 employed of more than 3.5:1, and an initial weight ratio of hydrogen peroxide (100% by weight):water of not more than 0.82:1.
2. A process according to claim 1 wherein

the reaction is carried out at a temperature of from 30 to 46°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 15.

5. Perpropionic acid prepared by a process according to any one of claims 1 to 4.

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1	0.82	5	20	2.5
2	0.82	7	20	1.5
3	0.82	10	20	1.0
4	0.82	5	30	2.5
5	0.82	7	30	2
6	0.82	8	30	2
7	0.82	10	30	1.5
8	0.67	6	20	1.5
9	0.67	10	20	1
10	0.67	5	30	2.5
11	0.67	6	30	2
12	0.67	7	30	2
13	0.67	10	30	1
14	0.54	4	30	2
15	0.54	6	30	1
16	1.0	5.6	20	5
17	1.0	6.7	20	5
18	1.0	9.4	20	4
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5. Perpropionic acid prepared by a process according to any one of claims 1 to 4.

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